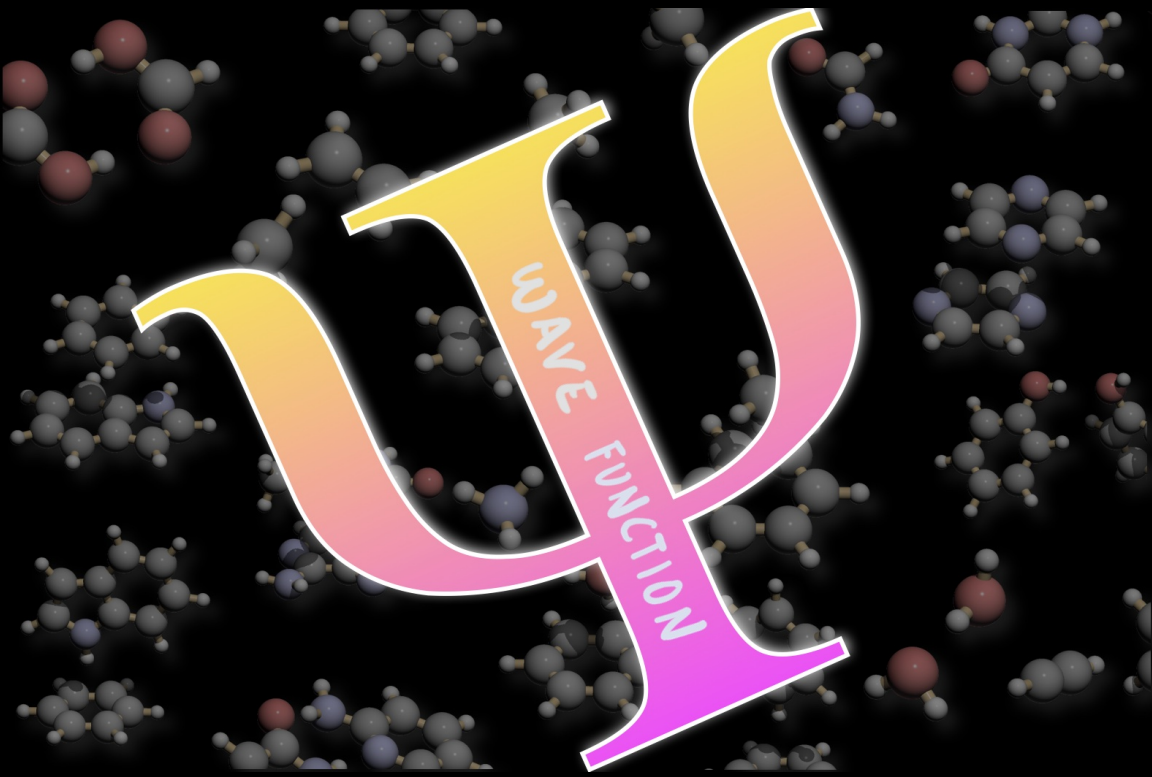
The Live Textbook of Physical Chemistry

Volume 2: Quantum Mechanics



Roberto Peverati

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The Live Textbook of Physical Chemistry, Volume 2

Beyond the Classical World

Quantum Mechanics, Atoms, Molecules, and Spectra

Roberto Peverati

15 November 2026

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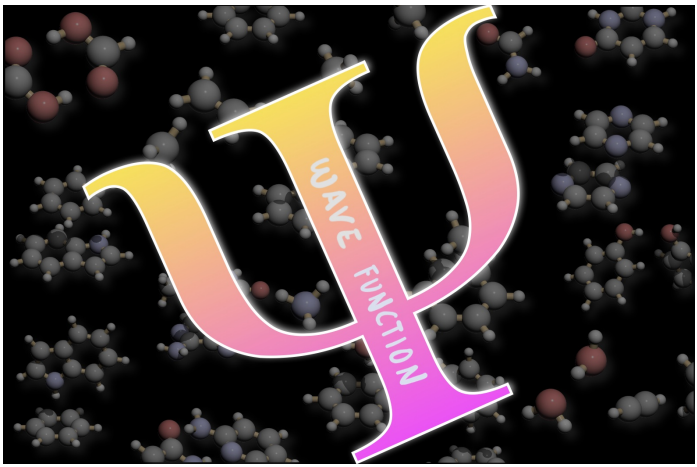
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Preface

Beyond the Classical World



This textbook is the official textbook for the Physical Chemistry 2 Course (CHM 3002) at Florida Tech.

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This live open textbook is distributed under the CC BY-NC-SA 4.0 License. The Python scripts that generate the figures are available under the MIT License. The first version of the book was funded in 2021 by the Florida Tech Open Educational Resources Grant Program, a collaboration of the Teaching Council, eEducation, and the Evans Library. That grant planted the seed; the current edition has since grown well beyond it, with a new structure, new chapters and sections, and new figures throughout.

How to use this book

If you have taken P-Chem 1 at Florida Tech, you should already be familiar with this format. Everything we did with the Live Textbook of P-Chem 1 will

be happening this semester with P-Chem 2. Please read this book carefully, since everything that will be in your exams is explained here. Since this book is specifically tailored for the CHM 3002 course at Florida Tech, there are no superfluous parts. In other words, everything in it might be subject to question in the quizzes and the final exam.

> Definitions and exercises are usually numbered and are highlighted in the text in this format (lighter grey, indented, and following a grey vertical bar). Please study the definitions carefully since they are fundamental concepts that will be used several times in the remainder of the text, and they will be subject to quizzes and exams. Exercises are essential for cementing the concepts, and you should attempt to execute them first without looking at the solution. Even if you were able to solve an exercise on your own, always read the solution after, since it might contain additional explanations expanding the main concepts in the text.

Navigating the book should be straightforward. On each page, there is a useful sidebar on the left that gives you an overview of all chapters, and a toolbar at the top with important tools. Arrows to shift between chapters might also be present, depending on your browser. If you are old-school and prefer a pdf, you can download a printout by clicking on the toolbar's corresponding icon. If you are *really* old-school and prefer a printed book, the best solution is to download the pdf and print it yourself. It is a LaTeX book, and I can promise you it will look good on paper. However, I cannot provide physical copies to each student. In the toolbar, you will find a useful search box that is capable of searching the entire book. The most adventurous will find in the toolbar a link to the raw GitHub source code. Feel free to head on over there and fork the book.

The appendices at the end of the book review the mathematical tools that we use (Appendix A), collect physical constants and unit conversions (Appendix B), and suggest further reading for when you want a second explanation or more depth (Appendix C).

A note on the use of AI. The November 2026 revision of this book was prepared with the help of Claude Code (Anthropic's Claude Opus 5.5), an AI assistant. The book, its structure, its scope, and its approach to teaching quantum chemistry are my own, developed over several years of teaching this course. In the revision, I used the AI as an assistant: to proofread the text, to rephrase passages, to draft new sections, figures, examples, and review questions following my outline and instructions, and to write the code for the computed and interactive figures. Every change was reviewed, corrected or rewritten, and approved by me, and I take full responsibility for the content of the book, including any remaining errors.

CHAPTER 1

Brief Summary of Classical Physics

Quantum mechanics cannot be derived from classical physics, but it was built by physicists who knew classical physics very well, and many of its ideas and equations are borrowed from it. Before discussing, in the next chapter, the experiments that classical physics could not explain, we will review the classical concepts that we will need the most: the description of motion through forces and through energy, the electrostatic interaction between charged particles, and the physics of waves.

1.1 Classical Mechanics

1.1.1 Newtonian Formulation

Classical mechanics as formulated by Isaac Newton (1643–1727) is all about forces. Newtonian mechanics works well for problems where we know the forces and have a reasonable coordinate system. In these cases, the net force acting on a system at position $\mathbf{r}$ in Cartesian 3-dimensional space $\{x, y, z\}$ is simply:

$$F_{\text{net}}(\mathbf{r}) = m\ddot{\mathbf{r}} = m\frac{d^2\mathbf{r}}{dt^2}. \tag{1.1}$$

Or, in other words, if we know the net force acting on a system of mass m at position $\mathbf{r}$ at some time t_0, we can use Eq. (1.1) to calculate the position of the system at any future (or past) time. We have completely determined the dynamical evolution of the system.[1]

[1] Notice that $\mathbf{r} \in \mathbb{R}^3$ is the position vector and $\dot{\mathbf{r}} \in \mathbb{R}^3$ is the velocity vector. As such, all the equations of classical mechanics are vector equations in 3-dimensional space, and not just simple numerical equations. To simplify the picture, we can restrict ourselves to a 1-dimensional space, replace $\mathbf{r}$ with x, and forget the complications of vector algebra, as we do in the examples.

Example 1.1: A ball tossed straight up (Newton)

A ball of mass m is at ground level and tossed straight up from an initial position x_0 with an initial velocity $\dot{x}_0$ and subject to gravity alone. Calculate the equation of motion for the ball (i.e. where is the ball going to be after some time t?).[2]

Solution: Since the only force acting on the ball is gravity, we can use the equation for the gravitational force to start our derivation:

$$F_{\text{gravity}} = -mg, \tag{1.2}$$

with g the gravitational acceleration ($g = 9.8$ m/s^2). We can then replace this expression into Eq. (1.1), to obtain:

$$\begin{aligned} -mg &= m\ddot{\mathbf{r}} \\ -g &= \ddot{\mathbf{r}} \\ -g &= \frac{d\dot{\mathbf{r}}}{dt}. \end{aligned} \tag{1.3}$$

Working in a 1-dimensional case, we can replace $\mathbf{r}$ with position x to obtain:

$$\begin{aligned} -mg &= m\ddot{x} \\ -g &= \ddot{x} \\ -g &= \frac{d\dot{x}}{dt}. \end{aligned} \tag{1.4}$$

which can then be integrated with respect to time, to obtain:

$$\begin{aligned} -g\int_{t=0}^{t} dt &= \int_{\dot{x}_0}^{\dot{x}} d\dot{x} \\ \dot{x} &= \dot{x}_0 - gt \\ \frac{dx}{dt} &= \dot{x}_0 - gt, \end{aligned} \tag{1.5}$$

which can be further integrated with respect to time, to give:

$$\begin{aligned} \int_{x_0}^{x} dx &= \int_{t=0}^{t} \dot{x}_0 dt - g\int_{t=0}^{t} t dt \\ x &= x_0 + \dot{x}_0 t - \frac{1}{2}gt^2. \end{aligned} \tag{1.6}$$

Example 1.1: A ball tossed straight up (Newton) *(continued)*

This final equation is the equation of motion for the ball, from which we can calculate the position of the ball at any time t. Notice how the equation of motion does not depend on the mass of the ball!
Numerical problem: How much time will a ball ejected from a height of 1 m at an initial velocity of 10 m/s take to hit the floor?
We can use the equation of motion obtained above to solve this problem, and obtain for this specific case $t \simeq 2.14$ s.[3]

Newton's equation is not the only way of writing the laws of classical mechanics. Physicists have developed other, equivalent formulations, which give exactly the same results but are more convenient for some problems. The most famous are the *Lagrangian* formulation, based on the difference between the kinetic and the potential energy of a system, and the *Hamiltonian* formulation, based on their sum.[4] Only the second one will be important for us, because it is the one that quantum mechanics is built upon.

1.1.2 Hamiltonian Formulation

Newton's mechanics is built around *forces*. Hamiltonian mechanics, instead, is built around *energy*. Its goal is to describe the motion of a system starting from a single function, the total energy, written in terms of where the particle is and how much momentum it has. This is exactly the starting point that we will use in quantum mechanics, which is why we need to get familiar with it now.

The first ingredient is the **momentum** of a particle of mass m moving with velocity $\dot{x}$ (we will work in one dimension to keep things simple):

$$p = m\dot{x}. \tag{1.7}$$

Momentum carries the same information as velocity, but, as we will see in the next chapter, it is the quantity that appears naturally when we describe particles in quantum mechanics.

The second ingredient is the total energy of the system, which is the sum of the kinetic energy, K, and the potential energy, V:

$$H = K + V. \tag{1.8}$$

When we write this total energy as a function of the position, x, and the momentum, p, we call it the **Hamiltonian** of the system, and we use the symbol

[3] This example is based on Rhett Allain's blog post on classical mechanics.
[3] Can you write a python program to do this calculation?
[4] The Lagrangian formulation is very powerful for complicated mechanical systems, such as a pendulum hanging from a moving support, but we will not need it in this textbook. Interested readers can find an introduction in the Wikipedia article on Lagrangian mechanics.

H. Since the kinetic energy is $K = \frac{1}{2}m\dot{x}^2$, and $\dot{x} = p/m$, we can write $K = \frac{p^2}{2m}$, and the Hamiltonian of a particle becomes:

$$H(x, p) = \frac{p^2}{2m} + V(x). \tag{1.9}$$

This equation is the most important result of this section. The first term depends only on the momentum, and it is the same for every system. The second term depends only on the position, and it is what makes each system different: a ball in the gravitational field of the Earth, an electron attracted by a nucleus, or two atoms connected by a chemical bond differ only in their potential energy, $V(x)$.

Once we know the Hamiltonian, the motion of the system can be obtained from two simple equations, called **Hamilton's equations**:

$$\begin{aligned} \dot{x} &= \frac{dx}{dt} = +\frac{\partial H}{\partial p}, \\ \dot{p} &= \frac{dp}{dt} = -\frac{\partial H}{\partial x}. \end{aligned} \tag{1.10}$$

These two equations are less mysterious than they look. If we apply them to Eq. (1.9), the first one gives $\dot{x} = \frac{p}{m}$, which is just the definition of momentum, Eq. (1.7), read backwards. The second one gives $\dot{p} = -\frac{dV}{dx}$. Since $\dot{p} = m\ddot{x}$, and since minus the derivative of the potential energy is the force, $F = -\frac{dV}{dx}$, this is just Newton's equation, $F = m\ddot{x}$, written in a different form. Hamilton's equations, in other words, contain no new physics: they are a different way of organizing the same information, starting from the energy instead of the forces.

Example 1.2: The same ball, using the Hamiltonian

Let's apply the Hamiltonian formulation to the same problem as in the previous example: a ball of mass m tossed straight up and subject only to gravity.
The potential energy of the ball at height x is $V(x) = mgx$, so the Hamiltonian, Eq. (1.9), is:

$$H = \frac{p^2}{2m} + mgx. \tag{1.11}$$

Hamilton's equations, Eq. (1.10), give:

$$\begin{aligned} \dot{x} &= \frac{\partial H}{\partial p} = \frac{p}{m}, \\ \dot{p} &= -\frac{\partial H}{\partial x} = -mg. \end{aligned} \tag{1.12}$$

Example 1.2: The same ball, using the Hamiltonian *(continued)*

The second equation tells us that the momentum of the ball decreases at a constant rate, $p(t) = p_0 - mgt$, where $p_0 = m\dot{x}_0$ is the initial momentum. Replacing it in the first equation, we obtain $\dot{x} = \dot{x}_0 - gt$, and integrating once more we obtain the same equation of motion that we found with Newton's method:

$$x = x_0 + \dot{x}_0 t - \frac{1}{2}gt^2. \tag{1.13}$$

So, if the Hamiltonian gives the same answers as Newton's equation, why do we bother? There are two reasons, both important for what follows:

1. **The Hamiltonian is the total energy, and the total energy is conserved.** We can check this for the ball in the previous example: replacing $p(t)$ and $x(t)$ in Eq. (1.11), all the terms that depend on time cancel out, and $H = \frac{p_0^2}{2m} + mgx_0$ at all times. As the ball rises, kinetic energy is converted into potential energy and vice versa, but their sum, H, never changes. Energy, and not force, is the central quantity in chemistry, and the energy levels of atoms and molecules are what we measure in experiments.

2. **The Hamiltonian is the bridge to quantum mechanics.** In quantum mechanics we will not be able to talk about the trajectory of a particle, so Newton's equation will be of little use. The Hamiltonian, on the other hand, will survive almost unchanged. In Chapter 6, we will see that the central equation of quantum mechanics, the Schrödinger equation, is obtained by taking Eq. (1.9) and replacing the momentum, p, with a mathematical operation (a derivative) acting on a wave function.

1.2 Coulomb's Law

Chemistry is, in the end, all about charged particles: positive nuclei and negative electrons. The force between them is described by **Coulomb's law**, discovered by Charles-Augustin de Coulomb in 1785. For two point charges q_1 and q_2 at a distance r from each other, the force is:

$$F = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}, \tag{1.14}$$

where $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$ is the *vacuum permittivity*, a constant that sets the strength of electric forces. The force acts along the line that joins the two charges, and Eq. (1.14) tells us two things:

- **The sign.** If the two charges have the same sign, $q_1 q_2 > 0$ and the force is positive: the charges repel each other. If they have opposite signs, as for an electron and a nucleus, $q_1 q_2 < 0$ and the force is negative: the charges attract each other.
- **The distance dependence.** The force decreases with the *square* of the distance: doubling the distance between the charges makes the force four times weaker.

You may also find the same law written in terms of the **electric field**, $\mathbf{E}$. We can think of each charge as creating a field around itself, and of the other charge as feeling a force $\mathbf{F} = q\mathbf{E}$ from that field. The two descriptions are equivalent, and we will mention the electric field again only when we discuss how light interacts with molecules (Chapter 13).

1.2.1 Electrostatic potential energy

In quantum mechanics, as we will see in Chapter 3, we do not work with forces, but with energies. So what we really need is the **potential energy** of two charges, $V(r)$. This is the energy stored in the pair of charges, and it is equal to the work that we have to do to bring them from very far apart (where they do not interact, and $V = 0$) to the distance r. Since the force changes with the distance, this work is an integral:

$$V(r) = -\int_{\infty}^{r} F(r')\,dr' = -\frac{q_1 q_2}{4\pi\varepsilon_0}\int_{\infty}^{r}\frac{dr'}{r'^2} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}. \tag{1.15}$$

(The minus sign is there because we push *against* the force: for two charges that repel, we need to do work to bring them closer, and the potential energy is positive.)

Eq. (1.15) is the most important result of this section, and it will appear in almost every chapter of this book. Notice how similar it is to Eq. (1.14), but with r instead of r^2 in the denominator. As a consequence, the potential energy decreases with distance more slowly than the force does.

For an electron ($q_1 = -e$) and a proton ($q_2 = +e$), with $e = 1.602 \times 10^{-19}$ C, the potential energy is always negative, and it becomes more and more negative as the two particles get closer:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0\, r}. \tag{1.16}$$

To get a feeling for the numbers, at a distance of 0.529 Å (the typical size of a hydrogen atom, as we will see in Chapter 2), Eq. (1.16) gives $V = -4.36 \times 10^{-18}$ J per electron–proton pair, or −2625 kJ/mol. This is several times larger than the energy of a typical chemical bond (a few hundred kJ/mol), which tells us that the Coulomb interaction is more than strong enough to hold atoms and molecules together.

1.3 Classical Waves

The last ingredient of classical physics that we need is the description of waves. Waves are everywhere: on the surface of water, in a vibrating guitar string, in sound, and in light. As we will see in the next two chapters, the central idea of quantum mechanics is that particles such as electrons also behave like waves, and the mathematics of quantum mechanics is, to a large extent, the mathematics of waves.

1.3.1 Describing a wave

A wave is a disturbance that repeats itself in space and time. Think of a long rope that you shake up and down at one end: a pattern of crests and troughs travels along the rope, even though each piece of rope only moves up and down. A snapshot of such a wave is shown in Fig. 1.1. We can describe it with a few quantities:

- The **amplitude**, A, is the maximum displacement from the rest position.
- The **wavelength**, λ, is the distance between two neighboring crests (or troughs).
- The **frequency**, ν, is the number of crests that pass by a fixed point every second. Its inverse, $1/\nu$, is the **period**, the time between two crests.
- The **speed**, v, is how fast the crests move. Since one wavelength passes by every period, the three quantities are related by:

$$v = \lambda\nu. \tag{1.17}$$

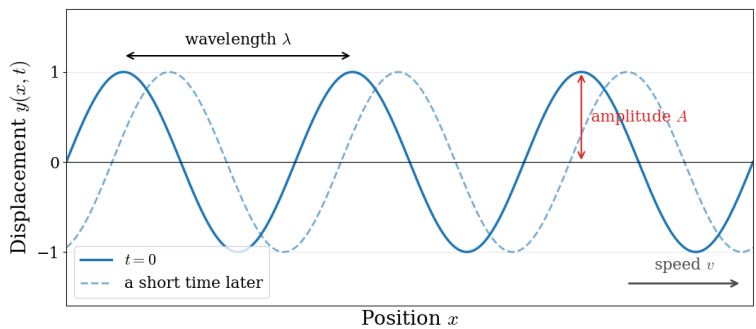


Figure 1.1 A traveling wave at $t = 0$ (solid line) and a short time later (dashed line), showing its wavelength and amplitude. The pattern moves to the right with speed v.

Mathematically, the displacement y of the rope at position x and time t for a wave moving to the right can be written as:

$$y(x,t) = A\sin(kx - \omega t), \tag{1.18}$$

where we have introduced two quantities that make the formulas simpler: the **wave vector**, $k = \frac{2\pi}{\lambda}$, which tells us how many radians the wave advances per unit length, and the **angular frequency**, $\omega = 2\pi\nu$, which tells us how many radians it advances per unit time. You can check that Eq. (1.18) repeats itself every time x increases by λ (at fixed t) or t increases by $1/\nu$ (at fixed x), and that the crests move with speed $v = \omega/k = \lambda\nu$.

A useful mathematical tool: complex waves

In quantum mechanics, waves are usually written using complex numbers instead of sines and cosines. The reason is **Euler's formula**, which connects the exponential function with the trigonometric functions:

$$e^{i\theta} = \cos\theta + i\sin\theta, \tag{1.19}$$

where $i = \sqrt{-1}$ is the imaginary unit (complex numbers are reviewed in Sec. A.1). Using this formula, we can write a wave as:

$$y(x,t) = A\,e^{i(kx-\omega t)} = A\cos(kx - \omega t) + iA\sin(kx - \omega t), \tag{1.20}$$

which contains both a cosine wave (the real part) and a sine wave (the imaginary part). The advantage is that exponentials are much easier to differentiate than sines and cosines: taking a derivative with respect to x simply multiplies the function by ik, since $\frac{d}{dx}e^{ikx} = ike^{ikx}$. We will start from exactly this form of a wave when we introduce the Schrödinger equation in Chapter 3.

1.3.2 The wave equation

Just as Newton's equation describes the motion of a particle, there is an equation that describes the motion of a wave. For a wave moving along a string, it is called the **classical wave equation**:

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}. \tag{1.21}$$

The left-hand side measures how curved the string is at a given point, and the right-hand side measures how fast that point accelerates up or down. In words, the equation says that the more a piece of string is curved, the faster it accelerates back towards a straight line. We can check that Eq. (1.18) is a solution: taking two derivatives with respect to x gives $-k^2 y$, and taking two derivatives with respect to t gives $-\omega^2 y$. Replacing them in Eq. (1.21), we obtain $-k^2 y = -\frac{\omega^2}{v^2}y$, which is true as long as $v = \omega/k$, the relation between speed, frequency, and wavelength that we already found.

An important property of the wave equation is that it is **linear**: if $y_1(x,t)$ and $y_2(x,t)$ are two solutions, their sum, y_1+y_2, is also a solution. This is called the **principle of superposition**, and it means that when two waves meet, their displacements simply add up. If the crests of the two waves coincide (they are *in phase*), they reinforce each other and produce a larger wave, which is called **constructive interference**. If the crests of one wave coincide with the troughs of the other (they are *out of phase*), they cancel each other, which is called **destructive interference**. The two cases are shown in Fig. 1.2. Interference is the signature of wave behavior, and we will see in Chapter 8 that it is also observed for electrons.

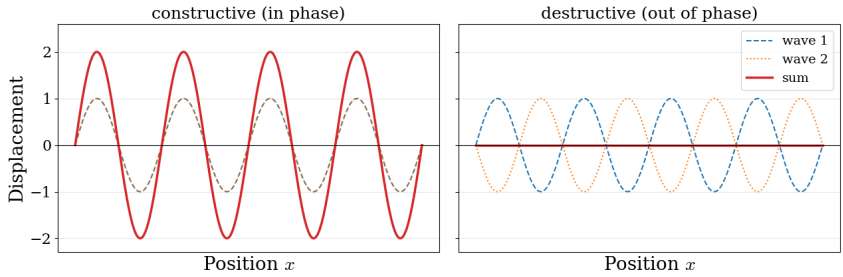


Figure 1.2 Superposition of two waves with the same wavelength. Left: when the waves are in phase, they add up to a wave with twice the amplitude (constructive interference). Right: when they are out of phase, they cancel each other (destructive interference).

1.3.3 Standing waves on a string

Something very interesting happens when a wave is confined, as on a guitar string of length L fixed at both ends. The waves travel along the string, bounce back at the ends, and interfere with themselves. Most of them cancel out, and only a few special patterns survive. These patterns do not travel along the string; they just oscillate up and down in place, and they are called **standing waves**.

To find them, we look for solutions of the wave equation in which the shape of the string does not change, but only its size, which oscillates in time:

$$y(x,t) = \psi(x)\cos(\omega t). \tag{1.22}$$

Here $\psi(x)$ describes the shape of the string, and $\cos(\omega t)$ describes how it oscillates. Replacing Eq. (1.22) in the wave equation, Eq. (1.21), the time-dependent factor cancels out, and we are left with an equation for the shape only:

$$\frac{d^2\psi}{dx^2} = -k^2\psi(x), \qquad k = \frac{\omega}{v}. \tag{1.23}$$

The solutions of this equation are sines and cosines, $\psi(x) = a\sin(kx) + b\cos(kx)$. Now we use the fact that the string is fixed at both ends, which gives two **boundary conditions**:

- At $x = 0$, the string cannot move, so $\psi(0) = 0$. Since $\sin(0) = 0$ and $\cos(0) = 1$, this requires $b = 0$, and $\psi(x) = a\sin(kx)$.
- At $x = L$, the string cannot move either, so $\psi(L) = a\sin(kL) = 0$. If $a = 0$ the string does not vibrate at all, so we need $\sin(kL) = 0$, which is only true when kL is a whole multiple of π.

The second condition can only be satisfied by special values of k, and therefore of the wavelength, $\lambda = 2\pi/k$, and of the frequency, $\nu = v/\lambda$:

$$k_n = \frac{n\pi}{L}, \qquad \lambda_n = \frac{2L}{n}, \qquad \nu_n = \frac{nv}{2L}, \qquad n = 1, 2, 3, \ldots \tag{1.24}$$

and the corresponding shapes are:

$$\psi_n(x) = a\sin\left(\frac{n\pi x}{L}\right). \tag{1.25}$$

The first four standing waves are shown in Fig. 1.3.

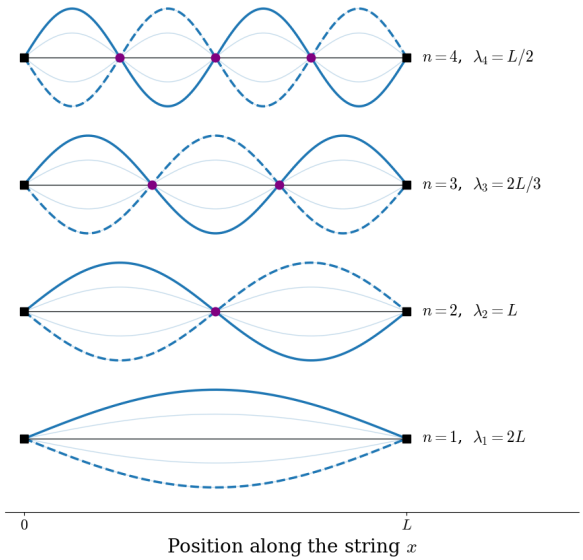


Figure 1.3 The first four standing waves on a string of length L fixed at both ends (black squares). The solid and dashed lines show the string at its two extreme positions, and the light lines show intermediate positions. The nodes are reported as purple dots.

Three things in these results are worth noticing:

1. **Quantization**: a confined wave can only have certain wavelengths and frequencies, labeled by a whole number, n. This is why a guitar string plays a definite note (the frequency with $n = 1$, called the *fundamental*) together with its *overtones* ($n = 2, 3, \ldots$), and not any frequency at all. Notice that nothing in the wave equation itself is quantized: the quantization comes entirely from the boundary conditions, i.e., from confining the wave.

2. **Nodes**: the standing wave with quantum number n has $n - 1$ points between the two ends where the string never moves, called **nodes**. The higher the frequency, the more nodes the wave has.

3. **The link with quantum mechanics**: in Chapter 4, we will solve the Schrödinger equation for an electron confined in a one-dimensional box, and we will obtain *exactly* the same functions as in Eq. (1.25), with the same conditions on the wavelength. The quantization of the energy of atoms and molecules has the same origin as the quantization of the notes of a guitar: a wave that is confined in a region of space.

1.3.4 Light as an electromagnetic wave

One more type of wave will be important for us: light. In the 19th century, James Clerk Maxwell showed that light is a wave of oscillating electric and magnetic fields, called an *electromagnetic wave*. In a vacuum, all electromagnetic waves travel at the same speed, the speed of light, $c = 2.998 \times 10^8$ m/s, so Eq. (1.17) becomes:

$$c = \lambda \nu. \tag{1.26}$$

Different wavelengths correspond to different types of radiation, which together form the *electromagnetic spectrum*: from radio waves (wavelengths of meters or more), to microwaves (millimeters to centimeters), infrared (micrometers), visible light (400–700 nm), ultraviolet, X-rays, and gamma rays (shorter than a billionth of a meter). In classical physics, the energy carried by an electromagnetic wave depends on its amplitude (the brighter the light, the more energy it carries), and not on its frequency. As we will see in the next chapter, this classical picture of light is one of the first things that quantum mechanics had to change.

1.4 Chapter Review

1.4.1 Key Ideas

- Newton's equation, $F = m\ddot{x}$, determines the trajectory of a particle once we know the forces and the initial conditions.

- The Hamiltonian, $H = \frac{p^2}{2m} + V(x)$, describes the same physics through the total energy, which is conserved. It is the bridge to quantum mechanics.
- Charged particles interact through the Coulomb potential energy, $V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$, which is negative (attractive) for an electron and a nucleus.
- Waves are described by their wavelength, frequency, and speed, $v = \lambda\nu$, and they are conveniently written as complex exponentials using Euler's formula.
- A wave confined between two fixed points can only have certain wavelengths: confinement leads to quantization, and higher frequencies mean more nodes.

1.4.2 Study Questions

1. If we know the net force acting on a particle, and its position and velocity at one instant, Newton's equation allows us to:

a. calculate only its average position
b. calculate only the probability of finding it at each position
c. calculate its position at any future (or past) time
d. calculate its energy, but not its position
e. calculate its position only if no force acts on it

2. The momentum of a particle of mass m moving with velocity $\dot{x}$ is:

a. $p = \frac{1}{2}m\dot{x}^2$
b. $p = m\ddot{x}$
c. $p = \dot{x}/m$
d. $p = mgx$
e. $p = m\dot{x}$

3. Which of the following is the Hamiltonian of a particle of mass m moving in one dimension with potential energy $V(x)$?

a. $H = \frac{p^2}{2m} - V(x)$
b. $H = m\ddot{x}$
c. $H = \frac{1}{2}mp^2 + V(x)$
d. $H = \frac{p^2}{2m} + V(x)$
e. $H = pV(x)$

4. Why is the Hamiltonian, rather than Newton's equation, the starting point of quantum mechanics?

a. because it is easier to integrate than Newton's equation
b. because it describes the system through its energy, which keeps its meaning even when trajectories do not

c. because it does not depend on the potential energy
d. because it gives different results from Newton's equation for heavy particles
e. because forces do not exist in quantum mechanics

5. The Coulomb force between an electron and a proton is:

a. repulsive, because the two charges have opposite signs
b. zero, because the two charges cancel each other
c. attractive, because the two charges have opposite signs
d. attractive only at large distances
e. independent of the distance between the particles

6. The electrostatic potential energy V of two point charges q_1 and q_2 separated by a distance r is:

a. $V = \dfrac{1}{4\pi\varepsilon_0}\dfrac{q_1 q_2}{r^2}$
b. $V = \dfrac{1}{4\pi\varepsilon_0} q_1 q_2 r$
c. $V = q_1 q_2 r^2$
d. $V = \dfrac{1}{4\pi\varepsilon_0}\dfrac{q_1 q_2}{r}$
e. $V = \dfrac{q_1 + q_2}{r}$

7. The speed v, wavelength λ, and frequency ν of a wave are related by:

a. $v = \lambda/\nu$
b. $v = \nu/\lambda$
c. $v = 2\pi\lambda\nu$
d. $v = \lambda^2\nu$
e. $v = \lambda\nu$

8. Euler's formula, which allows us to write waves using complex exponentials, is:

a. $e^{i\theta} = \cos\theta + i\sin\theta$
b. $e^{i\theta} = \cos\theta - i\sin\theta$
c. $e^{i\theta} = \sin\theta + i\cos\theta$
d. $e^{\theta} = \cos\theta + \sin\theta$
e. $e^{i\theta} = i\cos\theta\sin\theta$

9. A guitar string of length L is fixed at both ends. Which wavelengths can its standing waves have?

a. any wavelength
b. only $\lambda_n = 2L/n$, with $n = 1, 2, 3, \ldots$
c. only $\lambda = L$
d. only wavelengths longer than $2L$
e. only $\lambda_n = nL$, with $n = 1, 2, 3, \ldots$

10. How many nodes (points that never move, not counting the two

fixed ends) does the standing wave with quantum number n have?

a. $n-1$
b. n
c. $n+1$
d. $2n$
e. none

Answers

1.c, 2.e, 3.d, 4.b, 5.c, 6.d, 7.e, 8.a, 9.b, 10.a

CHAPTER 2

The Failure of Classical Physics

2.1 Historical Context

In the previous chapter, we reviewed the fundamental concepts of classical physics. In this chapter, we will see how these concepts fail when applied to atoms and light, and how these failures led to the development of quantum mechanics.

By the end of the 19th century, many physicists believed that their job was almost done. Newton's mechanics described the motion of everything from falling apples to planets, and Maxwell's equations described light as an electromagnetic wave. Only a few small puzzles were left to solve. Within thirty years, those few small puzzles had brought down the whole classical picture of the microscopic world, and replaced it with quantum mechanics: the theory that is at the foundation of all of modern chemistry.

The first cracks came from the discovery that atoms are not indivisible. J.J. Thomson discovered the electron in 1897, a year after Henri Becquerel had discovered radioactivity, which Marie and Pierre Curie then studied in depth. Atoms were clearly made of smaller charged pieces, and physicists started to build models of how these pieces fit together. Every attempt to describe them with classical physics, however, ran into contradictions. In 1911, Ernest Rutherford showed that the positive charge of an atom is concentrated in a tiny nucleus, with the electrons around it. According to classical electromagnetism, an electron orbiting a nucleus should continuously radiate energy and spiral into the nucleus in a fraction of a second. Atoms, in other words, should not exist.

The key idea that resolved these contradictions was *quantization*. In 1900, Max Planck showed that he could explain the light emitted by hot objects if he assumed that energy is exchanged only in discrete amounts, or "quanta." In 1905, Albert Einstein used the same idea to explain the photoelectric effect, proposing that light itself is made of quanta, later called photons. In 1913, Niels Bohr applied quantization to the hydrogen atom, assuming that the electron could move only on certain orbits with fixed energies, and that light is emitted or absorbed when the electron jumps between them. Bohr's model reproduced the spectrum of hydrogen with remarkable accuracy, but it worked only for atoms and ions with a single electron, and it had no justification other than

the fact that it worked. In 1924, Louis de Broglie suggested that, if light waves can behave like particles, then particles such as electrons might behave like waves.

A complete theory finally arrived in 1925–1926, in two different forms. Werner Heisenberg, together with Max Born and Pascual Jordan, developed *matrix mechanics*, a formulation based on arrays of numbers (matrices) that deals only with observable quantities, such as the frequencies and intensities of spectral lines. Shortly after, Erwin Schrödinger developed *wave mechanics*, based on the equation that now bears his name and that describes particles using waves. The two formulations looked completely different, but they were soon shown to be mathematically equivalent. Together, they form the theory that we will study in this textbook.

In the rest of this chapter, we will look in more detail at the experiments that classical physics could not explain, and at how their explanations led to the main ideas of quantum mechanics. These are the "ultraviolet catastrophe," the photoelectric effect, the line spectra of atoms, and the wave-particle duality.

2.2 The Ultraviolet Catastrophe

Every object emits electromagnetic radiation, and the hotter the object, the more radiation it emits and the shorter its wavelengths. This is why a piece of metal heated in a flame first glows red, then orange, and then white. To study this radiation without having to worry about the details of a specific material, physicists use an idealized object called a *black body*, which absorbs all the radiation that hits it and emits radiation that depends only on its temperature. The radiation emitted by a black body at a few temperatures is shown in Fig. 2.1.

Using classical electromagnetism and classical statistical mechanics, Lord Rayleigh and James Jeans derived an equation for the intensity of the radiation emitted by a black body at temperature T as a function of the wavelength λ. The result, known as the Rayleigh–Jeans law, is:

$$I(\lambda, T) = \frac{2ck_{\mathrm{B}}T}{\lambda^4}, \tag{2.1}$$

where I is the intensity of the radiation (more precisely, the power emitted per unit area of the emitting surface, per unit solid angle, and per unit wavelength, a quantity called *spectral radiance*), c is the speed of light, k_{B} is the Boltzmann constant, and T is the temperature in kelvins. This formula works well at long wavelengths, but it fails dramatically at short ones (dashed line in Fig. 2.1). If we take the limit for $\lambda \to 0$ in Eq. (2.1), we obtain $I \to \infty$. In other words, the shorter the wavelength (towards the UV and beyond), the more radiation the black body should emit, and the total energy emitted over all wavelengths should be infinite. This prediction is clearly absurd: if it were true, every warm object would be emitting an infinite amount of energy as UV

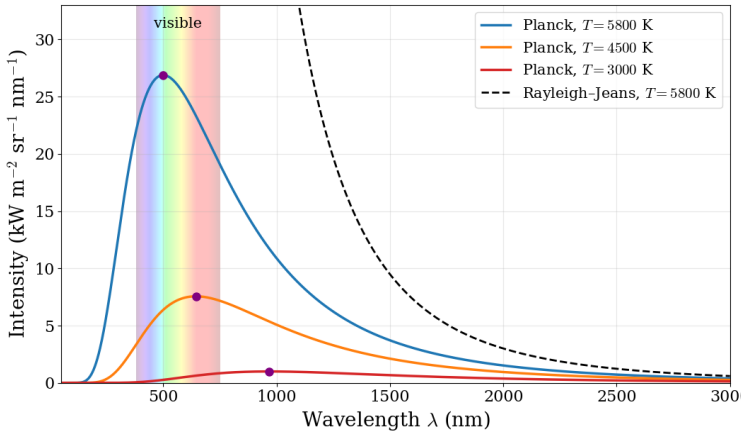


Figure 2.1 Intensity of the radiation emitted by a black body at three temperatures, calculated with Planck's law (solid lines). The purple dots mark the maximum of each curve. The dashed line is the classical Rayleigh–Jeans prediction at 5800 K, which diverges at short wavelengths. The shaded region is the visible part of the spectrum.

light, X-rays, and gamma rays. This failure of classical physics is called the **ultraviolet catastrophe** (or Rayleigh–Jeans catastrophe).

Max Planck solved the problem in 1900 by making an assumption that had no justification in classical physics: the energy of the oscillating electrons that emit the radiation cannot take any value, but only integer multiples of a minimum amount proportional to the frequency ν of the radiation:

$$E = nh\nu = nh\frac{c}{\lambda}, \tag{2.2}$$

with n a positive integer. With this assumption, Planck obtained the following formula for the intensity:

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_B T)} - 1}. \tag{2.3}$$

At short wavelengths, the exponential in the denominator grows much faster than λ^5 decreases, and I goes to zero as $\lambda \to 0$, in agreement with the experiments. (At long wavelengths, instead, $e^x - 1 \approx x$, and Planck's law reduces to the Rayleigh–Jeans law.) Physically, quantization works because at short wavelengths the minimum quantum of energy, hc/λ, becomes much larger than the typical thermal energy, $k_B T$, and the high-frequency oscillations are simply too "expensive" to be excited. By fitting Eq. (2.3) to the experimental data, Planck also obtained the value of the new constant, $h = 6.626 \times 10^{-34}$ J s, which is now called the *Planck constant*.

Let's look at what Fig. 2.1 tells us:

1. **Color and temperature**: as the temperature increases, the maximum of the curve moves to shorter wavelengths. The position of the maximum follows a simple rule, called *Wien's displacement law*, which can be derived from Eq. (2.3): $\lambda_{\max} T = 2.898 \times 10^{-3}$ m K. The surface of the Sun ($T \approx 5800$ K) has its maximum at $\lambda_{\max} \approx 500$ nm, in the middle of the visible region (our eyes evolved to see the light that the Sun emits the most). An incandescent light bulb ($T \approx 3000$ K) has its maximum at about 970 nm, in the infrared, which is why it looks yellowish and why most of its energy is wasted as heat. Our bodies ($T \approx 310$ K) emit mostly at about 9,000 nm, in the infrared, where thermal cameras can see it.

2. **Brightness and temperature**: the area under each curve, which is the total power emitted, grows very quickly with temperature (as T^4, a result known as the Stefan–Boltzmann law). Doubling the temperature of an object makes it emit sixteen times more energy.

3. **Where classical physics fails**: the classical and quantum curves agree at long wavelengths, where the quanta $h\nu$ are small compared to $k_B T$ and the energy behaves as if it were continuous. They disagree completely at short wavelengths, where the quanta are large. This is a pattern that we will see again: quantum effects become important when the spacing between energy levels is large compared to the thermal energy.

Planck himself considered quantization a mathematical trick rather than a property of nature, and the idea was not taken seriously until Einstein used it to explain the photoelectric effect.

2.3 The Photoelectric Effect

When light shines on a clean metal surface, electrons can be ejected from it. This phenomenon is called the photoelectric effect. It was first observed by Heinrich Hertz in 1887, and studied in detail by Philipp Lenard around 1900. Albert Einstein explained it in 1905, proposing that light energy is quantized into discrete particles, called photons, each with an energy proportional to its frequency.

To see why an explanation was needed, let's start from the classical prediction. As we saw at the end of Chapter 1, in classical physics light is a continuous electromagnetic wave, and the energy that it delivers every second depends on its amplitude (its brightness, or *intensity*), and not on its frequency. If we apply this picture to the photoelectric effect, we expect the electrons in the metal to absorb energy from the wave continuously, and to be ejected when they have accumulated enough of it to escape the surface. A brighter light delivers energy faster, so the electrons should come out with more energy. In other words, the kinetic energy of the ejected electrons, K, should be proportional to the intensity of the incident light, I_{in}:

$$K = c_{\text{PE}}\, I_{\text{in}}, \tag{2.4}$$

with c_{PE} being a constant that depends on the metal and on the characteristics of the incident light. The same picture also makes two other predictions: any color of light should be able to eject electrons, provided that it is bright enough, and with a very dim light the electrons should come out only after some delay, the time necessary to accumulate enough energy.

The experiments contradicted all three predictions. The kinetic energy of the ejected electrons does not depend on the intensity of the light at all (a brighter light ejects *more* electrons, but not faster ones), while it increases with the frequency of the light. Below a certain threshold frequency, which depends on the metal, no electrons are ejected, no matter how bright the light is. Above the threshold, electrons are ejected immediately, even with very dim light.

Einstein explained these results by proposing that a beam of light is not a continuous wave, but a stream of discrete packets of energy, the photons. The energy of each photon is equal to the smallest possible energy quantum in Planck's theory of the black body (corresponding to $n = 1$ in Eq. (2.2)):

$$E = h\nu. \tag{2.5}$$

Each photon interacts with a single electron, and gives it all of its energy at once. If the energy of the photon is smaller than the energy required to remove an electron from the metal, called the *work function*, ϕ, the electron cannot escape, and since there is no way of accumulating the energy of several photons, increasing the intensity (i.e., the number of photons) does not help. If the energy of the photon is larger than the work function, the electron escapes immediately, and the extra energy becomes its kinetic energy. The maximum kinetic energy of the ejected electrons, K_{max}, is therefore:

$$K_{\text{max}} = E_{\text{in}} - \phi = h\nu_{\text{in}} - \phi, \tag{2.6}$$

which depends on the frequency of the light, but not on its intensity, in agreement with the experiments. Eq. (2.6) is plotted for three metals in Fig. 2.2. For each metal, K_{max} is zero up to the threshold frequency, $\nu_0 = \phi/h$, and then increases linearly with the frequency. The lines for all metals are parallel, since their slope is always the Planck constant, h. In 1916, Robert Millikan measured these lines very carefully, confirming Einstein's prediction and obtaining a value of h in agreement with Planck's. Einstein received the Nobel Prize in Physics in 1921 for this explanation.

For example, the work function of sodium is about 2.3 eV.[1] The threshold wavelength is $\lambda_0 = hc/\phi \approx 1240/2.3 \approx 540$ nm, so green, blue, and violet light can eject electrons from sodium, but yellow and red light cannot, no matter

[1] The electronvolt, eV, is the energy gained by an electron accelerated through a potential difference of 1 volt: $1\ \text{eV} = 1.602 \times 10^{-19}$ J. It is a convenient unit for the energies of single electrons and photons. A useful shortcut for photons is $E(\text{eV}) \approx 1240/\lambda(\text{nm})$.

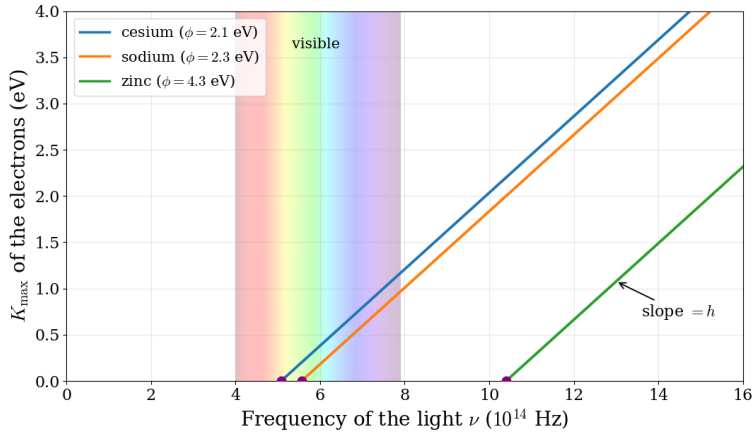


Figure 2.2 Maximum kinetic energy of the electrons ejected from three metals as a function of the frequency of the light, according to the photoelectric equation. The threshold frequencies are marked with purple dots, and the shaded region is the visible part of the spectrum. Work functions are approximate.

how bright. Ultraviolet light with $\lambda = 250$ nm carries photons of 4.96 eV, and ejects electrons with a maximum kinetic energy of $4.96 - 2.3 \approx 2.7$ eV, corresponding to a speed of about 10^6 m/s.

2.3.1 Why chemists care about photons

The energy of a single photon looks tiny in joules, but chemists usually think in terms of moles. A photon of green light ($\lambda = 500$ nm) has an energy of $E = hc/\lambda = 3.97 \times 10^{-19}$ J, or 2.48 eV. A mole of such photons carries 3.97×10^{-19} J $\times\ 6.022 \times 10^{23}$ mol^{-1} ≈ 239 kJ/mol. This is the same order of magnitude as the energy of a chemical bond (a C $-$ C single bond is about 350 kJ/mol). Ultraviolet photons ($\lambda = 250$ nm, 479 kJ/mol) carry enough energy to break chemical bonds, which is why UV light causes sunburns and can be used to sterilize surfaces, while visible photons can only excite electrons in molecules (which is how our eyes, and photosynthesis, work), and infrared photons can only make molecules vibrate. The interaction between light and molecules, one photon at a time, is the basis of spectroscopy, which we will discuss in Chapter 13.

Example 2.1: The photoelectric effect in sodium

Ultraviolet light with a wavelength of 250 nm shines on a sodium surface (work function $\Phi = 2.3$ eV). What is the maximum kinetic energy of the

Example 2.1: The photoelectric effect in sodium *(continued)*

ejected electrons?
Step 1: energy of one photon.

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m/s})}{250 \times 10^{-9}\ \text{m}} = 7.95{\times}10^{-19}\ \text{J} = 4.96\ \text{eV}.$$

(Per mole of photons, this is 7.95×10^{-19} J $\times$ 6.022×10^{23} mol^{-1} = 479 kJ/mol, more than enough to break most chemical bonds.)
Step 2: subtract the work function. Each photon gives all its energy to one electron, and 2.3 eV of it is needed to remove the electron from the metal:

$$K_{\max} = h\nu - \Phi = 4.96\ \text{eV} - 2.3\ \text{eV} = 2.7\ \text{eV}.$$

Notice that doubling the intensity of the light would double the number of ejected electrons, but would not change this value.

2.4 Atomic Spectra and the Bohr Model

The third failure of classical physics is the one that matters most for chemistry, since it concerns atoms themselves. When a gas of hydrogen atoms is heated or excited by an electric discharge, it emits light. If this light is passed through a prism, it does not produce a continuous rainbow, like the light from a black body, but a series of sharp lines, each with a precise wavelength. In the visible region, hydrogen emits only four lines: red (656 nm), blue-green (486 nm), violet (434 nm), and deep violet (410 nm). Every element has its own characteristic set of lines, which can be used to identify it, as a fingerprint (this is how helium was discovered in the spectrum of the Sun, before it was found on Earth).

In 1885, Johann Balmer found a simple formula that reproduces the wavelengths of the visible lines of hydrogen, and in 1888 Johannes Rydberg generalized it to all the lines of hydrogen, including those in the ultraviolet and infrared:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \qquad n_2 > n_1, \tag{2.7}$$

where n_1 and n_2 are positive integers, and $R_H = 1.0968 \times 10^7\ \text{m}^{-1}$ is the *Rydberg constant* for hydrogen. The lines with $n_1 = 1$ are in the ultraviolet (the *Lyman series*), those with $n_1 = 2$ are mostly in the visible (the *Balmer series*), and those with $n_1 = 3$ are in the infrared (the *Paschen series*). For example, for $n_1 = 2$ and $n_2 = 3$, Eq. (2.7) gives $1/\lambda = R_H \cdot \frac{5}{36}$, or $\lambda = 656$ nm, the

red line of hydrogen. The formula worked perfectly, but nobody knew why. Classical physics could not explain why atoms emit only certain wavelengths. Worse, as we mentioned at the beginning of this chapter, according to classical physics an electron orbiting a nucleus should continuously emit radiation of all wavelengths while spiraling into the nucleus.

In 1913, Niels Bohr proposed a model that explained the hydrogen spectrum by combining Rutherford's nuclear atom with Planck's idea of quantization. The **Bohr model** is based on two assumptions:

1. The electron moves around the nucleus only on certain circular orbits, called *stationary states*, on which it does not emit radiation. On these orbits, the angular momentum of the electron is quantized: it can only be a whole multiple of $\hbar = h/2\pi$, $L = n\hbar$, with $n = 1, 2, 3, \ldots$
2. The atom emits or absorbs light only when the electron jumps from one orbit to another. The energy of the photon is equal to the difference between the energies of the two orbits, $h\nu = E_{n_2} - E_{n_1}$.

Combining the first assumption with the classical laws of motion for an electron attracted by a proton (Coulomb's law, Chapter 1), Bohr found that the allowed energies of the electron are:

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{13.6\text{ eV}}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{2.8}$$

and the radius of the smallest orbit, now called the *Bohr radius*, is $a_0 = 0.529$ Å. The energy levels of Eq. (2.8) and the transitions between them are shown in Fig. 2.3.

This diagram explains three features of atomic spectra:

1. **Quantized energy levels explain line spectra**: since the electron can only have the energies of Eq. (2.8), the photons emitted when it jumps from a higher level to a lower one can only have the energies $E_{n_2} - E_{n_1} = 13.6\text{ eV}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$. Dividing by hc gives exactly the Rydberg formula, Eq. (2.7), with $R_H = 13.6\text{ eV}/hc = 1.097\times10^7\text{ m}^{-1}$, in perfect agreement with the experimental value.

2. **Ionization energy**: the levels get closer and closer as n increases, and they converge to $E = 0$, which corresponds to the electron completely separated from the proton. The energy needed to remove the electron from the lowest level, 13.6 eV (or 1,312 kJ/mol), is the ionization energy of hydrogen, again in perfect agreement with experiments.

3. **The meaning of the series**: all lines of a series end on the same lower level. The Lyman series, which ends on $n = 1$, involves the largest energy jumps, and it is in the ultraviolet. The Balmer series, which ends on $n = 2$, involves smaller jumps, and its first lines are visible.

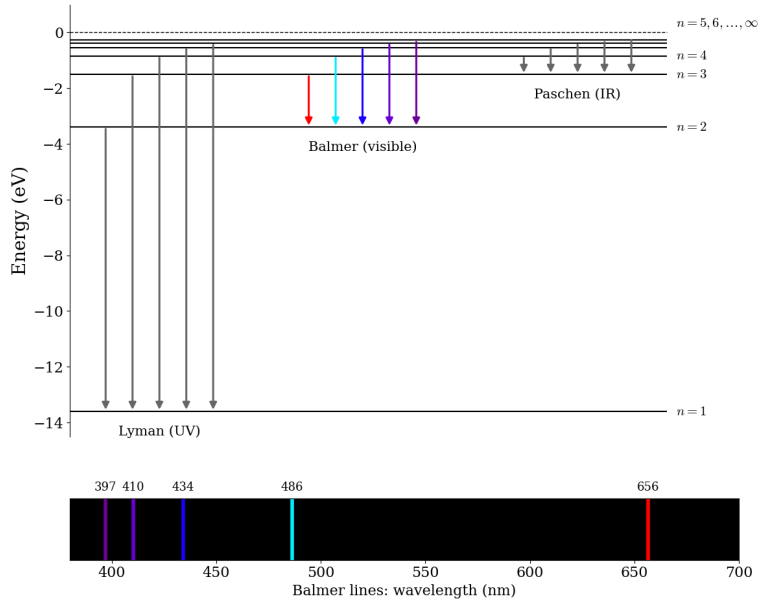


Figure 2.3 Top: energy levels of the hydrogen atom according to the Bohr model, and the transitions that produce the Lyman, Balmer, and Paschen series of emission lines. Bottom: the visible lines of the Balmer series, with their wavelengths in nm.

Despite this spectacular success, the Bohr model has serious problems. It works only for hydrogen and for ions with a single electron (such as He^+ and Li^{2+}), and it fails already for the helium atom. It cannot explain the intensities of the lines, nor why some lines split in a magnetic field. Most importantly, it does not explain *why* angular momentum should be quantized, or why an electron on an orbit should not radiate: these are assumptions made to fit the data. As we will see in Chapter 5, the Schrödinger equation gives exactly the same energies as Eq. (2.8), but without any of these assumptions, and with a completely different picture of the electron, which is not a particle moving on an orbit, but a wave.

2.5 Wave-Particle Duality

If light is made of particles, these particles should also carry momentum, and Einstein showed that the momentum of a photon is:

$$p = \frac{h}{\lambda}. \tag{2.9}$$

We can see where this result comes from in two steps. First, combining $E = h\nu$ for a photon with $\lambda\nu = c$ for an electromagnetic wave, we obtain the

energy of a photon as a function of its wavelength:

$$E = \frac{hc}{\lambda}. \tag{2.10}$$

Second, according to Einstein's theory of relativity, the energy of a particle with no mass, such as a photon, is related to its momentum by $E = pc$.[2] Replacing this relation in Eq. (2.10) and solving for λ we obtain:

$$\lambda = \frac{h}{p}, \tag{2.11}$$

which is equivalent to Eq. (2.9). Light, therefore, behaves as a wave in some experiments (it can be diffracted, and it has a wavelength) and as a particle in others (it comes in packets with energy $h\nu$ and momentum h/λ). In 1924, Louis de Broglie made the bold suggestion that this dual behavior is not unique to light, and that matter should also behave like a wave, with a wavelength given by the same Eq. (2.11). In 1927, Clinton Davisson and Lester Germer confirmed de Broglie's hypothesis by observing a diffraction pattern when they shot a beam of electrons at a nickel crystal, exactly as if the electrons were waves. We will discuss the wave behavior of electrons in more detail in Chapter 8.

Why don't we notice the wave nature of everyday objects? Because h is so small. A baseball with a mass of 0.145 kg thrown at 40 m/s has a de Broglie wavelength of $\lambda = h/mv \approx 1 \times 10^{-34}$ m, far too small to be observed in any experiment. An electron accelerated to a speed of 10^6 m/s, instead, has a wavelength of about 7×10^{-10} m, comparable to the size of an atom. This is why wave behavior dominates the world of electrons, atoms, and molecules, and why chemistry needs quantum mechanics.

Rewriting the previous equations in terms of the wave vector, $k = \frac{2\pi}{\lambda}$, and the angular frequency, $\omega = 2\pi\nu$, that we introduced in Chapter 1, we obtain the following two equations:

$$\begin{aligned} p &= \hbar k \\ E &= \hbar\omega, \end{aligned} \tag{2.12}$$

which are known as **de Broglie's equations**. We will use these equations to develop wave mechanics in the next chapter.

[2] This might be surprising, since in classical mechanics momentum is $p = mv$, and a particle without mass should have no momentum. In relativity, however, momentum and energy are more general concepts, and a massless particle that always travels at the speed of light can carry both. The fact that light carries momentum can be measured directly: light pushes on the objects that absorb or reflect it, a phenomenon called *radiation pressure*.

2.6 Summary

The four experiments discussed in this chapter, and the new ideas that they introduced, are summarized in Table 2.1.

Table 2.1 The experiments that led to quantum mechanics.

Experiment	Classical prediction	Observation	Quantum idea
Black-body radiation	Intensity grows without limit at short wavelengths	Intensity peaks and goes to zero at short wavelengths	Energy is exchanged in quanta, $E = nh\nu$ (Planck, 1900)
Photoelectric effect	Electron energy grows with light intensity; any color works	Electron energy depends only on frequency; threshold frequency	Light is made of photons, $E = h\nu$ (Einstein, 1905)
Atomic line spectra	Continuous emission; electrons spiral into the nucleus	Sharp lines at specific wavelengths; atoms are stable	Atoms have quantized energy levels (Bohr, 1913)
Electron diffraction	Electrons are particles and cannot interfere	Diffraction patterns, as for waves	Matter behaves as waves, $\lambda = h/p$ (de Broglie, 1924)

The common thread of all these results is that, at the scale of atoms and molecules, energy is not continuous, and particles and waves are not separate categories. In the next chapter, we will see how Schrödinger combined these ideas into a single equation.

2.7 Chapter Review

2.7.1 Key Ideas

- Black-body radiation could only be explained by assuming that energy is exchanged in quanta, $E = h\nu$ (Planck).
- The photoelectric effect showed that light is made of photons: the energy of the ejected electrons depends on the frequency of the light, not on its intensity.
- The sharp lines of atomic spectra show that atoms have discrete energy levels. The Bohr model explained hydrogen, but not why quantization happens.
- Particles behave as waves, with wavelength $\lambda = h/p$ (de Broglie). The effect matters only for very light particles such as electrons.
- At the scale of atoms, energy is not continuous, and particles and waves are not separate categories.

2.7.2 Study Questions

1. What did classical physics (the Rayleigh–Jeans law) predict for the radiation emitted by a black body?

a. the intensity peaks and then goes to zero at short wavelengths
b. the intensity grows without limit at short wavelengths
c. no radiation is emitted at room temperature
d. the intensity is the same at all wavelengths
e. only visible light is emitted

2. Which assumption did Planck introduce to explain black-body radiation?

a. light travels faster at short wavelengths
b. atoms have a nucleus
c. energy is exchanged only in multiples of $h\nu$
d. electrons are waves
e. energy is not conserved in the emission of light

3. As the temperature of a black body increases, the maximum of its emission:

a. moves to longer wavelengths
b. moves to shorter wavelengths
c. does not move
d. disappears
e. moves to longer wavelengths and becomes weaker

4. Light with a frequency below the threshold frequency shines on a metal. If we increase its intensity:

a. still no electrons are ejected
b. electrons are ejected with more kinetic energy
c. electrons are ejected after a short delay
d. more electrons are ejected, all with the same kinetic energy
e. the threshold frequency decreases

5. In the photoelectric effect, the kinetic energy of an ejected electron is:

a. proportional to the intensity of the light
b. $K = h\nu + \Phi$
c. $K = h\nu - \Phi$, where Φ is the work function of the metal
d. the same for all frequencies above the threshold
e. $K = \Phi/h\nu$

6. The energy of a single photon depends on:

a. the intensity of the light
b. the number of photons in the beam
c. the temperature of the source
d. its frequency only, $E = h\nu$

e. the size of the source

7. What do the sharp lines in the spectrum of hydrogen tell us?

a. that the electron spirals into the nucleus
b. that hydrogen emits light at all wavelengths
c. that light is a classical wave
d. that the hydrogen atom has many electrons
e. that the atom can only have certain discrete energies

8. Which of the following is a problem of the Bohr model?

a. it works only for atoms with one electron, and its assumptions have no justification
b. it cannot explain the lines of the hydrogen spectrum
c. it predicts that atoms are not stable
d. it gives the wrong value of the ionization energy of hydrogen
e. it does not use Planck's constant

9. The de Broglie wavelength of a particle with momentum p is:

a. $\lambda = hp$
b. $\lambda = p/h$
c. $\lambda = h\nu$
d. $\lambda = c/p$
e. $\lambda = h/p$

10. Why don't we observe the wave nature of a thrown baseball?

a. because a baseball has no momentum
b. because only charged particles have a wavelength
c. because a baseball moves faster than light
d. because its de Broglie wavelength is far smaller than any object or opening it could interact with
e. because its de Broglie wavelength is too long to be measured

Answers

1.b, 2.c, 3.b, 4.a, 5.c, 6.d, 7.e, 8.a, 9.e, 10.d

CHAPTER 3

The Schrödinger Equation

As we saw in the previous chapter, quantum mechanics was born in two different forms: Heisenberg's matrix mechanics and Schrödinger's wave mechanics. The two are mathematically equivalent, and we are free to start from either one. In this textbook, we start from Schrödinger's version, because it is written in the language of waves and differential equations, which is closer to the physics and mathematics that chemistry students already know. Schrödinger's main idea was simple: if matter behaves as a wave, as de Broglie had proposed, there should be a wave equation that describes it.

3.1 The Time-Independent Schrödinger Equation

The Schrödinger equation cannot be derived from classical physics, since it contains new physics that classical physics does not have. We can, however, make it *plausible*, by combining the mathematical description of a classical wave with de Broglie's relations. We start from the simplest wave that travels through space, the complex plane wave moving along x that we introduced in Sec. 1.3:

$$\psi(x,t) = \exp[i(kx - \omega t)], \tag{3.1}$$

where x is the position, t is time, $k = \frac{2\pi}{\lambda}$ is the wave vector, and $\omega = 2\pi\nu$ is the angular frequency of the wave. If we are not concerned with the time evolution, we can consider uniquely the derivatives of Eq. (3.1) with respect to the location, which are:

$$\begin{aligned} \frac{\partial\psi}{\partial x} &= ik\exp[i(kx-\omega t)] = ik\psi, \\ \frac{\partial^2\psi}{\partial x^2} &= i^2k^2\exp[i(kx-\omega t)] = -k^2\psi, \end{aligned} \tag{3.2}$$

where we have used the fact that $i^2 = -1$.

Assuming that particles behave as waves—as proposed by de Broglie—we can now use the first of de Broglie's equations, Eq. (2.12), to replace $k = \frac{p}{\hbar}$ and obtain:

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2\psi}{\hbar^2}, \tag{3.3}$$

which can be rearranged to:

$$p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2}. \tag{3.4}$$

The total energy associated with a wave moving in space is simply the sum of its kinetic and potential energies:

$$E = \frac{p^2}{2m} + V(x), \tag{3.5}$$

from which we can obtain:

$$p^2 = 2m[E - V(x)], \tag{3.6}$$

which we can then replace into Eq. (3.4) to obtain:

$$2m[E - V(x)]\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2}, \tag{3.7}$$

which can then be rearranged to the famous **time-independent Schrödinger equation (TISEq)**:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi, \tag{3.8}$$

Remember that we did not *prove* this equation: we only showed that it is consistent with a plane wave and with de Broglie's relations. Its real justification is that its predictions agree with experiments, as we will see in the following chapters. Notice also that the equation describes a single particle of mass m. If we want to describe the relative motion of two particles, such as the two atoms in a diatomic molecule or the electron and the proton in a hydrogen atom, we can use the same equation, as long as we replace m with the *reduced mass* of the two particles, $\mu = \frac{m_1 m_2}{m_1+m_2}$.

3.2 What Does the Wave Function Mean?

We now have an equation for the wave function, but we have not yet said what the wave function *is*. Unlike the displacement of a guitar string or the electric field of a light wave, the wave function of a particle is not something that we can measure directly. It is, in general, a complex function, so it cannot itself be a measurable quantity. Its physical meaning was proposed by Max Born in 1926, and it is known as **Born's interpretation**: the square magnitude of the wave function gives the probability of finding the particle at a given position. More precisely, for a particle moving along x:

$$\text{probability of finding the particle between } x \text{ and } x + dx = |\psi(x)|^2\, dx, \quad (3.9)$$

where $|\psi(x)|^2 = \psi^*(x)\psi(x)$ is called the **probability density**. Notice that, even if ψ is complex, $\psi^*\psi$ is always real and never negative, as a probability must be. This is similar to what happens for classical waves (Chapter 1), where the energy carried by a wave depends on the square of its amplitude, and not on the amplitude itself. For this reason, the wave function is sometimes called a *probability amplitude*.

Since the particle must be found somewhere, the probabilities of finding it at all possible positions must add up to one:

$$\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1. \quad (3.10)$$

This requirement is called the **normalization condition**, and a wave function that satisfies it is said to be *normalized*. For a particle moving in three dimensions, the integral runs over all three coordinates, $\int |\psi(\mathbf{r})|^2\, d\mathbf{r} = 1$. If we multiply a solution of the Schrödinger equation by any constant, we still have a solution, so the normalization condition is what fixes the overall size of the wave function. We will see how this works in practice for the particle in a box in Chapter 4.

The probabilistic interpretation is one of the most radical departures of quantum mechanics from classical physics. A classical particle has a definite position at every moment; a quantum particle, instead, is described by a wave function that tells us only how *likely* it is to be found at each position. Born's interpretation tells us how to *use* the wave function, and its predictions have never failed. What the wave function *is*, however, is still debated by physicists and philosophers, and we will come back to this question in Chapter 8.

Example 3.1: Normalizing a wave function

A particle confined between $x = 0$ and $x = a$ is described by $\psi(x) = N\,x(a - x)$ inside this region and $\psi = 0$ outside. Find the normalization constant N.

Step 1: write the normalization condition. Since ψ is real, $|\psi|^2 = \psi^2$:

$$\int_0^a N^2 x^2 (a - x)^2\, dx = 1.$$

Step 2: expand and integrate. $x^2(a - x)^2 = a^2x^2 - 2ax^3 + x^4$, so:

$$\int_0^a \left(a^2x^2 - 2ax^3 + x^4\right) dx = \frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5} = \frac{a^5}{30}.$$

Step 3: solve for N. $N^2\, a^5/30 = 1$, so $N = \sqrt{30/a^5}$.

Example 3.1: Normalizing a wave function *(continued)*

Notice that the units work out: N has units of (length)$^{-5/2}$, so that $|\psi|^2$ has units of (length)$^{-1}$, as a probability per unit length should.

3.3 The Time-Dependent Schrödinger Equation

The argument that we used in the previous section does not work for the time dependence of the wave function. Historically, Schrödinger also published the time-independent equation first, and only later proposed the more general time-dependent one. We will follow the same order, and simply state the time-dependent equation without derivation, as a basic assumption of the theory, whose justification is that its predictions agree with experiments. For a single particle moving in one dimension, the time-dependent Schrödinger equation (TDSEq) is:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{3.11}$$

where $V(x)$ is the potential energy of the system, which we assume does not depend on time. The TISEq is a special case of this equation. To see how, we try a wave function written as the product of a function of position and a function of time, $\psi(x,t) = \psi(x)f(t)$. Replacing it into Eq. (3.11), we obtain:

$$\psi(x)i\hbar\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x), \tag{3.12}$$

which can be rearranged to:

$$\frac{i\hbar}{f(t)}\frac{df(t)}{dt} = \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x). \tag{3.13}$$

The left-hand side of Eq. (3.13) depends only on t, and the right-hand side only on x. The only way for the two to be equal for every value of x and t is for both of them to be equal to the same constant. The right-hand side has the dimensions of energy, so we call this constant E. We have now split one partial differential equation into two ordinary differential equations:

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \tag{3.14}$$

and:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x). \tag{3.15}$$

The second equation is the TISEq that we obtained in the previous section. The first one is easy to solve, giving:

$$f(t) = e^{-iEt/\hbar} \tag{3.16}$$

This function oscillates in time, but its magnitude is always equal to one. Therefore, if the wave function is:

$$\psi(x,t) = \psi(x)\exp\left(\frac{-iEt}{\hbar}\right), \tag{3.17}$$

then $\psi(x,t)$ differs from $\psi(x)$ only by a phase factor that rotates in the complex plane without changing its size. As a consequence, the quantity $|\psi(x,t)|^2$ does not depend on time:

$$|\psi(x,t)|^2 = \psi^*(x,t)\psi(x,t) = \psi^*(x)\exp\left(\frac{iEt}{\hbar}\right)\psi(x)\exp\left(\frac{-iEt}{\hbar}\right) = \psi^*(x)\psi(x). \tag{3.18}$$

Wave functions of the form of Eq. (3.17) are called **stationary states**. As we saw in Sec. 3.2, $|\psi(x,t)|^2$ is a probability density, the quantity that we can measure, so in a stationary state nothing that we can observe changes in time. This does not mean that the particle is standing still, but only that its probability distribution does not change. This is why the solutions of the TISEq are so important: they are the states with a well-defined energy, and they do not change in time. Not every solution of the TDSEq is a stationary state, but every solution can be written as a linear combination (a *superposition*) of stationary states:[1]

$$\psi(\mathbf{r},t) = \sum_i c_i e^{-iE_i t/\hbar}\psi_i(\mathbf{r}). \tag{3.19}$$

3.4 Solution for the Free Particle

We will now show how to solve the time independent portion for the simple system of a particle in motion and not subject to any force. By definition, this free particle does not feel any external force, therefore $V(x) = 0$, and the TISEq is written simply:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x). \tag{3.20}$$

This equation can be rearranged to:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x), \tag{3.21}$$

[1] A similar presentation can be found in Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry notes.

which corresponds to a mathematical problem where the second derivative of a function should be equal to a constant, $-\frac{2mE}{\hbar^2}$, multiplied by the function itself. The most general solution to this problem is the function:

$$\psi(x) = A\exp(ikx) + B\exp(-ikx), \tag{3.22}$$

with A and B arbitrary (complex) constants. The first and second derivatives of this function are:

$$\begin{aligned} \frac{d\psi(x)}{dx} &= ikA\exp(ikx) - ikB\exp(-ikx) \\ \frac{d^2\psi(x)}{dx^2} &= -k^2A\exp(ikx) - k^2B\exp(-ikx) = -k^2\psi(x). \end{aligned} \tag{3.23}$$

Comparing the second derivative in Eq. (3.23) with Eq. (3.21), we immediately see that if we set:

$$k^2 = \frac{2mE}{\hbar^2}, \tag{3.24}$$

we solve the original differential equation. Considering de Broglie's equation, Eq. (2.12), we can replace $k = \frac{p}{\hbar}$, to obtain:

$$E = \frac{k^2\hbar^2}{2m} = \frac{p^2}{2m}, \tag{3.25}$$

which is exactly the classical value of the kinetic energy of a free particle moving in one direction of space. Since the function in Eq. (3.22) solves the Schrödinger equation for the free particle, it is called an *eigenfunction* (or *eigenstate*) of the TISEq. The energy result of Eq. (3.25) is called an *eigenvalue* of the TISEq. Notice that, since k is continuous in the eigenfunction, the energy eigenvalue is also continuous (i.e., all values of E are acceptable).

3.4.1 What does the free-particle solution look like?

Let's take a closer look at one of the solutions in Eq. (3.22), for example the one with $B = 0$, which describes a particle moving to the right with momentum $p = \hbar k$:

$$\psi(x) = A\,e^{ikx} = A\left[\cos(kx) + i\sin(kx)\right]. \tag{3.26}$$

Its real and imaginary parts are a cosine and a sine wave with wavelength $\lambda = 2\pi/k = h/p$, exactly as de Broglie proposed. As we saw in Sec. 3.2, however, the quantity that has a direct physical meaning is not the wave function itself, but its square magnitude, $|\psi(x)|^2$, which gives the probability of finding the particle at position x. For a plane wave, $|\psi(x)|^2 = |A|^2\left[\cos^2(kx) + \sin^2(kx)\right] = |A|^2$, a constant. The plane wave and its probability density are shown in Fig. 3.1.

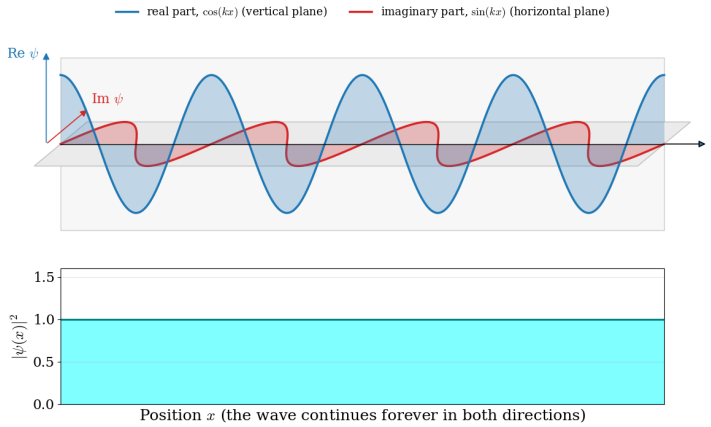


Figure 3.1 Top: a free-particle plane wave, $\psi(x) = e^{ikx}$, with its real part, $\cos(kx)$, in the vertical plane (blue) and its imaginary part, $\sin(kx)$, in a horizontal plane drawn in perspective (red). Bottom: its probability density, which is the same everywhere.

This result is surprising. A particle described by a plane wave has a perfectly well-defined momentum, $p = \hbar k$, but its probability density is the same everywhere: the particle is equally likely to be found at any point in the universe. The plane wave also extends forever in both directions, so the total probability, $\int |\psi|^2 dx$, is infinite, and the wave function cannot be normalized. A real particle, such as an electron shot from an electron gun, is certainly found somewhere in a limited region of space. Plane waves, therefore, are useful mathematical solutions, but they do not describe real particles by themselves.

3.4.2 Wave packets

The way out of this problem comes from the principle of superposition that we discussed for classical waves in Chapter 1. Since the Schrödinger equation is linear, any sum of plane waves with different wave vectors is also a solution. When we add waves with slightly different wavelengths, they interfere constructively in some regions and destructively in others. This is illustrated in Fig. 3.2.

Two waves produce a regular pattern of *beats*, the same effect that musicians use to tune two instruments to the same note. As we add more waves, with wave vectors spread over a range around a central value k_0, the regions of constructive interference get narrower and farther apart. With a continuous distribution of wave vectors, only one region of constructive interference survives, and the waves cancel each other everywhere else. The result is a **wave packet**: a wave that oscillates with wavelength close to $2\pi/k_0$ inside a limited region of space, and is essentially zero outside of it. Mathematically, a wave

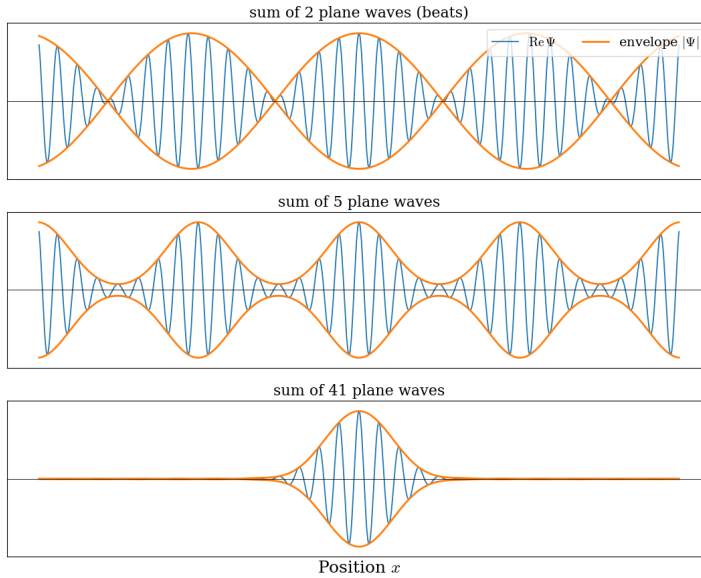


Figure 3.2 Superposition of plane waves with wave vectors close to k_0. Two waves produce a periodic pattern of beats; five waves produce sharper but still repeating bunches; many waves with a smooth distribution of wave vectors produce a single, localized wave packet. The thin line is the real part of the sum, and the thick line is its envelope.

packet is written as a continuous sum (an integral) of plane waves, each with its own amplitude, $\phi(k)$:

$$\Psi(x,t) = \int \phi(k)\, e^{i(kx-\omega(k)t)} dk, \qquad \omega(k) = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}, \tag{3.27}$$

where each plane wave evolves in time with its own frequency, as we saw in Eq. (3.17). Unlike a single plane wave, a wave packet can be normalized, and it describes a particle that is localized in a region of space. A wave packet is the quantum mechanical picture of a free particle such as an electron in a beam.

Wave packets teach us three important lessons:

1. **The price of localization**: to build a packet that is localized in space, we need plane waves with a *range* of wave vectors, and therefore a range of momenta, $p = \hbar k$. The more localized we want the particle to be, the wider the range of momenta that we need, as shown in Fig. 3.3. A plane wave is the extreme case of a perfectly defined momentum and a completely undefined position. A very narrow packet has a well-defined position, but a very uncertain momentum. For the packets in Fig. 3.3, the widths in position, Δx, and in wave vector, Δk, are related by $\Delta x\, \Delta k = \frac{1}{2}$,

or, using $p = \hbar k$, $\Delta x\, \Delta p = \frac{\hbar}{2}$. This is a first glimpse of the Heisenberg uncertainty principle, which we will discuss in Chapter 8.

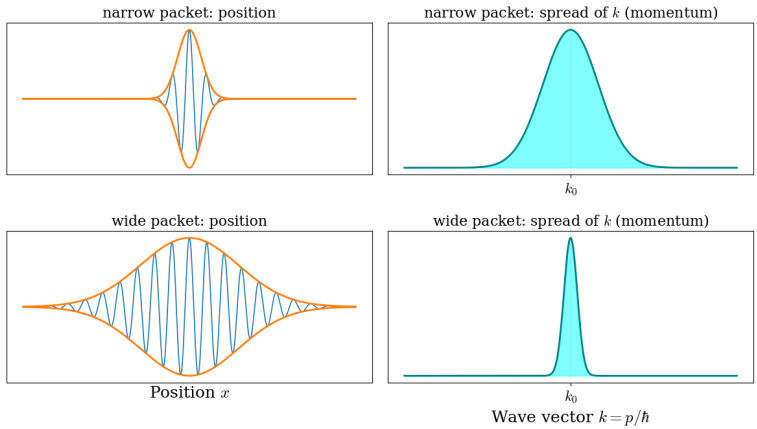


Figure 3.3 A narrow (top) and a wide (bottom) wave packet in position space (left), together with the corresponding distributions of wave vectors, and therefore of momenta (right). The more localized the particle is in space, the broader its distribution of momenta.

2. **Motion**: the wave packet moves, as shown in Fig. 3.4. Its center travels with velocity $v = \frac{d\omega}{dk} = \frac{\hbar k_0}{m} = \frac{p_0}{m}$, which is exactly the velocity of a classical particle with momentum p_0. (This velocity is called the *group velocity*. The individual crests inside the packet move at a different speed, but the packet as a whole, and with it the probability of finding the particle, moves at the classical speed.) This is how classical motion emerges from quantum mechanics: a well-localized wave packet follows the trajectory of a classical particle.

3. **Spreading**: as the packet moves, it also gets wider. Each plane wave in the packet travels at a slightly different speed (faster for larger k, slower for smaller k), so the packet gradually falls apart. For a packet with initial width Δx_0, the width doubles in a time of about $2m\Delta x_0^2/\hbar$. For an electron localized within 1 Å, this time is about 10^{-16} s: free electrons do not stay localized for long. For a baseball localized within one micrometer, it is about 10^{15} years, far longer than the age of the universe. This is why macroscopic objects always appear to be in a definite position, while quantum particles do not.

The wave packet gives us an important lesson that we will meet again many times: in quantum mechanics, a particle with a definite position is a superposition of states with different momenta, and vice versa. The states with a

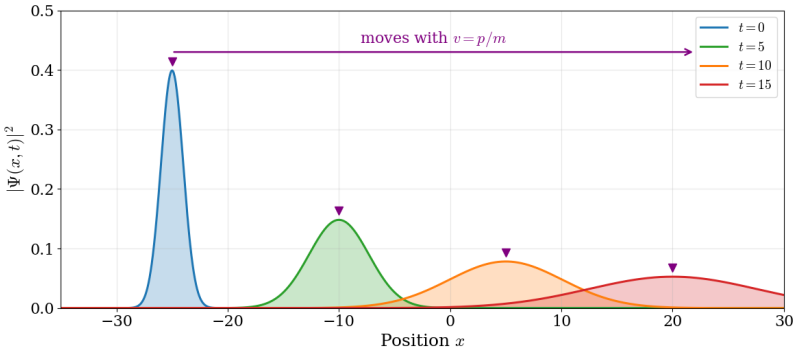


Figure 3.4 Probability density of a free-particle wave packet at four different times (in units where $\hbar = m = 1$). The center of the packet (purple triangles) moves at the classical velocity p/m, while the packet spreads out.

definite energy, the solutions of the TISEq, are stationary and do not move. Motion requires a superposition of different stationary states, as we will see again in Chapter 6.

3.5 Chapter Review

3.5.1 Key Ideas

- The Schrödinger equation, $\hat{H}\psi = E\psi$, cannot be derived from classical physics; it is justified by its agreement with experiments.
- The wave function itself is not observable: $|\psi|^2$ is a probability density (Born's interpretation), and the total probability must be one (normalization).
- Stationary states have a definite energy, and their probability density does not change in time.
- A free particle with a definite momentum is a plane wave, equally likely to be anywhere. Its energy is not quantized.
- A localized particle is a wave packet, a superposition of plane waves with a range of momenta: localization in space requires uncertainty in momentum.

3.5.2 Study Questions

1. **Which of the following is the time-independent Schrödinger equation for a particle in one dimension?**

   a. $-\frac{\hbar^2}{2m}\frac{d\psi}{dx} + V(x)\psi = E\psi$

b. $\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = V(x)$
c. $m\frac{d^2x}{dt^2} = -\frac{dV}{dx}$
d. $\psi = E\,V(x)$
e. $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$

2. How was the Schrödinger equation obtained?

a. it cannot be derived from classical physics; we can make it plausible, and it is justified by its agreement with experiments
b. it was derived from Newton's equation
c. it was derived from Coulomb's law
d. it was obtained by measuring wave functions
e. it was derived from the Bohr model

3. According to Born's interpretation, $|\psi(x)|^2dx$ is:

a. the energy of the particle at x
b. the charge of the particle
c. the fraction of the particle located at x
d. the probability of finding the particle between x and $x + dx$
e. the velocity of the particle at x

4. Why must a wave function be normalized, $\int |\psi|^2dx = 1$?

a. because the energy must be positive
b. because the particle must be found somewhere
c. because the wave function must be real
d. because the particle cannot move
e. because ψ must be zero everywhere

5. Why do we always use $|\psi|^2 = \psi^*\psi$, and not ψ itself, to compute probabilities?

a. because ψ can be complex, while $\psi^*\psi$ is always real and never negative
b. because ψ is always negative
c. because $\psi^*\psi$ is always larger than ψ
d. because ψ has no units
e. because $\psi^*\psi$ is easier to differentiate

6. For a stationary state, what does not change in time?

a. the wave function $\psi(x,t)$
b. the phase of the wave function
c. the probability density $|\psi(x,t)|^2$
d. the real part of the wave function
e. nothing: everything changes in time

7. A stationary state with energy E evolves in time by multiplication with which factor?

a. $e^{-Et/\hbar}$
b. $\cos(Et)$

c. $e^{iEx/\hbar}$
d. $e^{-iEt/\hbar}$
e. $E\,t$

8. The energy of a free particle is:

a. $E = \frac{p^2}{2m}$, but only integer multiples of $h\nu$
b. $E = \frac{p^2}{2m}$, and it can take any non-negative value
c. always zero
d. $E = mc^2$
e. $E = \frac{n^2h^2}{8ma^2}$

9. A particle described by a single plane wave, $\psi = e^{ikx}$, has:

a. a perfectly defined position, but undefined momentum
b. a perfectly defined position and momentum
c. zero momentum
d. a probability density that oscillates with x
e. a perfectly defined momentum, but the same probability of being found anywhere

10. To describe a particle localized in a small region of space, we need:

a. a single plane wave with a very large momentum
b. a single plane wave with zero momentum
c. a wave packet, a superposition of plane waves with a range of momenta
d. a wave function equal to zero everywhere
e. a classical trajectory

Answers

1.e, 2.a, 3.d, 4.b, 5.a, 6.c, 7.d, 8.b, 9.e, 10.c

CHAPTER 4

Analytically Solvable Models

The TISEq can be solved analytically only in a few special cases. We saw one of those special cases, the free particle, at the end of the previous chapter. In this chapter, we will analyze four others. Luckily, we can use these solutions to explain most of the effects in chemistry since we can combine them to describe the hydrogen atom upon which we can build more complex chemical systems, as we will show in the next chapters.

4.1 The Particle in a Box

We can start by considering a particle constrained to move in a single dimension, under the influence of a potential $V(x)$ which is zero for $0 \leq x \leq a$ and infinite elsewhere. Since the wavefunction is not allowed to become infinite, it must have a value of zero where $V(x)$ is infinite, so $\psi(x)$ is nonzero only within $[0, a]$. The Schrödinger equation is thus:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x) \qquad 0 \leq x \leq a. \tag{4.1}$$

In other words, inside the box $\psi(x)$ describes a free particle, but outside the box $\psi(x) = 0$. Since the Schrödinger equation involves derivatives, the function that solves it, $\psi(x)$, must be everywhere continuous. This fact means that the value of the wave function at the two extremes must be equal to zero:

$$\psi(0) = \psi(a) = 0. \tag{4.2}$$

Inside the box the solution will be the same as for the free particle:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{4.3}$$

where A and B are constants. Using the two constraints in Eq. (4.2), we get at $x = 0$:

$$\psi(0) = A + B = 0 \implies B = -A \tag{4.4}$$

And at $x = a$:

$$\psi(a) = Ae^{ika} + Be^{-ika} = 0. \tag{4.5}$$

Replacing Eq. (4.4) into Eq. (4.5) gives:

$$Ae^{ika} - Ae^{-ika} = 0 \tag{4.6}$$

which is then easily simplified into:

$$\begin{aligned} e^{ika} &= e^{-ika} \\ e^{i2ka} &= 1. \end{aligned} \tag{4.7}$$

This equation is solved when:

$$2ka = 2n\pi, \tag{4.8}$$

which is trivially solved for $n = 0$, giving either $k = 0$ or $a = 0$. This trivial solution is completely uninteresting, since it describes no particles in no boxes. A more interesting set of solutions however, are those for which:

$$k_n = \frac{n\pi}{a} \quad (n = 1, 2, 3, \dots, \infty), \tag{4.9}$$

which represents an infinite set of functions, $\psi_n(x)$, determined by a positive integer number n, called *quantum number*. Since these functions solve the TISEq, they are also called *eigenfunctions*, but they are not a continuous set, unlike in the previous case.

Using Eq. (4.4), the wave functions become:

$$\psi_n(x) = A\left(e^{i\frac{n\pi x}{a}} - e^{-i\frac{n\pi x}{a}}\right), \tag{4.10}$$

and using Euler's formula $\left(\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}\right)$, we get:

$$\psi_n(x) = 2iA\frac{e^{i\frac{n\pi x}{a}} - e^{-i\frac{n\pi x}{a}}}{2i} = C\sin\left(\frac{n\pi x}{a}\right) \tag{4.11}$$

where $C = 2iA$ is a complex constant.

To calculate the energy eigenvalues, we can replace Eq. (4.11) into Eq. (4.1), to obtain:

$$E_n = n^2\frac{\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \quad (n = 1, 2, \dots, \infty). \tag{4.12}$$

Eq. (4.12) tells us a few interesting things. First, although there is an infinite number of acceptable values of the energy (eigenvalues), these values are not continuous. Second, the lowest value of the energy is not zero, and it depends on the size of the box, a, since:

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} \neq 0. \tag{4.13}$$

This value is called *zero-point energy (ZPE)*, and is a purely quantum mechanical effect. Notice that we have not determined the constant C yet. We will do so in a moment, using the normalization condition of Chapter 3.

The most profound physical insight from the particle in a box solution comes from applying Born's interpretation of the wave function (Sec. 3.2). The probability of finding the particle in state n between positions x and $x + dx$ is $|\psi_n(x)|^2 dx$, so the probability densities $|\psi_n(x)|^2$ tell us where the particle is likely to be found inside the box.

Since the particle must be somewhere inside the box, the probability of finding it anywhere between $x = 0$ and $x = a$ must be equal to one. This is the normalization condition, Eq. (3.10), with the integral limited to the inside of the box (outside, the wave function is zero), and it is exactly what we need to determine the constant C:

$$\int_0^a |\psi_n(x)|^2 \, dx = |C|^2 \int_0^a \sin^2\Big(\frac{n\pi x}{a}\Big) dx = 1. \tag{4.14}$$

Using the trigonometric identity $\sin^2\theta = \frac{1-\cos(2\theta)}{2}$, the integral becomes:

$$\begin{aligned} \int_0^a \sin^2\Big(\frac{n\pi x}{a}\Big) dx &= \frac{1}{2}\int_0^a dx - \frac{1}{2}\int_0^a \cos\Big(\frac{2n\pi x}{a}\Big) dx \\ &= \frac{a}{2} - \frac{a}{4n\pi}\Big[\sin\Big(\frac{2n\pi x}{a}\Big)\Big]_0^a = \frac{a}{2}, \end{aligned} \tag{4.15}$$

since the sine vanishes at both limits. Replacing this result into Eq. (4.14) gives $|C|^2\frac{a}{2} = 1$, or $|C| = \sqrt{\frac{2}{a}}$. Only the magnitude of C is fixed by this condition, and we can choose it to be real and positive. The normalized eigenfunctions of the particle in a box are therefore:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\Big(\frac{n\pi x}{a}\Big) \quad (n = 1, 2, \ldots, \infty). \tag{4.16}$$

Notice that the normalization constant is the same for every n, and that it depends only on the size of the box: the larger the box, the more the probability is spread out, and the smaller the amplitude of the wave function. The same condition applies to any system: since the probability of finding the particle somewhere in space must be one, every acceptable wave function must satisfy $\int |\psi|^2 \, d\tau = 1$, where the integral runs over all the coordinates of the system. The probabilistic interpretation also puts some restrictions on what an acceptable wave function can look like. It must be *single-valued*, since the probability of finding the particle at a given point cannot have two different values. It must be *continuous* (and, where the potential is finite, so must be its first derivative), since the TISEq contains its second derivative. And it must be *finite* everywhere, and go to zero at large distances fast enough for the normalization integral to exist. We already used these conditions when we required the wave function to vanish at the walls of the box, and we will use them again for every system in this textbook.

For the particle in a box eigenfunctions in Eq. (4.11), the probability density is:

$$|\psi_n(x)|^2 = |C|^2 \sin^2\left(\frac{n\pi x}{a}\right). \tag{4.17}$$

This function tells us where the particle is *most likely* to be found if we measure its position.

4.1.1 Wave function analysis

The main results of the solution of the TISEq for the particle in a box are reported in Fig. 4.1. In this picture, the first five eigenfunctions are plotted together with their probability densities and spaced according to their energy levels. The non-trivial nodes are also reported.

Let's look at Fig. 4.1 and see what it tells us.

1. **Standing waves.** The wave functions are exactly the standing waves of a guitar string (Eq. (1.25) in Chapter 1). This is not a coincidence: in both cases, a wave is confined between two points where it must vanish, and only the waves that "fit" between them are allowed. For the string, this quantizes the frequency. For the particle, it quantizes the energy.
2. **The levels get farther apart.** Since $E_n \propto n^2$, the gap between two neighboring levels, $E_{n+1} - E_n \propto 2n + 1$, grows with n. The lowest levels are the closest together.
3. **Nodes.** The wave function ψ_n is zero, and so is the probability of finding the particle, at $n - 1$ points *inside* the box (the purple dots in the figure). The walls are also zero points, but they are imposed by the boundary conditions, so we do not count them as nodes. The rule "more energy, more nodes" is one that we will meet again in every system in this book.
4. **Where is the particle?** The probability density, $|\psi_n|^2$, is largest halfway between the nodes. In the ground state, the particle is most likely to be found at the center of the box, $x = a/2$. In the first excited state, instead, the center is a node: the particle is *never* found there, and it is most likely to be found at $x = a/4$ or $x = 3a/4$.

This last point is very different from what we would expect for a classical particle. A classical ball bouncing between the walls at constant speed spends the same amount of time everywhere in the box, so all positions are equally likely. Where does this classical picture come back? Using the identity $\sin^2\theta = \frac{1-\cos(2\theta)}{2}$, we can rewrite the probability density as:

$$|\psi_n(x)|^2 = \frac{|C|^2}{2}\left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right], \tag{4.18}$$

a uniform value, $|C|^2/2$, plus a wiggle whose wavelength gets shorter as n increases. For very large n the wiggles become so close together that no experiment could resolve them, and on average the particle is equally likely to be anywhere: the classical result.

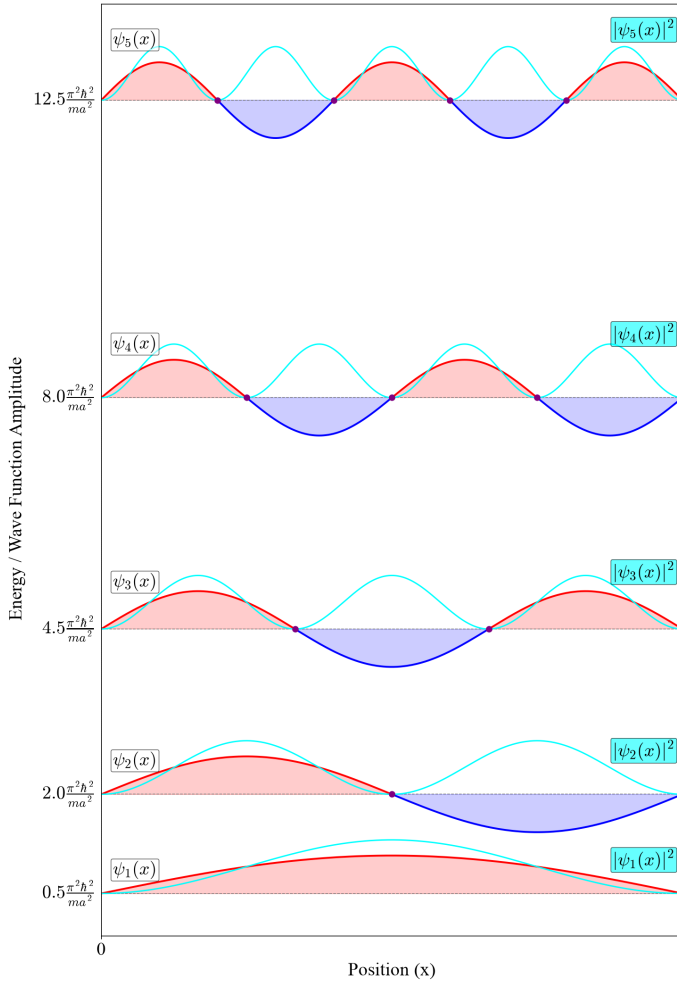


Figure 4.1 The first five eigenfunctions and energy levels of a particle confined inside a box by walls with infinite potential energy. The nodes of the wave functions are reported as purple dots. The probability density for each level is also plotted in cyan.

Example 4.1: An electron in a 1 nm box

An electron is confined in a one-dimensional box of length $a = 1.0$ nm, roughly the length of a conjugated molecule such as hexatriene. What are its two lowest energies, and what wavelength of light would it absorb going from $n = 1$ to $n = 2$?

Step 1: the ground state. With $m_e = 9.109 \times 10^{-31}$ kg:

Example 4.1: An electron in a 1 nm box *(continued)*

$$E_1 = \frac{h^2}{8m_e a^2} = \frac{(6.626\times10^{-34}\ \text{J s})^2}{8(9.109\times10^{-31}\ \text{kg})(1.0\times10^{-9}\ \text{m})^2} = 6.02\times10^{-20}\ \text{J} = 0.376\ \text{eV}.$$

Step 2: the first excited state. Since $E_n \propto n^2$, $E_2 = 4E_1 = 1.50$ eV.
Step 3: the transition. $\Delta E = E_2 - E_1 = 3E_1 = 1.13$ eV, and the corresponding wavelength is:

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ \text{J s})(2.998\times10^{8}\ \text{m/s})}{3\times6.02\times10^{-20}\ \text{J}} = 1.10\times10^{-6}\ \text{m} = 1100\ \text{nm},$$

in the near infrared. Notice how strongly the result depends on the size of the box: since $E \propto 1/a^2$, a box twice as long would absorb at a wavelength four times longer.

4.2 The Particle in a Three-Dimensional Box

Real particles move in three dimensions, so let's briefly extend the particle in a box to a rectangular box with sides a, b, and c, with the potential equal to zero inside and infinite outside. The Hamiltonian contains the kinetic energy along the three directions:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\,\psi(x,y,z). \tag{4.19}$$

Each term of the Hamiltonian acts on only one coordinate. This suggests that we try a wave function written as a product of three functions, each depending on one coordinate only, $\psi(x,y,z) = X(x)Y(y)Z(z)$. Replacing it in Eq. (4.19) and dividing by XYZ, the equation splits into three independent one-dimensional equations, one for each direction, each identical to the one that we just solved. This technique is called **separation of variables**, and we will use it again for the particle on a sphere and for the hydrogen atom. The solutions are products of the one-dimensional solutions, and the energies are sums of the one-dimensional energies:

$$\begin{aligned}\psi_{n_x n_y n_z} &= \sqrt{\frac{8}{abc}}\,\sin\frac{n_x\pi x}{a}\,\sin\frac{n_y\pi y}{b}\,\sin\frac{n_z\pi z}{c},\\ E_{n_x n_y n_z} &= \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right),\end{aligned} \tag{4.20}$$

with $n_x, n_y, n_z = 1, 2, 3, \ldots$ Notice that we now need *three* quantum numbers, one for each dimension of the motion.

Something new happens when the box is a cube ($a = b = c$). The energy becomes $E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$, and different states can have the same energy. The ground state, $(1,1,1)$, has $E = 3\frac{h^2}{8ma^2}$ and is unique, but the three states $(2,1,1)$, $(1,2,1)$, and $(1,1,2)$ all have $E = 6\frac{h^2}{8ma^2}$. Levels shared by more than one state are called **degenerate**, and the number of states with the same energy is the **degeneracy** of the level (three, in this case). Degeneracy is a consequence of symmetry: the three states have the same shape, just oriented along the three different axes of the cube, and since the three directions of a cube are equivalent, they must have the same energy. If we stretch the box along one direction, the symmetry is broken and the degeneracy disappears. We will meet degenerate levels again in all the systems that follow, starting from the particle on a ring.

4.3 The Particle on a Ring

We can extend our understanding of confined quantum systems by considering a particle constrained to move in a circle of fixed radius r. This model, known as the particle on a ring (or particle in a ring), represents the rotational motion of a particle about a fixed axis.

While this system seems to be a 2-dimensional problem, in reality it is closely related to the particle in a box, with the two endpoints of the box wrapping around themselves and touching each other. However, rather than working with a single linear coordinate, x, we can use the set of polar coordinates, (r, ϕ), where only the azimuthal angle ϕ varies (with $0 \leq \phi \leq 2\pi$). The radial coordinate r is held constant. The wave function $\psi(x)$ can be easily written as $\psi(\phi)$ by using $\phi = x/r$. Thus the second derivative becomes:

$$\frac{d^2\psi(x)}{dx^2} = \frac{1}{r^2}\frac{d^2\psi(\phi)}{d\phi^2}, \tag{4.21}$$

and the time-independent Schrödinger equation can be obtained directly from Eq. (4.1) as:

$$-\frac{\hbar^2}{2mr^2}\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi). \tag{4.22}$$

For a classical particle rotating about the origin in the xy-plane, its kinetic energy is expressed as:

$$E = \frac{L_z^2}{2I}, \tag{4.23}$$

where $I = mr^2$ is the moment of inertia of the particle about the axis of rotation and L_z is the component of the angular momentum along the z axis, perpendicular to the rotation plane. The TISEq can then be rewritten as:

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi), \tag{4.24}$$

where it is now evident that the energy of the quantum mechanical system is directly related to the component L_z of the angular momentum, as in the classical case. Since the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, $\mathbf{L}$ must point in the z-direction when $\mathbf{r}$ and $\mathbf{p}$ both lie on the xy-plane.

The boundary condition for the particle in a ring comes from the requirement that the wavefunction must be single-valued, meaning that as we traverse the ring from angle $\phi = 0$ to $\phi = 2\pi$, we must return to the same value:

$$\psi(\phi) = \psi(\phi + 2\pi) \tag{4.25}$$

Similarly to the previous cases, the general solution to the TISEq above is:

$$\psi(\phi) = Ae^{ik\phi} + Be^{-ik\phi} \tag{4.26}$$

where A and B are constants. Applying the single-valuedness boundary condition requires that $e^{ik\cdot 2\pi} = 1$, which is satisfied only when $k = m_\ell$, where m_ℓ is an integer (positive, negative, or zero) called *azimuthal quantum number*. The set of acceptable solutions is therefore:

$$\psi_{m_\ell}(\phi) = Ae^{im_\ell\phi} \quad (m_\ell = 0, \pm 1, \pm 2, \dots, \pm\infty). \tag{4.27}$$

The $m_\ell = 0$ solution is a constant function with zero energy (unlike the particle in a box, the particle on a ring has no zero-point energy), while the remaining solutions represent rotations in the counter-clockwise (positive solutions, L_z pointing upwards) and clockwise (negative solutions, L_z pointing downwards) directions, as seen from above the xy-plane.

To find the energy eigenvalues, we substitute the eigenfunction back into the Schrödinger equation. Taking the second derivative of $\psi_{m_\ell}(\phi)$:

$$\frac{d^2\psi_{m_\ell}}{d\phi^2} = -m_\ell^2 Ae^{im_\ell\phi} = -m_\ell^2\psi_{m_\ell}(\phi) \tag{4.28}$$

Replacing this derivative in the Schrödinger equation, we obtain:

$$-\frac{\hbar^2}{2mr^2}(-m_\ell^2)\psi_{m_\ell} = E\psi_{m_\ell}, \tag{4.29}$$

and the final energy levels, as:

$$E_{m_\ell} = \frac{\hbar^2 m_\ell^2}{2mr^2} = \frac{\hbar^2 m_\ell^2}{2I}. \tag{4.30}$$

The energy levels of the particle on a ring are plotted for the first five levels in Fig. 4.2.

Using the definition of kinetic energy for a classical system in Eq. (4.23), we get:

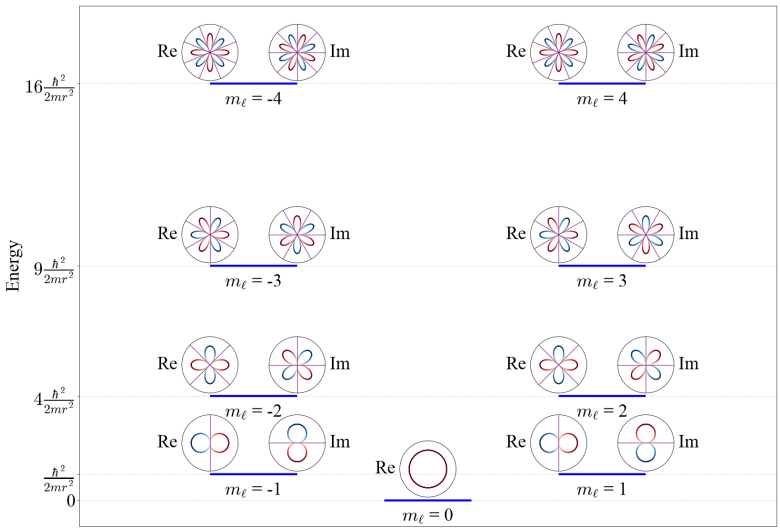


Figure 4.2 Energy level diagram and degeneracy pattern for the particle-on-a-ring. Both the real and imaginary parts of the wave functions of the first five energy levels are represented using polar plots (see text for explanation), with nodes reported as purple diameters of the physical ring (black circle).

$$\frac{L_z^2}{2I} = \frac{\hbar^2 m_\ell^2}{2I}, \tag{4.31}$$

which implies that the angular momentum along the z-axis is quantized in units of $\hbar$ as:

$$L_z = \hbar m_\ell \quad (m_\ell = 0, \pm 1, \pm 2, \dots, \pm\infty). \tag{4.32}$$

A rotating charged particle orbiting the ring generates a magnetic moment $\mu \propto \mathbf{L}$. Thus Eq. (4.32), which quantizes L_z, explains why m_ℓ is called the **magnetic quantum number**. Several important observations can be made from these results. First, the energy eigenvalues form a discrete set, as expected for a confined system. Second, except for the ground state ($m_\ell = 0$), each energy level is doubly degenerate: the states with m_ℓ and $-m_\ell$ have the same energy. This makes physical sense because rotation in the positive and negative directions (counter-clockwise and clockwise) should have the same energy. Third, the energy does not depend on the sign of m_ℓ, which is a consequence of the fact that energy depends on L_z^2, and $(-m_\ell)^2 = (m_\ell)^2$. This is the first instance we have seen of a degeneracy arising from the symmetry of the system itself (rotational symmetry).

4.3.1 Wave function analysis

The eigenfunctions in Eq. (4.27) are complex, and this makes them harder to picture than the sines of the particle in a box. Let's start from the most important property, the probability density:

$$|\psi_{m_\ell}(\phi)|^2 = \psi^*_{m_\ell}\psi_{m_\ell} = \frac{1}{2\pi}e^{-im_\ell\phi}e^{im_\ell\phi} = \frac{1}{2\pi}, \tag{4.33}$$

which is the same everywhere on the ring. In other words, a particle with a definite angular momentum is equally likely to be found anywhere on the ring. This makes sense: if the particle has no preferred position, it has no reason to prefer one point of the ring over another. Notice also that, since $|\psi|^2$ is never zero, **the wave function itself has no nodes**.

To see what the wave functions look like, we need to draw their real and imaginary parts separately, $\frac{1}{\sqrt{2\pi}}\cos(m_\ell\phi)$ and $\frac{1}{\sqrt{2\pi}}\sin(m_\ell\phi)$. The particle moves along a circle, so the most natural picture draws each part as a height above or below the ring, as in Fig. 4.3. Going once around the ring, each part oscillates $|m_\ell|$ times, and it crosses zero $2|m_\ell|$ times. These zero crossings are the nodes of the *real and imaginary parts*. They are not points where the particle cannot be found, since where one part is zero the other one is not.

The same information can be shown as a color map on the ring, seen from above (Fig. 4.4), with red for positive values and blue for negative ones, or as a polar plot (Fig. 4.5), where the distance from the center is the value of the function at each angle. Polar plots look a lot like the orbital pictures of general chemistry, so let's be careful: the "lobes" are not regions where the particle is more likely to be. The particle is always on the ring, and it is equally likely to be anywhere on it. The lobes are just another way of drawing how the real and imaginary parts change with the angle.

4.4 The Particle on a Sphere

Let's now move from a circle to the surface of a sphere: a particle free to move anywhere on a sphere of radius r, but never closer to or farther from the center. This model describes, for example, a rotating diatomic molecule (the *rigid rotor*, two masses at a fixed distance, which we will use in Chapter 13), and, as we will see in the next chapter, it gives the angular part of the hydrogen atom.

On a sphere, the natural coordinates are two angles: θ, measured down from the north pole ($0 \le \theta \le \pi$), and ϕ, measured around the z axis ($0 \le \phi < 2\pi$), exactly as on the ring (spherical coordinates are reviewed in Sec. A.4). Since r is fixed, only the angular part of the kinetic energy remains, and the TISEq is:

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta,\phi) = E\psi(\theta,\phi), \tag{4.34}$$

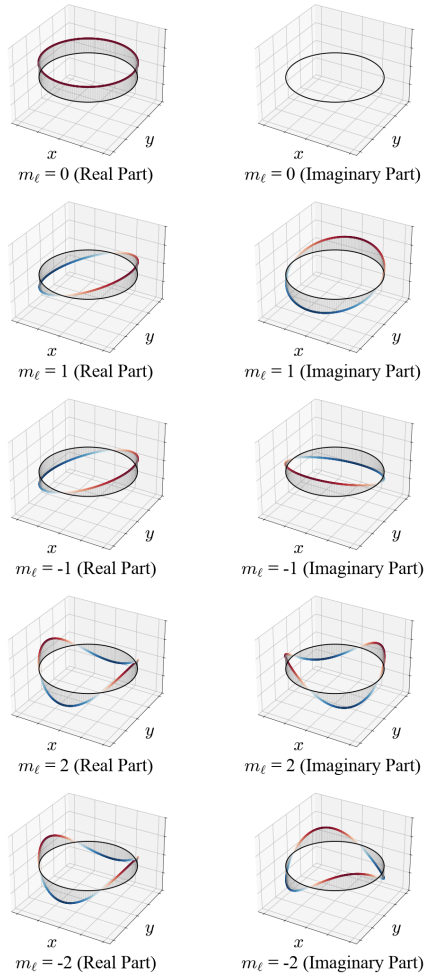


Figure 4.3 Real (left) and imaginary (right) parts of the particle-on-a-ring wave functions for $m_\ell = 0, \pm 1, \pm 2$, drawn as heights above and below the ring (black circle).

where $I = \mu r^2$ is the moment of inertia, as for the ring. This equation looks scary, but we do not need to solve it in detail to understand its solutions. The term in ϕ is the same as for the particle on a ring, so the dependence on ϕ is again $e^{im_\ell \phi}$. Solving for the dependence on θ takes more work, and gives polynomials in $\cos\theta$ and $\sin\theta$, called *associated Legendre polynomials*, $P_\ell^{|m_\ell|}$. The complete solutions are called **spherical harmonics**:

$$Y_\ell^{m_\ell}(\theta, \phi) = N P_\ell^{|m_\ell|}(\cos\theta)\, e^{im_\ell \phi}, \tag{4.35}$$

with N a normalization constant, and the energies are:

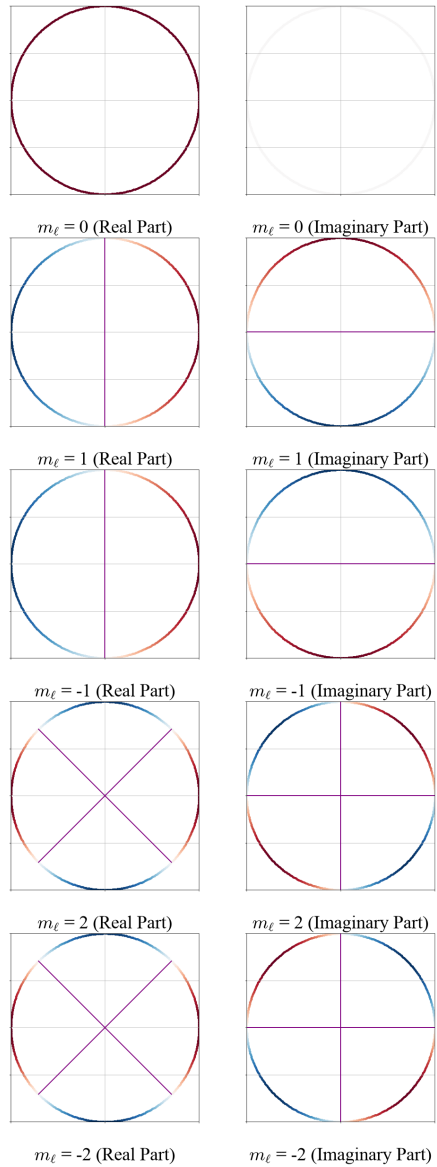


Figure 4.4 The same wave functions as in Fig. 4.3, seen from above as color maps on the ring (red: positive, blue: negative, white: zero).

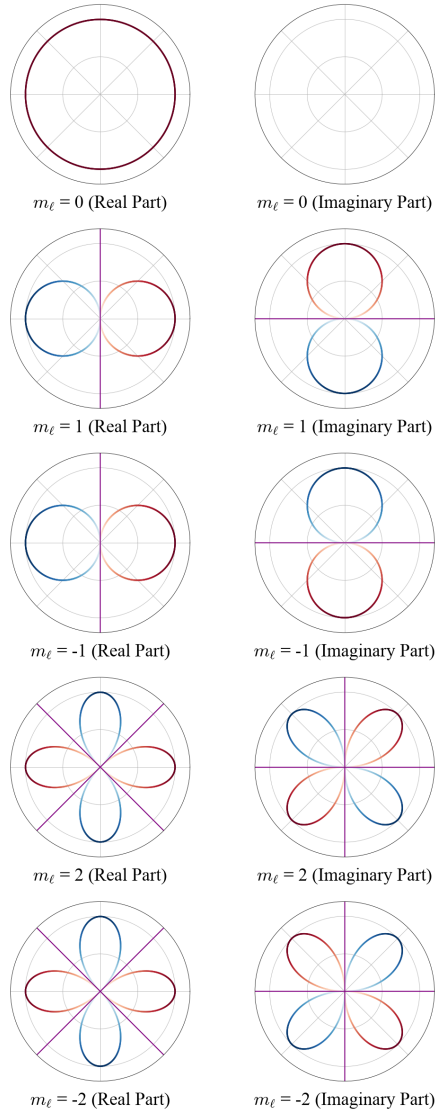


Figure 4.5 Polar plots of the real (left) and imaginary (right) parts of the particle-on-a-ring wave functions: the distance from the center is the value of each part at the angle ϕ. The lobes are not regions of higher probability: $|\psi|^2$ is the same everywhere on the ring.

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \quad (\ell = 0, 1, 2, \ldots). \tag{4.36}$$

Two things are new compared with the ring:

1. **Two quantum numbers.** The particle on a sphere has two degrees of freedom, so it needs two quantum numbers: $\ell = 0, 1, 2, \ldots$ and $m_\ell = -\ell, \ldots, +\ell$. The first one fixes the *magnitude* of the angular momentum, $|\mathbf{L}| = \hbar\sqrt{\ell(\ell+1)}$, and therefore the energy. The second one fixes its *component along z*, $L_z = m_\ell\hbar$, as for the ring.
2. **Degeneracy.** The energy depends only on ℓ. Since the sphere looks the same in every direction, the energy cannot depend on how the angular momentum is oriented, that is, on m_ℓ (we will come back to this idea in Sec. 7.4). Each level is therefore $(2\ell+1)$-fold degenerate, as shown in Fig. 4.6.

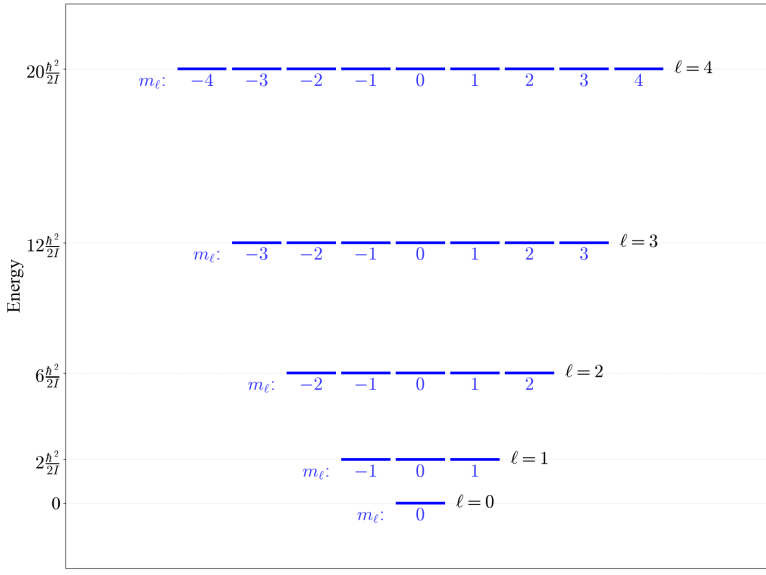


Figure 4.6 Energy level diagram and degeneracy pattern for the particle-on-a-sphere.

4.4.1 Wave function analysis

The spherical harmonics are simple functions of the angles. Those for the first three levels, $\ell = 0, 1, 2$, are listed in the box below, each written in two ways: with the angles θ and ϕ, and with the Cartesian coordinates x, y, z (on a sphere of radius r).

Details: the spherical harmonics for $\ell = 0, 1, 2$

$\ell = 0$:

$$Y_0^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}.$$

$\ell = 1$:

$$Y_1^{-1}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\, e^{-i\phi}\sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\frac{x-iy}{r},$$
$$Y_1^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\frac{z}{r},$$
$$Y_1^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\, e^{i\phi}\sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\frac{x+iy}{r}.$$

$\ell = 2$:

$$Y_2^{-2}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\, e^{-2i\phi}\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\frac{(x-iy)^2}{r^2},$$
$$Y_2^{-1}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\, e^{-i\phi}\sin\theta\cos\theta = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\frac{(x-iy)z}{r^2},$$
$$Y_2^0(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3\cos^2\theta - 1) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,\frac{3z^2 - r^2}{r^2},$$
$$Y_2^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\, e^{i\phi}\sin\theta\cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\frac{(x+iy)z}{r^2},$$
$$Y_2^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\, e^{2i\phi}\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\frac{(x+iy)^2}{r^2}.$$

As for the ring, the functions with $m_\ell \neq 0$ are complex, so we draw their real and imaginary parts separately. The most faithful picture is a color map on the sphere itself (Fig. 4.7 for the real parts and Fig. 4.8 for the imaginary parts): red where the function is positive, blue where it is negative, and white where it is zero. These zero lines are the angular nodes. Each real or imaginary part has ℓ of them, the same rule "more energy, more nodes" that we found for the box and the ring.

The probability of finding the particle at each point of the sphere is $|Y_\ell^{m_\ell}|^2$, shown in Fig. 4.9. Unlike the ring, this probability is **not** uniform. The formulas in the box above make this easy to see:

- Y_0^0 is a constant, so the particle is equally likely to be anywhere on the sphere.
- $|Y_1^0|^2 \propto \cos^2\theta$ is largest at the poles and zero on the equator.
- $|Y_1^{\pm 1}|^2 \propto \sin^2\theta$ is largest on the equator and zero at the poles. The two functions with $+1$ and -1 have exactly the same probability density:

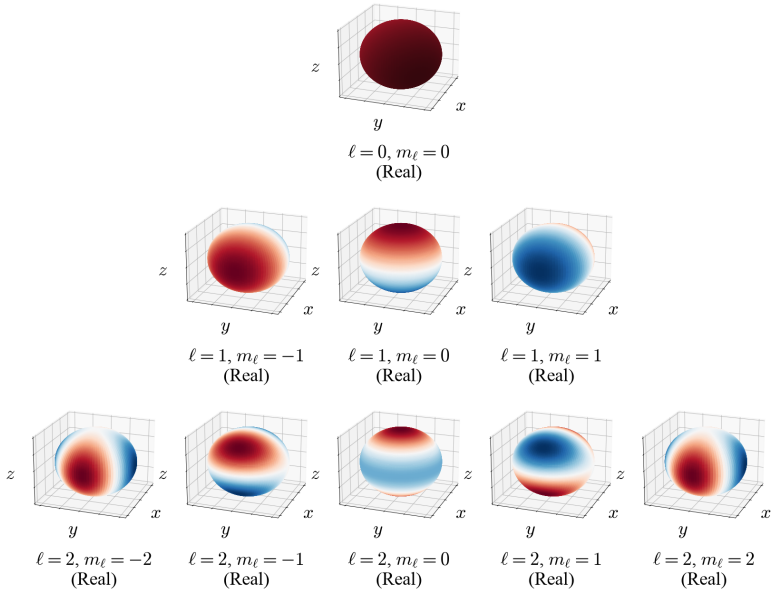


Figure 4.7 Real parts of the spherical harmonics for $\ell = 0, 1, 2$, as color maps on the sphere (red: positive, blue: negative, white: nodes).

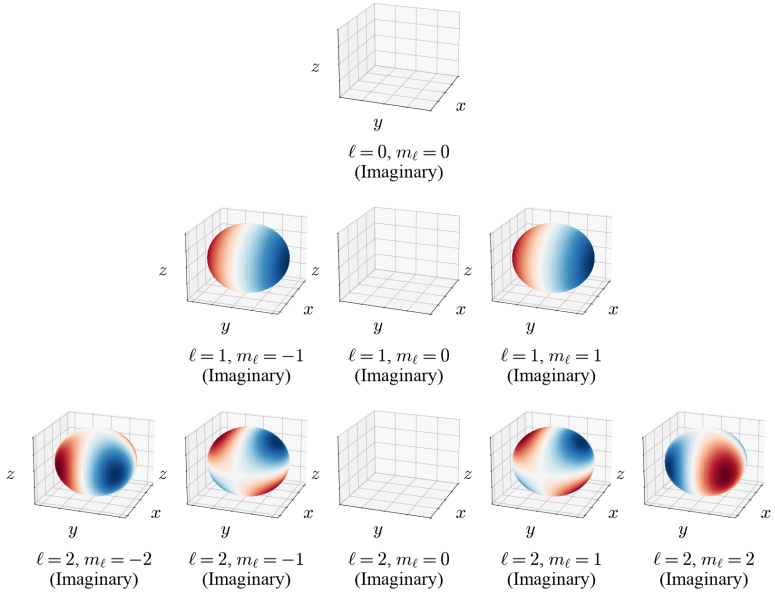


Figure 4.8 Imaginary parts of the spherical harmonics for $\ell = 0, 1, 2$, as color maps on the sphere (red: positive, blue: negative, white: nodes).

they differ only in the direction of rotation around z, counterclockwise or clockwise, as for the ring.

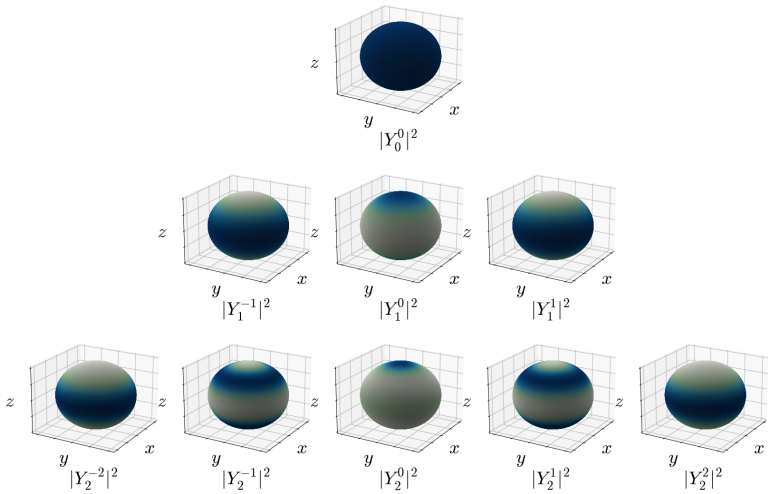


Figure 4.9 Probability density $|Y_\ell^{m_\ell}|^2$ on the sphere (darker: higher probability).

Finally, the spherical harmonics are often drawn as in Fig. 4.10 and Fig. 4.11: each point of the sphere is pushed outward by an amount proportional to the absolute value of the real (or imaginary) part, and colored by its sign. These are the three-dimensional versions of the polar plots of the ring, and they show the nodes as flat planes (or cones, as for Y_2^0). They also look very much like the "orbital pictures" of general chemistry, so the same warning applies here: **the lobes are not where the particle is.** The particle is always on the surface of the sphere. The lobes are just a way of drawing the angular function, and their size has nothing to do with the size of anything physical. We will meet the same warning again, and for the same reason, when we discuss the orbitals of the hydrogen atom in Chapter 5.

4.5 The Harmonic Oscillator

Our last model is a particle of mass μ attached to a spring. When the particle is displaced by x from its equilibrium position, the spring pulls it back with a force proportional to the displacement, $F = -kx$ (Hooke's law), where k is the *force constant*: the stiffer the spring, the larger k. The corresponding potential energy is:

$$V(x) = -\int (-kx)\,dx = \frac{1}{2}kx^2, \tag{4.37}$$

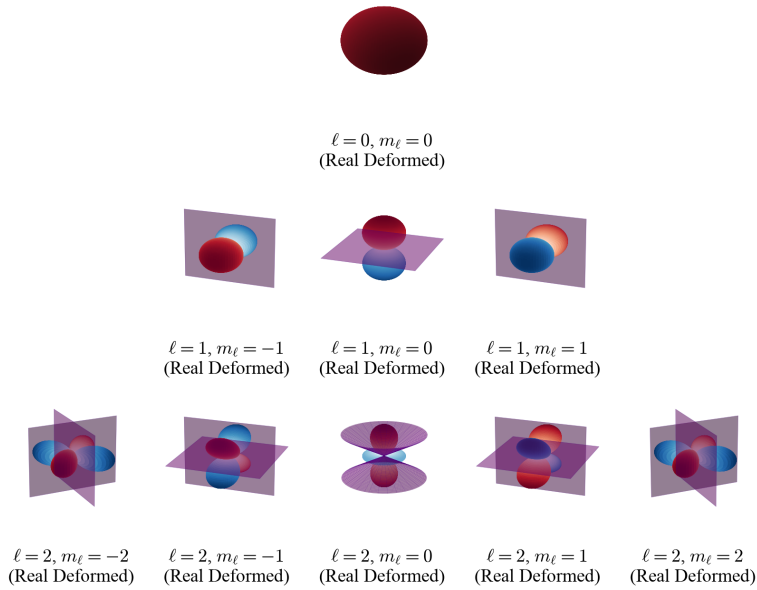


Figure 4.10 Real parts of the spherical harmonics drawn as deformed spheres: the distance from the center is proportional to the absolute value of the function, the color gives its sign, and the nodal planes and cones are shown in purple. The lobes do not represent where the particle is: it is always on the surface of the sphere.

where we have chosen $V = 0$ at the equilibrium position. This simple parabola is more important than it looks: close to the bottom of *any* potential energy well, the potential looks like a parabola. This is why the harmonic oscillator is the starting point for describing the vibrations of molecules (Chapter 10 and Chapter 13), where μ is the reduced mass of the vibrating atoms. The TISEq is:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x). \tag{4.38}$$

We will not solve this equation step by step, but we can understand the form of its solutions. Far from the center, the potential grows very quickly, and the wave function must die off quickly; the function that does this is a Gaussian, $e^{-\alpha x^2/2}$. Near the center, the wave function can oscillate, and the oscillations are described by a polynomial. The solutions are:

$$\psi_n(x) = N_n\, H_n\!\left(\sqrt{\alpha}\, x\right) e^{-\alpha x^2/2} \quad (n = 0, 1, 2, \ldots), \tag{4.39}$$

where $\alpha = \sqrt{k\mu}/\hbar$ sets the width of the Gaussian, N_n is a normalization constant, and H_n are polynomials called *Hermite polynomials*. The first three

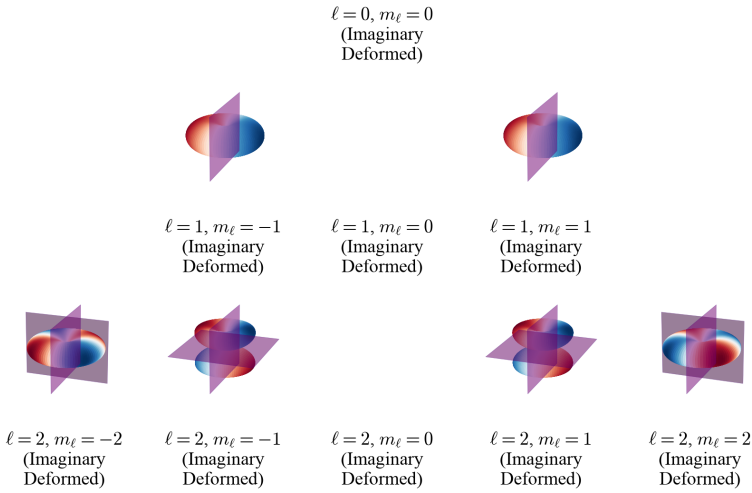


Figure 4.11 Imaginary parts of the spherical harmonics drawn as deformed spheres: the distance from the center is proportional to the absolute value of the function, the color gives its sign, and the nodal planes and cones are shown in purple. The lobes do not represent where the particle is: it is always on the surface of the sphere.

are simple, with $y = \sqrt{\alpha}\, x$:

$$H_0(y) = 1, \qquad H_1(y) = 2y, \qquad H_2(y) = 4y^2 - 2. \tag{4.40}$$

Notice that H_n has degree n, and therefore crosses zero n times. The energies are:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad \omega = \sqrt{\frac{k}{\mu}}, \tag{4.41}$$

where ω is the same angular frequency that a classical mass on a spring would have. As for the particle in a box, the energy is quantized, and the lowest level is not zero. The zero-point energy is:

$$E_0 = \frac{1}{2}\hbar\omega \neq 0. \tag{4.42}$$

This means that a quantum oscillator can never be completely at rest at the bottom of the well. Even at absolute zero, the atoms of a molecule keep vibrating. This zero-point vibration is real and measurable: for example, it is

the main reason why bonds to deuterium are slightly stronger than bonds to hydrogen (Chapter 8).

4.5.1 Wave function analysis

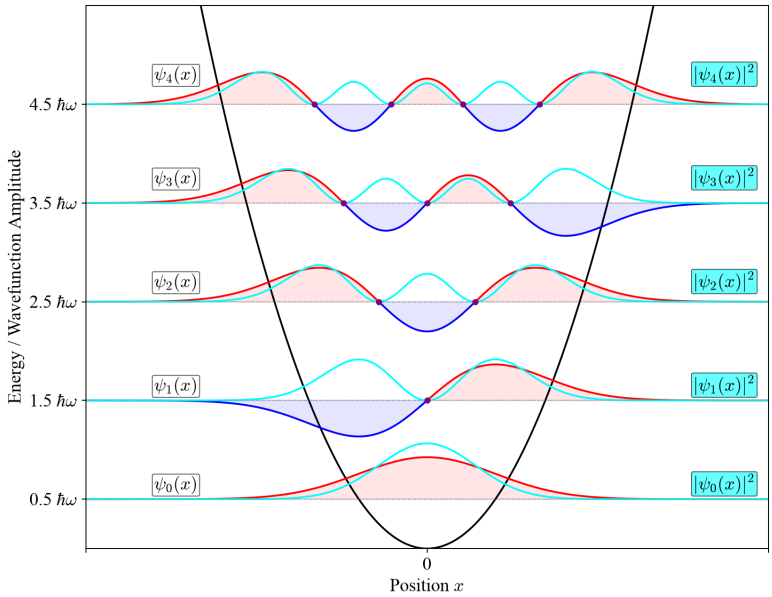


Figure 4.12 The first five eigenfunctions and energy levels of a particle confined inside a harmonic oscillator potential. The nodes of the wave functions are reported as purple dots. The probability density for each level is also plotted in cyan.

Let's look at Fig. 4.12:

1. **Equally spaced levels.** Unlike the particle in a box, the levels of the harmonic oscillator are all separated by the same amount, $\hbar\omega$. As we will see in Chapter 13, this is why a vibrating molecule absorbs light at one main frequency.
2. **Nodes.** The ground state ($n = 0$) is a Gaussian with no nodes, and each level adds one node: ψ_n has n nodes, the same rule "more energy, more nodes" that we found for all the other systems.
3. **Beyond the classical limits.** A classical oscillator with energy E can never go beyond the points where $V(x) = E$, called the *classical turning points*: there, all its energy is potential energy, and it turns back. The quantum wave functions, instead, do not stop at the turning points. They decay quickly but smoothly, so there is a small probability of finding the particle in the classically forbidden region. This is the same effect that allows a particle to tunnel through a barrier (Chapter 8).

4. **The classical limit again.** For large n, the probability density is largest near the turning points. This is what we expect classically: a mass on a spring moves slowest near the turning points, so it spends most of its time there.

4.6 Chapter Review

4.6.1 Key Ideas

- Confining a particle quantizes its energy. In a box, $E_n = \frac{n^2h^2}{8ma^2}$, and the lowest energy is not zero (zero-point energy).
- In every model, higher energy means more nodes (for the ring and the sphere, in the real and imaginary parts of the wave function).
- Symmetry produces degeneracy: equivalent directions in a cubic box, opposite rotations on a ring ($\pm m_\ell$), and all orientations on a sphere ($2\ell+1$ states).
- A particle on a ring or on a sphere has quantized angular momentum. The pictures of the spherical harmonics are drawings of functions, not of where the particle is.
- The harmonic oscillator has equally spaced levels, $E_n = \hbar\omega(n + \frac{1}{2})$. It is the model for molecular vibrations, and its wave functions extend beyond the classical turning points.

4.6.2 Study Questions

1. The energy levels of a particle of mass m in a one-dimensional box of length a are:

a. $E_n = \frac{nh^2}{8ma^2}$, with $n = 0, 1, 2, \ldots$
b. $E_n = \hbar\omega(n + \frac{1}{2})$
c. $E_n = \frac{n^2h^2}{8ma^2}$, with $n = 1, 2, 3, \ldots$
d. $E_n = -\frac{1}{2n^2}E_h$
e. any non-negative value

2. Why is the lowest energy of the particle in a box not zero?

a. because the walls repel the particle
b. because the particle always moves at the speed of light
c. because energy is never zero in classical physics
d. because $n = 0$ would give a wave function equal to zero everywhere, that is, no particle
e. because of the Coulomb attraction to the walls

3. How many nodes inside the box does the particle-in-a-box wave function ψ_n have?

a. $n-1$
b. n
c. $n+1$
d. $2n$
e. none, for every n

4. For the first excited state of the particle in a box ($n=2$), the probability of finding the particle at the center of the box is:

a. the largest in the box
b. the same as anywhere else in the box
c. one
d. zero
e. negative

5. In a cubic box, the states $(n_x, n_y, n_z) = (1,1,2)$, $(1,2,1)$, and $(2,1,1)$:

a. have different energies
b. are not allowed
c. have the same energy, because the three directions of the cube are equivalent
d. have zero energy
e. are the same state

6. For a particle on a ring, the energy levels with $m_\ell \neq 0$ are:

a. not degenerate
b. triply degenerate
c. all at zero energy
d. equally spaced
e. doubly degenerate, since $+m_\ell$ and $-m_\ell$ (rotation in opposite directions) have the same energy

7. For a particle on a ring in a state with definite angular momentum, the probability density is:

a. largest at $\phi = 0$
b. the same everywhere on the ring, and the wave function has no nodes
c. zero at $2|m_\ell|$ points
d. largest at the center of the ring
e. different for $+m_\ell$ and $-m_\ell$

8. How many states have the same energy E_ℓ for a particle on a sphere?

a. $2\ell+1$
b. ℓ
c. 2ℓ
d. ℓ^2
e. one

9. The energy levels of the harmonic oscillator are:

a. equally spaced by $\hbar\omega$, with the lowest one at zero
b. farther apart as n increases
c. closer together as n increases
d. continuous
e. equally spaced by $\hbar\omega$, with the lowest one at $\frac{1}{2}\hbar\omega$

10. Can a quantum harmonic oscillator be found beyond its classical turning points?

a. no, the wave function is exactly zero there
b. yes, with a small probability, since the wave function decays smoothly beyond them
c. yes, with the same probability as near the center
d. only in the ground state
e. only if its energy is larger than the potential

Answers

1.c, 2.d, 3.a, 4.d, 5.c, 6.e, 7.b, 8.a, 9.e, 10.b

CHAPTER 5

The Hydrogen Atom

The hydrogen atom, one proton and one electron, is the most important system in this book: it is the only atom for which we can solve the TISEq exactly, and its solutions, the hydrogen orbitals, are the building blocks that we will use for every other atom and molecule. Since the proton is about 1,836 times heavier than the electron, we can place it at the origin and think of the electron as moving around it (strictly speaking, the mass that enters the equations is the reduced mass of the two particles, μ, which is almost exactly the mass of the electron).

The potential energy is the Coulomb attraction between the electron and the proton (Eq. (1.16) in Chapter 1):

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \tag{5.1}$$

which depends only on the distance r between the two particles. The kinetic energy operator is the three-dimensional version of the one that we used for the particle in a box:

$$K = -\frac{\hbar^2}{2\mu}\nabla^2, \tag{5.2}$$

where the *Laplacian*, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, simply adds up the second derivatives along the three directions of space. The TISEq for the hydrogen atom is therefore:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = E\psi. \tag{5.3}$$

Since the potential depends only on r, it is much easier to work in spherical coordinates, (r, θ, ϕ), where the Laplacian becomes (Sec. A.4):

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi. \tag{5.4}$$

This equation looks scary, but we have already met most of it. The terms with θ and ϕ are exactly the ones of the particle on a sphere, Eq. (4.34) in Chapter 4, and the potential does not depend on the angles at all. This means that

we can write the wave function as a product of a *radial* part, which depends only on r, and an *angular* part, which is a spherical harmonic:

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\, Y_\ell^{m_\ell}(\theta,\phi). \tag{5.5}$$

The angular part is already solved: it is the same for every potential that depends only on r. All the physics that is specific to the hydrogen atom is in the radial part, which obeys the *radial equation*:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right]R(r) = E\,R(r). \tag{5.6}$$

Notice the extra term $\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}$, which acts as an additional, repulsive potential energy. It is the rotational energy of the electron, $L^2/2I$ with $I = \mu r^2$ (Chapter 6), and it pushes electrons with larger angular momentum away from the nucleus. Its solutions are a decaying exponential multiplied by a polynomial in r, which we will look at in a moment.

The solutions are labeled by three quantum numbers, one for each dimension of space:

- $n = 1, 2, 3, \ldots$, the **principal quantum number**, which comes from the radial equation and fixes the energy;
- $\ell = 0, 1, 2, \ldots, n-1$, the **angular momentum quantum number**;
- $m_\ell = -\ell, \ldots, +\ell$, the **magnetic quantum number**.

The functions $\psi_{n\ell m_\ell}$ are the **hydrogen atom orbitals** that you first encountered in general chemistry. Notice that an orbital is, by definition, a wave function that describes *one* electron, and that, as for the particle on a ring and on a sphere, it is in general a complex function.

The energies are:

$$E_n = -\frac{1}{n^2}\frac{e^2}{8\pi\varepsilon_0 a_0} \quad (n = 1, 2, 3, \ldots), \tag{5.7}$$

where $a_0 = \frac{\varepsilon_0 h^2}{\pi\mu e^2} \approx 0.529\,\text{Å}$ is the *Bohr radius*, the same length that we found with the Bohr model in Chapter 2. The energy depends only on n, and not on ℓ and m_ℓ: all the orbitals with the same n have the same energy. Some of this degeneracy comes from the rotational symmetry of the atom (the energy cannot depend on m_ℓ), and some from a special property of the $1/r$ potential (the energy does not depend on ℓ either), as we discussed in Sec. 7.4. So, for example:

- In the hydrogen atom, the $2s$ and $2p$ orbitals have the same energy.

This is often a surprise for students, since general chemistry textbooks usually show the $2s$ orbital below the $2p$. That splitting, however, only exists in

atoms with more than one electron, as we will see in Chapter 9. (Very precise experiments show a tiny difference between $2s$ and $2p$ even in hydrogen, called the *Lamb shift*, but it comes from effects beyond the Schrödinger equation, it is less than a millionth of the energy of the level, and it has nothing to do with the splitting of general chemistry.) The energy levels of the hydrogen atom are plotted in Fig. 5.1.

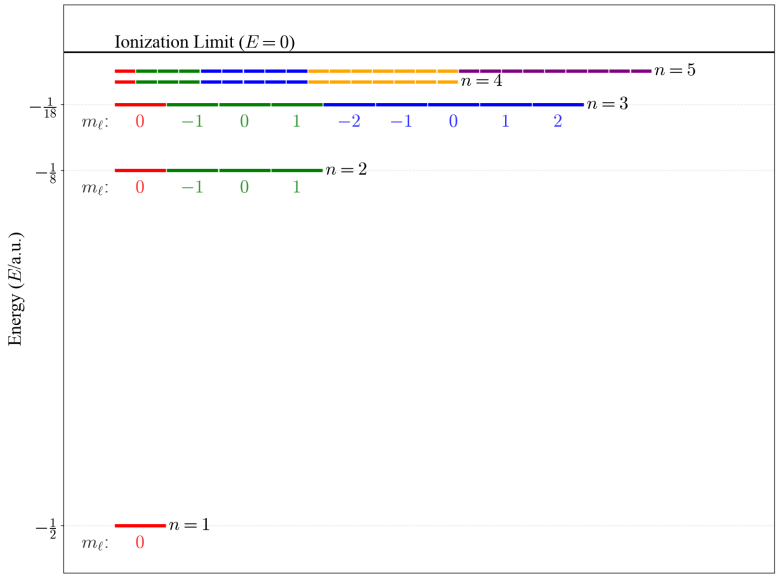


Figure 5.1 Energy level diagram and degeneracy pattern for the first five levels of the hydrogen atom, with energies in atomic units (see the next section).

5.1 Atomic Units

The hydrogen atom energies in Eq. (5.7) contain a combination of fundamental constants, $\frac{e^2}{4\pi\varepsilon_0 a_0}$, that will appear over and over again whenever we deal with electrons in atoms and molecules. Writing $\hbar$, m_e, e, and $4\pi\varepsilon_0$ in every equation quickly becomes tedious, and the numbers that come out (energies of the order of 10^{-18} J, distances of the order of 10^{-11} m) are inconvenient. For this reason, chemists and physicists who work with atoms and molecules use a set of units tailored to them, called **atomic units (a.u.)**. Atomic units are built by choosing the units of mass, charge, angular momentum, and permittivity so that:

$$\hbar = m_e = e = 4\pi\varepsilon_0 = 1. \tag{5.8}$$

With this choice, the constants simply disappear from the equations. The unit of length becomes the Bohr radius, a_0, and the unit of energy, called the **hartree** (E_h), is twice the ionization energy of the hydrogen atom:

$$1\,E_h = \frac{e^2}{4\pi\varepsilon_0 a_0} = 27.211\text{ eV} = 2{,}625.5\text{ kJ/mol}, \qquad 1\,a_0 = 0.529\,\text{Å}. \tag{5.9}$$

In atomic units, the energy levels of the hydrogen atom, Eq. (5.7), take the very simple form:

$$E_n = -\frac{1}{2n^2}\,E_h, \tag{5.10}$$

so the ground state is at $-\frac{1}{2}E_h$ (-13.6 eV, the value that we found with the Bohr model in Chapter 2), the first excited level at $-\frac{1}{8}E_h$, and so on, as shown in Fig. 5.1. Similarly, the Hamiltonian of the hydrogen atom becomes $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$, and the radial wave functions in the next section, which we write in terms of r/a_0, are already in atomic units. In the rest of this textbook we will often report energies in hartrees and distances in bohrs (a_0), together with their values in more familiar units. Atomic units are also the units used internally by all quantum chemistry programs.

Example 5.1: The red line of hydrogen

What is the wavelength of the light emitted when a hydrogen atom goes from $n = 3$ to $n = 2$?

Step 1: energy difference in atomic units. Using Eq. (5.10):

$$\Delta E = E_3 - E_2 = -\frac{1}{18}\,E_h - \left(-\frac{1}{8}\,E_h\right) = \frac{5}{72}\,E_h = 0.0694\,E_h.$$

Step 2: convert to familiar units. $0.0694\,E_h \times 27.211\text{ eV}/E_h = 1.89$ eV, or $0.0694 \times 2625.5 = 182$ kJ/mol.

Step 3: wavelength. $\Delta E = 0.0694 \times 4.360 \times 10^{-18}\text{ J} = 3.03 \times 10^{-19}\text{ J}$, so:

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{8}\text{ m/s})}{3.03 \times 10^{-19}\text{ J}} = 656\text{ nm}.$$

This is the red line of the Balmer series, the brightest line in the visible spectrum of hydrogen (Chapter 2).

5.2 The Radial Wave Functions

The radial wave functions for the first three energy levels are listed in the box below. They all have the same structure: a polynomial in r multiplied by a de-

caying exponential, e^{-r/na_0}. The exponential makes sure that the wave function goes to zero far from the nucleus, and it decays more slowly for larger n, so orbitals with larger n extend farther out. The polynomial is responsible for the nodes.

Details: the radial wave functions

For any n and ℓ, the radial functions can be written as:

$$R_{n\ell}(r) = -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right), \tag{5.11}$$

where $L_{n+\ell}^{2\ell+1}$ are polynomials called *associated Laguerre polynomials*. Working out these polynomials and the normalization constants for the first three energy levels, $n = 1, 2, 3$, gives (the overall sign, which has no physical meaning, has been chosen to make each function positive near the nucleus):

$$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \qquad (1s),$$

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0} \qquad (2s),$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}\,e^{-r/2a_0} \qquad (2p),$$

$$R_{30}(r) = \frac{2}{81\sqrt{3}}\left(\frac{1}{a_0}\right)^{3/2}\left[27-18\frac{r}{a_0}+2\left(\frac{r}{a_0}\right)^2\right]e^{-r/3a_0} \qquad (3s),$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right)e^{-r/3a_0} \qquad (3p),$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \qquad (3d).$$

The radial wave functions are plotted in Fig. 5.2. Let's look at them:

1. **Nodes.** R_{10} $(1s)$ is always positive. R_{20} $(2s)$ changes sign at $r = 2a_0$, where the polynomial $2 - r/a_0$ is zero: this is a *radial node*, a sphere around the nucleus on which the wave function is zero. As for the particle in a box, higher energy means more nodes. In general, $R_{n\ell}$ has $n - \ell - 1$ radial nodes.
2. **The nucleus.** The s functions are largest at the nucleus, while all the others start at zero, because of the factor r^ℓ: the rotational term in Eq. (5.6) keeps electrons with angular momentum away from the

nucleus.

3. **Angular nodes.** The radial nodes are not the only ones. The angular part, $Y_\ell^{m_\ell}$, adds ℓ more (Chapter 4), so that, as for all the other systems we have studied, the total number of nodes grows with the energy: $(n - \ell - 1) + \ell = n - 1$. For example, $2s$ has one radial node and no angular nodes, $2p$ has no radial nodes and one angular node, and $3d$ has two angular nodes. (As we saw for the particle on a sphere, the angular nodes are those of the real orbitals that we will meet below.)

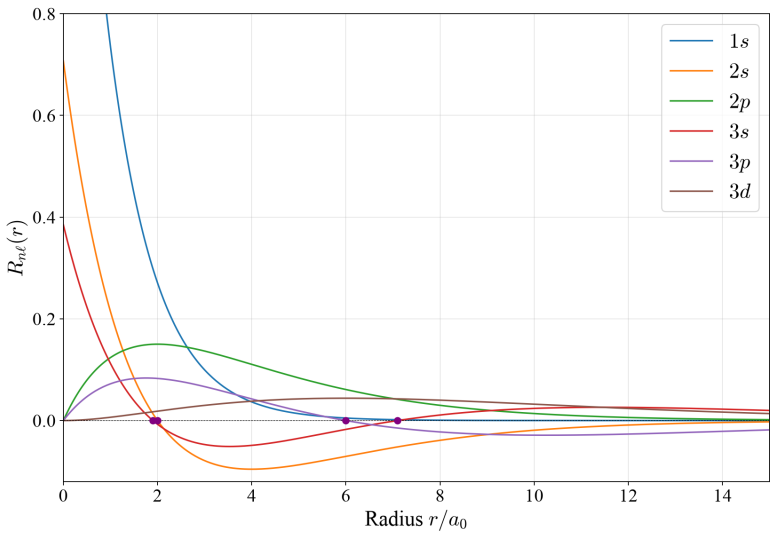


Figure 5.2 The radial wave functions of the hydrogen atom orbitals in the first three energy levels. The radial nodes are highlighted with purple dots.

How likely is the electron to be found at a certain distance from the nucleus? To answer this question, we need to add up the probability over all the points at distance r, which form a thin spherical shell. The volume of the shell, $4\pi r^2 dr$, grows with r, and this gives the **radial probability distribution**:

$$P(r) = r^2 |R_{n\ell}(r)|^2, \tag{5.12}$$

(the factor 4π is taken care of by the normalization of the spherical harmonics). $P(r)\,dr$ is the probability of finding the electron between r and $r + dr$, whatever the direction, and it is plotted in Fig. 5.3.

Notice how different $P(r)$ is from $|R_{n\ell}|^2$. For the $1s$ orbital, $|R_{10}|^2$ is largest at the nucleus, but there is very little volume close to the nucleus, so $P(r)$ is zero there. Its maximum, the most probable distance of the electron from the nucleus, is at exactly $r = a_0$, the radius of the Bohr model, although now the electron can be found at any distance. The $2s$ distribution has two maxima, at

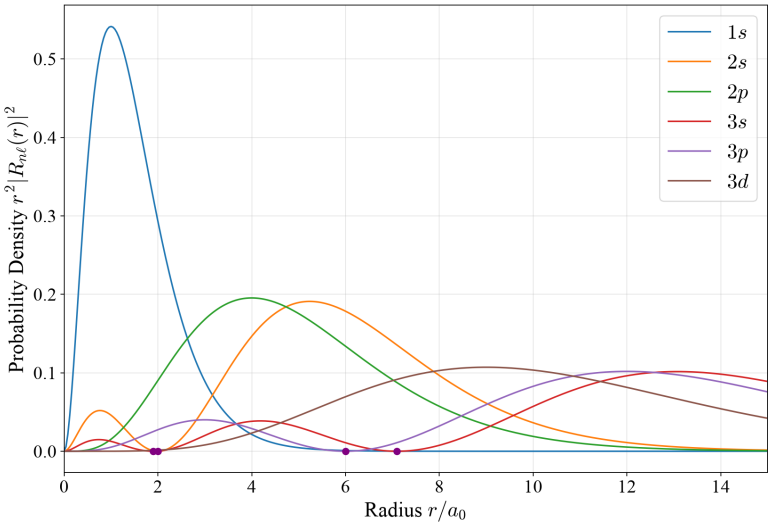


Figure 5.3 The radial probability functions of the hydrogen atom orbitals in the first three energy levels. The radial nodes are highlighted with purple dots.

about 0.76 a_0 and 5.24 a_0, separated by the radial node at $2a_0$: even though the $2s$ electron is mostly found far from the nucleus, it has a small but important probability of being found close to it. We will see in Chapter 9 that this small inner maximum is what makes the $2s$ orbital lower in energy than $2p$ in atoms with more than one electron.

5.3 The Angular Wave Functions

The angular part of the hydrogen orbitals is given by the spherical harmonics of the particle on a sphere (Chapter 4). As we saw there and in Chapter 6, they have a definite magnitude of the angular momentum and a definite component along z, and this is what the two angular quantum numbers mean:

- ℓ fixes the *magnitude* of the angular momentum of the electron, $|\mathbf{L}| = \hbar\sqrt{\ell(\ell+1)}$, and the number of angular nodes, ℓ. The letters that chemists use for the orbitals are just names for the values of ℓ: s for $\ell = 0$, p for $\ell = 1$, d for $\ell = 2$, f for $\ell = 3$.
- m_ℓ fixes the *component* of the angular momentum along the z axis, $L_z = m_\ell\hbar$. Its name comes from the fact that the energy of the atom in a magnetic field along z depends on it.

Together with n, which fixes the energy and how far from the nucleus the electron is likely to be found, these are the three labels of every orbital. An s electron has no angular momentum at all: there is nothing in classical physics

that resembles it, and it is one more reason to abandon the picture of an electron moving on an orbit.

5.4 Orbitals and Their Pictures

The complete orbital, Eq. (5.5), contains all the information about the state of the electron: the radial part tells us how the probability is distributed with the distance from the nucleus, and the angular part how it is distributed among the different directions. Drawing it, however, is not easy. An orbital is a function of three coordinates, so a complete plot would need four dimensions, and, since it is complex, we would need two of them, one for the real part and one for the imaginary part. A common compromise is to color the points of space around the nucleus by the value of the function, with a quarter of the space cut away so that we can see inside, as in Fig. 5.4 for the real parts and Fig. 5.5 for the imaginary parts.

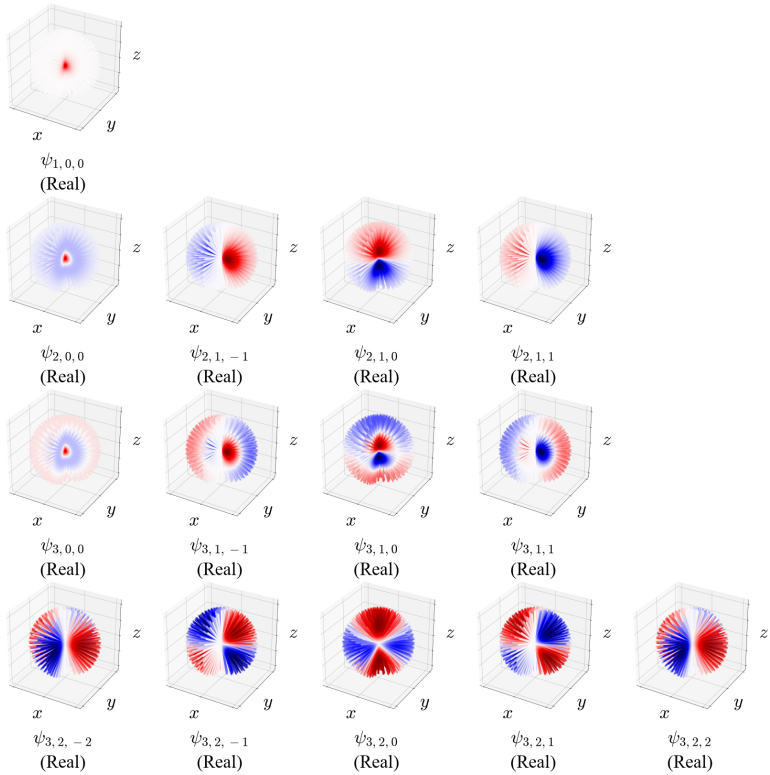


Figure 5.4 Real parts of some hydrogen orbitals, drawn as points around the nucleus colored by the value of the function, with a quarter of the space cut away (red: positive, blue: negative, white: nodes; distances in units of a_0).

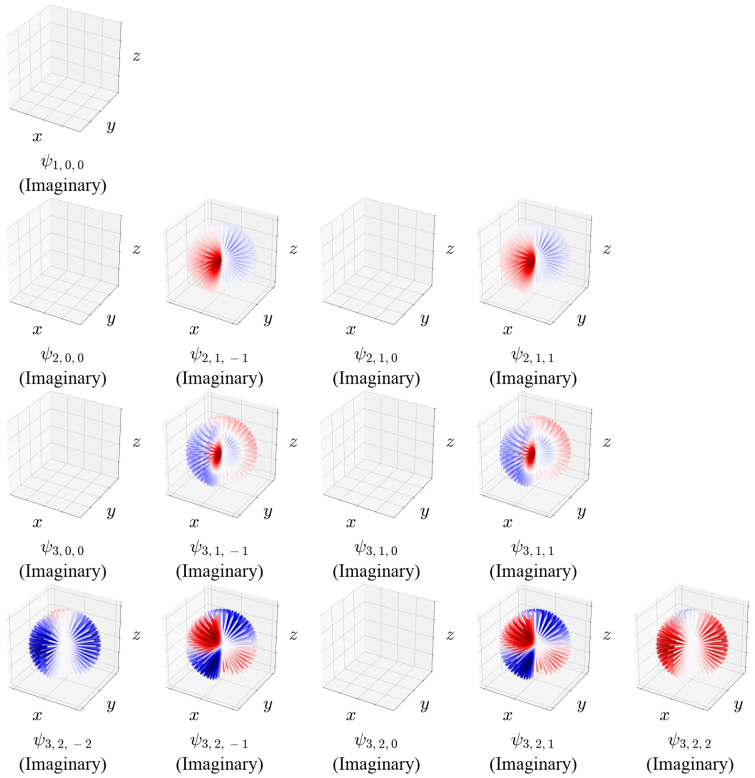


Figure 5.5 Imaginary parts of the same hydrogen orbitals as in Fig. 5.4 (red: positive, blue: negative, white: nodes).

5.4.1 Real orbitals

In chemistry, we usually do not use the complex orbitals, but real combinations of them. Since orbitals with the same n and ℓ have the same energy, any combination of them is still a solution of the TISEq with the same energy (Chapter 6). Combining the orbitals with opposite values of m_ℓ, we obtain, for example:

$$\begin{aligned} \psi_{2p_z} &= \psi_{2,1,0} \quad \text{(already real)}, \\ \psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,-1} - \psi_{2,1,+1}\right), \\ \psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,-1} + \psi_{2,1,+1}\right). \end{aligned} \tag{5.13}$$

These are the $2p_x$, $2p_y$, and $2p_z$ orbitals of general chemistry. The angular part of $2p_x$ is proportional to x/r, the one of $2p_y$ to y/r, and the one of $2p_z$

to z/r, which is where their names come from. The real and complex orbitals are two equally valid descriptions of the same set of states, and we can use whichever is more convenient: complex orbitals have a definite L_z, while real orbitals do not (they are superpositions of $m_\ell = +1$ and $m_\ell = -1$), but they are easier to draw, and they are the natural choice when we build molecules (Chapter 11).

5.4.2 What the pictures show, and what they do not

Pictures of orbitals such as those in Fig. 5.4 and Fig. 5.5 carry **no direct physical significance**. They plot a mathematical function, the wave function, which cannot be measured. They should never be interpreted as "regions of space" in which electrons live, or as objects with a shape. Unfortunately, such pictures are commonly presented as actual images of orbitals, and students are often led to believe that they represent a measurable, physical reality. **They do not!**

What has a physical meaning is the probability density, $|\psi_{n\ell m_\ell}|^2$, which tells us how likely we are to find the electron at each point of space if we measure its position. It can be drawn in several ways:

1. **Surfaces** that enclose a given fraction (for example, 80%) of the probability, as in Fig. 5.6.
2. **Volumetric plots**, where the color is denser where the probability is higher, as in Fig. 5.7.
3. **Dot-density plots**, where each dot represents one possible result of a measurement of the position of the electron, as in Fig. 5.8. These are probably the most honest pictures of all: if we could measure the position of the electron many times, each time on a freshly prepared atom, the results would accumulate exactly like these dots.

All three show the same information. Notice, however, that these pictures are colored by the *sign of the wave function*, a convention that you will find in almost every chemistry textbook. Strictly speaking, it mixes two different things, since the probability density is never negative. We keep the convention because it is everywhere and the sign of the wave function will be important when we build bonds (Chapter 11), but you should keep in mind what the colors mean.

5.4.3 Can we see an orbital?

Since the wave function is not an observable, orbitals cannot be measured directly. What experiments can measure are quantities related to them:

- **X-ray diffraction** measures the total electron density of a molecule or a crystal, the sum of the probability densities of all its electrons.

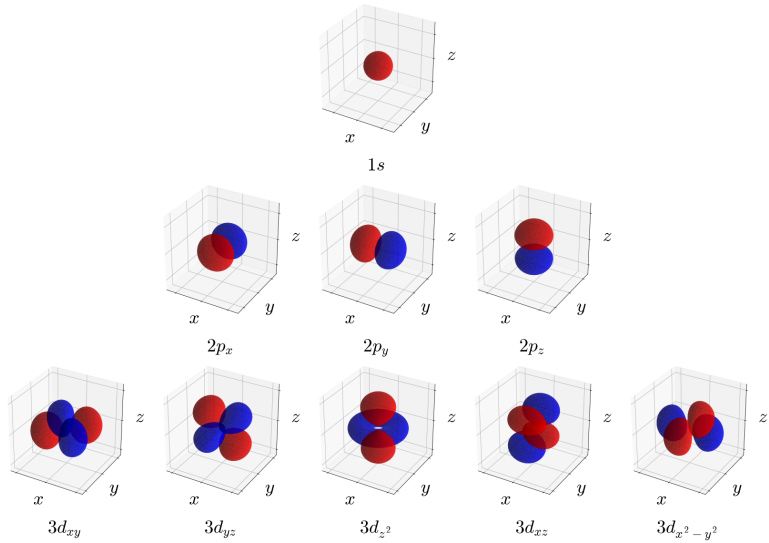


Figure 5.6 Surfaces that enclose 80% of the probability $|\psi|^2$ for a few hydrogen orbitals. Following the usual convention, the surfaces are colored by the sign of the wave function (red: positive, blue: negative), even though the probability itself is never negative.

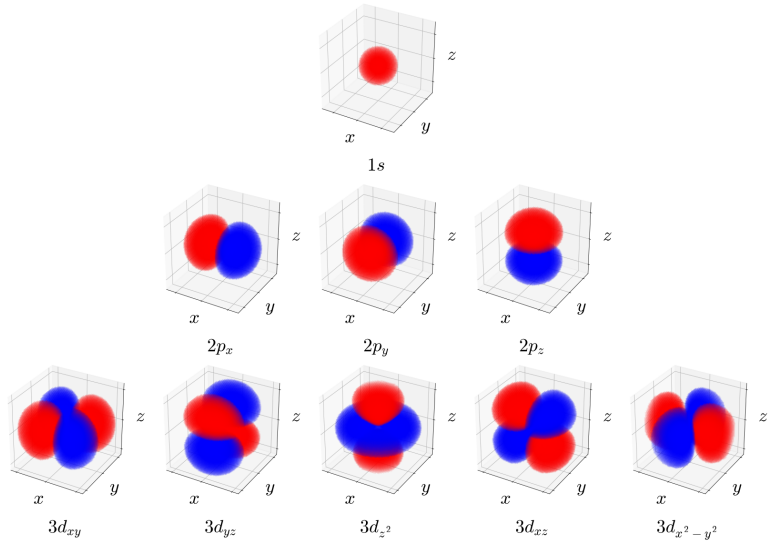


Figure 5.7 Volumetric plots of $|\psi|^2$ for a few hydrogen orbitals: the denser the color, the more likely the electron is to be found there. Colors give the sign of the wave function, as in Fig. 5.6.

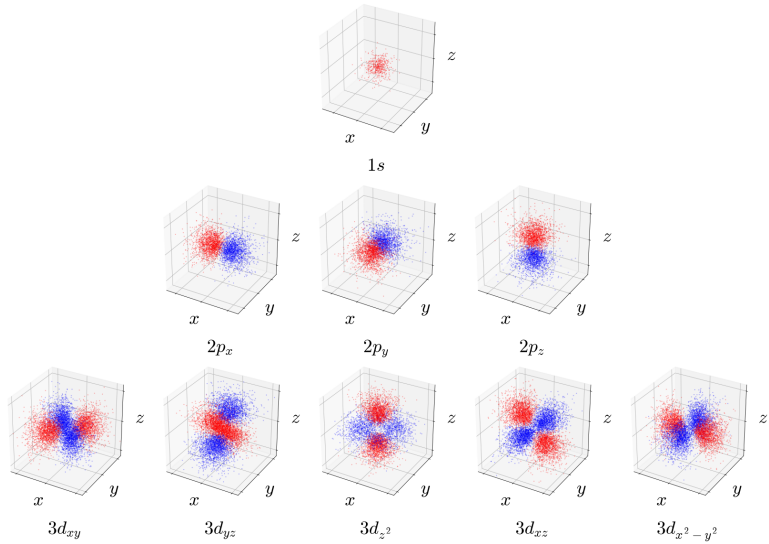


Figure 5.8 Dot-density plots for a few hydrogen orbitals: each dot is a possible result of a measurement of the position of the electron, so the dots are densest where $|\psi|^2$ is largest. Colors give the sign of the wave function, as in Fig. 5.6.

- **Photoelectron spectroscopy** measures the energy needed to remove an electron, which is closely related to the energy of the orbital that described it (we will see how in Chapter 12).
- **Scanning tunneling microscopy** of single molecules, like other modern experiments, can produce images that look remarkably like the pictures of individual orbitals, but they too measure probabilities, not wave functions, and they need theory to be interpreted.

Orbitals remain what they are: an extremely useful theoretical tool to describe electrons, not objects that we can observe.

5.5 Chapter Review

5.5.1 Key Ideas

- The hydrogen atom can be solved exactly. Its orbitals are products of a radial function and a spherical harmonic, $\psi_{n\ell m_\ell} = R_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)$.
- The energy depends only on n: $E_n = -\frac{1}{2n^2}E_h$ in atomic units. In hydrogen, $2s$ and $2p$ have the same energy.
- ℓ gives the magnitude of the angular momentum and the number of angular nodes, m_ℓ its z component, and there are $n-\ell-1$ radial nodes.

- The radial probability, $P(r) = r^2|R_{n\ell}|^2$, tells us how likely the electron is to be at each distance from the nucleus; for $1s$ it peaks at a_0.
- Orbitals are wave functions that describe one electron. Their pictures are plots of functions, not objects with a shape: only $|\psi|^2$ has a physical meaning.

5.5.2 Study Questions

1. Why can the hydrogen atom wave function be written as a product $R_{n\ell}(r)\, Y_\ell^{m_\ell}(\theta, \phi)$?

a. because the electron moves on a circular orbit
b. because the potential energy depends only on the distance r from the nucleus
c. because the proton is much lighter than the electron
d. because the energy depends on ℓ
e. because the wave function is always real

2. For $n = 3$, which values can the quantum number ℓ take?

a. $1, 2, 3$
b. $0, 1, 2, 3$
c. $-2, \ldots, +2$
d. $0, 1, 2$
e. only 3

3. In atomic units, the energy levels of the hydrogen atom are:

a. $E_n = -\frac{1}{n^2} E_h$, so the ground state is at $-1\, E_h = -13.6$ eV
b. $E_n = \frac{n^2}{2} E_h$
c. $E_n = -\frac{1}{2n} E_h$
d. $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$
e. $E_n = -\frac{1}{2n^2} E_h$, so the ground state is at $-0.5\, E_h = -13.6$ eV

4. In the hydrogen atom, the $2s$ and $2p$ orbitals:

a. are split, with $2s$ lower, because of penetration
b. have exactly the same energy (according to the Schrödinger equation)
c. are split, with $2p$ lower
d. have energies that depend on m_ℓ
e. are not solutions of the Schrödinger equation

5. How many radial nodes does the $3s$ orbital have?

a. 2
b. 0
c. 1
d. 3
e. 4

6. Why is the radial probability distribution $P(r) = r^2|R_{10}(r)|^2$ of the $1s$ orbital zero at the nucleus?

a. because R_{10} is zero at the nucleus
b. because the electron cannot be found near a positive charge
c. because the volume of a thin spherical shell, $4\pi r^2 dr$, goes to zero at $r = 0$
d. because of the Pauli principle
e. because $1s$ has a radial node at the nucleus

7. What does the quantum number ℓ tell us about an electron?

a. the shape of the region of space in which the electron lives
b. the size of its circular orbit
c. its spin
d. the magnitude of its angular momentum, $\hbar\sqrt{\ell(\ell+1)}$; s, p, d, f are names for $\ell = 0, 1, 2, 3$
e. its energy in the hydrogen atom

8. What does the magnetic quantum number m_ℓ tell us?

a. the component of the angular momentum along the z axis, $L_z = m_\ell \hbar$
b. the direction in which the orbital points
c. the magnetic moment of the nucleus
d. the number of radial nodes
e. the energy of the orbital in the absence of fields

9. The real $2p_x$ orbital is:

a. the orbital with $m_\ell = +1$
b. the orbital with $m_\ell = 0$
c. a different solution with a different energy from $2p_z$
d. an orbital that exists only in molecules
e. a combination of the complex orbitals with $m_\ell = +1$ and $m_\ell = -1$, so it does not have a definite L_z

10. Which of the following statements about the usual pictures of orbitals is correct?

a. they are photographs of the regions of space in which electrons live
b. they show the trajectory of the electron
c. they plot a mathematical function that cannot be measured; what has a physical meaning is $|\psi|^2$
d. they show the shape of the electron
e. they show where the electron is with certainty

Answers

1.b, 2.d, 3.e, 4.b, 5.a, 6.c, 7.d, 8.a, 9.e, 10.c

CHAPTER 6

Operators, Observables, and Measurements

So far, we have solved the TISEq for a few simple systems, one at a time. To go further, we need a more general language, and the language of quantum mechanics is built on the concept of an *operator*. An operator is a rule that takes a function and turns it into another function. You already know many of them: taking a derivative, $\frac{d}{dx}$, is an operator, and so is multiplying by x. Operators are not unique to quantum mechanics (in Chapter 1 we wrote the Hamiltonian of classical mechanics as a function that we can apply to a system), but in quantum mechanics they take center stage, since every physical quantity is represented by an operator. In this chapter, we will discuss the mathematics of quantum mechanical operators, and we will recast the results that we obtained for the analytically solvable models in this new language. As we will see, the new framework is actually simpler than what we have done so far. This simplicity, however, will open the door to the "stranger" side of quantum mechanics.

6.1 Operators in Quantum Mechanics

The central idea of this framework is that every *observable* (i.e., any quantity that can be measured in an experiment, such as position, momentum, or energy) is associated with an operator. To distinguish quantum mechanical operators from ordinary quantities, we write them with a hat, $\hat{}$, on top. The state of the system is described by its wave function, and the operator tells us what to do to the wave function to extract information about the corresponding observable. Since the result of a measurement is always a real number, the operators associated with observables must have real eigenvalues.[1] Operators with this property are called *Hermitian*, and we will discuss them in detail below.

In the wave mechanics formulation that we have used so far, wave functions are functions of the coordinates, and operators are combinations of derivatives and multiplications. An equivalent formulation, Heisenberg's matrix mechanics, represents the state of the system as a vector of numbers and operators as matrices. The two pictures are related in the same way as a function is related

[1] The operators themselves, however, do not need to be real, as for example the momentum operator, which contains the imaginary unit.

to the list of its coefficients in some basis set, an idea that we will use extensively when we describe molecules in Chapter 10.

The wave function itself is not directly observable. What we can measure in an experiment (or compute and compare with an experiment) are **expectation values**: averages of physical quantities. If we could prepare many identical hydrogen atoms, all in the ground state, and measure the distance between the electron and the proton in each one, the measurements would not all give the same result: they would scatter around some value. Their average is the expectation value of the distance, $\langle r \rangle$, and the size of the scatter is the uncertainty, Δr. For the 1s state of hydrogen, $\langle r \rangle = \frac{3}{2} a_0$ and $\Delta r = \frac{\sqrt{3}}{2} a_0 \approx 0.87\, a_0$. (Notice that the average distance is larger than the most probable distance, a_0, that we found from the radial probability distribution in Chapter 5, because the distribution has a long tail at large r.)

In general, the expectation value of the observable associated with an operator $\hat{A}$, for a system described by a normalized wave function $\psi(\mathbf{r})$, where $\mathbf{r} = \{x, y, z\}$ are the coordinates, is given by:

$$\langle A \rangle = \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r})\, d\mathbf{r}, \tag{6.1}$$

where the integral runs over all space. Notice the order of the three factors: the operator acts on the wave function first, and the result is then multiplied by the complex conjugate of the wave function and integrated. For an operator that simply multiplies by a function of the coordinates, such as the position, this reduces to the familiar formula for an average weighted by the probability density, $\langle r \rangle = \int r\, |\psi|^2\, d\mathbf{r}$. The uncertainty is calculated in the same way as a standard deviation in statistics, $\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$. We will discuss the meaning of expectation values in more detail later in this chapter, and the uncertainty in Chapter 8.

6.1.1 Basic Properties of Operators

Operators can be combined much like ordinary numbers, with one very important exception. We collect here the basic rules. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are defined by their action on a function f:

$$\begin{aligned} (\hat{A} + \hat{B}) f &= \hat{A} f + \hat{B} f \\ (\hat{A} - \hat{B}) f &= \hat{A} f - \hat{B} f. \end{aligned} \tag{6.2}$$

The product of two operators means applying them one after the other, starting from the one on the right:

$$\hat{A}\hat{B} f \equiv \hat{A}[\hat{B} f] \tag{6.3}$$

Two operators are equal if

$$\hat{A} f = \hat{B} f \tag{6.4}$$

for all functions f. The identity operator $\hat{1}$ does nothing (or multiplies by 1):

$$\hat{1}f = f \tag{6.5}$$

The associative law holds for operators:

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{6.6}$$

The exception is the commutative law, which does not hold for operators in general: $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. In other words, the order in which we apply two operators matters. For example, if $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x$, then $\hat{A}\hat{B}f = \frac{d}{dx}(xf) = f + x\frac{df}{dx}$, while $\hat{B}\hat{A}f = x\frac{df}{dx}$, and the two results differ by f. Since the difference between the two orders is so important, we give it a name:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{6.7}$$

which is called the **commutator** of $\hat{A}$ and $\hat{B}$. Note that the order matters, so that $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$. If $\hat{A}$ and $\hat{B}$ happen to commute, then $[\hat{A}, \hat{B}] = 0$.

6.1.2 Linear Operators

The operators that we use in quantum mechanics are linear. An operator $\hat{A}$ is linear if it satisfies the following two conditions:

$$\begin{aligned} \hat{A}(f+g) &= \hat{A}f + \hat{A}g, \\ \hat{A}(cf) &= c\hat{A}f, \end{aligned} \tag{6.8}$$

where c is a constant and f and g are functions. Linearity is what makes the superposition of states possible: if f and g are both solutions of a linear equation, so is any combination of them. For example, the derivative, $\frac{d}{dx}$, is linear, since:

$$\begin{aligned} \frac{d}{dx}[f(x) + g(x)] &= \frac{d}{dx}f(x) + \frac{d}{dx}g(x), \\ \frac{d}{dx}[cf(x)] &= c(d/dx)f(x). \end{aligned} \tag{6.9}$$

while the operator that squares a function, $()^2$, is not linear, since:

$$(f(x) + g(x))^2 \neq (f(x))^2 + (g(x))^2 \tag{6.10}$$

6.1.3 Hermitian Operators

We said at the beginning of this chapter that every observable is associated with an operator, and that the possible results of a measurement are the eigenvalues of that operator. This immediately puts a requirement on the operator: the

result of a measurement, such as an energy or a position, is always a *real* number, so the eigenvalues must be real. Operators that guarantee this are called **Hermitian**.

An operator $\hat{A}$ is Hermitian if, for any two well-behaved functions ψ_1 and ψ_2:

$$\int \psi_1^* (\hat{A}\psi_2)\, d\mathbf{r} = \int (\hat{A}\psi_1)^* \psi_2\, d\mathbf{r}. \tag{6.11}$$

In words: in an integral like this one, we can let the operator act on the function on the right or on the one on the left (complex conjugated), and we get the same result. The operators of Table 6.1 (position, momentum, kinetic energy, the Hamiltonian, angular momentum) are all Hermitian.

Hermitian operators have two properties that we will use over and over again:

1. **Their eigenvalues are real.** This is what makes them suitable to represent observables.
2. **Their eigenfunctions with different eigenvalues are orthogonal**, that is, if $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$ with $a \neq b$, then $\int \psi_a^* \psi_b\, d\mathbf{r} = 0$. Eigenfunctions with the *same* eigenvalue (degenerate ones) are not automatically orthogonal, but they can always be combined so that they are. This property is what allows us, in the next section, to calculate expectation values of superpositions so easily, and it is what we have already used, without saying it, for the particle in a box (Sec. A.3).

Both properties follow directly from Eq. (6.11), in a few lines that you can find below.

Proof: the eigenvalues are real

Take an eigenfunction of $\hat{A}$:

$$\hat{A}\psi_a = a\psi_a, \tag{6.12}$$

and use it as both ψ_1 and ψ_2 in Eq. (6.11):

$$a \int \psi_a^* \psi_a\, d\mathbf{r} = a^* \int \psi_a^* \psi_a\, d\mathbf{r} \quad \Rightarrow \quad (a - a^*) \int |\psi_a|^2 d\mathbf{r} = 0. \tag{6.13}$$

The integral of $|\psi_a|^2$ is positive (it is the total probability), so $a = a^*$: the eigenvalue is real.

Proof: eigenfunctions with different eigenvalues are orthogonal

Use two eigenfunctions, $\psi_1 = \psi_a$ and $\psi_2 = \psi_b$, in Eq. (6.11), and remember that a is real:

$$b \int \psi_a^* \psi_b \, d\mathbf{r} = a \int \psi_a^* \psi_b \, d\mathbf{r} \quad \Rightarrow \quad (b-a) \int \psi_a^* \psi_b \, d\mathbf{r} = 0. \tag{6.14}$$

Since $a \neq b$, the integral must be zero.

6.2 Eigenfunctions and Eigenvalues

As we have already seen, an eigenfunction of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant:

$$\hat{A} f = k f, \tag{6.15}$$

where k is a constant called the eigenvalue.

When a system is in an eigenstate of observable A (i.e., when the wave function is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wave function. Therefore, if:

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}), \tag{6.16}$$

then:

$$\begin{aligned} < A > &= \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) a \psi(\mathbf{r}) d\mathbf{r} \\ &= a \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = a, \end{aligned} \tag{6.17}$$

where we have used the fact that the wave function is normalized:

$$\int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = 1. \tag{6.18}$$

This property of wave functions is called normalization, and in the one-electron TISEq guarantees that the probability of finding the electron somewhere in the entire space is one.[2]

A unique property of quantum mechanics is that a wave function can be expressed not just as a simple eigenfunction, but also as a combination of several

[2] We used exactly this condition to find the constant C for the particle in a box in Chapter 4, Eq. (4.16).

of them. We have in part already encountered such property in the previous chapter, where complex hydrogen orbitals have been combined to form corresponding real ones. As a general example, let us consider a wave function written as a linear combination of two eigenstates of $\hat{A}$, with eigenvalues a and b:

$$\psi = c_a\psi_a + c_b\psi_b, \tag{6.19}$$

where $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$. Then, since ψ_a and ψ_b are orthogonal and normalized (usually abbreviated as orthonormal), the expectation value of A is:

$$\begin{aligned} < A > &= \int \psi^* \hat{A}\psi d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \hat{A}\left[c_a\psi_a + c_b\psi_b\right] d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \left[ac_a\psi_a + bc_b\psi_b\right] d\mathbf{r} \\ &= a|c_a|^2 \int \psi_a^*\psi_a d\mathbf{r} + bc_a^*c_b \int \psi_a^*\psi_b d\mathbf{r} \\ &\quad + ac_b^*c_a \int \psi_b^*\psi_a d\mathbf{r} + b|c_b|^2 \int \psi_b^*\psi_b d\mathbf{r} \\ &= a|c_a|^2 + b|c_b|^2. \end{aligned} \tag{6.20}$$

This result shows that the expectation value of A is a weighted average of the two eigenvalues, with weights given by the squared magnitudes of the coefficients, $|c_a|^2$ and $|c_b|^2$. Notice that $\langle A\rangle$ can be any number between a and b, but each individual measurement can only give either a or b, with probabilities $|c_a|^2$ and $|c_b|^2$, respectively. (What happens to the wave function after such a measurement is one of the most surprising aspects of quantum mechanics, and we will discuss it in Chapter 8.)[3]

Example 6.1: Measuring the energy of a superposition

A particle in a box is described by $\psi = \sqrt{\frac{1}{3}}\psi_1 + \sqrt{\frac{2}{3}}\psi_2$, where ψ_1 and ψ_2 are the two lowest eigenfunctions. What can a measurement of the energy give, with which probabilities, and what is the expectation value of the energy?

Step 1: possible results. The energy eigenvalues present in the superposition: E_1 or $E_2 = 4E_1$.

Step 2: probabilities. The squares of the coefficients: $P(E_1) = \frac{1}{3}$ and

[3] A similar presentation of these topics can be found in Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry notes.

Example 6.1: Measuring the energy of a superposition *(continued)*

$P(E_2) = \frac{2}{3}$. They add up to one, so ψ is normalized.
Step 3: expectation value. The weighted average of the possible results:

$$\langle E \rangle = \frac{1}{3}E_1 + \frac{2}{3}(4E_1) = 3E_1.$$

Notice that $3E_1$ is not an eigenvalue: no single measurement will ever give it. It is only the average of many measurements on identically prepared particles.

6.3 Common Operators in Quantum Mechanics

Some common operators occurring in quantum mechanics are collected in the table below:

Table 6.1 Common operators in quantum mechanics.

Observable Name	Symbol	Operator	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(\mathbf{r})$
Angular momentum	L^2	$\hat{L}^2$	$\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$
	L_x	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
	L_y	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$
	L_z	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

In the sections below we analyze in detail two main operators for the energy and the angular momentum.

6.3.1 Hamiltonian Operator

The most important observable in quantum chemistry is the total energy of the system, E. The operator corresponding to this quantity is called the *Hamiltonian*:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V, \tag{6.21}$$

where i is an index over all the particles of the system. Using the formalism of operators in conjunction with Eq. (6.21), we can write the TISEq just simply as:

$$\hat{H}\psi = E\psi. \tag{6.22}$$

Comparing Eq. (6.21) to the classical analog in Eq. (1.9), we notice how the first term in the Hamiltonian operator represents the corresponding kinetic energy operator, $\hat{K}$, while the second term represents the potential energy operator, $\hat{V}$. For a one-electron system—such as the ones we studied in Chapter 4—we can write:

$$\hat{K} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\nabla^2, \tag{6.23}$$

which is universal and applies to all systems. The potential energy operator $\hat{V}$ is what differentiates each system. Using Eq. (6.22), we can then simply obtain the TISEq for the free particle and for the particle in a box and the harmonic oscillator models discussed in Chapter 3 and Chapter 4 by simply using:

$$\begin{aligned} &\text{Free particle:} && \hat{V} = 0, \\ &\text{Particle in a box:} && \hat{V} = 0 \text{ inside the box, } \hat{V} = \infty \text{ outside the box,} \\ &\text{Harmonic oscillator:} && \hat{V} = \frac{1}{2}kx^2. \end{aligned} \tag{6.24}$$

While these three cases are simple to solve, the rigid rotor is more complicated, since the kinetic energy operator needs to be expressed in spherical polar coordinates, as we will see in the next section.

The Hamiltonian has a second, equally important role. Using the operator notation, the time-dependent Schrödinger equation, Eq. (3.11), can be written simply as:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{6.25}$$

In other words, the Hamiltonian is not only the operator associated with the total energy, but also the operator that determines how the wave function changes in time. For this reason, it is often said that the Hamiltonian *generates* the time evolution of the system. We will discuss the consequences of this equation in Sec. 6.4, at the end of this chapter.

6.3.2 Angular Momentum Operator

Angular momentum is the quantity that describes rotation, and rotation is everywhere in chemistry. We have already met it for the particle on a ring and

on a sphere (Chapter 4), and it will give us the quantum numbers ℓ and m_ℓ of the hydrogen orbitals (Chapter 5), the spin of the electron (Chapter 7), the term symbols of atoms (Chapter 9), and the rotational spectra of molecules (Chapter 13). So it is worth collecting here what we know about its operators.

As in classical mechanics, angular momentum is a vector with three components, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$. In practice, however, we almost never use the components $\hat{L}_x$ and $\hat{L}_y$. The two operators that we need are the *square* of the angular momentum, which tells us how fast the system rotates:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \tag{6.26}$$

and its component along one axis, by convention $\hat{L}_z$, which tells us how the rotation is oriented. Their eigenfunctions are the spherical harmonics of Chapter 4, and their eigenvalue equations are:

$$\hat{L}^2 Y_\ell^{m_\ell}(\theta,\varphi) = \hbar^2 \ell(\ell+1) Y_\ell^{m_\ell}(\theta,\varphi), \tag{6.27}$$

$$\hat{L}_z Y_\ell^{m_\ell}(\theta,\varphi) = \hbar m_\ell Y_\ell^{m_\ell}(\theta,\varphi), \tag{6.28}$$

with $\ell = 0, 1, 2, \ldots$ and $m_\ell = -\ell, \ldots, +\ell$. In words: the magnitude of the angular momentum can only take the values $|\mathbf{L}| = \hbar\sqrt{\ell(\ell+1)}$, and, for each of them, its z component can only take the $2\ell+1$ values $m_\ell\hbar$. Notice that $|\mathbf{L}|$ is always a bit larger than the largest possible $L_z = \ell\hbar$: the angular momentum can never point exactly along z.

Details: the angular momentum operators in coordinates

The components of the angular momentum are obtained from the classical definition, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, replacing the momentum with its operator, $\hat{\mathbf{p}} = -i\hbar\nabla$:

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),\\
\hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),\\
\hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).
\end{aligned} \tag{6.29}$$

In spherical coordinates, $\hat{L}_z$ becomes simply $-i\hbar\frac{\partial}{\partial\varphi}$, the operator that we used for the particle on a ring, and $\hat{L}^2$ contains all the angular derivatives of the Laplacian (Sec. A.4), which can be written as:

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{\hbar^2 r^2}, \tag{6.30}$$

where $\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ is the radial part. This is why the kinetic energy

Details: the angular momentum operators in coordinates *(continued)*

of any particle moving in three dimensions splits into a radial part and a rotational part, $\hat{L}^2/2\mu r^2$, the same form as the classical rotational energy $L^2/2I$. We will use this result for the hydrogen atom in Chapter 5.

Since $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ do not commute with each other (for example, $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$, and we will see the same relations for spin in Chapter 7), only one component can have a definite value at a time. This is why angular momentum is often pictured with the *vector model* of Fig. 6.1. For $\ell = 2$, the vector has length $\hbar\sqrt{6}$ and one of five possible z components. Its x and y components, instead, are not defined, so the vector is drawn anywhere on a cone around the z axis. The cone is only a picture, not a vector that rotates around the axis: in these states, a measurement of L_x or L_y gives a random result, and its average is zero.

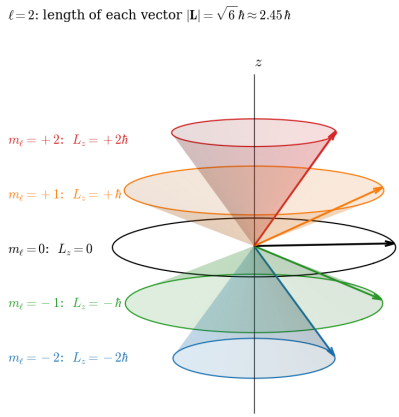


Figure 6.1 Vector model of the orbital angular momentum for $\ell = 2$. Each cone corresponds to one value of m_ℓ: the vector has length $\sqrt{6}\hbar$ and a well-defined projection $m_\ell\hbar$ on the z axis, while its direction around the cone (its x and y components) is undetermined.

6.3.3 Commuting operators and compatible observables

We can now come back to the commutator, Eq. (6.7), which turns out to be one of the most important quantities in quantum mechanics. Two facts make

it so important.

The first is a mathematical theorem, which we state without proof: **if two Hermitian operators commute, $[\hat{A}, \hat{B}] = 0$, they have a common set of eigenfunctions**. In other words, we can find wave functions that are eigenfunctions of $\hat{A}$ and $\hat{B}$ at the same time. A system described by one of these wave functions has a definite value of both A and B, and measuring one of them does not disturb the other. Observables of this kind are called *compatible*. We have already met an example: $\hat{L}^2$ and $\hat{L}_z$ commute, and the spherical harmonics are eigenfunctions of both, Eq. (6.27) and Eq. (6.28), so the magnitude of the angular momentum and its z component can be known at the same time. If two operators do *not* commute, instead, in general there is no wave function that is an eigenfunction of both, and the two observables cannot have definite values at the same time. They are called *incompatible*.

The second fact concerns the two most basic operators of all, position and momentum. In one dimension, $\hat{x}$ multiplies by x, and $\hat{p} = -i\hbar\frac{d}{dx}$. Applying their commutator to an arbitrary function $f(x)$, and using the result that we obtained above for $\frac{d}{dx}$ and x:

$$[\hat{x}, \hat{p}]f = x\left(-i\hbar\frac{df}{dx}\right) - \left(-i\hbar\frac{d}{dx}\right)(xf) = -i\hbar x\frac{df}{dx} + i\hbar\left(f + x\frac{df}{dx}\right) = i\hbar f. \tag{6.31}$$

Since this is true for any function, we can write the result as a relation between the operators themselves:

$$[\hat{x}, \hat{p}] = i\hbar. \tag{6.32}$$

This is called the **canonical commutation relation**. Position and momentum do not commute, so they are incompatible: no wave function can have both a definite position and a definite momentum. We have already seen this in the wave packets of Chapter 3, and we will make it quantitative with the uncertainty principle in Chapter 8. It is remarkable that the whole difference between classical and quantum mechanics can be traced back to the fact that the right-hand side of Eq. (6.32) is not zero: in classical mechanics, multiplying by x and by p in either order gives the same result.

6.4 Time Evolution

Eq. (6.25) tells us that, once we know the wave function at some initial time, the Hamiltonian determines it at all later times. In this section, we look at what this means in practice, using the solutions that we already know.

6.4.1 Stationary states

For a Hamiltonian that does not depend on time, we already found in Chapter 3 that an eigenfunction of the Hamiltonian with energy E evolves in time as $\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar}$ (Eq. (3.17)). The time evolution simply multiplies the wave function by a phase factor of magnitude one, so the probability density, $|\Psi|^2$, does not change in time, and neither does the expectation value of any observable. This is why the eigenfunctions of the Hamiltonian are called *stationary states*: nothing that we can measure on them changes in time.

6.4.2 Superpositions of stationary states

If the wave function is a superposition of eigenfunctions with *different* energies, the situation is very different. Since the TDSEq is linear, each term evolves with its own phase factor:

$$\Psi(\mathbf{r},t) = c_1\psi_1(\mathbf{r})e^{-iE_1t/\hbar} + c_2\psi_2(\mathbf{r})e^{-iE_2t/\hbar}. \tag{6.33}$$

Let's consider the simplest example: a particle in a box prepared in an equal superposition of the two lowest states, with $c_1 = c_2 = \frac{1}{\sqrt{2}}$. Using the normalized eigenfunctions of Eq. (4.16), the probability density is:

$$|\Psi(x,t)|^2 = \frac{1}{2}\left[\psi_1^2(x) + \psi_2^2(x)\right] + \psi_1(x)\psi_2(x)\cos\left(\frac{(E_2-E_1)t}{\hbar}\right). \tag{6.34}$$

The first term does not depend on time, but the second one oscillates with a period $T = \frac{2\pi\hbar}{E_2-E_1}$. The result is shown in Fig. 6.2.

What do these results mean?

1. **Motion**: the probability density sloshes back and forth between the left and the right side of the box, and the expectation value of the position oscillates around the center, $\langle x\rangle = \frac{a}{2} - \frac{16a}{9\pi^2}\cos\left(\frac{(E_2-E_1)t}{\hbar}\right)$. This is how a quantum particle moves: motion requires a superposition of states with different energies. A particle in a single stationary state, instead, never moves, in the sense that none of its measurable properties change in time.

2. **Frequency**: the oscillation frequency, $\nu = \frac{E_2-E_1}{h}$, is exactly the frequency of the photon that the particle would emit or absorb by jumping between the two states (Chapter 2). This is not a coincidence: an oscillating charge emits radiation at its oscillation frequency, and this is the quantum origin of spectroscopy (Chapter 13).

3. **Energy**: if we measure the energy of the particle, we obtain either E_1 or E_2, each with probability $|c_1|^2 = |c_2|^2 = \frac{1}{2}$, and the expectation value of

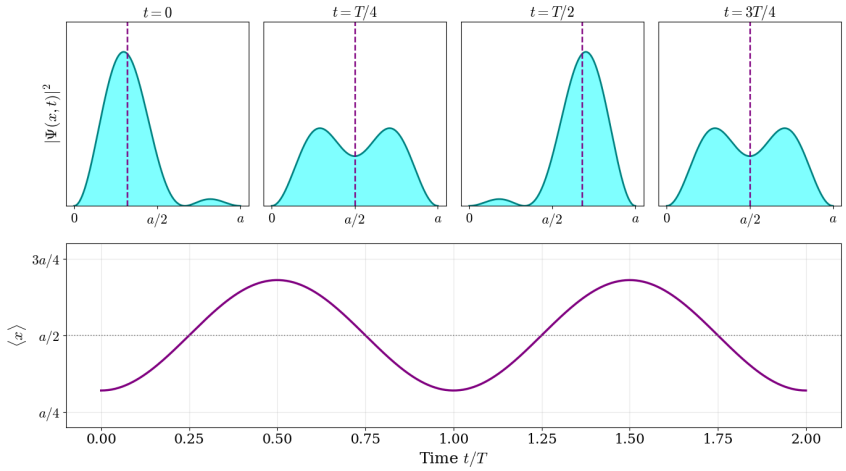


Figure 6.2 Top: probability density of a particle in a box in the superposition $\frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ at four different times, with the expectation value of the position marked by a purple dashed line. Bottom: the expectation value of the position as a function of time.

the energy is $\langle E \rangle = \frac{1}{2}(E_1 + E_2)$ at all times. The energy is conserved, even though the position changes.

6.4.3 Conservation of probability

An important property of the time evolution described by Eq. (6.25) is that it preserves the normalization of the wave function: if the total probability of finding the particle somewhere is equal to one at the beginning, it stays equal to one at all later times. We can see this in the example above: each phase factor has magnitude one, so the coefficients keep their magnitudes, and $|c_1|^2 + |c_2|^2 = 1$ at all times. The operator that takes the wave function at time 0 to the wave function at time t is, for a time-independent Hamiltonian, $e^{-i\hat{H}t/\hbar}$, and an operator that preserves the norm of the wave function in this way is called **unitary**. Notice the difference between the two types of operators that we have encountered: observables are represented by Hermitian operators, which have real eigenvalues, while time evolution is represented by a unitary operator, which preserves probabilities.

6.5 Chapter Review

6.5.1 Key Ideas

- Every observable is represented by a Hermitian operator. The possible results of a measurement are its eigenvalues, which are always real.
- The expectation value, $\langle A \rangle = \int \psi^* \hat{A} \psi \, d\mathbf{r}$, is the average of many measurements on identically prepared systems.
- For a superposition of eigenfunctions, each eigenvalue is measured with probability $|c_i|^2$.
- Operators that commute share eigenfunctions, and their observables can have definite values together. Position and momentum do not commute: $[\hat{x}, \hat{p}] = i\hbar$.
- The Hamiltonian determines the time evolution. Superpositions of states with different energies change in time, with frequencies $(E_2 - E_1)/h$.

6.5.2 Study Questions

1. If we measure an observable A on a system, the possible results are:

a. any real number
b. the eigenfunctions of $\hat{A}$
c. the eigenvalues of the operator $\hat{A}$
d. only the expectation value $\langle A \rangle$
e. the eigenvalues of the Hamiltonian, whatever A is

2. The expectation value $\langle A \rangle$ is:

a. the result of a single measurement
b. the largest possible result of a measurement
c. always an eigenvalue of $\hat{A}$
d. the uncertainty in the measurement of A
e. the average of the results of many measurements of A on identically prepared systems

3. For a normalized wave function ψ, the expectation value of $\hat{A}$ is:

a. $\langle A \rangle = \int \hat{A} \psi \, d\mathbf{r}$
b. $\langle A \rangle = \int \psi^* \hat{A} \psi \, d\mathbf{r}$
c. $\langle A \rangle = \int \psi^* \psi \, d\mathbf{r}$
d. $\langle A \rangle = \hat{A} \psi$
e. $\langle A \rangle = \int \psi \hat{A} \, d\mathbf{r}$

4. Why are the operators associated with observables Hermitian?

a. because Hermitian operators always commute with each other
b. because Hermitian operators are always real
c. because Hermitian operators have no eigenfunctions

d. because Hermitian operators have real eigenvalues, and the results of measurements are real numbers
e. because Hermitian operators do not depend on position

5. Eigenfunctions of a Hermitian operator with different eigenvalues are:

a. orthogonal
b. identical
c. always degenerate
d. complex conjugates of each other
e. normalized to zero

6. A system is described by $\psi = c_1\psi_a + c_2\psi_b$, where ψ_a and ψ_b are normalized eigenfunctions of $\hat{A}$ with eigenvalues a and b. A measurement of A gives:

a. always $c_1 a + c_2 b$
b. always a, the lowest eigenvalue
c. a and b at the same time
d. a with probability $|c_1|^2$, or b with probability $|c_2|^2$
e. a with probability c_1, or b with probability c_2

7. In one dimension, the momentum operator is:

a. $\hat{p} = -i\hbar\frac{d}{dx}$
b. $\hat{p} = m\frac{dx}{dt}$
c. $\hat{p} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$
d. $\hat{p} = x$
e. $\hat{p} = i\hbar x$

8. The commutator of position and momentum is $[\hat{x}, \hat{p}] = i\hbar$. This means that:

a. position and momentum can always be measured together exactly
b. no wave function can have a definite position and a definite momentum at the same time
c. momentum is always imaginary
d. position is quantized
e. the momentum of a particle is always zero

9. If two operators commute, $[\hat{A}, \hat{B}] = 0$:

a. they have the same eigenvalues
b. one of them must be the Hamiltonian
c. they have a common set of eigenfunctions, and both observables can have definite values at the same time
d. their observables cannot be measured
e. their eigenfunctions are always orthogonal to each other

10. A particle in a box is in a superposition of the two lowest energy eigenstates. Its probability density:

a. does not change in time
b. decays to zero
c. oscillates with frequency $\nu = E_1/h$
d. is the same everywhere in the box
e. oscillates back and forth with frequency $\nu = (E_2 - E_1)/h$

Answers

1.c, 2.e, 3.b, 4.d, 5.a, 6.d, 7.a, 8.b, 9.c, 10.e

CHAPTER 7

Spin

Spin is a special property of particles that has no classical analogue. Spin is an intrinsic form of angular momentum carried by elementary particles, such as the electron.

7.1 Stern-Gerlach Experiment

In 1922, Otto Stern and Walter Gerlach performed an experiment that unintentionally led to the discovery that electrons have their own intrinsic angular momentum (spin), independent of their orbital motion in an atom. The experiment was done by putting a silver foil in an oven to vaporize its atoms. The silver atoms were collected into a beam that passed through an inhomogeneous magnetic field. The result was that the magnetic field split the beam into two (and only two) separate ones. The Stern–Gerlach experiment demonstrated that the spatial orientation of angular momentum is quantized into two components (up and down). Thus an atomic-scale system was shown to have intrinsically quantum properties. The experiment is normally conducted using electrically neutral particles such as silver atoms. This avoids the large deflection in the path of a charged particle moving through a magnetic field and allows spin-dependent effects to dominate. A schematic of the apparatus is shown in Fig. 7.1.

If the particle is treated as a classical spinning magnetic dipole, it will precess in a magnetic field because of the torque that the magnetic field exerts on the dipole. If it moves through a homogeneous magnetic field, the forces exerted on opposite ends of the dipole cancel each other out and the trajectory of the particle is unaffected. However, if the magnetic field is inhomogeneous then the force on one end of the dipole will be slightly greater than the opposing force on the other end, so that there is a net force which deflects the particle's trajectory. If the particles were classical spinning objects, one would expect the distribution of their spin angular momentum vectors to be random and continuous. Each particle would be deflected by an amount proportional to its magnetic moment, producing some density distribution on the detector screen. Instead, the particles passing through the Stern–Gerlach apparatus are equally distributed among two possible values, with half of them ending up at an upper spot ("spin up"), and the other half at the lower spot ("spin down"). Since the particles are deflected by a magnetic field, spin is a magnetic property that is associated with some intrinsic form of angular momentum. As we saw

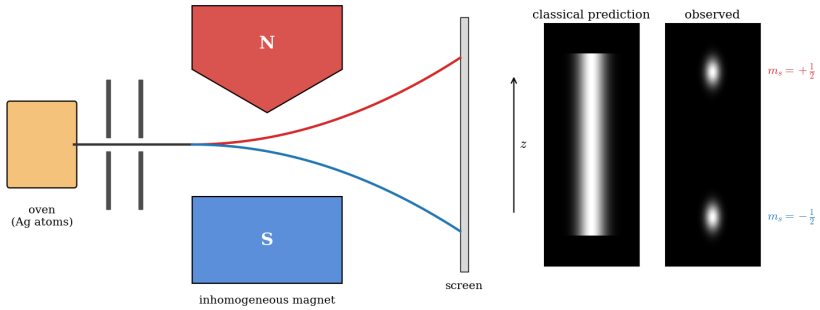


Figure 7.1 Schematic of the Stern–Gerlach experiment. A beam of silver atoms from an oven is collimated by two slits and passes between the poles of a magnet shaped to produce an inhomogeneous field. Right: the pattern on the screen expected for classical magnetic dipoles with random orientations (a continuous band) compared with the observed pattern (two separate spots).

in Chapter 6, the quantization of the angular momentum gives energy levels that are $(2\ell + 1)$-fold degenerate. Since along the direction of the magnet we observe only two possible eigenvalues for the spin, we conclude the following value for s:

$$2s + 1 = 2 \quad \Rightarrow \quad s = \frac{1}{2}. \tag{7.1}$$

The Stern-Gerlach experiment proves that electrons are spin-$\frac{1}{2}$ particles. These have only two possible spin angular momentum values measured along any axis, $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, a purely quantum mechanical phenomenon. Because its value is always the same, it is regarded as an intrinsic property of electrons, and is sometimes known as "intrinsic angular momentum" (to distinguish it from orbital angular momentum, which can vary and depends on the presence of other particles).

The act of observing (measuring) the spin angular momentum along the z direction corresponds to the operator $\hat{S}_z$, which projects the value of the total spin operator $\hat{S}^2$ along the z axis. The eigenvalue equation for this projection operator is:

$$\hat{S}_z \chi = \hbar m_s \chi, \tag{7.2}$$

where $m_s = \{-s, +s\} = \left\{-\frac{1}{2}, +\frac{1}{2}\right\}$ is the spin quantum number along the z component. The eigenvalues for the total spin operator $\hat{S}^2$—similarly to the angular momentum operator $\hat{L}^2$ seen in Eq. (6.27)—are:

$$\hat{S}^2 \chi = \hbar^2 s(s+1)\chi, \tag{7.3}$$

Notice that the magnitude of the spin angular momentum, $|\mathbf{S}| = \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar \approx 0.87\hbar$, is larger than its largest possible projection on the z axis, $\frac{1}{2}\hbar$. In other words, the spin vector can never point exactly along z. A common way of picturing this result, shown in Fig. 7.2, is to imagine the spin vector lying somewhere on the surface of a cone around the z axis: its z component is well defined ($+\frac{\hbar}{2}$ for α, and $-\frac{\hbar}{2}$ for β), while its x and y components are not. As we will see in the next sections, this is a consequence of the fact that the three components of spin cannot be measured at the same time.

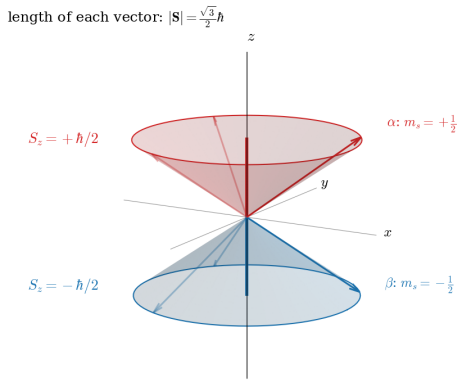


Figure 7.2 Vector model of the two spin states of an electron. The spin vector has length $\frac{\sqrt{3}}{2}\hbar$ and a well-defined projection on the z axis, $+\frac{\hbar}{2}$ (α, red) or $-\frac{\hbar}{2}$ (β, blue), but its direction around the cone (i.e., its x and y components) is undetermined. The lighter arrows show other possible orientations on the same cone.

The initial state of the particles in the Stern-Gerlach experiment is given by the following wave function:

$$\chi = c_1\,\alpha + c_2\,\beta, \tag{7.4}$$

where α and β are the two eigenfunctions of $\hat{S}_z$, corresponding to spin up ($\uparrow$, $m_s = +\frac{1}{2}$, eigenvalue $+\frac{\hbar}{2}$) and spin down ($\downarrow$, $m_s = -\frac{1}{2}$, eigenvalue $-\frac{\hbar}{2}$), respectively, and the coefficients c_1 and c_2 are complex numbers. The names α and β for the two spin functions are standard in chemistry, and we will use them for the rest of this textbook. In this initial state, spin can point in any direction. The expectation value of the operator $\hat{S}_z$ (the quantity that the Stern-Gerlach experiment measures), can be obtained using Eq. (6.20):

$$\begin{aligned} < S_z > &= \int \chi^* \hat{S}_z \chi \, d\mathbf{s} \\ &= +\frac{\hbar}{2}|c_1|^2 - \frac{\hbar}{2}|c_2|^2, \end{aligned} \tag{7.5}$$

where the integration is performed along a special coordinate **s** composed of only two values. Applying the normalization condition, Eq. (6.18), we can obtain:

$$|c_1|^2 + |c_2|^2 = 1 \quad \longrightarrow \quad |c_1|^2 = |c_2|^2 = \frac{1}{2}. \tag{7.6}$$

This equation is not sufficient to determine the values of the coefficients since they are complex numbers. Eq. (7.6), however, tells us that the squared magnitudes of the coefficients can be interpreted as probabilities of outcome from the experiment. This is true because their values are obtained from the normalization condition, and the normalization condition guarantees that the system is observed with probability equal to one. Summarizing, since we started with random initial directions, each of the two states, α and β, will be observed with equal probability of $\frac{1}{2}$.

Example 7.1: Spin probabilities

An electron is described by the spin function $\chi = \frac{\sqrt{3}}{2}\alpha + \frac{1}{2}\beta$. What are the probabilities of measuring spin up and spin down along z, and what is $\langle S_z \rangle$?

Step 1: check the normalization. $\left|\frac{\sqrt{3}}{2}\right|^2 + \left|\frac{1}{2}\right|^2 = \frac{3}{4} + \frac{1}{4} = 1.$

Step 2: probabilities. $P(\uparrow) = \frac{3}{4}$ and $P(\downarrow) = \frac{1}{4}$.

Step 3: expectation value. Each result is weighted by its probability:

$$\langle S_z \rangle = \frac{3}{4}\left(+\frac{\hbar}{2}\right) + \frac{1}{4}\left(-\frac{\hbar}{2}\right) = +\frac{\hbar}{4}.$$

As for any superposition, a single measurement gives either $+\hbar/2$ or $-\hbar/2$, never $\hbar/4$.

7.2 Sequential Stern-Gerlach Experiments

An interesting result can be obtained if we link multiple Stern–Gerlach apparatuses into one experiment and we perform the measurement along two orthogonal directions in space. As we showed in the previous section, all particles leaving the first Stern-Gerlach apparatus are in an eigenstate of the $\hat{S}_z$ operator (i.e., their spin is either "up" or "down" with respect to the z-direction). We can then take either one of the two resulting beams (for simplicity let's take

the "spin up" output), and perform another spin measurement on it. If the second measurement is also aligned along the z-direction then only one outcome will be measured, since all particles are already in the "spin up" eigenstate of $\hat{S}_z$. In other words, the measurement of a particle being in an eigenstate of the corresponding operator leaves the state unchanged. The possible combinations of sequential experiments discussed in this section are summarized in Fig. 7.3.

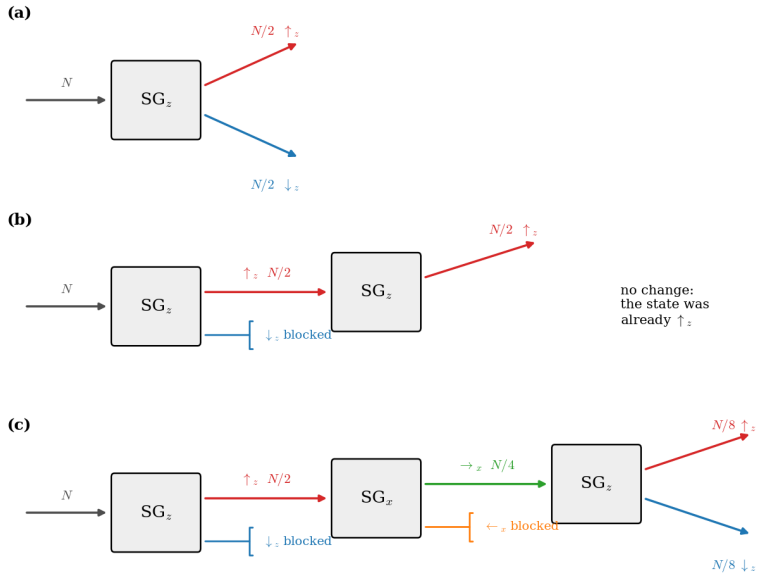


Figure 7.3 Sequential Stern–Gerlach experiments, with the number of particles in each beam. (a) A single apparatus along z splits a beam of N particles into two equal beams. (b) A second apparatus along z does not split the spin-up beam any further. (c) An apparatus along x splits the spin-up beam into two beams, spin right and spin left; a third apparatus along z then splits the spin-right beam again into spin up and spin down, as if the first measurement had never happened.

If, however, we perform the spin measurement along a direction perpendicular to the original z-axis (i.e., the x-axis) then the output will equally distribute among "spin up" or "spin down" in the x-direction, which in order to avoid confusion, we can call "spin left" and "spin right". Thus, even though we knew the state of the particles beforehand, in this case the measurement resulted in a random spin flip in either of the measurement directions. Mathematically, this property is expressed by the nonvanishing of the commutator of the spin operators:

$$\left[\hat{S}_z, \hat{S}_x\right] \neq 0. \tag{7.7}$$

We can finally repeat the measurement a third time, with the magnet aligned along the original z-direction. According to classical physics, after the second apparatus, we would expect to have one beam with characteristic "spin up" and "spin left", and another with characteristic "spin up" and "spin right". The outcome of the third measurement along the original z-axis should be one output with characteristic "spin up", regardless of which beam the magnet is applied (since the "spin down" component should have been "filtered out" by the first experiment, and the "spin left" and "spin right" component should be filtered out by the third magnet). This is not what is observed. The output of the third measurement is—once again—two beams in the z direction, one with "spin up" characteristic and the other with "spin down".

This experiment shows that spin is not a classical property. The Stern-Gerlach apparatus does not behave as a simple filter, selecting beams with one specific pre-determined characteristic. The second measurement along the x axis destroys the previous determination of the angular momentum in the z direction. This means that this property cannot be measured on two perpendicular directions at the same time.

7.3 Spin Operators

The mathematics of quantum mechanics tells us that $\hat{S}_z$ and $\hat{S}_x$ do not commute. As we saw in Sec. 6.3.3, when two operators do not commute, in general there is no state in which both of the associated quantities have a definite value: they cannot be known at the same time.

In 3-dimensional space there are three directions that are orthogonal to each other $\{x, y, z\}$. Thus, we can define a third spin projection operator along the y direction, $\hat{S}_y$, corresponding to a new set of Stern-Gerlach experiments where the second magnet is oriented along a direction that is orthogonal to the two that we considered in the previous section. The total spin operator, $\hat{S}^2$, can then be constructed similarly to the total angular momentum operator of Eq. (6.26), as:

$$\begin{aligned}\hat{S}^2 &= \hat{S}\cdot\hat{S} = \left(\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z\right)\cdot\left(\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z\right)\\ &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,\end{aligned} \tag{7.8}$$

with $\{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ the unit vectors in three-dimensional space.

Wolfgang Pauli explicitly derived the relationships between all three spin projection operators. Assuming the magnetic field along the z axis, Pauli's relations can be written using simple equations involving the two possible eigenstates α and β:

$$\begin{aligned}\hat{S}_x\alpha &= \frac{\hbar}{2}\beta \qquad \hat{S}_y\alpha = \frac{\hbar}{2}i\beta \qquad \hat{S}_z\alpha = \frac{\hbar}{2}\alpha\\ \hat{S}_x\beta &= \frac{\hbar}{2}\alpha \qquad \hat{S}_y\beta = -\frac{\hbar}{2}i\alpha \qquad \hat{S}_z\beta = -\frac{\hbar}{2}\beta,\end{aligned} \tag{7.9}$$

where i is the imaginary unit ($i^2 = -1$). In other words, for $\hat{S}_z$ we have eigenvalue equations, while the remaining components have the effect of permuting state α with state β after multiplication by suitable constants. We can use these equations, together with Eq. (6.7), to calculate the commutator for each pair of spin projection operators:

$$\begin{aligned}\left[\hat{S}_x, \hat{S}_y\right] &= i\hbar\hat{S}_z \\ \left[\hat{S}_y, \hat{S}_z\right] &= i\hbar\hat{S}_x \\ \left[\hat{S}_z, \hat{S}_x\right] &= i\hbar\hat{S}_y,\end{aligned} \tag{7.10}$$

In words: no two components of the spin commute with each other, so, as we saw for position and momentum, no state can have definite values of two different components at the same time. This is exactly what the sequential Stern–Gerlach experiments showed.

Proof: the commutators of the spin components

The commutators in Eq. (7.10) follow from Pauli's relations, Eq. (7.9), and the definition of commutator, Eq. (6.7). We apply both sides to α (applying them to β gives the same result). For the first pair:

$$\begin{aligned}\left[\hat{S}_x, \hat{S}_y\right]\alpha &= \hat{S}_x\hat{S}_y\alpha - \hat{S}_y\hat{S}_x\alpha \\ &= \hat{S}_x\left(\frac{\hbar}{2}i\beta\right) - \hat{S}_y\left(\frac{\hbar}{2}\beta\right) \\ &= \frac{\hbar}{2}i\left(\frac{\hbar}{2}\alpha\right) - \frac{\hbar}{2}\left(-\frac{\hbar}{2}i\alpha\right) \\ &= \left(\frac{\hbar^2}{4} + \frac{\hbar^2}{4}\right)i\alpha \\ &= \frac{\hbar^2}{2}i\alpha \\ &= i\hbar\hat{S}_z\alpha\end{aligned} \tag{7.11}$$

7.4 Operators Commuting with the Hamiltonian

We have now met several quantum numbers: n for the particle in a box, m_ℓ for the particle on a ring, ℓ and m_ℓ for the particle on a sphere, n, ℓ, and m_ℓ for the hydrogen atom, and now m_s for spin. At first sight, they look like a random collection of labels, each one coming out of a different calculation. To conclude this chapter, let's step back and see that they all have the same origin.

The key is the theorem that we discussed in Sec. 6.3.3: if an operator $\hat{A}$ commutes with the Hamiltonian, $[\hat{H}, \hat{A}] = 0$, we can find wave functions that are

eigenfunctions of both. Each of these wave functions then has a definite energy *and* a definite value of the observable A, and we can use the eigenvalue of $\hat{A}$ as a label for the state. Moreover, since $\hat{A}$ commutes with $\hat{H}$, which controls the time evolution (Sec. 6.4), this label does not change in time: the observable A is *conserved*. Physicists call such a label a **good quantum number**.

So, the question "which quantum numbers does a system have?" becomes "which operators commute with its Hamiltonian?". And, as we will see in the examples below, the answer to this second question comes from the **symmetry** of the system: every time the system looks the same after some operation (a shift, a reflection, a rotation), there is an operator that commutes with $\hat{H}$, and a quantum number that comes with it.

7.4.1 Free particle: shifts and momentum

A free particle feels no potential, so its Hamiltonian contains only the kinetic energy, $\hat{H} = \hat{p}^2/2m$. Its symmetry is that space looks the same everywhere: if we shift the whole system by any distance, nothing changes. The operator associated with this symmetry is the momentum, and since $\hat{H}$ contains only $\hat{p}$, the two commute:

$$[\hat{H}, \hat{p}] = 0. \tag{7.12}$$

This is why the free-particle solutions of Chapter 3, the plane waves e^{ikx}, have both a definite energy and a definite momentum, $p = \hbar k$, and why we can label them with k.

7.4.2 Particle in a box: no more momentum, but parity

Inside a box, the particle is still free, but the walls break the symmetry: if we shift the system, the walls move, and the problem changes. As a consequence, $\hat{p}$ no longer commutes with $\hat{H}$, and momentum is not a good quantum number. We can check this directly: the eigenfunctions of the particle in a box, $\sin(n\pi x/a)$, are not eigenfunctions of $\hat{p} = -i\hbar\frac{d}{dx}$, since the derivative turns a sine into a cosine. (Using Euler's formula, each sine is a combination of two plane waves, one moving to the right and one to the left, with opposite momenta. A measurement of momentum would give either one, but the state does not have a definite momentum.)

Some symmetry, however, survives. To see it, let's place the box symmetrically, between $-a/2$ and $+a/2$. This is the same box as in Chapter 4, only shifted so that its center is at $x = 0$. Moving the origin changes neither the energies nor the shapes of the wave functions, but it makes the symmetry easy to see: the system now looks the same when we reflect it through its center, $x \to -x$. The operator that performs this reflection is called the **parity operator**, $\hat{\Pi}$:

$$\hat{\Pi}\,\psi(x) = \psi(-x). \tag{7.13}$$

Whenever the potential is symmetric, $V(-x) = V(x)$, the Hamiltonian does not change under reflection, and it commutes with parity, $[\hat{H}, \hat{\Pi}] = 0$. The energy eigenfunctions can then be chosen to be eigenfunctions of parity too. Since reflecting twice brings us back to where we started, the only possible eigenvalues are $+1$ and -1:

- **Even** functions are unchanged by the reflection, $\psi(-x) = +\psi(x)$.
- **Odd** functions change sign, $\psi(-x) = -\psi(x)$.

As shown in Fig. 7.4, the states of the particle in a box alternate between even and odd as the energy increases. Parity is a simple label, but a very useful one: it is the origin of the g and u labels of molecular orbitals in Chapter 11, and of many selection rules in Chapter 13, since the integral of an odd function over a symmetric interval is zero (Sec. A.3).

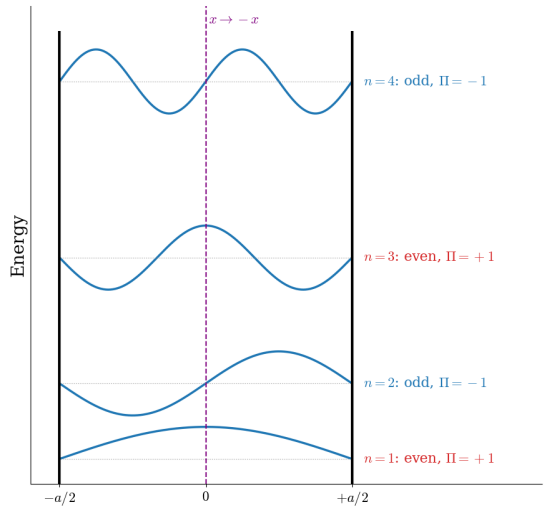


Figure 7.4 The first four eigenfunctions of a particle in a box placed symmetrically between $-a/2$ and $+a/2$. Even states (red labels) are unchanged by the inversion $x \to -x$ (reflection through the purple dashed line), and odd states (blue labels) change sign.

7.4.3 Particle on a ring and on a sphere: rotations and angular momentum

A particle on a ring looks the same if we rotate the ring by any angle around its axis, z. The operator associated with rotations around z is the z component of the angular momentum, so:

$$[\hat{H}, \hat{L}_z] = 0. \tag{7.14}$$

This is why the solutions of the particle on a ring, $e^{im_\ell \phi}$, have both a definite energy and a definite angular momentum, $L_z = m_\ell \hbar$ (Chapter 4), and why we can label them with m_ℓ.

A particle on a sphere looks the same after a rotation around *any* axis. Its Hamiltonian commutes with all three components of the angular momentum, and therefore also with $\hat{L}^2$. Since the components do not commute with each other (Chapter 6), we cannot use all of them as labels at the same time. The best we can do is to pick $\hat{L}^2$ and one component, by convention $\hat{L}_z$:

$$[\hat{H}, \hat{L}^2] = 0, \qquad [\hat{H}, \hat{L}_z] = 0, \tag{7.15}$$

which give the two quantum numbers ℓ (from $L^2 = \hbar^2 \ell(\ell+1)$) and m_ℓ (from $L_z = \hbar m_\ell$) of the spherical harmonics. There is one more consequence of the symmetry. Since the sphere has no preferred direction, the energy cannot depend on the orientation of the angular momentum, that is, on m_ℓ. This is why each level ℓ is $(2\ell + 1)$ times degenerate: the degeneracy *is* the rotational symmetry.

7.4.4 Hydrogen atom: one label more, and an extra degeneracy

The Coulomb potential of the hydrogen atom depends only on the distance from the nucleus, r, so the atom has the same rotational symmetry as the sphere, and $\hat{H}$ commutes with $\hat{L}^2$ and $\hat{L}_z$. Together with the energy itself, this gives the three labels n, ℓ, and m_ℓ of the hydrogen orbitals.

Rotational symmetry explains why the energy does not depend on m_ℓ. It does not explain, however, why the energy of hydrogen does not depend on ℓ either, so that, for example, the $2s$ and $2p$ orbitals have the same energy (Chapter 5). This additional degeneracy is a special property of the $1/r$ potential, which has a hidden symmetry that goes beyond simple rotations (its discussion is beyond the scope of this book). As soon as the potential is no longer exactly $1/r$, as for an electron in a many-electron atom shielded by the others, this degeneracy disappears, and the $2s$ and $2p$ energies split (Chapter 9).

7.4.5 Spin: why it matters

The hydrogen Hamiltonian that we used does not contain spin at all, so it automatically commutes with $\hat{S}^2$ and $\hat{S}_z$. Each spatial state (n, ℓ, m_ℓ) can therefore be combined with either spin function, α or β, giving a fourth label, $m_s = \pm\frac{1}{2}$, and doubling the number of states. In hydrogen, spin does not change the energies (except for the tiny spin–orbit effects that we will discuss in Sec. 9.4), but it changes the counting: this is why the first shell of the periodic table holds two elements, and the second one eight.

In atoms with many electrons, the same reasoning applies to the whole atom. The atom as a whole is still rotationally symmetric, so the *total* orbital angular momentum, L, and the *total* spin, S, become the good quantum numbers that label its states. These are the labels of the term symbols that we will meet in Sec. 9.4.

To summarize, every quantum number we use in chemistry can be traced back to a symmetry of the system, as collected in Table 7.1.

Table 7.1 Symmetries, commuting operators, and quantum numbers.

System	Symmetry	Commutes with $\hat{H}$	Quantum numbers
Free particle	shifts in space	$\hat{p}$	k
Symmetric box	reflection $x \to -x$	$\hat{\Pi}$	parity (even/odd)
Particle on a ring	rotations around z	$\hat{L}_z$	m_ℓ
Sphere, hydrogen atom	all rotations	$\hat{L}^2$, $\hat{L}_z$	ℓ, m_ℓ
Electron spin	(not in $\hat{H}$)	$\hat{S}^2$, $\hat{S}_z$	s, m_s
Many-electron atom	all rotations	$\hat{L}^2$, $\hat{S}^2$ (total)	L, S

7.5 Chapter Review

7.5.1 Key Ideas

- The Stern–Gerlach experiment shows that electrons have an intrinsic angular momentum, spin, with only two possible z components, $\pm\hbar/2$.
- The spin components do not commute with each other, so measuring one of them randomizes the others.
- A spin state $c_1\alpha + c_2\beta$ gives spin up with probability $|c_1|^2$ and spin down with probability $|c_2|^2$.
- Every quantum number comes from a symmetry of the system, through an operator that commutes with the Hamiltonian.
- Spin adds a fourth label, m_s, and doubles the number of states of each orbital.

7.5.2 Study Questions

1. **In the Stern–Gerlach experiment, a beam of silver atoms passing through an inhomogeneous magnetic field:**

a. is deflected into a continuous band
b. is not deflected
c. splits into three beams
d. is absorbed by the magnet
e. splits into two beams

2. The possible results of a measurement of the z component of the spin of an electron are:

a. $+\hbar$ and $-\hbar$
b. $+\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$
c. 0 and $\hbar$
d. any value between $-\frac{\hbar}{2}$ and $+\frac{\hbar}{2}$
e. $\frac{\sqrt{3}}{2}\hbar$

3. The magnitude of the spin of an electron, $\frac{\sqrt{3}}{2}\hbar$, is larger than its largest z component, $\frac{\hbar}{2}$. This means that:

a. the spin always points along z
b. the measurement of S_z is wrong
c. the spin can never point exactly along the z axis
d. the electron has two spins
e. the spin is not quantized

4. An electron is described by the spin function $c_1\alpha + c_2\beta$. The probability of measuring spin up along z is:

a. c_1
b. $|c_2|^2$
c. $\frac{1}{2}$, whatever the coefficients
d. $|c_1|^2$
e. $|c_1|^2 + |c_2|^2$

5. Electrons selected with spin up along z pass through an apparatus aligned along x, and then the spin-up-along-x beam is measured again along z. The result is:

a. both spin up and spin down along z, with equal probability
b. only spin up along z
c. only spin down along z
d. no electrons
e. a continuous distribution of values

6. The commutator $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \neq 0$ means that:

a. S_x and S_y are always zero
b. spin is a classical vector
c. the three spin components have the same value

d. an electron cannot have definite values of two different spin components at the same time
e. S_z cannot be measured

7. A quantum number is called a *good quantum number* when:

a. it is an eigenvalue of an operator that commutes with the Hamiltonian, so it does not change in time
b. it is an integer
c. it determines the energy
d. it is positive
e. it can only take two values

8. For a particle in a box placed symmetrically around $x = 0$, the energy eigenfunctions are:

a. all even
b. alternately even and odd under the reflection $x \to -x$
c. all odd
d. neither even nor odd
e. eigenfunctions of momentum

9. Why are the energy levels of a particle on a sphere $(2\ell + 1)$ times degenerate?

a. because the Hamiltonian does not commute with $\hat{L}_z$
b. because of the Pauli exclusion principle
c. because the sphere has no preferred direction, so the energy cannot depend on m_ℓ
d. because of spin
e. because the potential energy is $1/r$

10. Including spin, how many different states does the $n = 2$ level of the hydrogen atom have?

a. 2
b. 4
c. 6
d. 16
e. 8

Answers

1.e, 2.b, 3.c, 4.d, 5.a, 6.d, 7.a, 8.b, 9.c, 10.e

CHAPTER 8

Quantum Weirdness

In this chapter, we will delve deeper into the strangeness of quantum mechanics. In particular, we will explore quantum phenomena that don't have a classical counterpart, starting from perhaps the simplest but also one of the most revealing: the double-slit experiment.

8.1 The double-slit experiment

The double-slit experiment is considered by many the seminal experiment in quantum mechanics. The reason why we see it only at this advanced point is that its interpretation is not as straightforward as it might seem from a superficial analysis. The famous physicist Richard Feynman was so fond of this experiment that he used to say that all of quantum mechanics can be understood from carefully thinking through its implications.

The premises of the experiment are very simple: cut two slits in a solid material (such as a sheet of metal), send light or electrons through them, and observe what happens on a screen positioned at some distance on the other side. The results of this experiment, though, are far from straightforward.

Let's first consider the single-slit case. If light consisted of classical particles, and these particles were sent in a straight line through a single-slit and allowed to strike a screen on the other side, we would expect to see a pattern corresponding to the size and shape of the slit. However, when this "single-slit experiment" is actually performed, the pattern on the screen is a diffraction pattern in which the light is spread out. The smaller the slit, the greater the angle of spread. This behavior is typical of waves, where diffraction explains the pattern as being the result of the interference of the waves with the slit.

If one illuminates two parallel slits, the light from the two slits again interferes. Here the interference is a more pronounced pattern with a series of alternating light and dark bands. The width of the bands is a property of the frequency of the illuminating light. The pattern observed on the screen is the result of this interference, as shown in Fig. 8.1.

The interference pattern resulting from the double-slit experiment is observed not only with light, but also with a beam of electrons, and other small particles. This is the same wave behavior of electrons that Davisson and Germer first observed in 1927, when they diffracted electrons from a nickel crystal (Chapter 2).

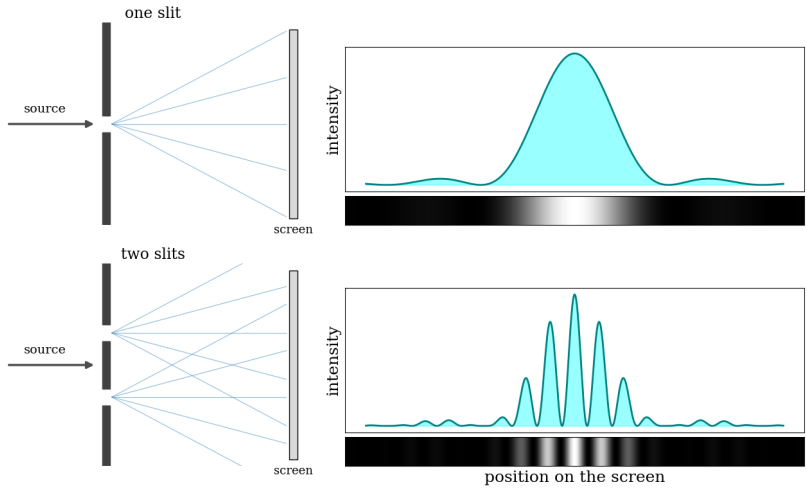


Figure 8.1 Diffraction through one slit (top) and interference through two slits (bottom). Left: schematic of the experiment. Right: intensity on the screen and the corresponding pattern of light and dark regions.

8.1.1 The individual particles experiment

The first twist in the plot is if we perform the experiment by sending individual particles (e.g., either individual photons, or individual electrons). Sending particles through a double-slit apparatus one at a time results in single particles appearing on the screen, as expected. Remarkably, however, an interference pattern emerges when these particles are allowed to build up one by one (Fig. 8.2). The resulting pattern on the screen is the same as if each individual particle had passed through both slits.

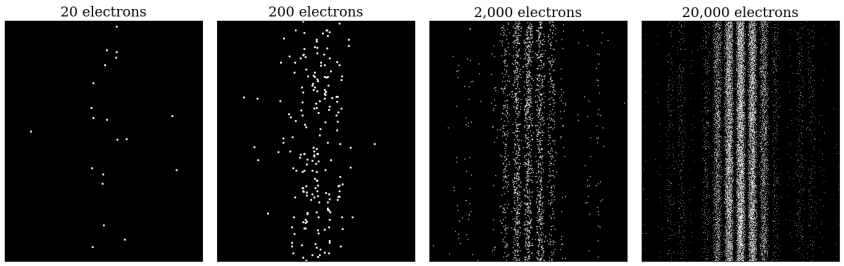


Figure 8.2 Simulated arrival of electrons, one at a time, on the screen of a double-slit experiment. Each electron arrives at a single random point, but as more electrons accumulate, the interference fringes emerge.

This variation of the double-slit experiment demonstrates the wave–particle

duality: the particle is measured as a single pulse at a single position, while the wave describes the probability of absorbing the particle at a specific place on the screen.

8.1.2 "Which way" experiment

A second twist happens if we place particle detectors at the slits with the intent of showing through which slit a particle goes. The interference pattern in this case will disappear. The two situations are compared in Fig. 8.3. Notice that a single detector, placed on one of the two slits, is enough: if it does not click, we know that the particle went through the other slit. With the detector on, the pattern on the screen is simply the sum of the patterns produced by each slit separately, exactly what we would expect from classical particles.

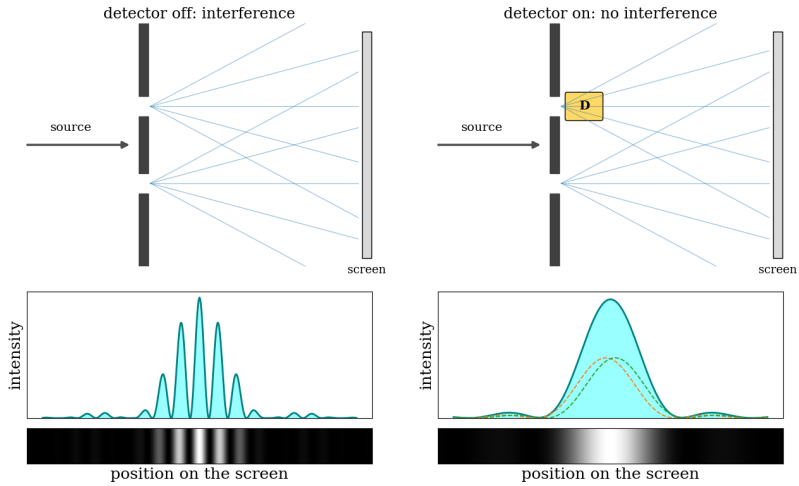


Figure 8.3 The which-way experiment. Left: without a detector, the particles produce interference fringes. Right: with a detector (D) on one slit, which reveals which slit each particle goes through, the fringes disappear, and the pattern is the sum of the two single-slit patterns (dashed lines).

This experiment illustrates that photons (and electrons) can behave as either particles or waves, but cannot be observed as both at the same time. In the language that we will introduce in the next section, the interaction with the detector on the slit makes the wave function of the particle *collapse* onto one of the two slits, and the interference pattern is therefore lost. This result also proves that in order to measure (detect) a photon, we must interact with it, an act that changes its wave function.

The interpretation of the results of this experiment is not simple. The problem is not that we cannot describe the experiment with mathematics: the wave function predicts the interference pattern perfectly. The problem is that the

wave function only gives *probabilities*, while each detector click, like every measurement in the macroscopic world, gives one definite result. How does a single, definite result come out of a wave function that describes all the possibilities at once? And why does looking at the slits change the outcome? These questions take us to the heart of what is called the **measurement problem**, the subject of the next section.

8.2 The Measurement Problem and Interpretations of Quantum Mechanics

8.2.1 Measurement and the collapse of the wave function

The which-way experiment shows that observing a quantum system is not a passive act: finding out which slit the particle goes through destroys the interference. To understand why, we need to look more closely at what quantum mechanics says about measurements.

In Chapter 6, we saw that if a system is in a superposition of eigenfunctions of an operator $\hat{A}$:

$$\Psi = \sum_i c_i \Psi_i, \qquad \hat{A}\Psi_i = a_i \Psi_i, \tag{8.1}$$

then a measurement of the observable A can only give one of the eigenvalues a_i, with probability $|c_i|^2$. Before the measurement, we cannot predict which one we will obtain: quantum mechanics only gives us the probabilities. This raises an obvious question: what happens to the wave function *after* the measurement?

The answer of quantum mechanics is that, immediately after a measurement that gives the value a_i, the wave function is no longer the superposition of Eq. (8.1), but the corresponding eigenfunction:

$$\Psi \xrightarrow{\text{measurement gives } a_i} \Psi_i. \tag{8.2}$$

This sudden change is called the **collapse of the wave function**. One way of seeing that it must happen is to repeat the measurement immediately after the first one: experiments show that we always obtain the same value again, a_i, with certainty. This is only possible if the system is now in the eigenstate Ψ_i, whose coefficient is one.

We have already seen the collapse at work in the sequential Stern–Gerlach experiments of Chapter 7 (Fig. 7.3). After the first apparatus along z, the atoms in the upper beam are in the state α, and a second measurement along z gives "spin up" with certainty. A measurement along x, however, makes the state collapse into one of the eigenstates of $\hat{S}_x$, which are superpositions of α and β. When we measure along z again, we find both "spin up" and "spin down" with equal probability: the information about the first measurement has been

erased by the second one. The measurement is not a "filter" that reveals a pre-existing property of the atom, but an act that changes its wave function.

The collapse is very different from the time evolution described by the TDSEq (Sec. 6.4). Time evolution is smooth, deterministic (if we know the wave function now, we can calculate it at any later time), and reversible. The collapse is sudden, random (we can only predict probabilities), and irreversible (after the collapse, we cannot reconstruct the superposition that we had before). Quantum mechanics, in its standard form, does not explain *what* exactly counts as a measurement, nor *how* or *when* the collapse happens. It only tells us that, when an interaction with a macroscopic instrument produces a definite result, the wave function must be updated accordingly. This is known as the **measurement problem**, and it is still debated by physicists and philosophers today. As we will see in this chapter, the collapse is at the heart of many of the most counterintuitive results of quantum mechanics.

8.2.2 Schrödinger's cat and decoherence

In 1935, Erwin Schrödinger proposed a thought experiment to show how strange the measurement problem becomes when we take it seriously. A cat is sealed in a box together with a single radioactive atom, a detector, and a vial of poison. If the atom decays, the detector triggers the release of the poison, and the cat dies. After one half-life, the atom is in an equal superposition of "decayed" and "not decayed." If the Schrödinger equation applies to everything, including the detector, the vial, and the cat, which are made of atoms too, then the cat should end up in a superposition of "alive" and "dead," at least until someone opens the box and looks. Schrödinger did not believe in such a cat. His point was that the rules of quantum mechanics, applied blindly to a macroscopic object, lead to an absurd conclusion. Where, then, does the quantum superposition stop, and where does a definite, classical result begin?

Part of the answer comes from **decoherence**. A macroscopic object is never isolated: it constantly interacts with its environment, by colliding with air molecules, absorbing and emitting photons, and so on. Each of these interactions leaves a trace of the state of the object in the environment, in the same way as the detector of the which-way experiment leaves a trace of the slit that the particle went through. Once this information has spread into the environment, the different parts of the superposition can no longer interfere with each other, and the object behaves, for all practical purposes, as if it were in one state or the other, with probabilities $|c_i|^2$. For a macroscopic object, this happens in an unimaginably short time, which is why we never see cats, or measuring devices, in superpositions. Decoherence is not an extra rule: it follows from the Schrödinger equation itself, and it has been observed in experiments, for example by watching the interference fringes of large molecules, such as fullerenes, fade away as gas is let into the interferometer. It also explains why the collapse looks irreversible: undoing it would require collecting back all the information

that has been scattered into the environment.

Decoherence, however, does not solve the whole measurement problem. It explains why we never see interference between macroscopic alternatives, and why the world around us looks classical. It does not explain why each experiment has a *single* outcome. After decoherence, the mathematics still contains all the possibilities, the living cat and the dead cat, only now they can no longer interfere. Why we observe only one of them, and which one, is the question that decoherence leaves open. The interpretations of quantum mechanics answer it in different ways.

8.2.3 Interpretations of quantum mechanics

The mathematics of quantum mechanics is not in question: it has been tested in countless experiments, and it has never failed. What is still debated is what the mathematics *means*. What is the wave function: a real physical object, or just a tool to compute probabilities? Does the collapse really happen, and if so, what causes it? Do particles have definite properties before we measure them? The different answers to these questions are called *interpretations* of quantum mechanics.

In this textbook, as in most chemistry textbooks, we use the language of the **Copenhagen interpretation**, developed in the 1920s mainly by Niels Bohr and Werner Heisenberg. In this view, the wave function encodes everything that can be known about a system, it evolves according to the Schrödinger equation between measurements, and it collapses when a measurement is made, as described above. The Copenhagen interpretation is convenient for calculations, and it is the reason why we talk about "measurements" and "collapse" at all. However, it is now widely regarded as antiquated and incomplete. It divides the world into a quantum system and a classical measuring apparatus, but it never says where the boundary between the two is, nor why the apparatus, which is itself made of atoms, should not obey quantum mechanics. It adds the collapse as a separate rule, without explaining it. In other words, the Copenhagen interpretation does not solve the measurement problem; it simply declares it out of bounds.

Many physicists, and even more chemists, are happy to stop here. The theory works, its predictions have never failed, and every interpretation gives the same numbers, so why worry about what the wave function "really" is? This pragmatic attitude is often summarized as **"shut up and calculate,"** a phrase coined by the physicist David Mermin in 1989 (and often wrongly attributed to Richard Feynman). It is a perfectly reasonable way to *use* quantum mechanics, and it is, in practice, the attitude of most working scientists and of this textbook. It does not, however, answer any of the questions above: it only decides not to ask them. The physicists and philosophers who do ask them have proposed many alternatives to the Copenhagen interpretation. All of them reproduce the successful predictions of quantum mechanics, but they paint very different pictures of reality. We can group them into four broad classes:

- **Hidden variables.** The idea that the wave function is an incomplete description, and that additional "hidden" variables determine the outcome of each measurement, goes back to Albert Einstein, who famously disliked the randomness of quantum mechanics. In 1964, John Bell proved that any theory of this kind that is also *local* (where nothing travels faster than light) must make predictions that differ from those of quantum mechanics. Experiments, starting in the 1970s and recognized with the Nobel Prize in Physics in 2022, have confirmed the predictions of quantum mechanics and ruled out local hidden variables. Hidden variable theories are still possible, but they must be *nonlocal*. The best known one is **Bohmian mechanics** (also called the de Broglie–Bohm or *pilot-wave* theory), proposed by Louis de Broglie in 1927 and developed by David Bohm in 1952. In this view, particles always have definite positions and follow well-defined trajectories, and the wave function is a real field that guides their motion. There is no collapse: a measurement simply reveals where the particles already are, and the randomness of the outcomes comes from our ignorance of their exact initial positions. This is the picture closest to the way chemists usually think: electrons are particles that are actually somewhere, and molecules have real shapes. Its price is nonlocality: the motion of each particle depends instantaneously on the positions of all the others. Moreover, Bohmian mechanics is built on particles with definite positions, and it is difficult to extend it to quantum field theory, the relativistic version of quantum mechanics in which particles can be created and destroyed.

- **Many worlds**, proposed by Hugh Everett in 1957, takes the opposite route: it keeps the Schrödinger equation and nothing else. There is no collapse and no special role for measurements. When a measuring device interacts with a superposition, the device, the observer, and eventually the whole universe become part of the superposition, which splits into *branches*, one for each possible outcome. Each branch contains a version of the observer who sees one definite result, and decoherence prevents the branches from interacting with each other. Many worlds is the most mathematically clean of all the interpretations, since it requires no additional rules beyond the equation that we already use. Its price is a reality much larger than the one we see, and the difficulty of explaining why the probabilities of the outcomes are given by $|c_i|^2$ (the **Born rule**, which we met in Sec. 3.2) when all of them actually happen. Deriving the Born rule within many worlds is possible, but far from trivial, and the proposed derivations are still debated.

- **Spontaneous collapse theories**, such as the one proposed by Giancarlo Ghirardi, Alberto Rimini, and Tullio Weber in 1986, treat the collapse as a real physical process and modify the Schrödinger equation to include it. In these theories, the wave function of any particle collapses spontaneously and at random, but extremely rarely (about once

every hundred million years for a single particle). A macroscopic object, however, contains so many particles that one of them collapses almost immediately, dragging the whole object with it, which explains why we never see a cat or a measuring device in a superposition. Unlike the other interpretations, these theories make predictions that differ slightly from standard quantum mechanics, and they are currently being tested in experiments.

- **Other interpretations.** Several more interpretations have a smaller, but active, following. *Neo-Copenhagen* views update Bohr's ideas, often by treating the wave function as a description of the information that we have about a system rather than of the system itself. *QBism* (quantum Bayesianism), developed by Christopher Fuchs, Rüdiger Schack, and others, goes further: the wave function expresses the personal degrees of belief of the agent who uses it, and the collapse is simply the agent updating those beliefs after seeing a result. *Relational quantum mechanics*, proposed by Carlo Rovelli in 1996, holds that the properties of a system are not absolute, but only defined relative to the other systems that interact with it. Other proposals include *consistent histories* (Robert Griffiths, Roland Omnès, Murray Gell-Mann, and James Hartle) and the *transactional interpretation* (John Cramer). The idea, suggested by John von Neumann and Eugene Wigner, that the collapse is caused by the consciousness of the observer, is now largely abandoned.

The main features of the Copenhagen interpretation and of the three main classes of alternatives are summarized in Table 8.1.

Table 8.1 Comparison of the Copenhagen interpretation with the three main classes of alternatives. The other interpretations are not included, since the answers depend on the details of each one.

	Copenhagen	Hidden variables	Many worlds	Spontaneous collapse
What is the wave function?	A tool to compute probabilities	A real field that guides the particles	Real, and the only thing that exists	Real
Collapse?	Yes, upon measurement (not explained)	No (only apparent)	No (branching instead)	Yes, as a random physical process
Definite positions?	No, until measured	Yes, always	Yes, in each branch	Only after a collapse
Deterministic?	No	Yes	Yes	No

	Copenhagen	Hidden variables	Many worlds	Spontaneous collapse
Pros	Simple and practical; the language of most textbooks	Particles are really somewhere, close to the chemist's intuition	Only the Schrödinger equation, with no extra rules	Explains the collapse and the classical world; can be tested
Cons	Does not say what a measurement is; collapse added by hand	Nonlocal; the hidden positions can never be observed; hard to extend to quantum field theory	A huge, unobservable reality; deriving the probabilities $\|c_i\|^2$ (the Born rule) is not trivial	Modifies the Schrödinger equation with new constants

For the purposes of chemistry, all these interpretations give the same answers: energy levels, spectra, bond lengths, and reaction rates do not depend on which one we choose (the tiny deviations predicted by spontaneous collapse theories are far too small to affect any chemical property). This is why, in the rest of this textbook, we will keep using the convenient language of the Copenhagen interpretation. You should be aware, however, that it is a language, and not the final word on what quantum mechanics tells us about reality.

8.3 Heisenberg's Uncertainty Principle

As we saw in Sec. 3.4.2, a free particle described by a single plane wave, $\psi(x) = Ae^{ipx/\hbar}$, has a perfectly defined momentum, but it is spread over all of space, so we cannot say where it is. To describe a particle that is localized, we need a wave packet: a superposition of many plane waves with different momenta, which interfere constructively in a small region of space and cancel everywhere else (Fig. 3.3). Written as a continuous sum over momenta, a wave packet is:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \varphi(p) \exp\left(\frac{ipx}{\hbar}\right) dp, \tag{8.3}$$

where $\varphi(p)$ gives the amplitude of each plane wave in the packet. The function $\varphi(p)$ is called the *wave function in momentum space*, and $|\varphi(p)|^2$ is the probability density of finding the particle with momentum p, just as $|\psi(x)|^2$ is the probability density of finding it at position x. In mathematical terms, $\varphi(p)$ is the *Fourier transform* of $\psi(x)$, and x and p are called *conjugate variables*.

The two functions contain exactly the same information, written in two different ways, and they cannot both be narrow: localizing the particle in space requires a broad mixture of momenta, and vice versa. This connection is shown in Fig. 8.4 for three wave packets of different width.

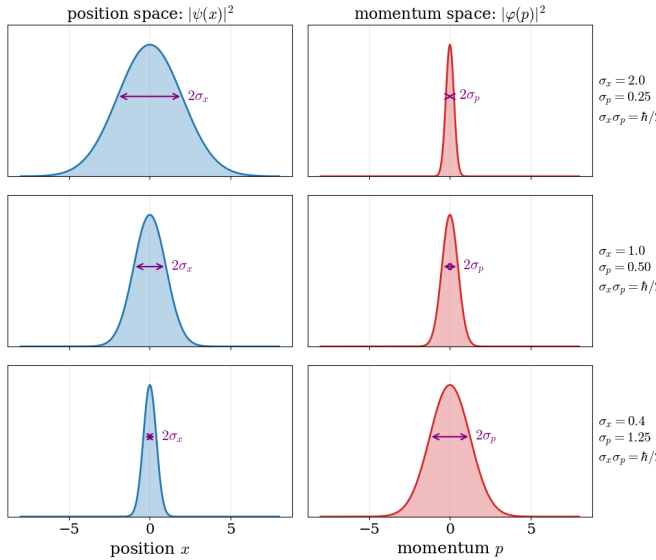


Figure 8.4 Probability densities in position space (left) and in momentum space (right) for three wave packets (in units where $\hbar = 1$). As the packet becomes narrower in position (from top to bottom), it becomes broader in momentum, and the product of the two standard deviations stays equal to $\hbar/2$.

One way to quantify the precision of the position and momentum is the standard deviation, σ. Since $|\psi(x)|^2$ is a probability density function for position, we calculate its standard deviation. The precision of the position is improved—i.e., reduced σ_x—by using many plane waves, thereby weakening the precision of the momentum—i.e., increased σ_p. Another way of stating this is that σ_x and σ_p have an inverse relationship (once we know one with absolute precision, the other becomes completely unknown). This fact was discovered by Werner Heisenberg and is now called **Heisenberg's uncertainty principle**. The mathematical treatment of this procedure results in the simple formula:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}. \tag{8.4}$$

The uncertainty principle is a direct consequence of the fact that position and momentum do not commute (Sec. 6.3.3). In fact, it is a special case of a general result: for any two observables A and B, the standard deviations of their measurements, in any state, satisfy:

$$\sigma_A \, \sigma_B \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right| . \tag{8.5}$$

This general uncertainty relation tells us that the precision with which two quantities can be known at the same time is limited by their commutator:

1. **Position and momentum.** Replacing the canonical commutation relation, $[\hat{x}, \hat{p}] = i\hbar$, in Eq. (8.5) gives $\sigma_x \sigma_p \geq \frac{1}{2}|i\hbar| = \frac{\hbar}{2}$, which is exactly Eq. (8.4). Since the commutator is a constant, this limit applies to every state, without exceptions.

2. **Components of spin and angular momentum.** For the spin components, $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ (Chapter 7), so $\sigma_{S_x}\sigma_{S_y} \geq \frac{\hbar}{2}|\langle S_z \rangle|$. For an electron in the state α, $\langle S_z \rangle = +\frac{\hbar}{2}$, so the x and y components cannot both be known precisely. This is the reason behind the results of the sequential Stern–Gerlach experiments and behind the cone picture of Fig. 7.2. The same is true for the components of the orbital angular momentum.

3. **Commuting observables.** If $[\hat{A}, \hat{B}] = 0$, the right-hand side of Eq. (8.5) is zero, and nothing prevents both observables from being known exactly. For example, the magnitude of the angular momentum and its z component can be known at the same time, which is why we can label the states of the hydrogen atom with both ℓ and m_ℓ.

You may also find in other textbooks an *energy–time* uncertainty relation, $\Delta E \, \Delta t \gtrsim \hbar/2$. Its meaning is different from Eq. (8.5), because time is not an observable described by an operator, but a parameter that labels the evolution of the system. The energy–time relation states that a state that lasts only for a short time, Δt (for example, an excited state that quickly emits a photon), does not have a perfectly defined energy, but an energy spread of about $\hbar/\Delta t$. This is the reason why spectral lines always have a finite width: the shorter the lifetime of the excited state, the broader the line.

Example 8.1: How uncertain is the velocity of an electron in an atom?

An electron in an atom is confined to a region of about 1 Å. Taking $\sigma_x = 1.0 \times 10^{-10}$ m, what is the smallest possible uncertainty in its velocity?
Step 1: minimum uncertainty in momentum. From $\sigma_x \sigma_p \geq \hbar/2$:

$$\sigma_p \geq \frac{\hbar}{2\sigma_x} = \frac{1.055 \times 10^{-34} \text{ J s}}{2 \times 1.0 \times 10^{-10} \text{ m}} = 5.3 \times 10^{-25} \text{ kg m/s}.$$

Step 2: velocity. $\sigma_v = \sigma_p / m_e = 5.3{\times}10^{-25}/9.109{\times}10^{-31} = 5.8{\times}10^{5}$ m/s. The uncertainty in the velocity is enormous, almost 600 km/s: it makes no sense to talk about the trajectory of an electron in an atom. For

Example 8.1: How uncertain is the velocity of an electron in an atom? *(continued)*

comparison, a 0.145 kg baseball localized to within 1 μm has $\sigma_v \approx 4 \times 10^{-28}$ m/s, which is why the uncertainty principle never shows up in everyday life.

8.4 Tunneling

Tunneling is the ability of a quantum particle to cross a barrier even when its energy is lower than the top of the barrier. The particle is said to "tunnel through" the barrier, a purely quantum mechanical phenomenon (Fig. 8.5).

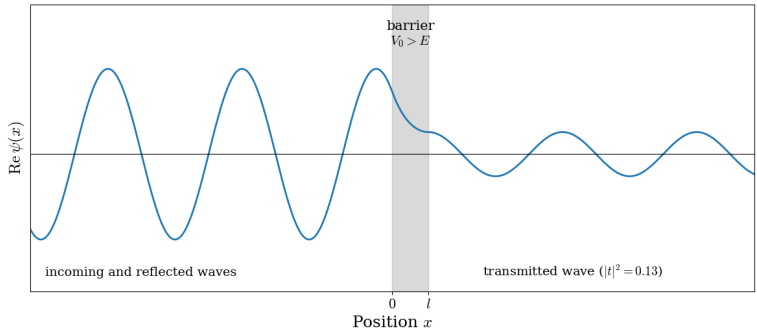


Figure 8.5 Real part of the wave function of a particle with energy E hitting a barrier of height $V_0 > E$ between 0 and l. The wave decays inside the barrier, and a smaller wave with the same wavelength continues on the other side: in this example, 13% of the particles are transmitted.

Classically, this is impossible. A ball rolling toward a hill with less energy than needed to reach the top simply rolls back. Inside the barrier, its kinetic energy would have to be negative, $K = E - V_0 < 0$, which makes no sense for a classical particle. For a quantum particle, however, the wave function does not have to stop abruptly at the wall of the barrier, and this is all we need for tunneling to happen.

Let's consider the simplest possible barrier: a particle of mass m and energy E moving along x, with the potential energy equal to zero everywhere except in a region of width l, where it is equal to $V_0 > E$:

$$V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } 0 \le x \le l \\ 0 & \text{if } x > l \end{cases}. \tag{8.6}$$

We can solve the TISEq separately in each of the three regions, and we already know all the ingredients:

- **Outside the barrier** ($x < 0$ and $x > l$) the particle is free, and the solutions are the plane waves of Chapter 3, $e^{\pm ikx}$, with $k = \frac{\sqrt{2mE}}{\hbar}$. On the left we have the incoming wave and a reflected one; on the right only a transmitted wave, moving away from the barrier.
- **Inside the barrier** the TISEq reads $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E - V_0)\psi$. Since $E - V_0$ is negative, the second derivative of ψ now has the *same* sign as ψ, and the solutions are not oscillating waves, but real exponentials:

$$\psi(x) = C\, e^{-\alpha x} + D\, e^{+\alpha x}, \qquad \alpha = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{8.7}$$

The solutions in the three regions must then be joined smoothly at $x = 0$ and $x = l$: both ψ and its first derivative must be continuous, otherwise the second derivative in the TISEq would be infinite. These four conditions fix all the coefficients. The algebra is long and not very instructive, so we will only look at the result, which is shown in Fig. 8.5: the wave function decays inside the barrier (the $e^{-\alpha x}$ term dominates), but it has not reached zero when it gets to the other side, and it continues as a smaller wave with the same wavelength.

The probability that the particle gets through, called the **transmission probability**, T, is the ratio between the probability densities of the transmitted and the incoming waves. For a barrier that is thick or high enough that the wave function decays a lot inside it ($\alpha l \gg 1$), the result of the calculation is approximately:

$$T \approx e^{-2\alpha l} = \exp\left(-\frac{2l\sqrt{2m(V_0 - E)}}{\hbar}\right), \tag{8.8}$$

where we have dropped a numerical factor in front of the exponential, which depends on E/V_0 and is of the order of one. All the physics is in the exponential, and Eq. (8.8) tells us three things:

1. **Tunneling is very sensitive to the width of the barrier.** T decreases *exponentially* with l: doubling the width of the barrier squares the (already small) transmission probability.
2. **Tunneling is very sensitive to the mass.** The mass appears under the square root in the exponent. For a barrier 1 eV higher than the energy of the particle and 5 Å wide, Eq. (8.8) gives $T \approx 6 \times 10^{-3}$ for an electron, but $T \approx 10^{-95}$ for a proton, which is about 1836 times heavier. This is why tunneling is common for electrons, important for hydrogen atoms in chemistry, and negligible for heavier atoms.
3. **Tunneling conserves energy.** The transmitted wave has the same k as the incoming one, so the particle has exactly the same energy before

and after the barrier. What changes is only the *probability* of finding it on the other side. The rest of the probability, $1 - T$, is reflected back.

In the two limits, Eq. (8.8) also behaves as we would expect: as the barrier becomes infinitely wide or infinitely high, $T \to 0$, and the barrier behaves like the walls of the particle in a box (Chapter 4). Tunneling of electrons is not an exotic curiosity: it is the principle behind the *scanning tunneling microscope*, which images individual atoms on a surface by measuring the tiny current of electrons that tunnel between a sharp metal tip and the sample. Since the current depends exponentially on the distance, the microscope is sensitive to changes in height much smaller than the size of an atom.

8.4.1 Tunneling in chemical reactions

The ammonia umbrella inversion reaction provides an excellent example of the impact of quantum mechanical tunneling on the kinetic isotope effect (KIE). The reaction involves the inversion of the nitrogen atom in ammonia, which changes its position from above the plane of the three hydrogen atoms to below it and vice versa. This is a rapid oscillation of the atom and substituents, classically described by the molecule passing through a planar transition state. The ammonia interconversion is, however, faster than classically predicted. At room temperature, ammonia inverts 30 billion times per second. Two factors contribute to the rapidity of the inversion: a low energy barrier (24.2 kJ/mol) and a narrow width of the barrier itself, which allows for frequent quantum tunneling of the hydrogen atoms. In contrast, phosphine (PH_3) inverts very slowly at room temperature (energy barrier: 132 kJ/mol).

One of the primary effects of tunneling can be seen on the KIE. The probability of tunneling depends strongly on the mass of the particle, since the mass appears under the square root in the exponent of Eq. (8.8). Lighter isotopes therefore tunnel much more efficiently than heavier ones. As a result, tunneling speeds up the reaction of the lighter isotope much more than the reaction of the heavier one, leading to an increase in the KIE compared to the classical prediction. In the case of the umbrella inversion reaction, replacing ammonia with its deuterated counterpart, ND_3, leaves the height of the barrier essentially unchanged (the potential energy does not depend on the mass of the nuclei), but it makes tunneling much less efficient: ND_3 inverts more than ten times slower than NH_3.

The KIE is defined as the ratio between the rate constants of the reactions involving the light and the heavy isotopes:

$$\mathrm{KIE} = \frac{k(\mathrm{H})}{k(\mathrm{D})}, \tag{8.9}$$

where $k(\mathrm{H})$ and $k(\mathrm{D})$ are the rate constants for the reaction involving hydrogen and deuterium, respectively. In the absence of tunneling, the KIEs of

reactions that involve the transfer of a hydrogen atom are typically smaller than about 7 at room temperature, since they arise mostly from the difference in the zero-point energies of the two isotopes (see the harmonic oscillator in Chapter 4). Significantly larger values, together with curved (non-linear) Arrhenius plots, are commonly taken as experimental evidence of tunneling, an effect that must be considered when studying chemical reactions involving light atoms.

8.5 Chapter Review

8.5.1 Key Ideas

- In the double-slit experiment, single particles build up an interference pattern, which disappears if we find out which slit each particle goes through.
- A measurement gives one eigenvalue and collapses the wave function onto the corresponding eigenfunction.
- Decoherence, the interaction with the environment, explains why we never see macroscopic superpositions such as Schrödinger's cat, but not why each measurement gives a single result.
- Different interpretations of quantum mechanics disagree on what the wave function is, but they give the same predictions for chemistry.
- The uncertainty principle, $\sigma_x \sigma_p \geq \hbar/2$, comes from the fact that the operators do not commute, not from imperfect instruments.
- Particles can tunnel through barriers higher than their energy. The probability decreases exponentially with the width of the barrier and with the square root of the mass, which makes tunneling important for electrons and hydrogen atoms.

8.5.2 Study Questions

1. In the double-slit experiment with electrons sent one at a time:

a. each electron splits into two halves
b. no pattern is ever formed
c. the electrons form two bright lines behind the slits, as classical particles
d. each electron is detected as a wave spread over the whole screen
e. each electron is detected at a single point, but many electrons build up an interference pattern

2. If we place detectors at the slits to find out which slit each electron goes through:

a. the interference pattern disappears
b. the interference pattern becomes sharper
c. the electrons stop going through the slits

d. the electrons go through both slits and are detected twice
e. nothing changes

3. A measurement of the observable A gives the eigenvalue a_i. Immediately after the measurement, the wave function is:

a. the same as before the measurement
b. zero
c. the eigenfunction ψ_i corresponding to a_i
d. a superposition of all the eigenfunctions of $\hat{A}$
e. the eigenfunction with the lowest eigenvalue

4. If we repeat the same measurement immediately after the first one, we obtain:

a. a random result
b. the same result, with certainty
c. the expectation value
d. zero
e. the next eigenvalue

5. The different interpretations of quantum mechanics (Copenhagen, hidden variables, many worlds, spontaneous collapse):

a. give different energy levels for atoms
b. have all been ruled out by experiments, except Copenhagen
c. disagree on the Schrödinger equation for the hydrogen atom
d. agree on the predictions for chemistry, but disagree on what the wave function is and on whether it collapses
e. are different names for the same theory

6. Heisenberg's uncertainty principle for position and momentum states that:

a. $\sigma_x \sigma_p = 0$
b. $\sigma_x \sigma_p \geq \frac{\hbar}{2}$
c. $\sigma_x + \sigma_p \geq \hbar$
d. $\sigma_x \sigma_p \leq \frac{\hbar}{2}$
e. $\sigma_x = \sigma_p$

7. What is the origin of the uncertainty principle?

a. our measuring instruments are not precise enough
b. the particle is disturbed by the light used to observe it
c. the particle moves too fast
d. the operators of the two observables do not commute
e. the Schrödinger equation is only an approximation

8. A particle tunnels through a barrier with transmission probability $T \approx e^{-2\alpha l}$. If the width l of the barrier doubles:

a. T doubles

b. T halves
c. T becomes the square of its previous value, which is much smaller
d. T does not change
e. T becomes one

9. Why do electrons tunnel much more easily than protons through the same barrier?

a. because the transmission probability decreases exponentially with the square root of the mass
b. because electrons are charged and protons are not
c. because protons have no wave function
d. because electrons have more energy than the barrier
e. because tunneling does not conserve energy

10. Which experimental evidence suggests that hydrogen tunneling is important in a chemical reaction?

a. a kinetic isotope effect close to one
b. a reaction rate that does not depend on the isotope
c. a linear Arrhenius plot
d. a very high activation energy
e. a large kinetic isotope effect and a curved Arrhenius plot

Answers

1.e, 2.a, 3.c, 4.b, 5.d, 6.b, 7.d, 8.c, 9.a, 10.e

CHAPTER 9

Many-Electron Atoms

As soon as a system contains two or more electrons, the TISEq can no longer be solved analytically. Since this is the case for every atom other than hydrogen, and for every molecule other than H_2^+, almost all of chemistry depends on approximate methods. In this and the following chapters we will introduce the most important of these approximations, starting from many-electron atoms. Keep in mind that, precisely because they are approximations, these methods are still an active field of research, and better ones are developed every year.

The electronic Hamiltonian for an atom with N electrons can be written as:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{r_{ij}}, \tag{9.1}$$

where Z is the nuclear charge, m_e and e are respectively the mass and charge of an electron, $\mathbf{r}_i$ and ∇_i^2 are the spatial coordinates and the Laplacian of each electron, $r_i = |\mathbf{r}_i|$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two electrons (all other symbols have been explained in previous chapters). The TISEq is easily written using Eq. (6.22).

It is worth looking at the three pieces of this Hamiltonian one at a time:

1. **Kinetic energy**: one term for each electron, identical to the one we used for the hydrogen atom.
2. **Electron–nucleus attraction**: also one term for each electron, identical to hydrogen except for the nuclear charge Z.
3. **Electron–electron repulsion**: one term for each *pair* of electrons. This is the only new ingredient, and it is the one that causes all the trouble. Each of these terms depends on the coordinates of two electrons at the same time, so the Hamiltonian can no longer be split into a sum of one-electron pieces, and the potential is no longer spherically symmetric for any one electron.

If the third term were not there, the TISEq for the atom would separate into N hydrogen-like equations that we already know how to solve. Most of the approximations in this chapter can be understood as different ways of dealing with this single term.

9.1 Many-Electron Wave Functions

9.1.1 Identical particles: fermions and bosons

When a system contains more than one electron, we need to deal with a property of quantum particles that has no classical counterpart: identical particles are truly *indistinguishable*. In classical mechanics, we could in principle paint one electron red and the other blue, and follow each of them along its trajectory. In quantum mechanics there are no trajectories, and two electrons are completely identical, so there is no experiment that can tell us which one is which.

To describe this mathematically, we need to include the spin of each electron. We define a variable $\mathbf{x}$ that collects all four coordinates of an electron: the three spatial coordinates $\mathbf{r}$, and one spin coordinate $\mathbf{s}$, i.e., $\mathbf{x} = \{\mathbf{r}, \mathbf{s}\}$, and we write the wave function of N electrons as $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$. Since the electrons are indistinguishable, swapping the coordinates of any two of them cannot change any measurable quantity, and in particular it cannot change the probability density:

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 . \tag{9.2}$$

This equation can be satisfied in two ways: the wave function can stay the same when we swap two particles (it is *symmetric*), or it can change sign (it is *antisymmetric*). Nature uses both options, for two different families of particles:

- **Bosons** have symmetric wave functions. Photons and helium-4 atoms are examples of bosons.
- **Fermions** have antisymmetric wave functions. Electrons, protons, and neutrons are fermions.

Which family a particle belongs to is determined by its spin: particles with integer spin ($s = 0, 1, 2, \ldots$) are bosons, and particles with half-integer spin ($s = \frac{1}{2}, \frac{3}{2}, \ldots$) are fermions. This connection is known as the *spin-statistics theorem*, and it can be proven only in the framework of relativistic quantum mechanics, so we will simply accept it here. Since electrons have $s = \frac{1}{2}$ (Chapter 7), they are fermions, and their wave function must be antisymmetric with respect to the exchange of any two of them:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{9.3}$$

This simple requirement has an enormous consequence. Suppose that we try to describe two electrons with exactly the same state, including their spin, so that $\mathbf{x}_1 = \mathbf{x}_2$. Swapping two identical things cannot change anything, so the wave function must be unchanged by the swap. At the same time, Eq. (9.3) says that it must change sign. The only number that is equal to minus itself is zero,

so the wave function must vanish: two electrons can never be in the same state. This is the **Pauli exclusion principle**, which we will see again, in a more familiar form, when we build many-electron wave functions below. Bosons, instead, have no such restriction, and any number of them can be described by the same state. This difference is responsible for the shell structure of atoms, and therefore for the whole of chemistry: if electrons were bosons, all of them would be described by the 1*s* orbital, and atoms would not form bonds the way they do.

9.1.2 Spin-orbitals and Slater determinants

A very important step in simplifying $\Psi(\mathbf{x})$ is to build it from one-electron functions. Since we need to take the spin coordinate into account as well, we define a new function, called **spin-orbital**, by multiplying a spatial orbital by one of the two spin functions, α (spin up, $m_s = +\frac{1}{2}$) or β (spin down, $m_s = -\frac{1}{2}$), that we introduced in Chapter 7:

$$\begin{aligned} \chi(\mathbf{x}) &= \psi(\mathbf{r})\alpha(\mathbf{s}), \\ \chi(\mathbf{x}) &= \psi(\mathbf{r})\beta(\mathbf{s}). \end{aligned} \tag{9.4}$$

For a given spatial orbital $\psi(\mathbf{r})$ we can therefore form two spin-orbitals, one with spin up and one with spin down (the spin coordinate $\mathbf{s}$ has only two possible values, as we discussed in Chapter 7). For the spatial orbitals we can use the same one-electron functions that solve the TISEq for the hydrogen atom, $\psi_{n\ell m_\ell}(\mathbf{r})$ (Eq. (5.5) in Chapter 5). Each spin-orbital then depends on four quantum numbers: the three of the spatial part, n, ℓ, m_ℓ, plus the spin quantum number m_s. We need to keep in mind, however, that the spin-orbitals $\chi_{n\ell m_\ell m_s}$ *are not* solutions of the many-electron TISEq, so any wave function that we build from them is an approximation, not the exact wave function of the system.

Once we have spin-orbitals, we can use them as the building blocks of the many-electron wave function, making sure that the result is antisymmetric. We start from the simplest case: two electrons, with coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$, and two spin-orbitals, χ_1 and χ_2. The most general wave function that we can build from products of these two spin-orbitals is:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) = &b_{11}\chi_1(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{12}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \\ &b_{21}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{22}\chi_2(\mathbf{x}_1)\chi_2(\mathbf{x}_2). \end{aligned} \tag{9.5}$$

For this function to change sign when we swap $\mathbf{x}_1$ and $\mathbf{x}_2$, we need $b_{12} = -b_{21}$ and $b_{11} = b_{22} = 0$, which gives:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = b_{12}\left[\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)\right]. \tag{9.6}$$

This wave function is sufficient to describe two-electron atoms and ions, such as helium. The coefficient is fixed by the normalization condition, $b_{12} =$

$\frac{1}{\sqrt{2}}$. For the ground state of helium, we can use the 1*s* hydrogen-like orbital, ψ_{100}, as the spatial part of both spin-orbitals, obtaining:

$$\begin{aligned}\Psi(\mathbf{x}_1,\mathbf{x}_2) &= \frac{1}{\sqrt{2}}\left[\psi_{100}(\mathbf{r}_1)\alpha(1)\,\psi_{100}(\mathbf{r}_2)\beta(2) - \psi_{100}(\mathbf{r}_1)\beta(1)\,\psi_{100}(\mathbf{r}_2)\alpha(2)\right] \\ &= \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right],\end{aligned} \tag{9.7}$$

where $\alpha(1)$ is short for $\alpha(\mathbf{s}_1)$, and so on. This equation shows that we need just one spatial orbital, ψ_{100}, to describe the system, while the antisymmetry is taken care of by the combination of spin functions, $\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$. Notice that we commit a small inaccuracy when we say that "two electrons occupy one spatial orbital, one electron has spin up, and the other electron has spin down," as is typically done in general chemistry textbooks with the configuration $[\uparrow\downarrow]$. The real spin state is more subtle: neither electron individually is "the up one"; instead, the ground state of helium is the combination $\frac{1}{\sqrt{2}}[\uparrow\downarrow - \downarrow\uparrow]$.

To go from two electrons to N, we can first observe that Eq. (9.6) is exactly the determinant of a 2×2 matrix built from the spin-orbitals:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1)\\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2)\end{vmatrix}, \tag{9.8}$$

where each column contains one spin-orbital, each row contains the coordinates of one electron, and the vertical bars mean that we take the determinant of the matrix. This construction is called a **Slater determinant**, and it is the standard way of building an N-electron wave function. Slater determinants can be written for any number of electrons, using the same number of spin-orbitals, and they automatically produce an antisymmetric wave function. A general Slater determinant is written:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1)\\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N)\end{vmatrix} = |\chi_1\,\chi_2\cdots\chi_N|, \tag{9.9}$$

where the notation $|\cdots|$ on the right is a compact shorthand for the whole determinant (including its normalization factor), in which we only list the spin-orbitals that appear on its diagonal. When a spin-orbital is used in the Slater determinant to describe an electron, we say that it is *occupied*, and orbitals that are not used are called *unoccupied* (or *virtual*). This is convenient language, and we will use it throughout the textbook, but it should not be taken

literally: orbitals are not boxes that contain electrons, but mathematical functions that we use to describe them.

Two properties of determinants that you may remember from linear algebra have important physical consequences here:

1. **Swapping two rows changes the sign of a determinant.** Swapping two rows means swapping the coordinates of two electrons, so a Slater determinant is always antisymmetric, as required by Eq. (9.3).
2. **A determinant with two identical columns is zero.** If we try to describe two electrons with the same spin-orbital (same n, ℓ, m_ℓ, *and* same m_s), two columns become identical and the wave function vanishes everywhere. In other words, such a state does not exist. This is the familiar form of the Pauli exclusion principle from general chemistry, "no two electrons in an atom can have the same four quantum numbers," which here appears as a direct consequence of the antisymmetry of the wave function.

9.2 Approximated Hamiltonians

To solve the TISEq for a many-electron atom we also need to deal with the Hamiltonian, since analytic solutions of the full Hamiltonian in Eq. (9.1) cannot be found. The most important tool that chemists use for this purpose is called the *variational method*.

9.2.1 Variational method

The idea behind the variational method is simple. We guess a "trial" wave function that contains some adjustable numbers, called *variational parameters*. We then calculate the energy of the trial function and change the parameters until this energy is as low as possible. The trial function with the lowest energy, and that energy itself, are our best approximations to the true ground-state wave function and energy.

Why should the lowest energy be the best answer? The energy of a trial function Φ is the expectation value of the Hamiltonian:

$$E[\Phi] = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}, \tag{9.10}$$

where $\tau = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ collects the spatial coordinates of all electrons, so the integrals are $3N$-dimensional. The denominator takes care of normalization, so Φ does not need to be normalized. The justification of the method is the **variational theorem**: the energy calculated from any trial wave function is always greater than or equal to the exact ground-state energy, $\mathcal{E}_0$:

$$E[\Phi] \geq \mathcal{E}_0. \tag{9.11}$$

and the equality holds only if Φ is the exact ground state. In other words, we can never "overshoot" the exact energy from below. This gives us a clear strategy: any change in the trial function that lowers its energy brings the energy closer to the exact answer. (As the energy goes down, the wave function usually gets better too, although "better" for a wave function is harder to define than for a number, and it is guaranteed to be exact only when $\Phi = \Psi_0$.)

Proof: the variational theorem

The proof uses a nice trick. Even if we cannot solve the TISEq, its exact eigenfunctions Ψ_i (with energies $\mathcal{E}_0 \leq \mathcal{E}_1 \leq \mathcal{E}_2 \leq \ldots$) still exist and form a complete set. We can therefore imagine expanding our trial function in terms of them:

$$\Phi = \sum_i c_i \Psi_i. \tag{9.12}$$

We never need to know the Ψ_i or the c_i; the expansion is only a tool for the proof. Inserting it in Eq. (9.10), we obtain:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \int \Psi_i^* \hat{H} \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \tag{9.13}$$

Since each Ψ_j is an eigenfunction of $\hat{H}$, we can replace $\hat{H}\Psi_j$ with $\mathcal{E}_j \Psi_j$:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \mathcal{E}_j \int \Psi_i^* \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \tag{9.14}$$

The eigenfunctions of a Hermitian operator are orthonormal (or can be chosen to be, Chapter 6), so all integrals with $i \neq j$ vanish and those with $i = j$ are equal to one:

$$E[\Phi] = \frac{\sum_i |c_i|^2 \mathcal{E}_i}{\sum_i |c_i|^2}. \tag{9.15}$$

This equation already tells the whole story: the energy of the trial function is a weighted average of the exact energies, with weights $|c_i|^2$, and an average can never be lower than its smallest member. To make this explicit, we subtract $\mathcal{E}_0$ from both sides:

$$E[\Phi] - \mathcal{E}_0 = \frac{\sum_i |c_i|^2 (\mathcal{E}_i - \mathcal{E}_0)}{\sum_i |c_i|^2}. \tag{9.16}$$

Every term on the right-hand side is greater than or equal to zero, because $|c_i|^2 \geq 0$ and $\mathcal{E}_i \geq \mathcal{E}_0$. Therefore, $E[\Phi] \geq \mathcal{E}_0$.

9.2.2 Approximated solution for the helium atom

We now have all the ingredients for the simplest approximate solution of the TISEq for a many-electron atom. We start by writing the wave function as the Slater determinant of Eq. (9.9), in which each spatial orbital is used to describe two electrons of opposite spin:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_1\, \chi_2 \cdots \chi_N| = |\psi_1\alpha\, \psi_1\beta \cdots \psi_{\frac{N}{2}}\alpha\, \psi_{\frac{N}{2}}\beta|, \tag{9.17}$$

and we insert it into the TISEq for N electrons. This results in a set of N one-electron equations, one for each electron. When we try to solve each of them, however, we run into the problem that we identified at the beginning of this chapter: because of the electron-electron repulsion term, the potential felt by each electron does not have spherical symmetry, and the one-electron TISEq cannot be solved in spherical polar coordinates as we did for the hydrogen atom in Chapter 5. The crudest way around the problem is to neglect the electron-electron repulsion altogether (i.e., to pretend that the electrons do not interact with each other). For a two-electron atom the Hamiltonian then becomes a sum of two one-electron Hamiltonians:

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \tag{9.18}$$

each of them identical to the Hamiltonian of a hydrogen-like atom with nuclear charge Z. This Hamiltonian does not depend on spin, so we can drop the spin part of Eq. (9.7) and write the wave function for the ground state of helium simply as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2). \tag{9.19}$$

The TISEq then separates into two independent one-electron equations:

$$\begin{aligned} \hat{H}_1\psi_{100}(\mathbf{r}_1) &= E_1\psi_{100}(\mathbf{r}_1) \\ \hat{H}_2\psi_{100}(\mathbf{r}_2) &= E_2\psi_{100}(\mathbf{r}_2), \end{aligned} \tag{9.20}$$

which we already know how to solve (Chapter 5), and whose solutions combine to give:

$$E = E_1 + E_2. \tag{9.21}$$

In this approximation, the energy of the helium atom is twice the energy of a 1s electron in a hydrogen-like atom with $Z = 2$. The energies in Eq. (5.7) scale as Z^2 when the nuclear charge is Z instead of 1, so the 1s energy is $-\frac{Z^2}{2}E_h$ and the total is $E = 2 \times \left(-\frac{Z^2}{2}\right)E_h = -4\,E_h$, or about −10,500 kJ/mol,[1] compared with the exact value of $-2.9037\,E_h = -7{,}624$ kJ/mol. The error is enormous, about 40%, because we have neglected a large positive contribution to

[1] E_h is the hartree, the atomic unit of energy that we introduced in Sec. 5.1: $1\,E_h = 27.211$ eV = 2,625.5 kJ/mol.

the energy. We can partially fix it by keeping the same orbitals and adding back the *average* repulsion between the two electrons, which for two 1*s* electrons is $\frac{5}{8}Z\,E_h$ ($1.25\,E_h = 3{,}282$ kJ/mol for helium). The result, $-2.75\,E_h = -7{,}220$ kJ/mol, is already much better, with an error of about 5%.

Optimizing the effective nuclear charge

We can do better using the variational method. The two electrons do not feel the full charge of the nucleus, since each of them is partially *shielded* from it by the other. We can account for this by using, for both electrons, a 1*s* orbital with an adjustable charge ζ in place of Z:

$$\psi_{1s}(r) = \sqrt{\frac{\zeta^3}{\pi a_0^3}}\, e^{-\zeta r/a_0}, \tag{9.22}$$

and treat ζ as a variational parameter. Calculating the expectation value of the full Hamiltonian, Eq. (9.1), with $\Psi = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$, gives three contributions (in E_h): the kinetic energy of the two electrons, ζ^2; their attraction to the nucleus of charge Z, $-2Z\zeta$; and their mutual repulsion, $+\frac{5}{8}\zeta$. Summing them:

$$E(\zeta) = \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta. \tag{9.23}$$

This energy is plotted in Fig. 9.1. To find its minimum, we set the derivative to zero:

$$\frac{dE}{d\zeta} = 2\zeta - 2Z + \frac{5}{8} = 0 \quad\longrightarrow\quad \zeta_{\min} = Z - \frac{5}{16} = 1.6875, \tag{9.24}$$

and replacing this value in Eq. (9.23) gives $E(\zeta_{\min}) = -\left(Z - \frac{5}{16}\right)^2 = -2.8477\,E_h = -7{,}477$ kJ/mol.

Let's see what these results tell us:

1. **The variational theorem at work**: every point of the curve in Fig. 9.1 lies above the exact energy, as guaranteed by Eq. (9.11). The minimum gets within 147 kJ/mol (about 2%) of the exact value, using a single adjustable number.

2. **Shielding**: the optimal value $\zeta_{\min} = 1.6875$ is smaller than the real nuclear charge, $Z = 2$. We can interpret it as the **effective nuclear charge**, Z_{eff}, felt by each electron. Each electron spends part of its time between the nucleus and the other electron, partially canceling the attraction that the other electron feels. The amount of shielding, $\frac{5}{16} \approx 0.31$ of a proton charge, is much less than a full electron charge because the two electrons occupy the same region of space: a 1*s* electron is only rarely found "inside" the other one.

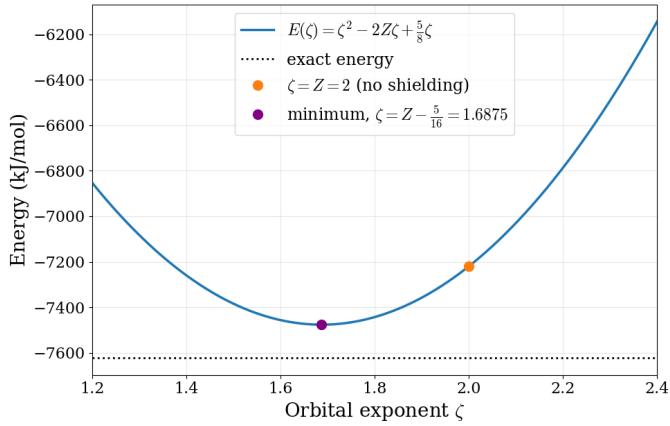


Figure 9.1 Variational energy of the helium atom as a function of the orbital exponent ζ. The orange dot is the energy of the unshielded orbitals ($\zeta = Z = 2$, with the average repulsion included), the purple dot is the variational minimum, and the dotted line is the exact energy.

3. **Orbital size**: since $\langle r \rangle \propto 1/\zeta$, a smaller effective charge means a larger orbital. The shielded 1*s* orbitals of helium are about $2/1.6875 \approx 1.19$ times larger than the unshielded ones.

4. **What is still missing**: even the best possible orbitals cannot reach the exact energy if we keep the product form of Eq. (9.19). We will come back to this point at the end of this chapter, when we discuss electron correlation.

The results obtained with the different approximations are summarized in Fig. 9.2, which also reports the Hartree–Fock limit that we will discuss in the next chapter.

9.3 Shielding and Penetration

The helium example shows that the main effect of the other electrons on any given electron is to reduce the nuclear charge that it feels. We can generalize this idea to any atom by writing the effective nuclear charge felt by an electron as:

$$Z_{\text{eff}} = Z - \sigma, \tag{9.25}$$

where σ is called the **shielding constant**, and it measures how much the other electrons screen the nucleus. In the simplest model of a many-electron atom, called the **central-field approximation**, each electron moves in the

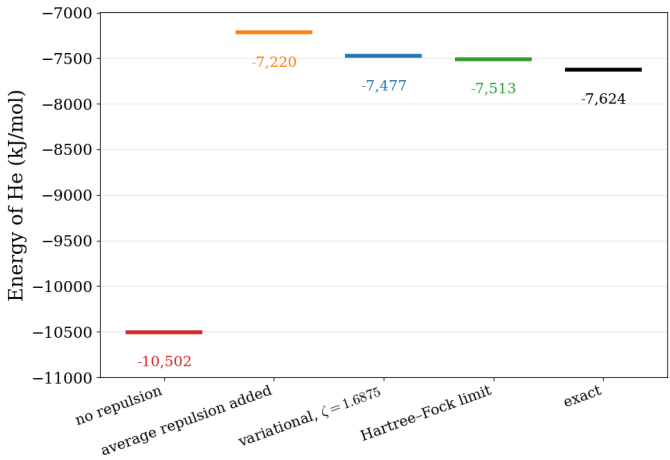


Figure 9.2 Energy of the helium atom computed with the approximations discussed in this chapter, compared with the exact value.

field of the nucleus plus the *spherically averaged* field of all other electrons. Since this effective potential depends only on r, the angular part of the TISEq is the same as for hydrogen, and the orbitals keep the familiar shapes of the spherical harmonics and the labels n, ℓ, m_ℓ. The radial part, however, changes, and with it the energies. What the central-field approximation does *not* include is the instantaneous repulsion between electrons: each electron feels only the average position of the others, not where they actually are at any given moment.

Inner-shell electrons are very effective at shielding the outer ones, while electrons of the same shell shield each other only partially (as we saw for helium). As a result, outer electrons feel a much smaller effective charge than inner electrons, they are held less tightly, and their orbitals are more diffuse. This explains why the valence electrons of an atom are the ones involved in chemistry, while the core electrons are not.

The most important consequence of shielding, however, is that it breaks the degeneracy of orbitals with the same n and different ℓ. Recall from Chapter 5 that in the hydrogen atom the $2s$ and $2p$ orbitals have exactly the same energy. In a many-electron atom this is no longer the case. To understand why, consider the lithium atom, which has two core electrons, described by the $1s$ orbital, and one valence electron. The radial probability distributions of the $2s$ and $2p$ orbitals, compared with that of the $1s^2$ core, are plotted in Fig. 9.3.

The $2s$ orbital has a small inner lobe, the one that we already noticed for hydrogen in Chapter 5, which places part of its probability *inside* the $1s^2$ core. When it is there, a $2s$ electron feels almost the full nuclear charge. We say that the $2s$ orbital **penetrates** the core. The $2p$ orbital, instead, starts at zero

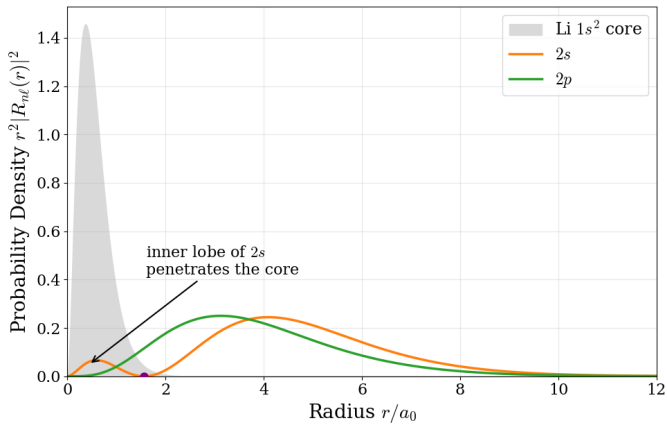


Figure 9.3 Radial probability distributions of the $2s$ and $2p$ orbitals of lithium compared with the $1s^2$ core (gray), computed using hydrogen-like functions with effective nuclear charges. The radial node of the $2s$ orbital is highlighted with a purple dot.

at the nucleus and has no inner lobe, so it is more effectively shielded by the core electrons. As a result, a $2s$ electron feels a larger Z_{eff} than a $2p$ electron, and it is lower in energy. This is the $2s$–$2p$ splitting that general chemistry textbooks show in their orbital energy diagrams. In general, for the same n, penetration decreases as ℓ increases (because of the r^ℓ behavior of the radial functions close to the nucleus), so the energies of the orbitals follow the order $ns < np < nd < nf$.

The effective nuclear charges felt by the $1s$, $2s$, and $2p$ electrons of the second-row atoms can be obtained from variational calculations similar to the one we did for helium. Some of the results are reported in Table 9.1.

Table 9.1 Effective nuclear charges for the orbitals of the ground-state configurations of the second-row atoms, from variational calculations by Clementi and Raimondi (Clementi and Raimondi 1963).

Atom	Z	$Z_{\text{eff}}(1s)$	$Z_{\text{eff}}(2s)$	$Z_{\text{eff}}(2p)$
Li	3	2.69	1.28	—
Be	4	3.68	1.91	—
B	5	4.68	2.58	2.42
C	6	5.67	3.22	3.14
N	7	6.67	3.85	3.83
O	8	7.66	4.49	4.45

Atom	Z	$Z_{\text{eff}}(1s)$	$Z_{\text{eff}}(2s)$	$Z_{\text{eff}}(2p)$
F	9	8.65	5.13	5.10
Ne	10	9.64	5.76	5.76

Notice how the $1s$ electrons feel almost the full nuclear charge (they are shielded only by each other, as in helium), while the valence electrons feel a much smaller charge. Notice also how $Z_{\text{eff}}(2s)$ is larger than $Z_{\text{eff}}(2p)$, as expected from penetration, although the difference becomes small for the heavier atoms of the row. When the electrons of an atom are described using the orbitals in order of increasing energy, following the Pauli exclusion principle, the different penetration of s, p, d, and f orbitals produces the familiar **aufbau** order, $1s < 2s < 2p < 3s < 3p < 4s < 3d < \ldots$, and with it the structure of the periodic table.

9.4 Atomic States and Term Symbols

An electron configuration, such as $1s^2 2s^2 2p^2$ for carbon, tells us which orbitals are used to describe the electrons, but it does not tell us everything about the state of the atom. In the carbon configuration, the two $2p$ electrons can be described using any of the three $2p$ orbitals, with either spin, in several different ways, and these arrangements do not all have the same energy. Since electrons repel each other, the energy depends on how their orbital motions and their spins are arranged relative to each other. As a result, a single configuration gives rise to several distinct energy levels, called *atomic states*. These are the levels that we actually observe in atomic spectra, and chemists and spectroscopists label them using *term symbols*.

9.4.1 Total angular momenta

In an atom with several electrons, the individual orbital angular momenta (quantum numbers ℓ_i and $m_{\ell,i}$) and spins ($s_i = \frac{1}{2}$ and $m_{s,i}$) combine into a **total orbital angular momentum** and a **total spin**. Their projections on the z axis are simply the sums of the individual projections:

$$M_L = \sum_i m_{\ell,i}, \qquad M_S = \sum_i m_{s,i}. \tag{9.26}$$

The total angular momenta are described by two new quantum numbers, L and S, which play the same role as ℓ and s for a single electron: M_L can take the $2L + 1$ values $-L, \ldots, +L$, and M_S the $2S + 1$ values $-S, \ldots, +S$. A great simplification comes from the fact that a closed subshell (such as $1s^2$ or $2p^6$, where every spin-orbital of the subshell is used) always has $M_L = 0$ and

$M_S = 0$ for every possible arrangement, and therefore contributes $L = 0$ and $S = 0$. Only the electrons of open subshells need to be considered.

9.4.2 Term symbols

The states that arise from a configuration are labeled with a **term symbol**:

$$^{2S+1}L_J, \tag{9.27}$$

where:

- L is written with a capital letter, following the same code used for orbitals: S for $L = 0$, P for $L = 1$, D for $L = 2$, F for $L = 3$, and so on. (Notice the unfortunate double use of the letter S, both for $L = 0$ and for the total spin.)
- The left superscript, $2S + 1$, is called the **multiplicity**. States with $S = 0$ (all spins paired) have multiplicity 1 and are called *singlets*; states with $S = \frac{1}{2}$ are *doublets*; states with $S = 1$ are *triplets*, and so on.
- J is the quantum number of the **total angular momentum**, obtained by combining L and S. It can take the values $J = |L-S|, |L-S|+1, \ldots, L+S$.

For example, a sodium atom ([Ne] $3s^1$) has a single electron outside closed shells, so $L = 0$, $S = \frac{1}{2}$, and $J = \frac{1}{2}$: its ground state is $^2S_{1/2}$ (read "doublet S one-half"). The noble gases, and any atom with only closed subshells, have the ground state $^1S_0$.

9.4.3 The terms of carbon

When a subshell contains more than one electron, a single configuration produces several terms. To find them, we proceed in three steps: list all the possible ways of describing the electrons, sort them by M_L and M_S, and then group them into terms.

Step 1: list the microstates. Each $2p$ electron can be described by one of six spin-orbitals: three values of m_ℓ ($+1, 0, -1$), each with spin up ($\uparrow$) or down ($\downarrow$). For two electrons, we need two *different* spin-orbitals (Pauli principle), and since electrons are indistinguishable, the order does not matter. There are $\frac{6\times5}{2} = 15$ ways of choosing them, called **microstates**. For example, $(+1\uparrow, 0\uparrow)$ is the microstate in which one electron has $m_\ell = +1$ and spin up, and the other has $m_\ell = 0$ and spin up. For each microstate, we can calculate M_L and M_S by adding the values of the two electrons (Eq. (9.26)). For $(+1\uparrow, 0\uparrow)$, $M_L = +1 + 0 = +1$ and $M_S = +\frac{1}{2} + \frac{1}{2} = +1$.

Step 2: sort them in a grid. We now arrange the 15 microstates in a grid, with one row for each value of M_L and one column for each value of M_S, as shown in Fig. 9.4. Notice that some cells contain more than one microstate, and that some are empty. For example, $M_L = +2$ requires both electrons to

have $m_\ell = +1$, and the Pauli principle then forces them to have opposite spins, so $M_L = +2$ is only possible with $M_S = 0$.

	$M_S = +1$	$M_S = 0$	$M_S = -1$
$M_L = +2$	—	$(+1\uparrow, +1\downarrow)$	—
$M_L = +1$	$(+1\uparrow, 0\uparrow)$	$(+1\uparrow, 0\downarrow)$ $(+1\downarrow, 0\uparrow)$	$(+1\downarrow, 0\downarrow)$
$M_L = 0$	$(+1\uparrow, -1\uparrow)$	$(+1\uparrow, -1\downarrow)$ $(+1\downarrow, -1\uparrow)$ $(0\uparrow, 0\downarrow)$	$(+1\downarrow, -1\downarrow)$
$M_L = -1$	$(0\uparrow, -1\uparrow)$	$(0\uparrow, -1\downarrow)$ $(0\downarrow, -1\uparrow)$	$(0\downarrow, -1\downarrow)$
$M_L = -2$	—	$(-1\uparrow, -1\downarrow)$	—

Figure 9.4 The 15 microstates of the $2p^2$ configuration, sorted by M_L (rows) and M_S (columns). Each microstate lists the m_ℓ value and the spin of the two electrons.

Step 3: group them into terms. The key idea is that each term with quantum numbers L and S contains exactly $(2L + 1)(2S + 1)$ states: one for each combination of $M_L = -L, \ldots, +L$ and $M_S = -S, \ldots, +S$. In the grid, a term therefore looks like a *rectangle*: $2L+1$ rows tall and $2S+1$ columns wide, with exactly one microstate in each cell. The terms can then be found by "peeling off" rectangles from the grid, starting from the largest values of M_L, as shown in Fig. 9.5:

1. **The ^1D term.** The largest value of M_L in the grid is +2. A microstate with $M_L = +2$ must belong to a term with $L = 2$ (a D term), since a term with smaller L cannot reach $M_L = +2$. This term must also contain all the other values of M_L from +2 down to −2, so it is 5 rows tall. Since the $M_L = +2$ row has a microstate only in the $M_S = 0$ column, the term has only $M_S = 0$, so $S = 0$, and it is 1 column wide. This is a ^1D term, a rectangle of $5 \times 1 = 5$ microstates, one in each row of the $M_S = 0$ column (Fig. 9.5b).

2. **The ^3P term.** After removing the five ^1D states, the largest remaining value of M_L is +1, which now appears in all three columns, $M_S = +1, 0, -1$. This must be a term with $L = 1$ (a P term) and $S = 1$ (since M_S reaches +1). It is a rectangle 3 rows tall ($M_L = +1, 0, -1$) and 3 columns wide: a ^3P term with $3 \times 3 = 9$ microstates (Fig. 9.5c).

3. **The ^1S term.** Only one microstate is left, with $M_L = 0$ and $M_S = 0$. It is a term with $L = 0$ and $S = 0$: a ^1S term with a single state (Fig. 9.5d).

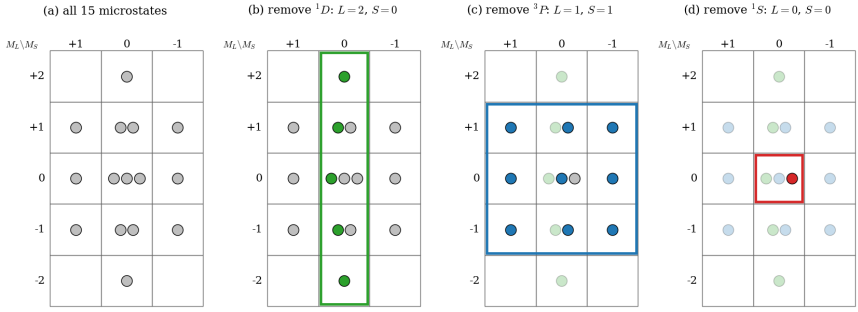


Figure 9.5 Finding the terms of the $2p^2$ configuration. (a) Each dot is one microstate in the grid of the previous figure. (b)–(d) Each term occupies a rectangle of the grid, with one microstate in each cell: ^1D (5 states, green), ^3P (9 states, blue), and ^1S (1 state, red). Microstates already assigned to a term are shown faded.

Notice that, in the cells with more than one microstate, we do not need to decide *which* microstate belongs to which term: only the number of states in each cell matters. (In fact, the real states of each term are combinations of the microstates in the same cell.) The $2p^2$ configuration of carbon therefore produces three terms, ^3P, ^1D, and ^1S, with $9 + 5 + 1 = 15$ states in total. Their experimental energies are shown in Fig. 9.6.

Notice three things in this diagram:

1. **The size of the splitting**: the three terms are separated by about 10,000 cm^{-1} (more than 100 kJ/mol), comparable to the energy of chemical processes. The configuration alone, which is all that the simple orbital picture provides, is not enough to describe the atom.

2. **The triplet is lowest**: the term with the highest multiplicity, ^3P, has the lowest energy. In the triplet, the two electrons have parallel spins, and the antisymmetry of the wave function keeps electrons with the same spin away from each other (two electrons with the same spin can never be found at the same point), which reduces their repulsion. We will see this effect again in Chapter 10, where it appears as the exchange term of the Fock operator.

3. **Spin–orbit coupling is much smaller**: the three levels of the ^3P term are only a few tens of cm^{-1} apart, a thousand times less than the separation between terms (see below).

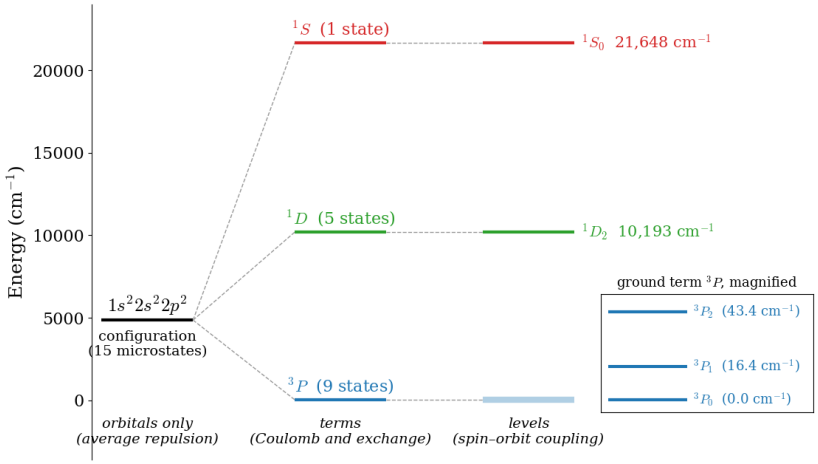


Figure 9.6 Energy levels arising from the $1s^2 2s^2 2p^2$ configuration of carbon (experimental values from the NIST Atomic Spectra Database (Kramida et al., n.d.)). Electron–electron repulsion splits the configuration into three terms, and spin–orbit coupling further splits the ^3P term into three levels with different J (inset, magnified).

9.4.4 Hund's rules

Finding all the terms of a configuration can be tedious, but in most cases we only need the ground state. This can be found using three empirical rules, formulated by Friedrich Hund in the 1920s:

1. The term with the **largest multiplicity** (largest S) has the lowest energy.
2. For terms with the same multiplicity, the one with the **largest** L has the lowest energy.
3. If the open subshell has **fewer than half** of its maximum number of electrons, the level with the **lowest** J has the lowest energy; if it has **more than half**, the level with the **highest** J is lowest.

For carbon, the first rule selects ^3P as the ground term, and the third rule ($2p^2$ has fewer than half of the six possible $2p$ electrons) selects $J = 0$: the ground state of carbon is $^3P_0$, in agreement with Fig. 9.6. Oxygen ($2p^4$) has the same terms as carbon, since the $2p^4$ configuration lacks two electrons with respect to the closed $2p^6$ subshell, and behaves like $2p^2$ (the two missing electrons are often called "holes"), but it has more than half of the six possible $2p$ electrons, and its ground state is $^3P_2$. In practice, the ground term can be found quickly with the orbital diagrams of general chemistry, used here only as a bookkeeping device: we describe the electrons one at a time using the orbitals with the largest m_ℓ first, keeping their spins parallel as long as possible, and then reading S from the number of unpaired electrons and L from the sum

of the m_ℓ values. The ground states of the first ten elements obtained in this way are reported in Table 9.2.

Table 9.2 Ground-state configurations and term symbols of the first ten elements.

Element	Configuration	Ground state
H	$1s^1$	$^2S_{1/2}$
He	$1s^2$	$^1S_0$
Li	$[\mathrm{He}]2s^1$	$^2S_{1/2}$
Be	$[\mathrm{He}]2s^2$	$^1S_0$
B	$[\mathrm{He}]2s^2 2p^1$	$^2P_{1/2}$
C	$[\mathrm{He}]2s^2 2p^2$	$^3P_0$
N	$[\mathrm{He}]2s^2 2p^3$	$^4S_{3/2}$
O	$[\mathrm{He}]2s^2 2p^4$	$^3P_2$
F	$[\mathrm{He}]2s^2 2p^5$	$^2P_{3/2}$
Ne	$[\mathrm{He}]2s^2 2p^6$	$^1S_0$

Example 9.1: The ground state of oxygen

Find the ground-state term symbol of the oxygen atom, $1s^2 2s^2 2p^4$, using Hund's rules.
Step 1: only the open subshell matters. Filled subshells have $L = 0$ and $S = 0$, so we only need the four $2p$ electrons.
Step 2: maximize S (first rule). The three $2p$ spin-orbitals with $m_s = +\frac{1}{2}$ describe three electrons, and the fourth one must have $m_s = -\frac{1}{2}$: $M_S = \frac{3}{2} - \frac{1}{2} = 1$, so $S = 1$ (a triplet).
Step 3: maximize L (second rule). The fourth electron can use $m_\ell = +1$, so $M_L = (+1 + 0 - 1) + 1 = 1$, and $L = 1$: a ^3P term.
Step 4: choose J (third rule). J can be 2, 1, or 0. The subshell is *more* than half filled (four of six electrons), so the lowest level has the largest J: the ground state is $^3P_2$, in agreement with Table 9.2.

9.4.5 Spin–orbit coupling

Term symbols include the quantum number J because of an effect that we have neglected so far: **spin–orbit coupling**. From the point of view of the electron, the charged nucleus is the one that moves around it, and this moving charge produces a magnetic field proportional to the orbital angular momentum. This field interacts with the magnetic moment associated with its spin.

This interaction adds to the energy a term proportional to $\mathbf{L}\cdot\mathbf{S}$, which depends on whether the spin and orbital angular momenta are aligned or opposed, and therefore on J. It splits each term with $L > 0$ and $S > 0$ into its levels with different J.

Spin–orbit coupling is small for light atoms, but it grows very rapidly with the nuclear charge (approximately as Z^4), and it is important for heavy elements. A familiar example is the yellow light of sodium street lamps, which comes from the transition from the first excited configuration, [Ne] $3p^1$, to the ground state, $^2S_{1/2}$. The $3p^1$ configuration gives a single term, ^2P, which spin–orbit coupling splits into two levels, $^2P_{1/2}$ and $^2P_{3/2}$, separated by 17 cm^{-1}. As a result, the sodium emission is not a single line, but a pair of lines at 589.6 and 589.0 nm, known as the *sodium D lines*. Their small splitting was one of the first experimental clues that led to the discovery of the electron spin.

9.5 Electron Correlation

Even with the best possible orbitals, a wave function built as a product of orbitals (or as a single Slater determinant) does not give the exact energy. The best energy that can be obtained in this way is called the **Hartree–Fock limit**, and for helium it is $-2.8617\,E_h = -7{,}513$ kJ/mol. This value is still 110 kJ/mol above the exact energy (Fig. 9.2). The difference is called the **correlation energy**:

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}. \tag{9.28}$$

The origin of this error is the same approximation that is at the heart of the central-field model. In an orbital-based wave function, each electron moves in the *average* field of the others, and the probability of finding electron 1 at some position does not depend on where electron 2 is at that moment. Real electrons, however, repel each other and tend to stay away from each other: if electron 1 is on one side of the nucleus, electron 2 is more likely to be found on the other side. In other words, the motions of the electrons are *correlated*, and an orbital-based wave function misses part of this correlation. Since the correlated electrons avoid each other more effectively, their repulsion is lower, and the exact energy is lower than the Hartree–Fock limit.

The correlation energy is a small fraction of the total energy (about 1.5% for helium), but it is of the same order of magnitude as the energy of a chemical bond, so it can be very important for chemistry. We will see a dramatic example in Chapter 11, when we look at the breaking of the bond in the hydrogen molecule. Methods that go beyond the Hartree–Fock limit are called *correlated methods*, and they are among the most important tools of modern quantum chemistry.

The procedure that we used for helium can be extended to atoms with more than two electrons, and to molecules, resulting in the Hartree–Fock method.

We will explain it in more detail in the next chapter, since it is also the simplest approximation that can describe the chemical bond.

9.6 Chapter Review

9.6.1 Key Ideas

- The electron–electron repulsion makes many-electron atoms impossible to solve exactly, so we need approximations.
- Electrons are fermions: their wave function is antisymmetric, which we build with Slater determinants, and the Pauli principle follows.
- The variational theorem guarantees that the energy of any trial wave function is an upper bound to the exact energy.
- Shielding and penetration explain effective nuclear charges and why $2s$ is lower than $2p$ in many-electron atoms.
- A configuration gives several atomic states, labeled by term symbols ${}^{2S+1}L_J$. Hund's rules find the ground state.
- The difference between the exact energy and the best single-determinant energy is the correlation energy.

9.6.2 Study Questions

1. Why can the Schrödinger equation not be solved exactly for an atom with two or more electrons?

a. because the nucleus is too heavy
b. because electrons have spin
c. because the kinetic energy operator is not Hermitian
d. because the electrons move too fast
e. because the electron–electron repulsion couples the coordinates of different electrons

2. Electrons are fermions. This means that the total wave function of a system of electrons:

a. does not change when we swap two electrons
b. changes sign when we swap the coordinates (including spin) of two electrons
c. is always real
d. is zero for more than two electrons
e. does not depend on spin

3. What happens to a Slater determinant if two electrons are described by the same spin-orbital?

a. it becomes zero, which is the Pauli exclusion principle
b. it doubles
c. it changes sign

d. it describes an excited state
e. nothing: it remains a valid wave function

4. According to the variational theorem, the energy calculated with any trial wave function is:

a. always equal to the exact ground-state energy
b. greater than or equal to the exact ground-state energy
c. always lower than the exact ground-state energy
d. always positive
e. equal to the energy of the first excited state

5. In the variational treatment of helium, the optimal orbital exponent is $\zeta = 1.6875$, smaller than the nuclear charge $Z = 2$. This is because:

a. the nucleus of helium has a charge of 1.6875
b. the electrons have spin
c. the variational method always underestimates charges
d. each electron is partially shielded from the nucleus by the other electron
e. the two electrons attract each other

6. In atoms with more than one electron, why is the $2s$ orbital lower in energy than $2p$?

a. because $2s$ has a smaller principal quantum number
b. because $2p$ has a radial node
c. because the $2s$ electron penetrates the $1s^2$ core and feels a larger effective nuclear charge
d. because of spin–orbit coupling
e. because $2s$ has more angular momentum

7. What are the values of S, L, and J for an atomic state with term symbol $^3P_2$?

a. $S = 1, L = 1, J = 2$
b. $S = 3, L = 1, J = 2$
c. $S = 1, L = 2, J = 3$
d. $S = \frac{3}{2}, L = 1, J = 2$
e. $S = 1, L = 0, J = 2$

8. According to Hund's first rule, among the terms of a configuration, the lowest in energy is:

a. the one with the largest L
b. the one with the smallest S
c. the one with the largest J
d. the one with the largest total spin S
e. the one with the most microstates

9. What is the ground-state term symbol of the carbon atom ($1s^2 2s^2 2p^2$)?

a. $^1D_2$
b. $^1S_0$
c. $^3P_2$
d. $^2P_{1/2}$
e. $^3P_0$

10. The correlation energy is:

a. the energy of the electron–electron repulsion
b. the energy needed to remove an electron from the atom
c. the difference between the exact energy and the best energy obtainable from a single Slater determinant (the Hartree–Fock limit)
d. the difference between the energies of two terms
e. the energy of spin–orbit coupling

Answers

1.e, 2.b, 3.a, 4.b, 5.d, 6.c, 7.a, 8.d, 9.e, 10.c

CHAPTER 10

Introduction to Molecules

In the previous chapter we saw that a single extra electron is enough to make the TISEq impossible to solve exactly. Molecules add a further complication: they contain several nuclei, which can also move. In this chapter we will introduce the two approximations that make molecules tractable: the Born–Oppenheimer approximation, which separates the motion of the nuclei from that of the electrons, and the Hartree–Fock method, which extends the ideas that we used for the helium atom to molecular orbitals.

10.1 The Molecular Hamiltonian

For a molecule, we can decompose the Hamiltonian operator as:

$$\hat{H} = \hat{K}_N + \hat{K}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee} \tag{10.1}$$

where we have decomposed the kinetic energy operator into nuclear and electronic terms, $\hat{K}_N$ and $\hat{K}_e$, as well as the potential energy operator into terms representing the interactions between nuclei, $\hat{V}_{NN}$, between electrons, $\hat{V}_{ee}$, and between electrons and nuclei, $\hat{V}_{eN}$. Each term can then be calculated using:

$$\begin{aligned}
\hat{K}_N &= -\sum_{i}^{\text{nuclei}} \frac{\hbar^2}{2M_i} \nabla^2_{\mathbf{R}_i} \\
\hat{K}_e &= -\sum_{i}^{\text{electrons}} \frac{\hbar^2}{2m_e} \nabla^2_{\mathbf{r}_i} \\
\hat{V}_{NN} &= \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{R}_j\right|} \\
\hat{V}_{eN} &= -\sum_i \sum_j \frac{Z_i e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{r}_j\right|} \\
\hat{V}_{ee} &= \sum_i \sum_{j>i} \frac{e^2}{4\pi\varepsilon_0 \left|\mathbf{r}_i - \mathbf{r}_j\right|},
\end{aligned} \tag{10.2}$$

where M_i, Z_i, and $\mathbf{R}_i$ are the mass, atomic number, and coordinates of nucleus i, respectively, and all other symbols are the same as those used in

Eq. (9.1) for the many-electron atom Hamiltonian. Notice that the two potential energy terms between like particles ($\hat{V}_{NN}$ and $\hat{V}_{ee}$) are positive (repulsive), while the term between electrons and nuclei is negative (attractive). The chemical bond is the result of a delicate balance between these three terms and the kinetic energy.

10.1.1 Small terms in the molecular Hamiltonian

Eq. (10.1) is often called the "exact" non-relativistic Hamiltonian of a molecule, but it is worth remembering what it leaves out. The first missing piece is relativity. The valence electrons of light atoms move at a small fraction of the speed of light (less than 1% for the electron in the hydrogen atom), but the inner electrons of heavy atoms are pulled so strongly by the nucleus that relativistic effects become important. The second missing piece is the coupling between the spin of each electron and its orbital motion. We can picture it by sitting on the electron: from its point of view, the charged nucleus is the one that moves around it, and this moving charge creates a magnetic field proportional to the orbital angular momentum, **L**. The electron carries its own magnetic moment, proportional to its spin, **S**, and the interaction between the two gives an energy term proportional to $\mathbf{L} \cdot \mathbf{S}$, called *spin–orbit coupling*. Both effects grow quickly with the nuclear charge, so they are small for the molecules made of first- and second-row atoms that we discuss in this textbook, and we will neglect them from now on.

10.2 The Born–Oppenheimer Approximation

Before looking at molecules, let's recall a general property that we already used for the helium atom. If a Hamiltonian can be written as the sum of two terms, each depending on a different set of coordinates, q_1 and q_2:

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2), \tag{10.3}$$

then its eigenfunctions are products of the eigenfunctions of each piece, and its eigenvalues are sums of their eigenvalues:

$$\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2), \qquad E = E_1 + E_2. \tag{10.4}$$

A big problem is broken into smaller ones, which is exactly what we did when we wrote the wave function of helium as a product of two hydrogen-like orbitals.

Proof: separable Hamiltonians

Take $\psi_1(q_1)$ and $\psi_2(q_2)$ as eigenfunctions of $\hat{H}_1$ and $\hat{H}_2$, with eigenvalues E_1 and E_2. Since $\hat{H}_1$ acts only on q_1 and $\hat{H}_2$ only on q_2, applying $\hat{H}$ to

Proof: separable Hamiltonians *(continued)*

their product gives:

$$\begin{aligned}\hat{H}\psi(q_1,q_2) &= (\hat{H}_1+\hat{H}_2)\psi_1(q_1)\psi_2(q_2)\\ &= \psi_2(q_2)\hat{H}_1\psi_1(q_1)+\psi_1(q_1)\hat{H}_2\psi_2(q_2)\\ &= E_1\psi_1(q_1)\psi_2(q_2)+E_2\psi_1(q_1)\psi_2(q_2)\\ &= (E_1+E_2)\psi_1(q_1)\psi_2(q_2)\\ &= E\psi(q_1,q_2).\end{aligned} \tag{10.5}$$

So the product is an eigenfunction of $\hat{H}$ with eigenvalue E_1+E_2.

Can we use this trick to separate the electrons from the nuclei in Eq. (10.1)? Not exactly, because the electron–nucleus attraction, $\hat{V}_{eN}$, depends on the coordinates of both electrons and nuclei at the same time. However, nuclei are much heavier than electrons (a proton is about 1,836 times heavier than an electron), so they move much more slowly. From the point of view of the electrons, the nuclei are almost standing still; from the point of view of the nuclei, the electrons adjust almost instantaneously to any change in their positions. This suggests that we can write the total wave function, approximately, as:

$$\psi(\mathbf{r},\mathbf{R}) \approx \psi_e(\mathbf{r};\mathbf{R})\psi_N(\mathbf{R}), \tag{10.6}$$

where $\psi_e(\mathbf{r};\mathbf{R})$ is the electronic wave function calculated with the nuclei held fixed at positions $\mathbf{R}$. The semicolon indicates that ψ_e is a function of the electronic coordinates $\mathbf{r}$ that depends only *parametrically* on $\mathbf{R}$: for each arrangement of the nuclei we get a different electronic wave function, but the nuclear positions are not variables of the electronic problem. This approximation is called the **Born–Oppenheimer approximation**, and it is accurate for the vast majority of chemical applications.

In practice, we fix the nuclei at some configuration, $\mathbf{R_a}$, and solve the TISEq for the electrons only, using the **electronic Hamiltonian**:

$$\hat{H}_{\mathrm{e}} = \hat{K}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r};\mathbf{R_a}) + \hat{V}_{ee}(\mathbf{r}), \tag{10.7}$$

where we have dropped the nuclear kinetic energy, $\hat{K}_N$, since the nuclei are fixed (and, in any case, $\hat{K}_N$ is smaller than $\hat{K}_e$ by roughly the ratio $\frac{m_e}{M_i}$). We have also left out $\hat{V}_{NN}(\mathbf{R_a})$, since for fixed nuclei it is just a constant that shifts all the eigenvalues by the same amount and can be added back at the end. The electron–nucleus attraction stays in the electronic Hamiltonian, but now it depends on $\mathbf{R_a}$ only as a parameter. The electronic Hamiltonian results in the following TISEq:

$$\hat{H}_e\psi_e(\mathbf{r};\mathbf{R_a}) = E_e(\mathbf{R_a})\psi_e(\mathbf{r};\mathbf{R_a}), \tag{10.8}$$

which is the equation that we will use to explain the chemical bond in the next chapter. Notice that Eq. (10.8) is not the total TISEq of the system, since it says nothing about the motion of the nuclei. As is customary in quantum chemistry, in the remainder of this textbook we will use the term "total energy" for the "total energy at fixed geometry," which is E_e of Eq. (10.8) plus the constant nuclear–nuclear repulsion, $V_{NN}(\mathbf{R_a})$ (i.e., everything except the nuclear kinetic energy).

10.2.1 Potential energy surfaces

The Born–Oppenheimer approximation has a very important consequence. If we repeat the electronic calculation for many different arrangements of the nuclei, we obtain the total energy at fixed geometry as a function of the nuclear coordinates:

$$U(\mathbf{R}) = E_e(\mathbf{R}) + V_{NN}(\mathbf{R}). \tag{10.9}$$

This function is called the **potential energy surface (PES)**, and it is the potential energy that the nuclei feel when they move. The motion of the nuclei (vibrations, rotations, and chemical reactions) can then be described by solving a second TISEq for the nuclei, with the PES playing the role of the potential: $\left[\hat{K}_N + U(\mathbf{R})\right]\psi_N(\mathbf{R}) = E\,\psi_N(\mathbf{R})$.

For a diatomic molecule, the only coordinate that matters is the internuclear distance, R, and the PES reduces to a curve. The potential energy curve of the hydrogen molecule is plotted in Fig. 10.1.

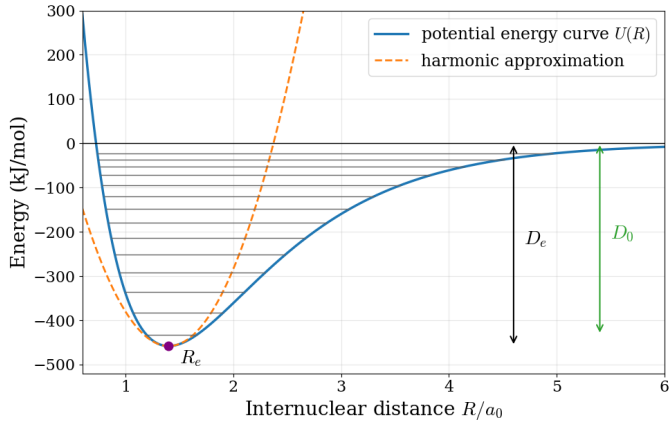


Figure 10.1 Potential energy curve of the hydrogen molecule (blue), compared with its harmonic approximation (orange, dashed). The horizontal lines are the vibrational energy levels, and the energy is measured from the separated atoms. The purple dot marks the equilibrium bond distance.

This single curve contains a lot of chemistry:

1. **Equilibrium geometry**: the minimum of the curve, at $R_e = 1.40\,a_0 = 0.74\,\text{Å}$, is the equilibrium bond distance of the molecule. For larger molecules, minima of the PES correspond to stable structures, and finding them is called *geometry optimization*.

2. **Bond energy**: the depth of the well, $D_e = 458\,\text{kJ/mol}$, is the energy needed to separate the two atoms starting from the bottom of the well. The molecule, however, can never sit exactly at the bottom: even in its lowest vibrational level it has a zero-point energy, as we saw for the harmonic oscillator in Chapter 4. The experimentally measurable dissociation energy, $D_0 = D_e - \text{ZPE} = 432\,\text{kJ/mol}$, is measured from the lowest vibrational level.

3. **Vibrations**: close to the minimum, the curve looks like a parabola, and the harmonic oscillator of Chapter 4 is a good model, with force constant equal to the curvature of the PES at the minimum, $k = \left.\frac{d^2U}{dR^2}\right|_{R_e}$. As the energy increases, the real curve becomes wider than the parabola, and it flattens out towards the dissociation limit. As a consequence, the vibrational levels get closer to each other as they approach dissociation, unlike the equally spaced levels of the harmonic oscillator. We will see how these features show up in experiments in Chapter 13.

For a molecule with N_{at} atoms, the PES depends on $3N_{\text{at}} - 6$ internal coordinates ($3N_{\text{at}} - 5$ for linear molecules), and it is a surface in many dimensions. We cannot draw it, but we can get a feeling for its features using a model surface in two dimensions, such as the one in Fig. 10.2.

Each minimum (A, B, and C) corresponds to a stable structure of the molecule, such as a reactant, a product, or an intermediate. To go from one minimum to another, the molecule must pass over a mountain pass, called a **saddle point**: a point that is a maximum along the path that connects the two minima, but a minimum along every other direction. In chemistry, these saddle points are the **transition states** of chemical reactions, and the energy difference between a minimum and the transition state is the activation energy of the reaction.

If we want to go from one minimum to another, there are infinitely many possible paths on the surface, but the most important one is the path of lowest energy, which follows the bottom of the valleys and crosses each mountain pass exactly at the saddle point. This path is called the **minimum energy path**, and it is shown as a dashed line in Fig. 10.2a. The distance traveled along this path, measured from the starting minimum, is called the **reaction coordinate**. It is a single number that tells us how far the reaction has progressed, even though, in a real molecule, moving along it may require changing many bond lengths and angles at the same time. If we plot the energy along the reaction coordinate, as in Fig. 10.2b, the many-dimensional surface reduces

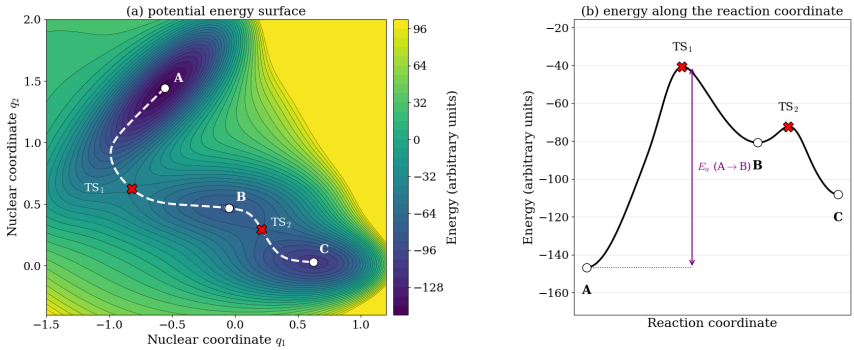


Figure 10.2 (a) Contour plot of a model two-dimensional potential energy surface (the Müller–Brown surface). White dots mark minima, red crosses mark saddle points (transition states), and the dashed line is the minimum energy path that connects them. (b) Energy along the minimum energy path, plotted as a function of the distance traveled along it: the reaction coordinate.

to the familiar one-dimensional *reaction profile* of general chemistry and kinetics courses: reactants and products are minima, the transition state is the maximum between them, and the height of the barrier is the activation energy. Notice that the reaction profile hides most of the information contained in the surface: the reaction coordinate is not one of the nuclear coordinates q_1 or q_2, but a curved path through both of them. The PES is therefore the bridge between quantum mechanics and chemical reactivity: structures, vibrational frequencies, reaction paths, and activation energies are all properties of the PES.

Example 10.1: Bond energy and zero-point energy of H_2

The depth of the potential energy curve of H_2 is $D_e = 458$ kJ/mol, and its vibrational wavenumber is $\tilde{\nu} = 4401\ \text{cm}^{-1}$. How much energy is actually needed to break the bond?

Step 1: the molecule is never at the bottom of the well. As we saw for the harmonic oscillator (Chapter 4), the lowest vibrational level is the zero-point energy, $E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\tilde{\nu}$, above the minimum.

Step 2: compute the zero-point energy.

$$E_0 = \tfrac{1}{2}(6.626\times10^{-34}\ \text{J s})(2.998\times10^{10}\ \text{cm/s})(4401\ \text{cm}^{-1}) = 4.37\times10^{-20}\ \text{J},$$

or $4.37\times10^{-20}\ \text{J}\times 6.022\times10^{23}\ \text{mol}^{-1} = 26$ kJ/mol.

Step 3: the dissociation energy. Starting from the lowest vibrational level, $D_0 = D_e - E_0 = 458 - 26 = 432$ kJ/mol, which is the experimental

Example 10.1: Bond energy and zero-point energy of H_2 *(continued)*

bond energy of H_2.

10.3 Solving the Electronic Eigenvalue Problem

Once we have invoked the Born–Oppenheimer approximation, we can try to solve the electronic TISEq in Eq. (10.8). For any molecule with more than one electron (i.e., all molecules except H_2^+ and a few exotic ions), we need to keep in mind the antisymmetry of the wave function, so we write the electronic wave function as a Slater determinant, as we did for atoms in Chapter 9. Then we need to approximate the Hamiltonian, since the electron-electron repulsion term does not allow an analytic solution. Similarly to the many-electron atom case, the simplest approximation is to use the variational method and to treat the electron-electron repulsion only in an average way, as we did for the helium atom in the previous chapter. This approximation is called the Hartree–Fock method.

10.3.1 The Hartree–Fock Method

The main difference when we apply the variational principle to a molecular Slater determinant is that we need orbitals (one-electron wave functions) that extend over the entire molecule. We can build them by assuming that, close to each nucleus, a molecular orbital looks similar to the orbitals of the corresponding atom. The molecular orbital can then be written as a linear combination of atomic contributions. This method is called **linear combination of atomic orbitals (LCAO)**. In practice, we expand each molecular orbital $\psi(\mathbf{r})$ as a linear combination of suitable basis functions $f_i(\mathbf{r})$ centered on the atoms:

$$\psi(\mathbf{r}) = \sum_i^m c_i f_i(\mathbf{r}). \tag{10.10}$$

A consequence of the LCAO method is that basis functions on two different atoms are not orthogonal to each other, so the simplification that we used to go from Eq. (9.14) to Eq. (9.15) is not possible anymore. Using the following notation for the integrals:

$$H_{ij} = \int f_i^* \hat{H} f_j d\tau\,, \qquad S_{ij} = \int f_i^* f_j d\tau, \tag{10.11}$$

the variational energy of Eq. (9.10) becomes:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j S_{ij}}. \tag{10.12}$$

The integrals S_{ij} are called **overlap integrals**, and they measure how much two basis functions share the same region of space. To find the best orbital, we minimize this energy with respect to all the coefficients c_i, setting each derivative to zero. This gives a set of m linear equations for the coefficients, which have a non-trivial solution only if the following **secular determinant** is equal to zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2m} - ES_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \cdots & H_{mm} - ES_{mm} \end{vmatrix} = 0, \tag{10.13}$$

where m is the number of basis functions. Expanding the determinant gives a polynomial of degree m in E, whose m roots are the energies of the molecular orbitals. For each root, the linear equations give the corresponding coefficients. We will solve this problem explicitly for the simplest molecules in the next chapter.

The Fock operator

What Hamiltonian should we use in Eq. (10.11)? For a one-electron molecule, such as H_2^+, it is simply the electronic Hamiltonian of Eq. (10.7). For more than one electron, the Hartree–Fock method replaces the true many-electron problem with a set of one-electron problems, one for each occupied spin-orbital χ_i:

$$\hat{f}\,\chi_i = \varepsilon_i\,\chi_i, \tag{10.14}$$

where ε_i is the energy of the orbital, and $\hat{f}$ is an effective one-electron Hamiltonian called the **Fock operator**:

$$\hat{f} = \hat{h} + \sum_{j}^{\text{occupied}} \left(\hat{J}_j - \hat{K}_j\right). \tag{10.15}$$

Each piece of $\hat{f}$ has a clear physical meaning:

1. $\hat{h}$ is the **core Hamiltonian**: the kinetic energy of one electron plus its attraction to all nuclei. This is all there is in a one-electron molecule.
2. $\hat{J}_j$ is the **Coulomb operator**: the repulsion felt by an electron because of the *average* charge distribution, $|\chi_j|^2$, of the electron described by orbital χ_j. This is the "average repulsion" that we added back for the helium atom in Chapter 9.
3. $\hat{K}_j$ is the **exchange operator**. It has no classical analog, and it appears because the wave function is a Slater determinant. It acts only between electrons with the same spin, and it lowers their repulsion, since the antisymmetry of the wave function keeps same-spin electrons away from

each other (two electrons with the same spin can never be found at the same point, as a consequence of the Pauli exclusion principle).

Eq. (10.14) are called the **Hartree–Fock equations**. They look like ordinary one-electron TISEqs, but there is a catch: the Fock operator depends, through $\hat{J}_j$ and $\hat{K}_j$, on the occupied orbitals, which are the solutions we are looking for. The equations are coupled with each other, since every orbital affects the operator that determines all other orbitals. When we expand the orbitals using the LCAO method, Eq. (10.10), the Hartree–Fock equations take the form of the secular determinant in Eq. (10.13), with the integrals H_{ij} replaced by the matrix elements of the Fock operator, $F_{ij} = \int f_i^* \hat{f} f_j \, d\tau$.

The self-consistent-field procedure

Since the Fock operator and its solutions depend on each other, the Hartree–Fock equations cannot be solved in one step. Instead, they are solved iteratively, using a cycle called the **self-consistent-field (SCF) procedure**, which is summarized in Fig. 10.3. Starting from an initial guess of the coefficients, we build the Fock operator, solve the secular determinant, and obtain new coefficients. These are used to build an improved Fock operator, and the cycle is repeated until neither the orbitals nor the energy change anymore (within a chosen threshold). At that point, the orbitals are "consistent" with the field that they generate, and the energy of the molecule can be calculated from them.

The SCF procedure is too tedious to perform by hand, even for small molecules, but it is easily done by computer programs. Every time that you run a quantum chemistry calculation, the first thing the program does is solve this cycle.

10.4 Chapter Review

10.4.1 Key Ideas

- The Born–Oppenheimer approximation separates the motion of the electrons from that of the much heavier nuclei.
- The electronic energy as a function of the nuclear positions is the potential energy surface: its minima are stable structures, and its saddle points are transition states.
- In the LCAO method, molecular orbitals are linear combinations of atom-centered basis functions, and the variational method leads to the secular determinant.
- The Hartree–Fock method describes each electron in the average field of the others through the Fock operator, which includes the exchange term.
- The Hartree–Fock equations are solved iteratively with the self-consistent-field (SCF) procedure.

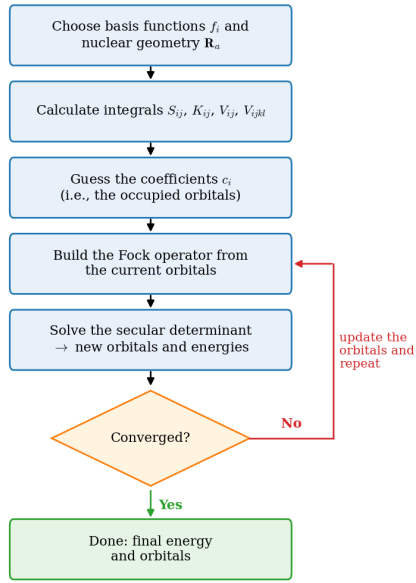


Figure 10.3 Flowchart of the self-consistent-field (SCF) procedure used to solve the Hartree–Fock equations.

10.4.2 Study Questions

1. What justifies the Born–Oppenheimer approximation?

a. electrons and nuclei have the same mass
b. nuclei are much heavier than electrons, so they move much more slowly
c. nuclei do not interact with electrons
d. electrons are fermions
e. the molecule is always at its equilibrium geometry

2. A potential energy surface is:

a. the surface of the molecule
b. the probability density of the electrons
c. the kinetic energy of the nuclei
d. the electronic energy of a molecule as a function of the positions of its nuclei
e. the energy of a molecule as a function of temperature

3. The minimum of the potential energy curve of a diatomic molecule corresponds to:

a. the dissociated atoms
b. the transition state
c. the equilibrium bond length

d. the zero-point energy
e. the ionization energy

4. The depth of the well of the potential energy curve of H_2 is:

a. the energy needed to remove an electron
b. the zero-point energy
c. the energy of the first excited state
d. the energy needed to separate the two atoms (the bond energy)
e. the kinetic energy of the nuclei

5. On a potential energy surface, the transition state of a reaction is:

a. the deepest minimum
b. the point where the energy is zero
c. the geometry of the products
d. any point with a high energy
e. a saddle point, the highest point along the minimum energy path between reactants and products

6. How many internal coordinates are needed to describe the geometry of a water molecule?

a. 1
b. 6
c. 3
d. 9
e. 4

7. In the LCAO method, each molecular orbital is written as:

a. a product of atomic orbitals
b. a linear combination of basis functions centered on the atoms
c. a single atomic orbital
d. a Slater determinant of atomic orbitals
e. the sum of all the atomic orbitals of the molecule, with equal coefficients

8. The overlap integral $S_{ij} = \int f_i^* f_j \, d\mathbf{r}$ between two basis functions on different atoms:

a. measures how much the two functions share the same region of space, and is in general not zero
b. is always zero, because basis functions are orthogonal
c. is always equal to one
d. is the energy of the bond
e. is negative for bonding orbitals

9. The exchange operator $\hat{K}$ in the Fock operator:

a. describes the attraction of the electrons to the nuclei
b. describes the kinetic energy of the electrons
c. is the classical repulsion between two charge distributions
d. describes the repulsion between nuclei

e. has no classical analog, and it appears because the wave function is a Slater determinant

10. Why must the Hartree–Fock equations be solved iteratively, with the SCF procedure?

a. because the Fock operator depends on the orbitals that are the solutions of the equations
b. because computers cannot solve linear equations directly
c. because the nuclei move during the calculation
d. because the basis set changes at each step
e. because the energy is not variational

Answers

1.b, 2.d, 3.c, 4.d, 5.e, 6.c, 7.b, 8.a, 9.e, 10.a

CHAPTER 11

The Chemical Bond in Diatomic Molecules

In this chapter we will see a couple of examples of how the concept and mathematics of quantum mechanics can be applied to understand the chemical bond in molecules. We will start from the simplest molecule, the H_2^+ molecular ion, we will then move on to the simplest two-electron bond in the hydrogen molecule, and finally we will use the same ideas to understand the bonds in the diatomic molecules of the second row, such as N_2 and O_2. To simplify the notation, in this chapter we will use the atomic units that we introduced in Sec. 5.1, in which $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$, energies are measured in hartrees ($1\,E_h = 2{,}625.5$ kJ/mol), and distances in bohrs ($1\,a_0 = 0.529$ Å).

11.1 The Chemical Bond in the Hydrogen Molecular Cation

This system has only one electron, but since its geometry is not spherical (Fig. 11.1), the TISEq cannot be solved analytically as for the hydrogen atom.

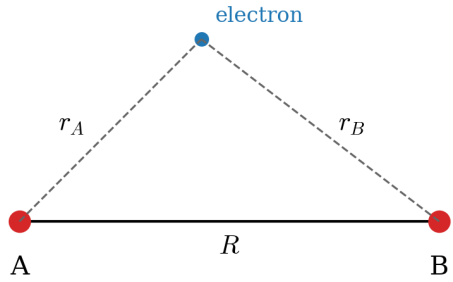


Figure 11.1 Geometry of the hydrogen molecular cation, H_2^+.

The electron is at point P, while the two protons are at positions A and B at a fixed distance R. Using the Born-Oppenheimer approximation we can write the one-electron molecular Hamiltonian in a.u. as:

$$\hat{H} = \hat{H}_e + \frac{1}{R} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B}\right) + \frac{1}{R} \tag{11.1}$$

As a first approximation to the variational wave function, we can build the one-electron molecular orbital (MO) by linearly combining two 1*s* hydrogenic orbitals centered at A and B, respectively:

$$\varphi = c_1 a + c_2 b, \tag{11.2}$$

with:

$$\begin{aligned} a &= 1s_A = (\psi_{100})_A \\ b &= 1s_B = (\psi_{100})_B \,. \end{aligned} \tag{11.3}$$

Using Eq. (10.11) and considering that the nuclei are identical, we can define the integrals $H_{aa} = H_{bb}, H_{ab} = H_{ba}$ and $S_{ab} = S$ (while $S_{aa} = 1$ because the hydrogen atom orbitals are normalized). The integral H_{aa} is called the *Coulomb integral*, and it is the energy of an electron described by orbital a, including its attraction to the second nucleus, B. The integral H_{ab} is called the *resonance integral* (or exchange integral), and it has no classical counterpart: it describes the energy associated with the electron being shared between the two centers. It is negative, and it is responsible for the bond. The secular equation, Eq. (10.13), can then be written (determinants and secular equations are reviewed in Sec. A.5):

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{aa} - E \end{vmatrix} = 0 \tag{11.4}$$

The expansion of the determinant results in:

$$\begin{aligned} (H_{aa} - E)^2 &= (H_{ab} - ES)^2 \\ H_{aa} - E &= \pm(H_{ab} - ES), \end{aligned} \tag{11.5}$$

with roots:

$$\begin{aligned} E_+ &= \frac{H_{aa} + H_{ab}}{1 + S} = H_{aa} + \frac{H_{ba} - SH_{aa}}{1 + S}, \\ E_- &= \frac{H_{aa} - H_{ab}}{1 - S} = H_{aa} - \frac{H_{ba} - SH_{aa}}{1 - S}, \end{aligned} \tag{11.6}$$

the first corresponding to the ground state, the second to the first excited state. Solving for the best value for the coefficients of the linear combination for the ground state E_+, we obtain:

$$c_1 = c_2 = \frac{1}{\sqrt{2 + 2S}}, \tag{11.7}$$

which gives the bonding MO:

$$\varphi_+ = \frac{a+b}{\sqrt{2+2S}}. \tag{11.8}$$

Proceeding similarly for the excited state, we obtain:

$$c_1 = \frac{1}{\sqrt{2-2S}} \qquad c_2 = -\frac{1}{\sqrt{2-2S}}, \tag{11.9}$$

which gives the antibonding MO:

$$\varphi_- = \frac{a-b}{\sqrt{2-2S}}. \tag{11.10}$$

Derivation: the coefficients of the molecular orbitals

The secular determinant comes from two linear equations for the coefficients (Sec. A.5):

$$(H_{aa}-E)\,c_1 + (H_{ab}-ES)\,c_2 = 0, \qquad (H_{ab}-ES)\,c_1 + (H_{aa}-E)\,c_2 = 0.$$

For $E = E_+$, Eq. (11.5) with the plus sign gives $H_{aa} - E_+ = H_{ab} - E_+S$, so the first equation becomes $(H_{aa} - E_+)(c_1 + c_2) = 0$, and therefore $c_2 = c_1$. For $E = E_-$, the minus sign gives $H_{aa} - E_- = -(H_{ab} - E_-S)$, and therefore $c_2 = -c_1$. The remaining constant is fixed by normalization. For $\varphi_+ = c_1(a+b)$:

$$\int \varphi_+^2\, d\mathbf{r} = c_1^2\left(\int a^2 d\mathbf{r} + \int b^2 d\mathbf{r} + 2\int ab\, d\mathbf{r}\right) = c_1^2\,(1+1+2S) = 1,$$

which gives $c_1 = 1/\sqrt{2+2S}$. The same steps for $\varphi_- = c_1(a-b)$ give $c_1 = 1/\sqrt{2-2S}$.

These results can be summarized in the molecular orbital diagram of Fig. 11.2. We notice that the splitting of the doubly degenerate atomic level under the interaction is non-symmetric for $S \neq 0$, the antibonding level being pushed up more than the bonding level is pushed down, compared with the symmetric case that would occur for $S = 0$.

11.1.1 Wave function analysis

The bonding and antibonding molecular orbitals are plotted in Fig. 11.3 as color maps in a plane that contains the two nuclei, and in Fig. 11.4 along the internuclear axis, together with their probability densities.

What do these plots tell us about the bond?

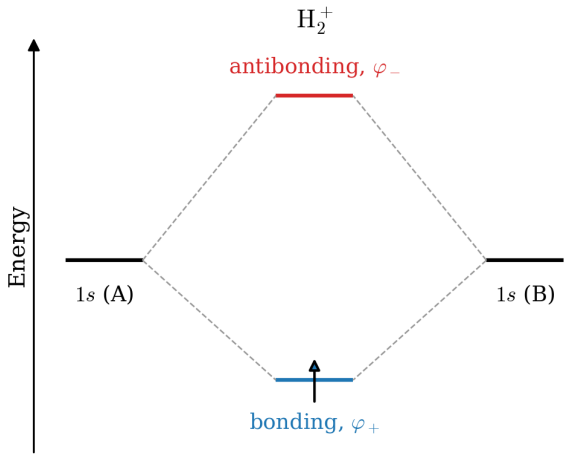


Figure 11.2 Molecular orbital diagram of the hydrogen molecular cation. The antibonding orbital is pushed up more than the bonding orbital is pushed down.

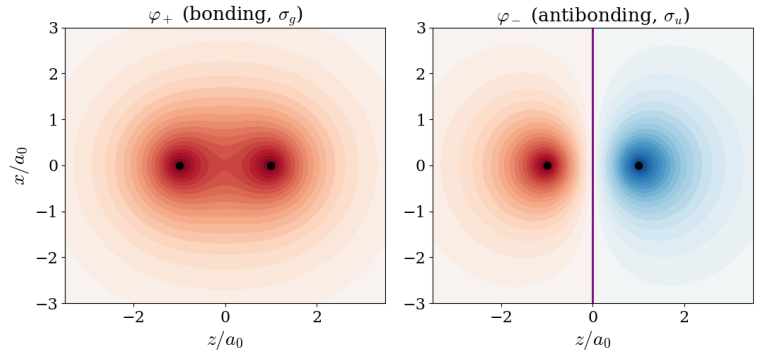


Figure 11.3 Color maps of the bonding (left) and antibonding (right) molecular orbitals of the hydrogen molecular cation at $R = 2\,a_0$, in a plane that contains the two nuclei (black dots). Color scheme: red (positive), blue (negative), white/light (close to zero). The nodal plane of the antibonding orbital is reported in purple.

1. **Constructive and destructive interference**: the bonding orbital is the sum of the two atomic orbitals, which add up in the region between the nuclei, just like two waves that interfere constructively. The antibonding orbital is their difference, and the two atomic orbitals cancel each other exactly halfway between the nuclei, like two waves that interfere destructively.

2. **Nodes**: as for all the systems that we have studied so far, the higher energy state has more nodes. The bonding orbital has no nodes, while

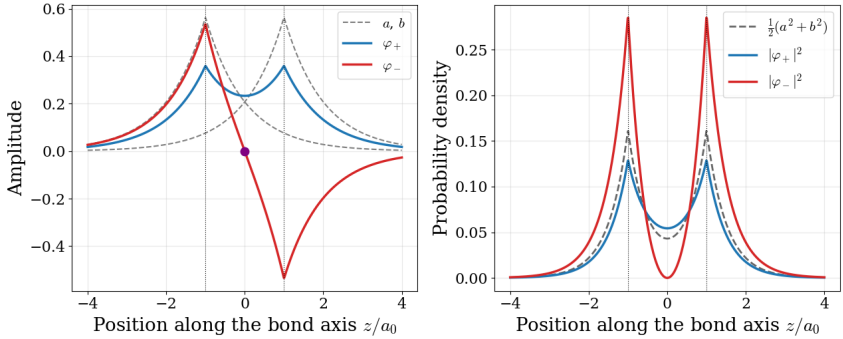


Figure 11.4 Left: the bonding (blue) and antibonding (red) molecular orbitals of the hydrogen molecular cation along the internuclear axis at $R = 2\,a_0$, compared with the two atomic orbitals a and b (gray, dashed). The node of the antibonding orbital is reported as a purple dot. Right: the corresponding probability densities, compared with the average density of the two atomic orbitals (gray, dashed). The positions of the nuclei are marked by dotted vertical lines.

the antibonding orbital has a nodal plane perpendicular to the bond axis, where the probability of finding the electron is exactly zero.

3. **Charge accumulation**: the probability density of the bonding orbital is *larger* than the average density of the atomic orbitals in the region between the nuclei, at the expense of the regions close to the nuclei and behind them. An electron in this region is attracted by both nuclei at the same time, and this is the origin of the chemical bond. The antibonding orbital does the opposite: it removes probability from the region between the nuclei, leaving the two protons less shielded from each other.

4. **Symmetry labels**: both orbitals are symmetric with respect to rotations around the bond axis, which is why they are called σ orbitals. If we invert any point through the center of the molecule, the bonding orbital stays the same, while the antibonding orbital changes sign. These two behaviors are labeled g (from the German *gerade*, even) and u (*ungerade*, odd). Therefore, the bonding orbital is called σ_g, and the antibonding orbital σ_u.

To obtain the energy as a function of the internuclear distance, we need to calculate the values of the integrals, and to repeat the calculation for different distances, R. For $1s$ orbitals, all the integrals can be calculated analytically. For example, the overlap integral is $S = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$, which goes from 1 when the two nuclei coincide to 0 when they are far apart. The resulting energies of the two states, measured from the separated fragments (one hydrogen atom and one proton), are plotted in Fig. 11.5. The energy of the ground state

is negative for a wide range of distances, which means that, in this range, the molecule is more stable than the separated fragments. The minimum of the curve is at $R = 2.49\,a_0$ and $E_+ = -0.065\,E_h = -170$ kJ/mol, which is a reasonable first approximation to the exact values ($R = 2.00\,a_0$ and -269 kJ/mol). The excited state, instead, is repulsive at all distances: if the electron is promoted to the antibonding orbital, the molecule falls apart.

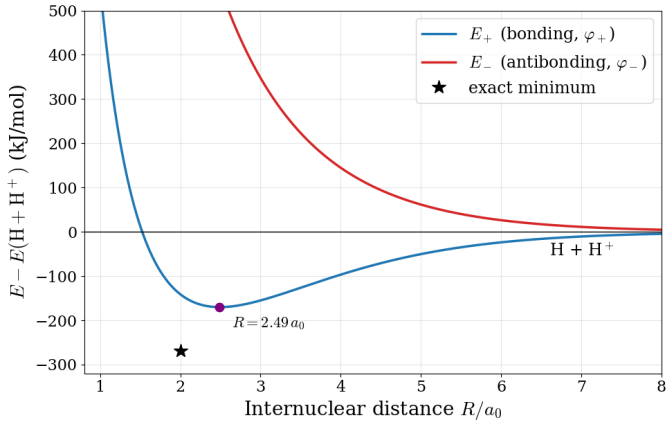


Figure 11.5 Born–Oppenheimer potential energy curves for the ground (bonding) and first excited (antibonding) states of the hydrogen molecular cation, computed with the LCAO wave functions. The purple dot marks the LCAO minimum, and the black star the exact minimum.

11.2 The Chemical Bond in the Hydrogen Molecule

We can now examine the formation of the two-electron chemical bond in the H_2 molecule. With reference to Fig. 11.6, the molecular Hamiltonian for H_2 in a.u. in the Born-Oppenheimer approximation will be:

$$\begin{aligned}\hat{H} &= \hat{H}_e + \frac{1}{R} \\ &= \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{A2}} - \frac{1}{r_{B2}}\right) + \frac{1}{r_{12}} + \frac{1}{R} \\ &= \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R},\end{aligned} \tag{11.11}$$

where $\hat{h}$ is the one-electron Hamiltonian. As for the previous case, we can build the first approximation to the molecular wave function from two 1s

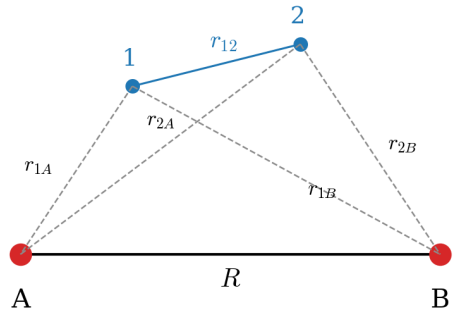


Figure 11.6 Geometry of the hydrogen molecule, H_2.

atomic orbitals, a and b, centered at A and B, respectively, with overlap S. If we neglect the electron-electron repulsion term, $\frac{1}{r_{12}}$, the Hamiltonian is a sum of two identical one-electron Hamiltonians, and the molecular orbitals are exactly the same as those we obtained for H_2^+. The most important difference is that now we need to consider the spin of the two electrons. Proceeding as we did for the helium atom in Chapter 9, we can build an antisymmetric wave function for H_2 using a Slater determinant in which the lowest molecular orbital, the bonding σ_g orbital of Eq. (11.8), is used to describe two electrons with opposite spin:[1]

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\sigma_g\alpha\ \sigma_g\beta| = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right], \qquad (11.12)$$

where:

$$\sigma_g = \varphi_+ = \frac{(\psi_{100})_A + (\psi_{100})_B}{\sqrt{2+2S}}. \qquad (11.13)$$

A Slater determinant in which each spatial orbital is used to describe two electrons with opposite spin is called a **restricted Hartree–Fock (RHF)** wave function, since both electrons are restricted to be described by the same spatial orbital. The energies and the resulting MO diagram are similar to those for H_2^+, with the only difference that two electrons are described by the same σ_g MO (Fig. 11.7).

As for the many-electron atoms, the Hartree–Fock method is just an approximation to the exact solution. The accurate theoretical value for the bond energy at the equilibrium distance, $R_e = 1.4\ a_0$, is $-0.17447\ E_h$ (-458 kJ/mol). The variational result obtained with the wave function

[1] Compare this equation to Eq. (9.7) for the helium atom.

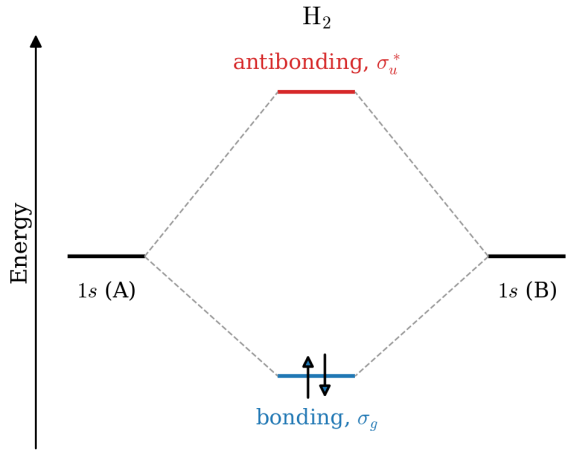


Figure 11.7 Molecular orbital diagram of the hydrogen molecule, with both electrons described by the bonding orbital, with opposite spins.

in Eq. (11.12) is −0.12778 E_h (−335 kJ/mol), which is about 73% of the exact value. In this calculation, the exponent of the 1s orbitals, c_0 in $\psi_{100} = \sqrt{\frac{c_0^3}{\pi}}\exp[-c_0 r]$, is used as a variational parameter, exactly as we did for helium in Chapter 9. Its optimal value at R_e is $c_0 = 1.1695$, larger than 1: in the molecule, each electron feels the attraction of two nuclei, and the orbitals contract.

If we scan the Born–Oppenheimer potential energy curve with the wave function in Eq. (11.12), as we did for H_2^+, we obtain the red curve in Fig. 11.8.

The Hartree–Fock results for H_2 describe the formation of the bond qualitatively around the equilibrium distance (the minimum of the curve), but they fail completely at dissociation: instead of going to the energy of two hydrogen atoms, the curve keeps rising, and at large distances the molecule is predicted to be *less* stable than the separated atoms by hundreds of kJ/mol. To understand why, we can write the spatial part of Eq. (11.12) in terms of the atomic orbitals:

$$\begin{aligned}\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2) &= \frac{1}{2+2S}\,[a(1)+b(1)]\,[a(2)+b(2)] \\ &= \frac{1}{2+2S}\Big[\underbrace{a(1)b(2)+b(1)a(2)}_{\text{covalent: H–H}} + \underbrace{a(1)a(2)+b(1)b(2)}_{\text{ionic: H}^-\ \text{H}^+\ \text{and H}^+\ \text{H}^-}\Big],\end{aligned} \tag{11.14}$$

where $a(1)$ is short for $a(\mathbf{r}_1)$, and so on. The first two terms describe one electron on each atom, the covalent picture of the bond. The last two terms describe both electrons on the same atom, i.e., an H^- ion next to a bare proton. The RHF wave function always contains the two types of terms *with the same*

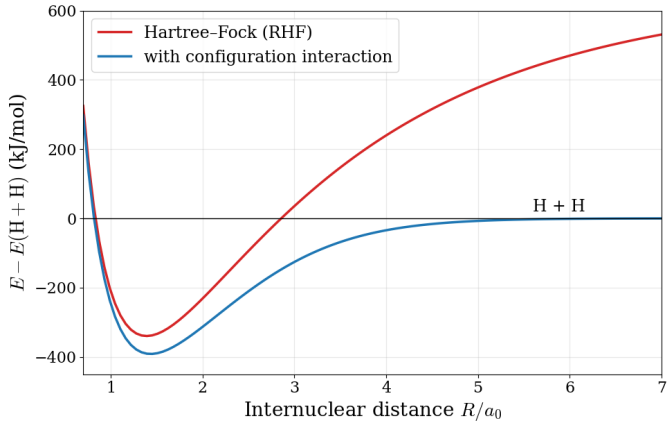


Figure 11.8 Born–Oppenheimer potential energy curves for the hydrogen molecule computed with the restricted Hartree–Fock wave function (red) and with configuration interaction (blue). Both calculations use a minimal basis of 1*s* functions with the exponent optimized at each distance (approximated with three gaussian functions, so the numbers differ slightly from those in the text). Energies are measured from two separated hydrogen atoms.

weight, whatever the distance between the nuclei. Close to equilibrium this is not too bad, since the ionic terms give a reasonable description of the electrons being shared between the two nuclei. At dissociation, however, the correct answer is two neutral hydrogen atoms, and the ionic terms (which describe the much less stable H^- + H^+ pair) should disappear completely. The RHF wave function cannot do that, and its energy at large distance is too high.

11.2.1 Beyond Hartree–Fock

This failure is not a failure of quantum mechanics, but of the approximation that we used: it is an extreme example of the electron correlation that we discussed in Chapter 9. In the RHF wave function the two electrons are described by the same orbital and move independently of each other, so there is nothing that prevents them from being found on the same atom. In reality, when the two atoms are far apart, if one electron is on atom A the other is almost certainly on atom B: their motions are strongly correlated.

We can fix the problem by mixing into the wave function a second Slater determinant, in which both electrons are described by the antibonding orbital, $\sigma_u = \varphi_-$:

$$\Psi_{\mathrm{CI}} = c_1\,|\sigma_g\alpha\;\sigma_g\beta| + c_2\,|\sigma_u\alpha\;\sigma_u\beta|, \tag{11.15}$$

where the coefficients c_1 and c_2 are determined with the variational method. Expanding the spatial part of the second determinant as we did in Eq. (11.14),

we obtain $\sigma_u(1)\sigma_u(2) \propto [a(1)a(2) + b(1)b(2)] - [a(1)b(2) + b(1)a(2)]$: the same ionic and covalent terms, but with opposite relative sign. By choosing c_2 negative, we can therefore reduce the weight of the ionic terms. At equilibrium the variational method gives a small c_2, while at dissociation it gives $c_2 = -c_1$, which removes the ionic terms completely and leaves the correct covalent wave function. The resulting potential energy curve is the blue curve in Fig. 11.8. It goes smoothly to the energy of two hydrogen atoms at dissociation, and it is also lower than the RHF curve near the minimum, since it recovers part of the correlation energy.

A wave function written as a linear combination of several Slater determinants, such as Eq. (11.15), is called a **configuration interaction (CI)** wave function, and it is the simplest example of a *correlated method*. Modern quantum chemistry programs routinely use correlated methods to compute bond energies to within a few kJ/mol of the experimental values.

11.3 Homonuclear Diatomic Molecules of the Second Row

We can now use what we learned for H_2^+ and H_2 to understand the bonds formed by the atoms of the second row of the periodic table, from lithium to neon. Here we will not perform the calculations explicitly, but we will use the same ideas to build qualitative MO diagrams, which are one of the most powerful tools that chemists have to reason about bonding.

11.3.1 Building the molecular orbitals

Each second-row atom has a $1s$ core and valence electrons, described by the $2s$ and $2p$ orbitals. As we saw in Chapter 9, the core orbitals are very compact and very low in energy, so the $1s$ orbitals of the two atoms barely overlap, and they combine into a bonding and an antibonding orbital, which together describe the four core electrons and have almost the same energy as the atomic orbitals. Their effects cancel out, and we can ignore them. The interesting chemistry happens in the valence shell, where each atom contributes four atomic orbitals, $2s$, $2p_x$, $2p_y$, and $2p_z$, for a total of eight. The LCAO method of Chapter 10 would then give an 8×8 secular determinant. Fortunately, we do not need to solve it to understand the results, because of two simple rules:

1. **Only orbitals with similar energies interact strongly.** The difference between the energies of the atomic orbitals enters the solution of the secular determinant in the same way as H_{aa} did for H_2^+: the closer two atomic orbitals are in energy, the more they mix and the larger the splitting between the resulting bonding and antibonding orbitals.
2. **Only orbitals with the same symmetry with respect to the bond axis can interact.** If we take the bond axis as z, the $2s$ and $2p_z$ orbitals

are symmetric with respect to rotations around the axis, and they form σ orbitals, as we saw for hydrogen. The $2p_x$ and $2p_y$ orbitals are perpendicular to the axis, and they change sign when we rotate the molecule by 180° around it. Their overlap with an orbital of σ symmetry is exactly zero (the positive and negative lobes cancel), so they form separate molecular orbitals, called π orbitals.

Using these two rules, the 8×8 problem splits into smaller pieces. To a first approximation, the two $2s$ orbitals combine into a bonding $\sigma_g 2s$ and an antibonding $\sigma_u^* 2s$ orbital, exactly as the $1s$ orbitals did in H_2. The two $2p_z$ orbitals, which point towards each other, combine into a bonding $\sigma_g 2p$ and an antibonding $\sigma_u^* 2p$ orbital. Finally, the $2p_x$ orbitals on the two atoms combine side by side into a bonding $\pi_u 2p$ and an antibonding $\pi_g^* 2p$ orbital, and the same happens for the $2p_y$ orbitals. The two π_u orbitals (one from p_x and one from p_y) have the same energy, and so do the two π_g^* orbitals. (The asterisk is a common way of marking antibonding orbitals.) The orbitals formed by the $2p$ functions are plotted in Fig. 11.9.

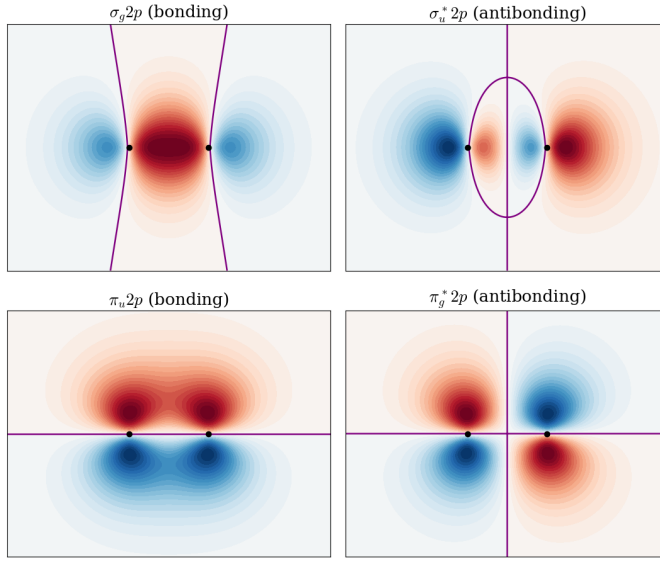


Figure 11.9 Color maps of the molecular orbitals formed by the $2p$ atomic orbitals in a homonuclear diatomic molecule, in a plane that contains the two nuclei (black dots, bond axis horizontal). Color scheme: red (positive), blue (negative). Nodal surfaces are reported in purple.

Notice three things in these orbitals:

1. σ **versus** π **overlap**: the $2p_z$ orbitals point directly at each other and overlap strongly along the bond axis. The $2p_x$ orbitals overlap side by

side, above and below the axis, and their overlap is smaller. As a consequence, the splitting between π_u and π_g^* is usually smaller than the splitting between $\sigma_g 2p$ and $\sigma_u^* 2p$.

2. **Nodes**: as always, the antibonding orbitals have an extra nodal plane perpendicular to the bond axis, halfway between the nuclei. The π orbitals also have a nodal plane that *contains* the bond axis, so the electrons in a π bond are found above and below the axis, never on it.

3. **Symmetry labels**: if we invert the π bonding orbital through the center of the molecule, the upper positive lobe goes into the lower negative lobe, so the orbital changes sign and is labeled u. The π antibonding orbital, instead, does not change sign, and is labeled g. Notice that this is the opposite of what happens for σ orbitals, where the bonding orbital is g and the antibonding one is u.

11.3.2 Molecular orbital diagrams of N_2 and O_2

Once we know the molecular orbitals and their approximate order, we can use them to describe the valence electrons of the molecule, at most two electrons (with opposite spins) for each orbital, starting from the lowest, and following the Pauli exclusion principle as we did for many-electron atoms. The resulting MO diagrams for N_2 (10 valence electrons) and O_2 (12 valence electrons) are shown in Fig. 11.10.

The two diagrams are not identical: in N_2 the $\pi_u 2p$ orbitals are *below* the $\sigma_g 2p$ orbital, while in O_2 the order is reversed. The reason is a mixing between the $2s$ and $2p_z$ orbitals, which we neglected in the simple picture above. The $\sigma_g 2s$ and $\sigma_g 2p$ orbitals have the same symmetry, so, according to the second rule, they can interact. When they do, the lower orbital is pushed further down, and the upper one, $\sigma_g 2p$, is pushed up, above the $\pi_u 2p$ orbitals. According to the first rule, this mixing is important only if the $2s$ and $2p$ atomic orbitals are close in energy. As we saw in Chapter 9, the $2s$ orbitals are lower than the $2p$ orbitals because they penetrate the core. This effect grows across the row, as the nuclear charge increases (see the difference between $Z_{\text{eff}}(2s)$ and $Z_{\text{eff}}(2p)$ in Table 9.1, multiplied by the larger charges). For the first part of the row (from Li_2 to N_2), the $2s$–$2p$ gap is small, the mixing is strong, and $\pi_u 2p$ is below $\sigma_g 2p$. For O_2 and F_2, the gap is large, the mixing is small, and $\sigma_g 2p$ is the lower of the two. This change in order is confirmed experimentally by photoelectron spectroscopy, which measures the energies needed to remove electrons from each orbital.

11.3.3 Bond order and magnetic properties

A simple way of summarizing an MO diagram is the **bond order**:

$$\text{bond order} = \frac{1}{2}\left(n_{\text{bonding}} - n_{\text{antibonding}}\right), \tag{11.16}$$

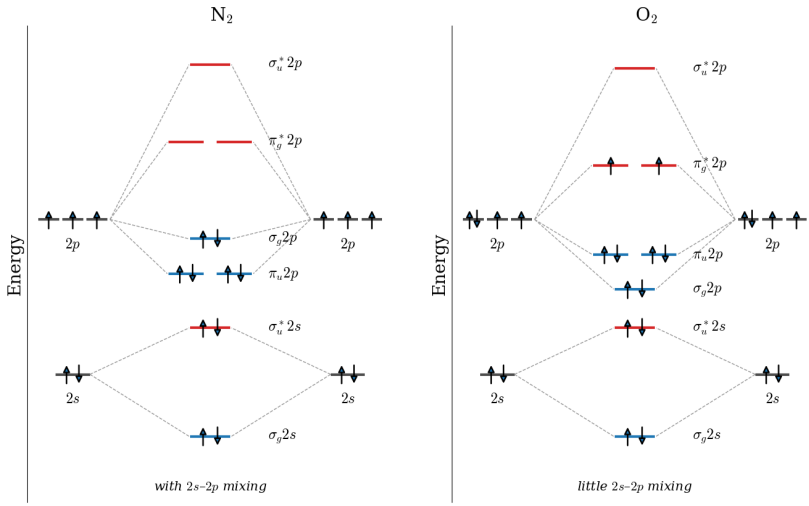


Figure 11.10 Qualitative valence molecular orbital diagrams of N_2 (left) and O_2 (right). The atomic orbitals of the two atoms are on the sides, and the molecular orbitals in the middle (blue: bonding, red: antibonding). The 1*s* core orbitals are not shown.

where n_{bonding} and $n_{\text{antibonding}}$ are the numbers of electrons described by bonding and antibonding orbitals, respectively. Since each electron described by a bonding orbital stabilizes the molecule and each electron described by an antibonding orbital destabilizes it by a similar (slightly larger) amount, the bond order measures the net number of bonds between the two atoms. For H_2 it is $\frac{1}{2}(2-0) = 1$, a single bond. From Fig. 11.10 we obtain:

- N_2: 8 electrons described by bonding orbitals ($\sigma_g 2s$, $\pi_u 2p$, $\sigma_g 2p$) and 2 by antibonding orbitals ($\sigma_u^* 2s$), so the bond order is $\frac{1}{2}(8-2) = 3$. This is the triple bond of the Lewis structure, N ≡ N, made of one σ and two π bonds.
- O_2: 8 electrons described by bonding orbitals and 4 by antibonding orbitals ($\sigma_u^* 2s$ and $\pi_g^* 2p$), so the bond order is $\frac{1}{2}(8-4) = 2$, the double bond of the Lewis structure, O = O.

So far, the MO diagrams agree with the Lewis structures. The most interesting difference is in the last two electrons of O_2. They are described by two orbitals with exactly the same energy, the two π_g^* orbitals, and there are two ways of doing so: using the same orbital for both electrons, with opposite spins, or a different orbital for each electron. As for the many-electron atoms (where this is known as Hund's rule), the lowest energy is obtained by describing the two electrons with different orbitals, with *parallel* spins. Electrons described

by different orbitals are, on average, farther apart and repel each other less, and electrons with the same spin are kept even farther apart by the antisymmetry of the wave function, which is the origin of the exchange term that we saw in the Fock operator in Chapter 10. Molecular oxygen, therefore, has two unpaired electrons. Since each unpaired electron behaves like a tiny magnet (Chapter 7), the molecule is attracted by a magnetic field: it is **paramagnetic**. This can be seen in a classic demonstration, in which liquid oxygen poured between the poles of a strong magnet stays suspended between them, while liquid nitrogen, which has no unpaired electrons (it is *diamagnetic*), flows straight through. The Lewis structure of O_2, which pairs all electrons, cannot explain this behavior, while the MO diagram predicts it naturally. This was one of the earliest and most convincing successes of molecular orbital theory.

The same procedure can be applied to all the homonuclear diatomic molecules of the second row, and the results are summarized in Table 11.1.

Table 11.1 Bond orders predicted by MO theory for the homonuclear diatomic molecules of the second row, compared with approximate experimental bond lengths and bond energies.

Molecule	Valence electrons	Bond order	Unpaired electrons	Bond length (pm)	Bond energy (kJ/mol)
Li_2	2	1	0	267	105
Be_2	4	0	0	—	~10
B_2	6	1	2	159	289
C_2	8	2	0	124	599
N_2	10	3	0	110	942
O_2	12	2	2	121	494
F_2	14	1	0	142	154
Ne_2	16	0	0	—	~0

Notice how the experimental data follow the predicted bond orders: as the bond order increases from Li_2 to N_2, the bonds get shorter and stronger, and as it decreases from N_2 to F_2, they get longer and weaker. The molecules with a bond order of zero, Be_2 and Ne_2, are not chemically bound (they exist only as extremely weak van der Waals complexes at very low temperatures). Notice also that MO theory correctly predicts that B_2, like O_2, is paramagnetic: because of the $2s$–$2p$ mixing, its last two electrons are described by the two degenerate π_u orbitals, with parallel spins.

Example 11.1: Removing an electron from O_2

What happens to the bond of O_2 when we remove one electron to form O_2^+?
Step 1: which electron is removed? The highest occupied orbitals of O_2 are the two π_g^* antibonding orbitals, which describe the last two electrons (Fig. 11.10). The electron that is removed is one of these.
Step 2: new bond order. O_2^+ has 8 electrons described by bonding orbitals and 3 by antibonding orbitals:

$$\text{bond order} = \frac{8-3}{2} = 2.5,$$

larger than the bond order of O_2, 2.
Step 3: predictions. Since an antibonding electron was removed, the bond becomes *stronger and shorter*: experimentally, the bond length decreases from 121 pm in O_2 to 112 pm in O_2^+. With one unpaired electron, O_2^+ is still paramagnetic. Notice how different this is from removing an electron from N_2, where the electron comes from a bonding orbital and the bond becomes weaker.

11.4 Heteronuclear Diatomic Molecules

When the two atoms of a diatomic molecule are different, the two rules that we used to build the molecular orbitals still apply, but with an important difference: the atomic orbitals of the two atoms no longer have the same energy. Recall from Chapter 9 that the energy of an atomic orbital depends on the effective nuclear charge, which increases across a row of the periodic table. Orbitals of more electronegative atoms are therefore lower in energy. This has two consequences, which we can understand by going back to the 2×2 secular determinant of H_2^+, with $H_{aa} \neq H_{bb}$:

1. **Smaller splitting.** The larger the energy difference between the two atomic orbitals, the less they mix, and the smaller the stabilization of the bonding orbital. Orbitals that are very far apart in energy do not mix at all, even if they have the same symmetry.
2. **Unequal sharing.** The bonding orbital is closer in energy to the lower atomic orbital, and it has a larger coefficient on the more electronegative atom. The antibonding orbital, instead, resembles the higher atomic orbital, and it is concentrated on the less electronegative atom. In other words, an electron described by the bonding orbital is more likely to be found near the more electronegative atom: the bond is **polar**.

These ideas are illustrated by the MO diagrams of hydrogen fluoride and carbon monoxide in Fig. 11.11.

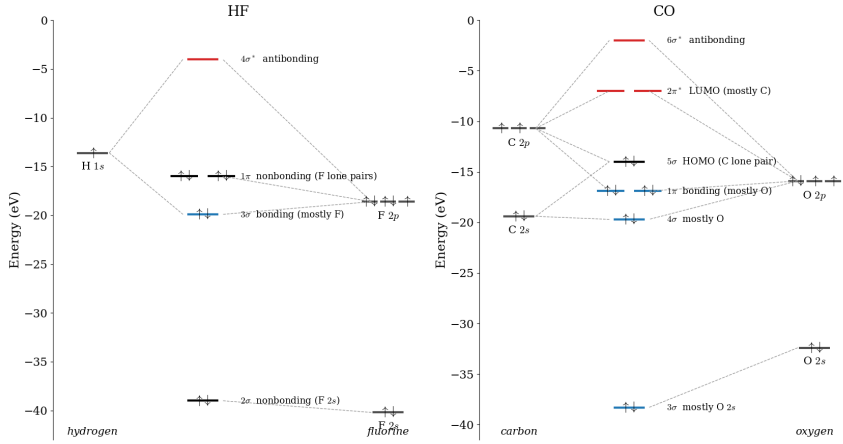


Figure 11.11 Qualitative valence molecular orbital diagrams of HF (left) and CO (right). The atomic levels are placed at the approximate energies of the valence atomic orbitals, and the occupied molecular orbitals of CO at the negative of the experimental ionization energies (blue: bonding, red: antibonding, black: nonbonding).

Hydrogen fluoride. The 1*s* orbital of hydrogen (−13.6 eV) is much higher in energy than the valence orbitals of fluorine, whose large effective nuclear charge pulls the 2*s* orbital down to about −40 eV and the 2*p* orbitals to about −19 eV. By symmetry, the hydrogen 1*s* orbital can only combine with the fluorine orbitals of σ symmetry, 2*s* and $2p_z$, and the 2*s* is too low in energy to mix significantly. The bond is therefore formed by the hydrogen 1*s* and the fluorine $2p_z$ orbitals, which give a bonding orbital (3σ) much closer to the fluorine level, and therefore mostly localized on fluorine, and an antibonding orbital ($4\sigma^*$) mostly localized on hydrogen. The fluorine 2*s* (2σ) and the two fluorine 2*p* orbitals perpendicular to the bond (1π) have no partner on hydrogen, and they remain *nonbonding*: they are the three lone pairs of the Lewis structure of HF. The eight valence electrons are described by 2σ, 3σ, and 1π, so the bond order is $\frac{1}{2}(2-0) = 1$, a single bond. Since the two bonding electrons are found mostly near fluorine, the molecule has a large dipole moment (1.83 D), with the negative end on fluorine.

Carbon monoxide. CO has the same number of valence electrons as N_2 (it is *isoelectronic* with it), and its MO diagram looks similar: the bond order is $\frac{1}{2}(8-2) = 3$, a triple bond, and CO is, in fact, one of the strongest bonds known (1,072 kJ/mol). The orbitals of oxygen are lower in energy than those of carbon, so the bonding orbitals (3σ, 4σ, and 1π) are concentrated on oxygen, and the antibonding orbitals on carbon. Two orbitals deserve special attention, since they control the chemistry of CO. They are shown in Fig. 11.12.

1. **The HOMO (5σ)** is mostly a carbon orbital, a combination of carbon 2*s*

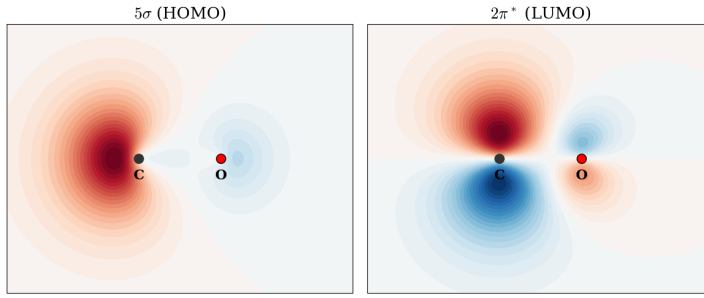


Figure 11.12 Schematic color maps of the frontier orbitals of CO, in a plane that contains the bond axis (red: positive, blue: negative). Left: the highest occupied orbital, 5σ, is a lone pair on carbon pointing away from oxygen. Right: the lowest unoccupied orbital, $2\pi^*$, has its largest lobes on carbon. The maps are drawn from simple combinations of atomic orbitals and are meant to show the qualitative shape only.

and $2p_z$ that points *away* from the oxygen atom. It is essentially a lone pair on carbon, the same lone pair that appears in the Lewis structure $:\mathrm{C}\equiv\mathrm{O}:$.

2. **The LUMO ($2\pi^*$)** is a pair of antibonding π orbitals, which, as the antibonding orbitals of a polar bond, have their largest lobes on carbon.

These two orbitals explain why CO binds to metal atoms through carbon, and not through the more electronegative oxygen. In metal carbonyls, such as $Ni(CO)_4$, and in the binding of CO to the iron atom of hemoglobin (which is why CO is so toxic), the carbon lone pair donates electron density to an empty orbital on the metal (σ donation), while filled d orbitals of the metal donate electron density back into the $2\pi^*$ orbitals of CO (π back-donation). Both interactions involve orbitals that are concentrated on carbon, so carbon is the end that binds. The back-donation also weakens the C–O bond, since it adds electron density to an antibonding orbital, which is observed experimentally as a lower C–O vibrational frequency in metal carbonyls (around 2,000 cm^{-1}) than in free CO (2,143 cm^{-1}, Chapter 13).

The MO picture also explains a famous puzzle: despite the much larger electronegativity of oxygen, the dipole moment of CO is very small (0.11 D), and its negative end is on *carbon*. The polarization of the bonding orbitals towards oxygen is almost exactly compensated by the carbon lone pair (5σ), which places electron density on the outer side of the carbon atom.

These qualitative MO diagrams are the starting point of molecular orbital theory, but they only work so well for diatomic molecules. For a molecule with more than two atoms, such as water, we cannot easily guess the order and shape of the molecular orbitals, and we need to solve the Hartree–Fock

equations explicitly, as we will do in the next chapter.

11.5 Chapter Review

11.5.1 Key Ideas

- In H_2^+, the in-phase combination of two 1*s* orbitals is bonding and the out-of-phase one antibonding; the antibonding orbital is destabilized more.
- Hartree–Fock describes the H_2 bond well near equilibrium, but fails at dissociation; configuration interaction fixes this.
- Atomic orbitals interact strongly only if they have similar energies and the same symmetry with respect to the bond axis.
- The bond order, $\frac{1}{2}(n_{\text{bonding}} - n_{\text{antibonding}})$, predicts bond strengths and lengths, and MO theory explains why O_2 is paramagnetic.
- In heteronuclear molecules, electrons are shared unequally, and the composition of the frontier orbitals explains reactivity, as for CO binding to metals through carbon.

11.5.2 Study Questions

1. **In the bonding orbital of H_2^+, $\varphi_+ = (a + b)/\sqrt{2 + 2S}$:**
   a. the two atomic orbitals cancel between the nuclei
   b. the electron is found only near nucleus a
   c. there is a node between the nuclei
   d. the energy is higher than that of the separated atoms
   e. the two atomic orbitals add up in phase, and the probability between the nuclei increases

2. **Compared with the energy of a hydrogen 1*s* orbital, the antibonding orbital of H_2^+ is:**
   a. pushed up exactly as much as the bonding orbital is pushed down
   b. pushed down
   c. at the same energy
   d. pushed up more than the bonding orbital is pushed down
   e. pushed up less than the bonding orbital is pushed down

3. **Which integral is mainly responsible for the formation of the bond in H_2^+?**
   a. the overlap integral S
   b. the Coulomb integral H_{aa}
   c. the nuclear repulsion
   d. the kinetic energy of the proton
   e. the resonance integral H_{ab}, which is negative

4. Why does the Hartree–Fock wave function give the wrong energy when the H_2 molecule is dissociated?

a. because the Hamiltonian is wrong at large distances
b. because the basis set is too large
c. because the electrons have the same spin
d. because it contains equal amounts of covalent and ionic (H^+H^-) terms at all distances
e. because the variational theorem does not apply to molecules

5. How can the wave function of H_2 be improved at large distances?

a. by removing the electron spin
b. by using a single atomic orbital
c. by mixing in a second Slater determinant (configuration interaction)
d. by neglecting electron–electron repulsion
e. by fixing the nuclei closer together

6. Two atomic orbitals interact strongly to form molecular orbitals only if:

a. they are on the same atom
b. they have similar energies and the same symmetry with respect to the bond axis
c. they have different symmetries
d. they have very different energies
e. they are both core orbitals

7. What is the bond order of N_2?

a. 1
b. 2
c. 3
d. 2.5
e. 0

8. Why is O_2 paramagnetic?

a. because its last two electrons are described by two degenerate π^* orbitals with parallel spins
b. because it has a triple bond
c. because its bond order is zero
d. because oxygen nuclei are magnetic
e. because all its electrons are paired

9. In hydrogen fluoride, the bonding molecular orbital:

a. is mostly made of the hydrogen 1*s* orbital
b. is mostly made of the fluorine orbital, so the electrons are shared unequally
c. has equal contributions from the two atoms
d. is made only of fluorine core orbitals
e. does not exist, because the energies are too different

10. Why does carbon monoxide bind to metal atoms through carbon, not through oxygen?

a. because its highest occupied orbital, 5σ, is mostly a carbon orbital pointing away from oxygen
b. because carbon is more electronegative than oxygen
c. because oxygen has no lone pairs
d. because the dipole moment of CO is large
e. because CO has a single bond

Answers

1.e, 2.d, 3.e, 4.d, 5.c, 6.b, 7.c, 8.a, 9.b, 10.a

CHAPTER 12

The Chemical Bond in Polyatomic Molecules

In the previous chapter, we built the molecular orbitals of diatomic molecules using two simple rules: atomic orbitals interact only if they have similar energies and the same symmetry. For a diatomic molecule, these rules are enough to guess the order and shape of the molecular orbitals without solving any equation. As soon as a molecule has three or more atoms, however, guessing becomes much harder: the orbitals of the outer atoms can combine in several ways, and many of them have the same symmetry and can mix. In this chapter, we will see how the LCAO-MO method and the Hartree–Fock procedure of Chapter 10 are used to solve this problem for a real polyatomic molecule, water, and how the results compare with experiments and with the familiar Lewis picture of bonds and lone pairs. In the last part of the chapter, we will introduce Hückel theory, a much simpler approximation that captures the essential physics of the π electrons in conjugated organic molecules.

12.1 The Chemical Bond in the Water Molecule Using a Minimal Basis

For a minimal representation of the two hydrogen atoms, we need two 1*s* functions, one centered on each atom. Some of the electrons of oxygen are described by orbitals of the second shell ($n = 2$), so we will need one 1*s*, one 2*s*, and three 2*p* functions (one each of p_x, p_y, and p_z). Summarizing, for a minimal representation of the water wave function we need five orbitals on oxygen, plus one each on the hydrogen atoms, for a total of 7 functions. From these atomic functions, we can build a total wave function using the LCAO method of Chapter 10, and then we can use the variational principle, in conjunction with the Hartree–Fock (HF) method, to build and solve a secular determinant that is similar to that in Eq. (10.13), with $m = 7$ being the total number of basis functions. The approximated Hamiltonian operator in the HF method is called the Fock operator, and it can be divided into one-electron integrals, comprising the kinetic and potential energy contributions:

$$
\begin{aligned}
K_{ij} &= \int \phi_i^* \hat{K} \phi_j \, d\tau = \int \phi_i^* \left(-\frac{1}{2} \nabla^2 \right) \phi_j \, d\tau \\
V_{ij} &= \int \phi_i^* \hat{V} \phi_j \, d\tau = \int \phi_i^* \left(-\sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right) \phi_j \, d\tau,
\end{aligned}
\tag{12.1}
$$

as well as two-electron integrals describing the Coulomb repulsion between electrons:

$$
V_{ijkl} = \iint \phi_i^* \phi_j^* \hat{r}_{12}^{-1} \phi_k \phi_l \, d\tau_1 \, d\tau_2 = \iint \phi_i^* \phi_j^* \left(\frac{1}{r_{12}} \right) \phi_k \phi_l \, d\tau_1 \, d\tau_2. \tag{12.2}
$$

Even with such a small basis set, the number of integrals that we need is large, since each of the indices i, j, k, and l can be any of the 7 basis functions. There are $7 \times 7 = 49$ kinetic energy integrals, and 49 nuclear attraction integrals for each of the three nuclei, $7 \times 7 \times 3 = 147$, for a total of 196 one-electron integrals. For the two-electron integrals, there are $7 \times 7 \times 7 \times 7 = 2{,}401$ combinations. In total, we need almost 2,600 integrals for a very simple calculation on a very small molecule.[1]

12.1.1 Using symmetry

Before computing anything, we can use the symmetry of the molecule to simplify the problem, exactly as we did for diatomic molecules. We place the water molecule in the yz plane, with the oxygen atom at the origin and the z axis bisecting the H–O–H angle. The molecule has two mirror planes: the plane of the molecule itself (yz), and the plane perpendicular to it that contains the z axis (xz). Reflecting the molecule through either plane leaves it unchanged, so the Hamiltonian is unchanged too, and every molecular orbital must be either symmetric (unchanged) or antisymmetric (changing sign) with respect to each reflection. We can then sort the seven basis functions according to their behavior:

1. **Symmetric with respect to both planes**: the oxygen 1s, 2s, and 2p_z orbitals, and the in-phase combination of the two hydrogen orbitals, $H_a + H_b$. Orbitals of this type are labeled a_1.

[1] These numbers assume that each basis function is a single function. In real calculations, each basis function is itself a fixed combination of simpler gaussian functions, called *primitives*. In the simplest case, the STO-3G basis set, each basis function is made of 3 primitives, so each one-electron integral requires $3 \times 3 = 9$ integrals over primitives, for a total of $9 \times 196 = 1{,}764$. Each two-electron integral requires $3^4 = 81$ integrals over primitives, for a total of $81 \times 2{,}401 = 194{,}481$. Notice how the two-electron integrals dominate the cost of the calculation, and how their number grows as the fourth power of the size of the basis set. A similar discussion of the minimal-basis calculation on water can be found in Prof. C.J. Cramer's lecture notes.

2. **Antisymmetric with respect to the perpendicular (xz) plane only**: the oxygen $2p_y$ orbital and the out-of-phase combination $H_a - H_b$. These are labeled b_2.
3. **Antisymmetric with respect to the molecular (yz) plane**: only the oxygen $2p_x$ orbital, which is perpendicular to the plane of the molecule. This is labeled b_1.

The labels come from group theory, but here we will simply use them as names.[2] As we saw for the σ and π orbitals of diatomic molecules, two functions of different symmetry have zero overlap and do not mix. As a consequence, the 7×7 secular determinant splits into three independent blocks: a 4×4 block for the a_1 functions, a 2×2 block for the b_2 functions, and a 1×1 block for $2p_x$, which cannot mix with anything and forms a molecular orbital by itself. We will see these blocks appear in the matrices of the next section, as patterns of zeros, and in the final molecular orbitals.

All this work is needed to find just 5 occupied molecular orbitals (10 electrons, two described by each orbital) for the final Slater determinant. The situation is less hopeless than it looks, though. If we use gaussian functions in place of the hydrogen-like orbitals, every integral has an analytic formula that depends only on the positions of the atoms and on the exponents of the functions. Evaluating all of them requires roughly a million floating-point operations, which a modern computer performs in a tiny fraction of a second. In addition, the symmetry of the molecule makes many integrals identical (or exactly zero), so the number that actually needs to be computed is smaller.

12.2 Hartree-Fock Calculation for Water

To find the Hartree-Fock (HF) molecular orbitals (MOs) we need to solve the following secular determinant:

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{17} - ES_{17} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{27} - ES_{27} \\ \vdots & \vdots & \ddots & \vdots \\ F_{71} - ES_{71} & F_{72} - ES_{72} & \cdots & F_{77} - ES_{77} \end{vmatrix} = 0 \tag{12.3}$$

with S_{ij} being the overlap integrals of Eq. (10.11), and F_{ij} the matrix elements of the Fock operator, defined using the one- and two-electron integrals in Eq. (12.1) and Eq. (12.2) as:

$$F_{ij} = K_{ij} + V_{ij} + \sum_{kl} P_{kl} \left[V_{ijkl} - \frac{1}{2} V_{ikjl} \right], \tag{12.4}$$

with the density matrix elements P_{kl} defined as:

[2] The symmetry group of the water molecule is called C_{2v}, and a_1, b_1, and b_2 are the names of its irreducible representations.

$$P_{kl} = 2 \sum_{i}^{\text{occupied}} a_{ki} a_{li}, \tag{12.5}$$

where the a values are the coefficients of the basis functions in the occupied molecular orbitals. These values will be determined using the SCF procedure, which proceeds as follows: At the first step we simply guess what these are, then we iterate through solution of the secular determinant to derive new coefficients and we continue to do so until self-consistency is reached (i.e. the $N + 1$ step provides coefficients and energies that are equal to those in the N step).

We can try to solve the SCF procedure for water using a fixed geometry of the nuclei close to the experimental structure: O-H bond lengths of 0.95 Å and a valence bond angle at oxygen of 104.5°. To do so, we can use a minimal basis set composed of the following seven orbitals: basis function #1 is an oxygen 1s orbital, #2 is an oxygen 2s orbital, #3 is an oxygen $2p_x$ orbital, #4 is an oxygen $2p_y$ orbital, #5 is an oxygen $2p_z$ orbital, #6 is one hydrogen 1s orbital, and #7 is the other hydrogen 1s orbital. The corresponding integrals introduced in the previous section can be calculated using a quantum chemistry code. The calculated overlap matrix elements are:

$$\mathbf{S} = \begin{bmatrix} \text{O } 1s & \text{O } 2s & \text{O } 2p_x & \text{O } 2p_y & \text{O } 2p_z & \text{H}_a\ 1s & \text{H}_b\ 1s & \\ 1.000 & & & & & & & \text{O } 1s \\ 0.237 & 1.000 & & & & & & \text{O } 2s \\ 0.000 & 0.000 & 1.000 & & & & & \text{O } 2p_x \\ 0.000 & 0.000 & 0.000 & 1.000 & & & & \text{O } 2p_y \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & & \text{O } 2p_z \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & & \text{H}_a\ 1s \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 & \text{H}_b\ 1s \end{bmatrix} \tag{12.6}$$

The matrix $\mathbf{S}$ is shown in lower triangular form, since $S_{ji} = S_{ij}$, and its diagonal elements are all equal to 1, since each basis function is normalized. The other elements tell us a lot about the shape of the basis functions:

1. **Symmetry zeros**: the three 2p orbitals on oxygen are orthogonal to each other and to the s orbitals on the same atom, so their overlaps are zero. The two s orbitals on oxygen, instead, overlap ($S_{12} = 0.237$), because they are not pure hydrogen-like orbitals (which would be orthogonal) but functions optimized for the oxygen atom.
2. **Core versus valence**: the oxygen 1s orbital overlaps with the hydrogen orbitals about ten times less than the oxygen 2s orbital, since the 1s orbital is much more compact and decays quickly away from the oxygen nucleus.

3. **Orientation of the p orbitals**: the $2p_x$ orbital does not overlap at all with the hydrogen $1s$ orbitals. The hydrogen atoms lie in the nodal plane of $2p_x$, so the positive overlap on one side of the plane exactly cancels the negative overlap on the other. The $2p_y$ orbital overlaps with the two hydrogen orbitals by the same amount but with opposite sign, since each hydrogen faces a different lobe. The $2p_z$ orbital points along the axis that bisects the molecule, so it overlaps in the same way with both hydrogens.

The kinetic energy matrix (in a.u.) is:

$$\mathbf{K} = \begin{bmatrix} 29.003 & & & & & & \\ -0.168 & 0.808 & & & & & \\ 0.000 & 0.000 & 2.529 & & & & \\ 0.000 & 0.000 & 0.000 & 2.529 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & \\ -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & \\ -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 \end{bmatrix} \tag{12.7}$$

All diagonal elements are positive and much larger than the off-diagonal ones. Recall that the kinetic energy integrals in Eq. (12.1) contain the Laplacian, ∇^2, which measures how quickly a function curves in space. For a diagonal element, we multiply a function by its own curvature, which is large where the function is large, so the integral accumulates a large value. For two functions centered on different atoms, one function is usually almost flat (and therefore has almost no curvature) wherever the other is large, so the integral is small. Notice also that the largest element by far is the one for the oxygen $1s$ orbital: the more compact a function is, the more it curves, and the higher its kinetic energy. Off-diagonal elements can be negative, since they are not the kinetic energy of anything; they are just integrals that enter the secular determinant. As for the overlap, symmetry keeps the p orbitals from mixing with the s orbitals on the same atom or with each other. The nuclear attraction matrix is:

$$\mathbf{V} = \begin{bmatrix} -61.733 & & & & & & \\ -7.447 & -10.151 & & & & & \\ 0.000 & 0.000 & -9.926 & & & & \\ 0.000 & 0.000 & 0.000 & -10.152 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & -10.088 & & \\ -1.778 & -3.920 & 0.000 & -0.228 & -0.184 & -5.867 & \\ -1.778 & -3.920 & 0.000 & 0.228 & 0.184 & -1.652 & -5.867 \end{bmatrix} \tag{12.8}$$

As for the kinetic energy, the diagonal elements are the largest, since an electron described by a basis function is attracted most strongly by the nucleus

on which the function is centered, and two functions on different atoms are rarely large in the same place. All diagonal elements are negative, as they must be, since an electron described by a single function is always attracted by the nuclei. Off-diagonal elements involving two different functions can be either negative or positive. Notice also that the three $2p$ orbitals have different nuclear attraction integrals, even though they are attracted in the same way by the oxygen nucleus. The difference comes from the hydrogen nuclei: the $2p_x$ orbital is zero at both hydrogen nuclei (they lie in its nodal plane), so it has the weakest attraction. The $2p_y$ orbital has a slightly larger amplitude at the hydrogen nuclei than the $2p_z$ orbital, since the bond angle (104.5°) is larger than 90°, so its attraction is slightly stronger. (If the angle were 90°, the two orbitals would have the same amplitude at the hydrogen nuclei and the same attraction.)

The sum of the kinetic and nuclear attraction matrices is called the *core* (or one-electron) part of the Fock matrix, $\mathbf{h} = \mathbf{K} + \mathbf{V}$, and the Fock matrix can be written as $\mathbf{F} = \mathbf{h} + \mathbf{G}$, where $\mathbf{G}$ contains the contributions of the two-electron integrals (cf. Eq. (12.4)). To build $\mathbf{G}$ we need the density matrix, and to build the density matrix we need the coefficients of the occupied orbitals, which are what we are trying to find. This is the circular problem that the SCF procedure solves, as we discussed in Chapter 10. We start with a guess of the coefficients (there are many ways of making one, and in principle any reasonable guess will do), and from it we compute the density matrix using Eq. (12.5):

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & \\ -0.456 & 2.010 & & & & & \\ 0.000 & 0.000 & 2.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 \end{bmatrix} \tag{12.9}$$

With $\mathbf{P}$, we can compute the remaining contribution of $\mathbf{G}$ to the Fock matrix. We will not list all 406 unique two-electron integrals here (many of the 2,401 integrals are identical by permutational symmetry). Instead, we will simply write the total Fock matrix:

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & \\ -5.163 & -2.453 & & & & & \\ 0.000 & 0.000 & -0.395 & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 \end{bmatrix} \tag{12.10}$$

With **F** and **S** in hand, we can finally solve the secular determinant. Its roots are the orbital energies, and the corresponding coefficients give a new set of occupied orbitals. From them we build a new density matrix and a new Fock matrix, and we repeat the cycle until the energy, the density matrix, and the coefficients do not change anymore (within thresholds chosen by the user).

In our water calculation, if we monitor the energy at each step we find:

$$\begin{aligned}
E(RHF) &= -74.893\,002\,803 && \text{a.u. after 1 cycle}\\
E(RHF) &= -74.961\,289\,145 && \text{a.u. after 2 cycles}\\
E(RHF) &= -74.961\,707\,247 && \text{a.u. after 3 cycles}\\
E(RHF) &= -74.961\,751\,946 && \text{a.u. after 4 cycles}\\
E(RHF) &= -74.961\,753\,962 && \text{a.u. after 5 cycles}\\
E(RHF) &= -74.961\,754\,063 && \text{a.u. after 6 cycles}\\
E(RHF) &= -74.961\,754\,063 && \text{a.u. after 7 cycles}
\end{aligned} \tag{12.11}$$

The energy of our initial guess was off by about 0.07 a.u., or roughly 184 kJ/mol, and, as guaranteed by the variational principle, it was too high. The first iteration recovers almost all of this difference, the second one an additional 0.000 42 a.u., and after seven iterations the energy does not change anymore to within one nanohartree (less than 10^{-5} kJ/mol).

The final optimized MOs for water are:

	1	2	3	4	5	6	7
E	−20.24094	−1.27218	−.62173	−.45392	−.39176	.61293	.75095
1	.99411	−.23251	.00000	−.10356	.00000	−.13340	.00000
2	.02672	.83085	.00000	.53920	.00000	.89746	.00000
3	.00000	.00000	.00000	.00000	1.0000	.00000	.00000
4	.00000	.00000	.60677	.00000	.00000	.00000	.99474
5	−.00442	−.13216	.00000	.77828	.00000	−.74288	.00000
6	−.00605	.15919	.44453	−.27494	.00000	−.80246	−.84542
7	−.00605	.15919	−.44453	−.27494	.00000	−.80246	.84542

(12.12)

where the first row reports the eigenvalue of each MO in E_h (i.e., the energy of one electron described by that orbital), and each column contains the coefficients of the basis functions in that MO. If we add up the energies of the occupied orbitals (twice each, since each orbital describes two electrons), we obtain $2(-20.24094-1.27218-0.62173-0.45392-0.39176) = -45.961\,060$. This sum is *not* the electronic energy, and it is too high. The reason is that the energy of each orbital contains the repulsion of its electron with all other electrons, so when we add up the orbital energies the repulsion between each

pair of electrons is counted twice. If we subtract the electron-electron repulsion energy once, 38.265 406, we get −84.226 466, and if we add the nuclear repulsion energy, 9.264 701, we get a total energy of −74.961 765. The small difference with the converged result above (−74.961 754) comes from rounding the orbital energies to 5 decimal places. Notice that all five occupied MOs have negative energies, so their electrons are bound to the molecule, while the two unoccupied (or *virtual*) MOs have positive energies, meaning that the molecule would not gain energy by accepting an extra electron described by them.

12.3 The Molecular Orbitals of Water

Looking at the coefficients of the occupied MOs in Eq. (12.12), we see that the lowest orbital (by far) is almost a pure oxygen 1*s* orbital: its coefficient is very close to 1, and all others are close to 0. This is the core orbital of oxygen, which is basically unaffected by the formation of the bonds. (Keep in mind that the coefficients are not percentages, since the basis functions are not orthogonal to each other.) The second MO is dominated by the oxygen 2*s* function, but it has significant contributions from other functions as well, and it is difficult to describe it from the numbers alone. As we did for the hydrogen atom in Chapter 5, the best way to understand an orbital is to look at it. We can compute the square of each orbital on a three-dimensional grid of points, and plot the surface where the probability density has a chosen value, for example 0.04 a_0^{-3}. This *isodensity surface* encloses the region where the electron is most likely to be found, and we can color it according to the sign of the wave function, blue where it is positive and red where it is negative. The five occupied and two unoccupied MOs of water are plotted in this way in Fig. 12.1.

12.3.1 The MO diagram of water

Using the symmetry labels of the previous section, the seven MOs of water are, in order of increasing energy, $1a_1$, $2a_1$, $1b_2$, $3a_1$, $1b_1$, $4a_1$, and $2b_2$ (the number counts the orbitals of each symmetry, starting from the lowest). We can check in Eq. (12.12) that each MO contains only basis functions of one symmetry. For example, MO 5 contains only the $2p_x$ function (basis function 3), and MOs 3 and 7 contain only $2p_y$ and the out-of-phase combination of the hydrogen orbitals (their coefficients on H_a and H_b have opposite sign). The energies and the main atomic contributions to each MO can be summarized in the MO diagram of Fig. 12.2.

Let's go through this diagram from the bottom up:

1. **Core orbital**: $1a_1$ (not shown, at $-20.24\,E_h = -551$ eV) is the oxygen 1*s* orbital, which does not participate in bonding.

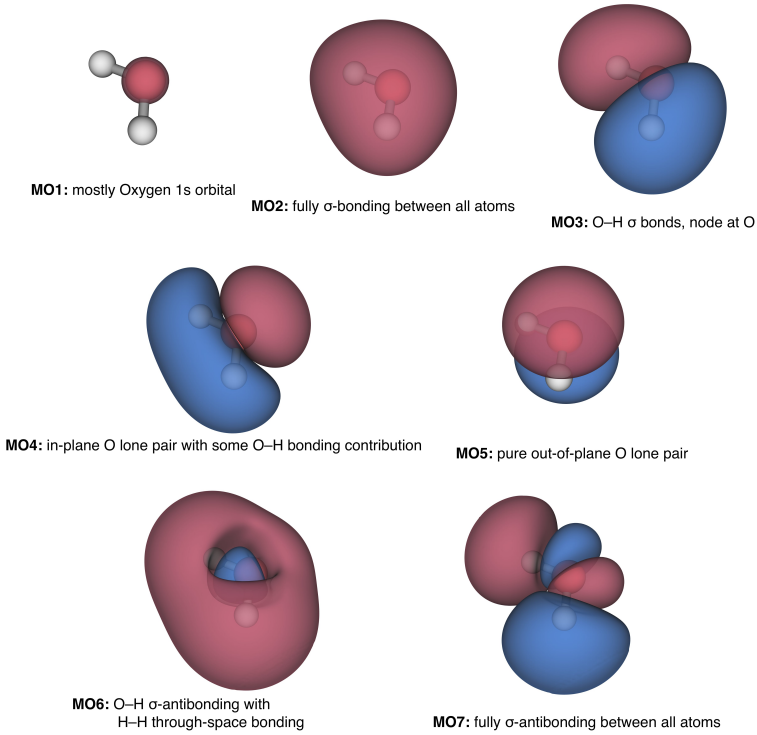


Figure 12.1 Isodensity maps of the Molecular Orbitals (MOs) of water.

2. **Bonding orbitals**: $2a_1$ is mainly oxygen $2s$, combined in phase with both hydrogen orbitals, and it is bonding over the whole molecule. $1b_2$ combines oxygen $2p_y$ with the out-of-phase hydrogen combination: it is also bonding, with one lobe on each O–H bond and a nodal plane between them. Notice that each of these two orbitals describes *both* O–H bonds at the same time.

3. **Lone pairs**: $3a_1$ is mainly oxygen $2p_z$ mixed with $2s$, and it points away from the hydrogen atoms along the symmetry axis, with only a small bonding contribution from the hydrogens. $1b_1$, the highest occupied MO (HOMO), is a pure oxygen $2p_x$ orbital, perpendicular to the plane of the molecule. Since it cannot mix with any other function, it is completely nonbonding: an electron described by it feels the hydrogen atoms only through the average field of the other electrons and nuclei.

4. **Antibonding orbitals**: $4a_1$ and $2b_2$ are the antibonding partners of $2a_1/3a_1$ and $1b_2$, respectively. They are not used to describe any electron in the ground state. The lowest of them, $4a_1$, is the lowest unoccupied MO (LUMO).

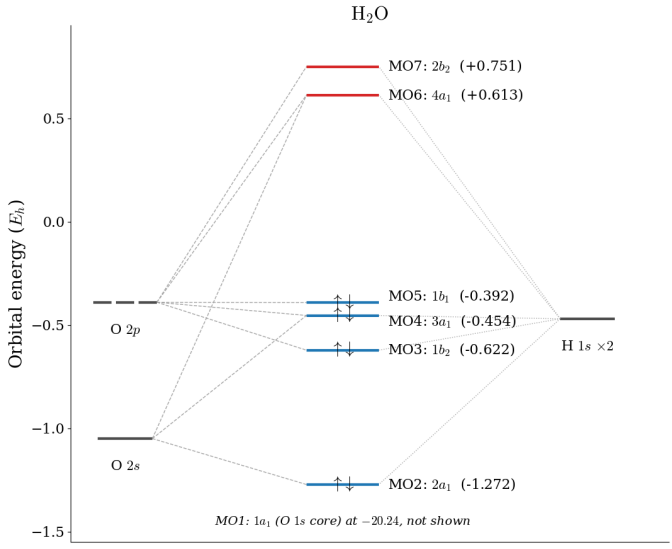


Figure 12.2 Molecular orbital diagram of water from the minimal-basis Hartree–Fock calculation. The MO energies (in E_h) are those of the converged calculation; the positions of the atomic levels are qualitative. Dashed lines connect each MO with its main atomic contributions (blue: occupied, red: unoccupied). Each MO is labeled with its number, as in the previous figure, and with its symmetry label.

12.3.2 Comparison with experiment: Koopmans' theorem

How can we test this picture experimentally? The orbital energies are not directly observable, but they are closely related to a quantity that is: the energy needed to remove an electron from the molecule. **Koopmans' theorem** states that, if we assume that the other orbitals do not change when one electron is removed, the ionization energy needed to remove an electron described by orbital i is equal to minus its orbital energy:

$$IE_i \approx -\varepsilon_i. \tag{12.13}$$

Ionization energies from each orbital can be measured with **photoelectron spectroscopy**, an experiment based on the same principle as the photoelectric effect of Chapter 2: the molecule is hit with photons of known energy (ultraviolet light for valence electrons, X-rays for core electrons), and the kinetic energy of the ejected electrons is measured. The difference between the two is the ionization energy. Each occupied orbital gives a separate band in the spectrum. The results for water are compared with the minimal-basis Hartree–Fock orbital energies in Table 12.1.

Table 12.1 Orbital energies of water from the minimal-basis Hartree–Fock calculation, compared with the experimental ionization energies measured by photoelectron spectroscopy (approximate values).

MO	ε_i (E_h)	$-\varepsilon_i$ (eV)	Experimental IE (eV)
$1b_1$ (HOMO)	-0.392	10.7	12.6
$3a_1$	-0.454	12.4	14.7
$1b_2$	-0.622	16.9	18.5
$2a_1$	-1.272	34.6	32.2
$1a_1$ (O 1s)	-20.241	550.8	539.9

The agreement is not quantitative (with such a small basis set, we should not expect it to be), but the important point is that the experiment finds *four* distinct valence bands, in the same order as the calculated orbitals. In particular, the two highest bands, at 12.6 and 14.7 eV, correspond to the two "lone pair" orbitals, $1b_1$ and $3a_1$, which have clearly different energies.

12.3.3 Canonical and localized orbitals

Let's now compare these results with the Lewis structure of water that we learn in general chemistry. In the Lewis picture, there is one pair of electrons in each of the two O–H σ bonds, and two equivalent lone pairs on oxygen. The four pairs point towards the corners of a tetrahedron, since the oxygen atom is considered sp^3 hybridized.

The MOs in Fig. 12.1 and Fig. 12.2 look very different: the two lone pairs are not equivalent at all, and no orbital describes a single O–H bond. Does this mean that the Lewis structure of water is wrong? Not exactly. The two pictures answer different questions, and they are more closely related than they look.

The MOs that we obtain from the Hartree–Fock equations are called **canonical orbitals**. They are the orbitals with well-defined energies, and they are the ones that we need to describe experiments in which we add or remove a single electron, such as photoelectron spectroscopy. The total wave function, however, is a Slater determinant, and a determinant does not change (except, possibly, for its sign) if we replace its columns with linear combinations of each other. This means that we can mix the occupied orbitals among themselves in any way we like (as long as the new orbitals stay orthonormal) without changing the total wave function, the total electron density, or the total energy. The canonical orbitals are just one possible choice.

A different, and very useful, choice is to mix the occupied orbitals so that each new orbital is as compact as possible. The resulting orbitals are called

localized molecular orbitals. There are several ways of defining "as compact as possible." One of the most common, called *Boys localization*, chooses the combinations that place the center of each orbital as far as possible from the centers of all the others. If we apply it to the four valence orbitals of water ($2a_1$, $1b_2$, $3a_1$, and $1b_1$), we obtain the orbitals in Fig. 12.3.

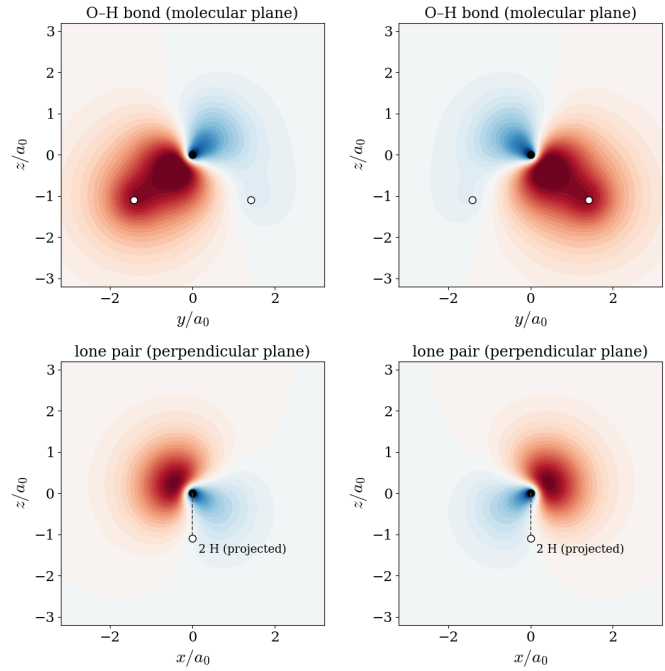


Figure 12.3 Boys-localized valence orbitals of water, obtained by mixing the four occupied valence MOs of the converged calculation. Top: the two O–H bond orbitals, in the plane of the molecule (black dot: oxygen; white dots: hydrogen). Bottom: the two lone-pair orbitals, in the plane perpendicular to the molecule that contains the symmetry axis (the two hydrogen atoms lie in front of and behind this plane, and their projection onto it is shown as a white dot below the oxygen). Color scheme: red (positive), blue (negative).

The localized orbitals look exactly like the Lewis structure: two equivalent orbitals, each describing one O–H bond, and two equivalent lone pairs on oxygen, above and below the plane of the molecule, pointing away from the hydrogens (they are often called "rabbit ears"). The centers of the two lone pairs form an angle of about 119° at the oxygen atom, and those of the two bonds an angle of about 104°, close to the tetrahedral picture of the Lewis structure. Neither set of orbitals is "more correct" than the other: they describe exactly the same wave function. The canonical orbitals are the natural choice to discuss energies and spectroscopy, while the localized orbitals are the natural choice

to discuss the chemical structure and connect with the Lewis picture.

This is why the sp^3 picture of water works well to explain, for example, hydrogen bonding. In liquid water, each molecule donates two hydrogen bonds to its neighbors and accepts two more, creating a network that is tetrahedral around each oxygen atom. To see where this comes from, we can look at the total electron density instead of the individual orbitals, since a neighboring molecule does not see the orbitals of water, but only the combined effect of all of its electrons and nuclei **together**. We can choose a surface of constant electron density (e.g., 0.02 a.u.), and color it according to the electrostatic potential: the energy that a positive test charge would feel at each point of the surface, negative where it would be attracted and positive where it would be repelled. The result is shown in Fig. 12.4. The negative potential is entirely on the oxygen side, and the positive potential on the hydrogen side. Moreover, the negative region bulges out towards the two tetrahedral directions where the Lewis lone pairs would be, and the positive regions are centered on the hydrogen atoms: exactly the pattern needed for a tetrahedral network of hydrogen bonds.

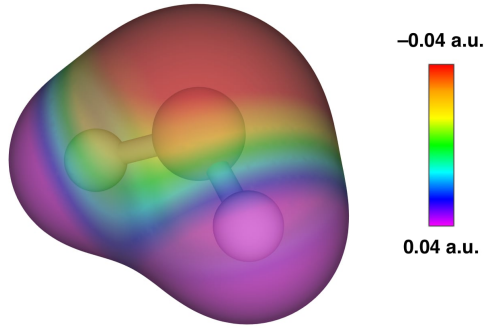


Figure 12.4 Molecular electrostatic potential of water plotted on a 0.02 a.u. isodensity surface.

12.4 Hückel Theory for Conjugated π Systems

The Hartree–Fock calculation on water required thousands of integrals and a computer. Long before computers were available, however, chemists found that a drastically simplified version of the LCAO method could explain many properties of an important class of molecules: the conjugated hydrocarbons, such as butadiene and benzene, where single and double bonds alternate. This simplified method was proposed by Erich Hückel in 1931, and it is still one of the most useful qualitative tools in organic chemistry.

12.4.1 The Hückel approximations

In a planar conjugated molecule, each carbon atom forms three σ bonds in the plane of the molecule, and has one $2p$ orbital left over, perpendicular to the plane. Following the symmetry argument that we used for water, these $2p$ orbitals are antisymmetric with respect to the molecular plane, while all the orbitals that form the σ bonds are symmetric, so the two sets do not mix. We can therefore treat the π electrons separately, as if they moved in a fixed framework provided by the σ bonds. For a molecule with N conjugated carbon atoms, each π molecular orbital is written as a linear combination of the N carbon $2p$ orbitals, p_j:

$$\psi = \sum_{j=1}^{N} c_j \, p_j, \tag{12.14}$$

and the coefficients are found by solving the secular determinant of Eq. (10.13). Hückel's idea was to replace all the integrals in the determinant with simple parameters:

1. All overlap integrals between different atoms are neglected: $S_{jk} = 0$ for $j \neq k$, and $S_{jj} = 1$.
2. All diagonal integrals are equal: $H_{jj} = \alpha$. The parameter α, called the *Coulomb integral*, is the energy of an electron described by a carbon $2p$ orbital in the molecule. It is negative.
3. The off-diagonal integrals are equal to β for two carbon atoms that are directly bonded to each other, and zero otherwise: $H_{jk} = \beta$ if j and k are neighbors, $H_{jk} = 0$ if they are not. The parameter β, called the *resonance integral*, is the same quantity that is responsible for the bond in H_2^+ (Chapter 11), and it is also negative.[3]

With these approximations, the whole molecule is described by just two numbers and by the list of which atoms are bonded to which.

12.4.2 Ethylene and butadiene

The simplest case is ethylene, with two carbon atoms. The secular determinant is:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \longrightarrow \quad (\alpha - E)^2 = \beta^2 \quad \longrightarrow \quad E = \alpha \pm \beta, \tag{12.15}$$

which is the same result we obtained for H_2^+ in Eq. (11.6), with $S = 0$. Since β is negative, the bonding π orbital, $\frac{1}{\sqrt{2}}(p_1 + p_2)$, has energy $\alpha + \beta$, below α,

[3] The symbols α and β for the Hückel parameters are universally used, and they should not be confused with the spin functions α and β of Chapter 7.

and the antibonding orbital, $\frac{1}{\sqrt{2}}(p_1 - p_2)$, has energy $\alpha - \beta$, above α. The two π electrons are described by the bonding orbital, and the total π energy is $2\alpha + 2\beta$.

For butadiene, with four carbon atoms in a chain (1–2–3–4), it is convenient to divide every element of the determinant by β and define $x = \frac{\alpha - E}{\beta}$:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = x^4 - 3x^2 + 1 = 0. \tag{12.16}$$

Notice how the determinant reflects the structure of the molecule: there is a 1 in position (j, k) only if atoms j and k are bonded. The equation is quadratic in x^2, and its solutions are $x^2 = \frac{3 \pm \sqrt{5}}{2}$, or $x = \pm 1.618$ and $x = \pm 0.618$. Since $E = \alpha - x\beta$, the four π orbital energies are $\alpha \pm 1.618\beta$ and $\alpha \pm 0.618\beta$. The four π electrons are described by the two lowest orbitals, and the total π energy is:

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta. \tag{12.17}$$

If the two double bonds of butadiene were independent of each other, as in two separate ethylene molecules, the π energy would be $2 \times (2\alpha + 2\beta) = 4\alpha + 4\beta$. The difference, 0.472β, is called the **delocalization energy**. It is negative, so butadiene is more stable than two isolated double bonds, because its π electrons can spread over all four atoms.

The coefficients of the butadiene orbitals are plotted in Fig. 12.5, together with something that might look familiar.

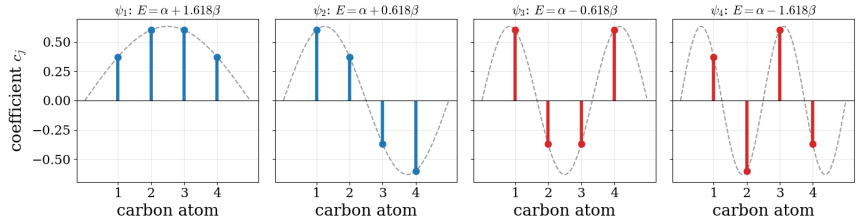


Figure 12.5 Coefficients c_j of the four Hückel π orbitals of butadiene on each carbon atom (blue: occupied, red: unoccupied), compared with the particle-in-a-box wave functions $\sqrt{2/a}\sin(n\pi x/a)$ with $n = 1, \ldots, 4$ and $a = 5$ (gray dashed lines).

These orbitals should look familiar:

1. **Nodes**: the lowest orbital has no nodes, and each following orbital has one more node, exactly as for the particle in a box (Chapter 4) and for all the other systems that we have studied.

2. **Particle in a box**: the coefficients fall exactly on the particle-in-a-box wave functions, sampled at the positions of the carbon atoms. This is not a coincidence: for a chain of N atoms, the Hückel equations can be solved exactly, giving

$$\begin{aligned} E_k &= \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right), \\ c_{jk} &= \sqrt{\frac{2}{N+1}} \sin\left(\frac{jk\pi}{N+1}\right), \qquad k = 1, \ldots, N. \end{aligned} \tag{12.18}$$

   The π electrons of a conjugated chain behave like particles in a one-dimensional box, which is why the particle in a box is a good model for the colors of conjugated molecules.

3. **Bonding character**: in the lowest orbital, all the coefficients have the same sign, and the orbital is bonding between every pair of neighbors. In the second orbital, the HOMO, the coefficients have the same sign on atoms 1 and 2 and on atoms 3 and 4, but opposite signs on atoms 2 and 3. The HOMO is therefore bonding between C_1–C_2 and C_3–C_4, and antibonding between C_2–C_3. Adding the contributions of the two occupied orbitals, the outer bonds have more double-bond character than the central one, in agreement with the experimental bond lengths of butadiene (1.34 Å for the outer bonds and 1.46 Å for the central one).

Example 12.1: Hückel theory for the allyl system

The allyl system, CH_2=CH–CH_2, has three carbon atoms in a chain. Find its Hückel π energies, and the delocalization energy of the allyl cation (two π electrons).

Step 1: the determinant. Dividing every element by β and writing $x = (\alpha - E)/\beta$, as we did for butadiene:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 - 2x = x(x^2 - 2) = 0.$$

Step 2: the energies. The roots are $x = 0$ and $x = \pm\sqrt{2}$, which give $E = \alpha + \sqrt{2}\beta$ (bonding), $E = \alpha$ (non-bonding), and $E = \alpha - \sqrt{2}\beta$ (antibonding).

Step 3: the delocalization energy. The two electrons of the cation are described by the lowest orbital, so its π energy is $2\alpha + 2\sqrt{2}\beta$. A localized double bond (as in ethylene) would have $2\alpha + 2\beta$. The difference, $2(\sqrt{2} - 1)\beta = 0.828\beta$, is negative (since $\beta < 0$): the allyl cation is stabilized by delocalization, which is why it is much more stable than other primary carbocations.

12.4.3 Polyenes and benzene

The π energy levels of ethylene, butadiene, hexatriene, and benzene are compared in Fig. 12.6.

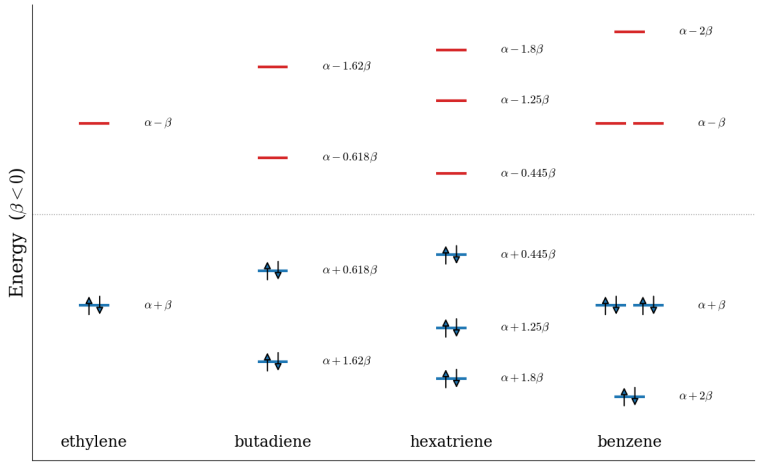


Figure 12.6 Hückel π energy levels of ethylene, butadiene, hexatriene, and benzene (blue: bonding, red: antibonding), with their π electrons. The dotted line marks the energy α of an isolated carbon $2p$ orbital. Since $\beta < 0$, levels with $+\beta$ are lower in energy.

As the chain gets longer, the levels get closer to each other, and the gap between the HOMO and the LUMO decreases: it is $2|\beta|$ for ethylene, $1.236|\beta|$ for butadiene, and $0.890|\beta|$ for hexatriene. The lowest electronic transition of these molecules (Chapter 13) changes the description of one electron from the HOMO to the LUMO, so their absorption moves to longer wavelengths as the chain grows. This is exactly what is observed: ethylene absorbs at about 165 nm, butadiene at 217 nm, and hexatriene at 258 nm. Long polyenes, such as β-carotene, with 11 conjugated double bonds, absorb visible light (around 450 nm), which gives carrots their orange color.

For benzene, the six carbon atoms form a ring, so atom 6 is also bonded to atom 1, and the Hückel determinant has one extra 1 in its corners. The solutions are:

$$E_k = \alpha + 2\beta \cos\left(\frac{2\pi k}{6}\right), \qquad k = 0, \pm 1, \pm 2, 3, \tag{12.19}$$

which gives one level at $\alpha+2\beta$, two degenerate levels at $\alpha+\beta$, two degenerate levels at $\alpha - \beta$, and one level at $\alpha - 2\beta$. The pattern of a single lowest level followed by pairs of degenerate levels is the same that we found for the particle on a ring in Chapter 4, where the states with $\pm m_\ell$ have the same energy. The

π electrons of benzene behave like particles on a ring. The six π electrons are described by the three bonding orbitals, so:

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta. \tag{12.20}$$

Three isolated double bonds would have π energy $3\times(2\alpha+2\beta) = 6\alpha+6\beta$, so the delocalization energy of benzene is 2β, much larger than that of butadiene. This is the extra stability of aromatic molecules. Comparing the experimental heat of hydrogenation of benzene with that of three isolated double bonds gives a stabilization of about 150 kJ/mol, which corresponds to $\beta \approx -75$ kJ/mol. (Values of β obtained from different types of experiments vary considerably, which is a reminder of how crude the Hückel approximations are.)

The same calculation explains why not all rings are aromatic. For cyclobutadiene, a ring of four carbon atoms, the levels are $\alpha + 2\beta$, two degenerate levels at α, and $\alpha - 2\beta$. Two of its four π electrons are described by the lowest orbital, and the other two by the two degenerate nonbonding orbitals, one each, (as for O_2 in Chapter 11). The total π energy, $4\alpha + 4\beta$, is the same as that of two isolated double bonds, so cyclobutadiene has no delocalization energy at all, and it is in fact extremely unstable. In general, every bonding level of a ring describes pairs of electrons with opposite spins (a closed shell) only when the number of π electrons is $2, 6, 10, \ldots$, or $4n + 2$: this is the origin of **Hückel's rule** for aromaticity.

Hückel theory neglects electron-electron repulsion entirely, and it treats all overlaps as zero, so its energies are only qualitative. Nevertheless, it captures the essential physics of π electrons with a few lines of algebra, and it shows clearly how the shape and connectivity of a molecule determine its energy levels. More accurate methods, such as the Hartree–Fock method that we used for water, follow exactly the same logic, with the parameters α and β replaced by integrals computed from the actual orbitals.

12.5 Chapter Review

12.5.1 Key Ideas

- For polyatomic molecules, MOs are obtained by solving the Hartree–Fock equations numerically. Symmetry splits the problem into smaller pieces.
- The SCF energy decreases at each iteration until it converges.
- Koopmans' theorem relates orbital energies to ionization energies measured by photoelectron spectroscopy.
- Canonical and localized orbitals are equivalent descriptions; localized orbitals recover the Lewis picture.
- Hückel theory describes conjugated π systems with two parameters, α and β. It explains delocalization energies, the decreasing HOMO–LUMO gap of polyenes, and aromaticity.

12.5.2 Study Questions

1. How many basis functions does a minimal basis set have for the water molecule?

a. 3
b. 5
c. 7
d. 10
e. 14

2. Why does the symmetry of a molecule simplify the calculation of its molecular orbitals?

a. because symmetric molecules have no electrons in core orbitals
b. because all integrals become equal
c. because the Hamiltonian becomes zero
d. because the molecular orbitals become atomic orbitals
e. because only basis functions with the same symmetry can mix, so the problem splits into smaller pieces

3. During the SCF iterations of the water calculation, the total energy:

a. increases at each step
b. stays constant
c. oscillates without converging
d. decreases at each step until it converges
e. becomes positive

4. The highest occupied molecular orbital of water, $1b_1$, is:

a. a bonding orbital between oxygen and hydrogen
b. a pure oxygen $2p$ orbital perpendicular to the plane of the molecule, which is a non-bonding lone pair
c. the oxygen $1s$ orbital
d. an antibonding orbital
e. a hydrogen $1s$ orbital

5. According to Koopmans' theorem, the energy needed to remove an electron described by orbital i is approximately:

a. ε_i
b. the total energy of the molecule
c. $-\varepsilon_i$, minus the orbital energy
d. zero for the HOMO
e. $2\varepsilon_i$

6. The photoelectron spectrum of water shows four distinct valence bands. This shows that:

a. the two lone pairs of water are not equivalent, as predicted by the canonical molecular orbitals
b. water has four equivalent sp^3 orbitals

c. water has four lone pairs
d. Koopmans' theorem is wrong
e. water has only two valence electrons

7. Canonical and localized molecular orbitals:

a. give different energies
b. describe different molecules
c. differ in the number of electrons
d. cannot both be obtained from the same calculation
e. give the same total wave function and energy; they are just different choices of orbitals

8. In Hückel theory, the π orbital energies of ethylene are:

a. $\alpha + \beta$ and $\alpha - \beta$, with the bonding orbital lower since $\beta < 0$
b. α and β
c. 2α and 2β
d. $\alpha + 2\beta$ and $\alpha - 2\beta$
e. both equal to α

9. As a conjugated polyene gets longer, the energy gap between its HOMO and LUMO:

a. increases
b. does not change
c. becomes negative
d. decreases, so the molecule absorbs light of longer wavelength
e. decreases, so the molecule absorbs light of shorter wavelength

10. What is the delocalization energy of benzene in Hückel theory?

a. 0
b. 2β
c. β
d. 6β
e. 0.472β

Answers

1.c, 2.e, 3.d, 4.b, 5.c, 6.a, 7.e, 8.a, 9.d, 10.b

CHAPTER 13

Spectroscopy

Everything that we know experimentally about the energy levels of atoms and molecules comes, one way or another, from shining light on them. Experiments that study the interaction between electromagnetic radiation and matter are called spectroscopies. Since the energy levels of atoms and molecules are quantized, a molecule can absorb or emit light only when the energy of the photon, $h\nu$, matches the difference between two of its levels:

$$h\nu = E_{\text{final}} - E_{\text{initial}}. \tag{13.1}$$

The spectrum, therefore, is a direct map of the energy levels of the system. Not every pair of levels, however, gives rise to a signal. Some transitions are observed (we call them *allowed*), and others are not (*forbidden*). The reason is that light interacts with a molecule mainly through its electric field, which pushes on the charges of the molecule. A transition between an initial state ψ_i and a final state ψ_f can happen only if the integral $\int \psi_f^* \hat{\mu}\, \psi_i \, d\tau$, called the *transition dipole moment*, is different from zero, where $\hat{\mu}$ is the dipole moment operator of the molecule. Working out when this integral vanishes for each type of motion results in simple rules on how the quantum numbers can change during a transition, which are called **selection rules**.

To summarize, a spectrum is the result of three ingredients:

- The energy levels of the atoms or molecules, which determine the *positions* of the signals.
- The population of the energy levels, which determines (together with the transition dipole moment) the *intensities* of the signals.
- The selection rules, which determine *which* signals are observed.

Spectroscopy is also the most important experimental test of quantum mechanics, since it allows us to compare the energy levels that we calculate with those that nature actually has. In this chapter, we will see how the models that we studied in Chapter 4 explain the rotational, vibrational, and electronic spectra of diatomic molecules. Keep in mind, however, that this chapter is only a gentle introduction. Spectroscopy is a huge field of science in its own right: a whole semester course would barely scratch its surface, and entire textbooks are dedicated to it. Here, we will only present its foundations. If you want to go further, Appendix C suggests some good textbooks on spectroscopy.

13.1 Where Selection Rules Come From

Light is an electromagnetic wave, and the oscillating electric field of the wave pushes the positive and negative charges of a molecule in opposite directions. The interaction energy between the field and the molecule is proportional to the molecule's **dipole moment operator**, $\hat{\mu} = \sum_k q_k \hat{\mathbf{r}}_k$, the sum of the charges of all electrons and nuclei multiplied by their positions. Quantum mechanics shows that the probability that the light drives a transition from an initial state ψ_i to a final state ψ_f is proportional to the square of the **transition dipole moment**:

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \, \psi_i \, d\tau, \qquad \text{intensity} \propto |\mu_{fi}|^2. \tag{13.2}$$

If this integral is zero, the transition does not happen (it is *forbidden*), no matter how intense the light. Selection rules are simply lists of the conditions under which the integral is different from zero, and very often they can be found from symmetry alone, without calculating anything.

As an example, let's consider the vibration of a diatomic molecule, modeled as a harmonic oscillator. Close to the equilibrium geometry, the dipole moment changes approximately linearly with the displacement x from equilibrium, so $\hat{\mu} \approx \mu_0 + \left(\frac{d\mu}{dx}\right) x$. The constant μ_0 does not contribute to the integral, since the wave functions of different states are orthogonal, and the transition dipole moment is proportional to $\frac{d\mu}{dx} \int \psi_f \, x \, \psi_i \, dx$. This gives two results:

1. **The dipole moment must change during the vibration** ($\frac{d\mu}{dx} \neq 0$). Homonuclear diatomics, whose dipole moment is always zero, are IR inactive.
2. **Only $\Delta v = \pm 1$ is allowed.** The integrands for two transitions starting from $v = 0$ are shown in Fig. 13.1. Recall from Chapter 4 that the harmonic oscillator wave functions are alternately even ($v = 0, 2, 4, \ldots$) and odd ($v = 1, 3, \ldots$). For $v = 0 \to 1$, the product $\psi_1 \, x \, \psi_0$ is even (odd times odd times even), it is positive everywhere, and its integral is different from zero. For $v = 0 \to 2$, the product is odd, its positive and negative parts cancel exactly, and the integral is zero. Calculating the integrals for all pairs of levels shows that only neighboring levels are connected.

The same reasoning, applied to the other types of motion, gives all the selection rules of this chapter:

- **Rotations**: a rotating molecule can only interact with the light if it has a permanent dipole moment. Using the spherical harmonics of the rigid rotor, the integral is different from zero only for $\Delta J = \pm 1$. Physically, a photon carries one unit of angular momentum, so absorbing or emitting it changes the angular momentum of the molecule by one unit.

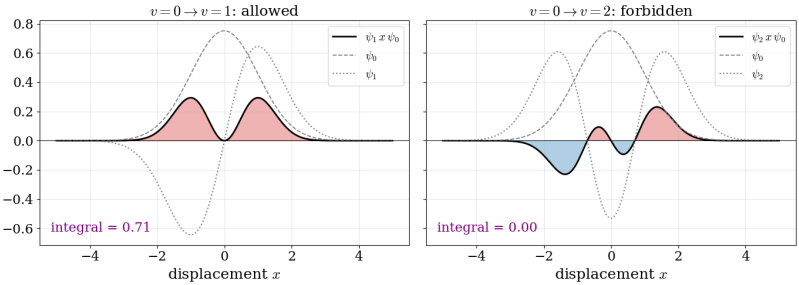


Figure 13.1 The integrand of the transition dipole moment, $\psi_f\, x\, \psi_0$, for two vibrational transitions of a harmonic oscillator. For $v = 0 \to 1$ (left), the integrand is positive everywhere, and the transition is allowed. For $v = 0 \to 2$ (right), the positive (red) and negative (blue) areas cancel exactly, and the transition is forbidden.

- **Spin**: the dipole moment operator depends on the positions of the charges, but not on their spins. Since spin functions with different total spin are orthogonal, the integral vanishes unless the initial and final states have the same total spin: $\Delta S = 0$. Transitions between singlets and triplets are therefore forbidden. As we will see at the end of this chapter, this rule is responsible for the difference between fluorescence and phosphorescence.

Selection rules derived in this way are exact only within the models that we used to derive them. Real molecules are not perfectly harmonic, and spin–orbit coupling mixes singlets and triplets slightly, so "forbidden" transitions are often observed, but much more weakly than the allowed ones.

13.2 Rotational Spectroscopy

Rotational spectroscopy measures the energies of transitions between the quantized rotational states of molecules in the gas phase. These energies are small, and the corresponding photons are in the microwave and far-infrared regions of the electromagnetic spectrum (roughly $1 - 100$ cm^{-1}). For this reason, rotational spectroscopy is often called *microwave spectroscopy*. It is also the tool that astronomers use, with radio telescopes, to identify the molecules present in interstellar clouds.

13.2.1 Rotation of diatomic molecules

The simplest model of a rotating diatomic molecule is the rigid rotor: two point masses, m_1 and m_2, held at a fixed distance d by a rigid bond. We already solved this problem in Chapter 4, where we saw that it is equivalent to a particle of

mass equal to the reduced mass, $\mu = \frac{m_1 m_2}{m_1+m_2}$, moving on the surface of a sphere. The energy levels are:

$$E_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0, 1, 2, \ldots \tag{13.3}$$

where J is the rotational quantum number (the same as ℓ for the particle on a sphere), and I is the moment of inertia of the molecule:

$$I = \mu d^2 = \frac{m_1 m_2}{m_1 + m_2} d^2. \tag{13.4}$$

Each level is $(2J + 1)$-fold degenerate, since the quantum number M (the same as m_ℓ) can take the values $-J, -J + 1, \ldots, J$. Spectroscopists prefer to work with energies in wavenumbers, $\tilde{\nu} = E/hc$, usually in cm^{-1}. Dividing Eq. (13.3) by hc, we obtain the rotational *term values*:

$$F(J) = \frac{E_J}{hc} = BJ(J+1) \qquad J = 0, 1, 2, \ldots \tag{13.5}$$

where all the properties of the molecule are collected in a single number, called the **rotational constant**:

$$B = \frac{\hbar^2}{2Ihc} = \frac{h}{8\pi^2 cI}. \tag{13.6}$$

Light can drive a rotational transition only if the molecule has a *permanent* electric dipole moment, which the electric field of the light can grab and rotate. This is why molecules such as HCl and CO have rotational spectra, while H_2 and N_2 do not. Evaluating the transition dipole moment with the spherical harmonics of the rigid rotor gives the selection rule:

$$\Delta J = J' - J'' = \pm 1, \tag{13.7}$$

where, following the spectroscopic convention, J' denotes the upper level and J'' the lower level of the transition. In absorption, a molecule in level J'' can only go to $J' = J'' + 1$, and the position of the corresponding line is:

$$\tilde{\nu}_{J' \leftarrow J''} = F(J'' + 1) - F(J'') = 2B(J'' + 1) \qquad J'' = 0, 1, 2, \ldots \tag{13.8}$$

The rotational levels and the resulting spectrum are shown in Fig. 13.2. The levels get farther apart as J increases, but, since each transition connects two neighboring levels, the lines in the spectrum are equally spaced, with a separation of $2B$. Each arrow in the top part of the figure produces one line in the spectrum below it.

The equal spacing makes it very easy to measure B from a spectrum, and from B we can obtain the bond length. For example, the rotational constant of carbon monoxide, $^{12}C^{16}O$, is $B = 1.9313\ \mathrm{cm}^{-1}$, so its first lines are at 3.86, 7.73, 11.59 cm^{-1}, and so on. Inverting Eq. (13.6), we obtain:

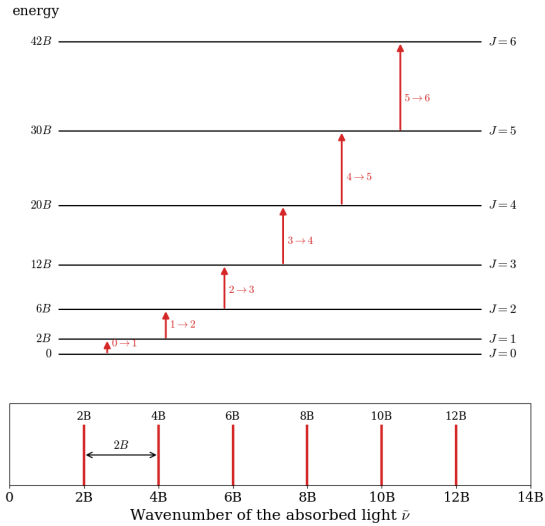


Figure 13.2 Top: rotational energy levels of a rigid rotor, $BJ(J+1)$, and the absorption transitions allowed by the selection rule $\Delta J = +1$. Bottom: the corresponding lines in the spectrum, which are equally spaced by $2B$.

$$I = \frac{h}{8\pi^2 cB} = 1.449 \times 10^{-46}\ \text{kg m}^2, \tag{13.9}$$

and, using the reduced mass of CO, $\mu = 6.856$ amu $= 1.1385 \times 10^{-26}$ kg, Eq. (13.4) gives $d = \sqrt{I/\mu} = 1.128{\times}10^{-10}$ m $= 1.128$ Å. This is how most of the bond lengths of small molecules that you find in tables have been measured, often with five or more significant figures.

The intensities of the lines depend, first of all, on how many molecules are in the initial level of each transition. At thermal equilibrium, the ratio between the number of molecules in a level with energy E_J and the number in the ground level is given by the Boltzmann distribution, multiplied by the degeneracy of the level:

$$\frac{N_J}{N_0} = (2J+1)\exp\left[-\frac{E_J}{kT}\right] = (2J+1)\exp\left[-\frac{hcBJ(J+1)}{kT}\right], \tag{13.10}$$

where k is the Boltzmann constant and T is the absolute temperature. The two factors in this expression pull in opposite directions: the degeneracy, $2J+1$, increases with J, while the exponential decreases. The result is a population that first grows and then decays, as shown in Fig. 13.3 for CO at room temperature:

$$\text{population} \propto (2J+1)\exp\left[-\frac{E_J}{kT}\right]. \tag{13.11}$$

The most populated level is the maximum of Eq. (13.11), at:

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}. \tag{13.12}$$

Derivation: the most populated rotational level

Treating J as a continuous variable and writing $x = hcB/kT$, the population is proportional to $f(J) = (2J+1)\,e^{-xJ(J+1)}$. At the maximum, the derivative is zero:

$$\frac{df}{dJ} = 2\,e^{-xJ(J+1)} - (2J+1)^2\,x\,e^{-xJ(J+1)} = 0 \quad \Rightarrow \quad (2J+1)^2 = \frac{2}{x} = \frac{2kT}{hcB},$$

which gives Eq. (13.12).

For CO at 298 K, $J_{\max} \approx 6.8$, so the most populated level is $J = 7$, and the strongest lines of the spectrum are found around $2B(J+1) \approx 30{-}45$ cm^{-1}. Notice that, even at room temperature, dozens of rotational levels are populated, since B is much smaller than $kT/hc \approx 207$ cm^{-1}.

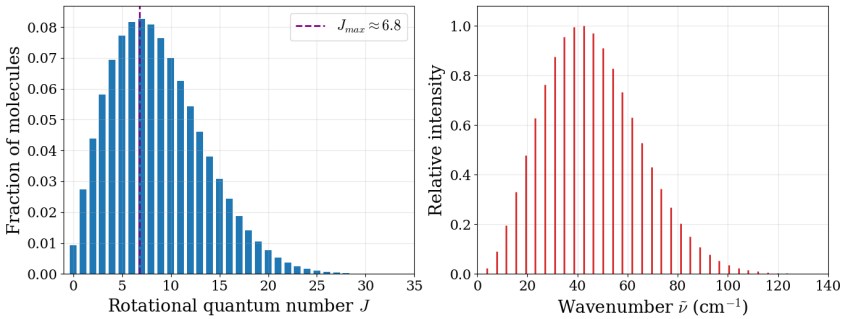


Figure 13.3 Left: population of the rotational levels of CO at 298 K, calculated with the Boltzmann distribution. The purple dashed line marks the most populated level, $J_{\max}$. Right: the corresponding simulated rotational absorption spectrum.

For non-linear molecules, there are up to three different moments of inertia, and the rotational energy levels are more complicated. Only a few special cases (such as symmetric tops like NH_3) can be solved analytically, and the other cases are treated numerically. The principle, however, is the same: from the measured lines we obtain the moments of inertia, and from them the geometry of the molecule.

13.3 Vibrational Spectroscopy

Vibrational spectroscopy measures the energies of transitions between the quantized vibrational states of molecules. These transitions are usually found in the mid-infrared (IR) region, at approximately $4{,}000 - 400\ \text{cm}^{-1}$ (wavelengths of $2.5 - 25\ \mu$m), and vibrational spectroscopy is therefore often called *IR spectroscopy*. Vibrational energies are much larger than rotational energies, so in the gas phase each vibrational transition is accompanied by many rotational transitions, which give the spectrum a *fine structure*. Transitions that change both the vibrational and the rotational state are called *rovibrational* transitions. As before, we will discuss the simplest case of a diatomic molecule. For polyatomic molecules, the spectra are more complicated to calculate, but they are one of the most widely used tools to identify chemical structures.

13.3.1 Vibration of heteronuclear diatomic molecules

A diatomic molecule AB has only one way of vibrating: the stretching of the A − B bond. As we saw in Chapter 10, close to its minimum the potential energy curve of the molecule can be approximated by a parabola, so we can use the harmonic oscillator of Chapter 4 as our model. In wavenumbers, the vibrational term values are:

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) \qquad v = 0, 1, 2, \ldots , \tag{13.13}$$

where v is the vibrational quantum number, and $\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ is the harmonic vibrational wavenumber, which depends on the force constant of the bond, k, and on the reduced mass of the molecule, μ. Since the molecule also rotates, each vibrational level has a ladder of rotational levels on top of it, and the total term values are obtained by summing the two contributions:

$$G(v) + F_v(J) = \omega_e \left(v + \frac{1}{2}\right) + B_v J(J+1), \tag{13.14}$$

where B_v is the rotational constant in the vibrational level v. B_v decreases slightly as v increases, because the average bond length gets longer when the molecule vibrates more.[1]

For a vibration to absorb IR light, the dipole moment of the molecule must *change* as the bond stretches. This is why heteronuclear diatomics, such as HCl and CO, are IR active. For the harmonic oscillator, the transition dipole moment is different from zero only between neighboring levels, and the selection rules for the rovibrational transitions of a diatomic molecule are:

[1] This is just a first approximation to rovibrational spectroscopy. Corrections for anharmonicity and centrifugal distortion are necessary to closely match experimental spectra.

$$\Delta v = \pm 1,\ \Delta J = \pm 1. \tag{13.15}$$

The transition from $v = 0$ to $v = 1$ is called the *fundamental transition*. Since real bonds are not perfectly harmonic, transitions with $\Delta v = \pm 2, \pm 3, \ldots$, called *overtones*, are also observed, but they are much weaker. The selection rules have two important consequences:

1. Both quantum numbers must change. A purely vibrational transition, with $\Delta v = +1$ and $\Delta J = 0$ (which would be called the Q-branch), is forbidden.
2. The rotational energy is either added to ($\Delta J = +1$) or subtracted from ($\Delta J = -1$) the vibrational energy. The two cases give rise to two series of lines, called the R-branch and the P-branch, respectively.

If we neglect the small difference between B_1 and B_0, the lines of the fundamental band are found at:

$$\begin{aligned} \tilde{\nu}_R &= \tilde{\nu}_0 + 2B(J'' + 1) \qquad J'' = 0, 1, 2, \ldots \\ \tilde{\nu}_P &= \tilde{\nu}_0 - 2BJ'' \qquad\quad J'' = 1, 2, 3, \ldots \end{aligned} \tag{13.16}$$

where $\tilde{\nu}_0 = G(1) - G(0)$ is the position of the (missing) purely vibrational transition, called the *band center*.

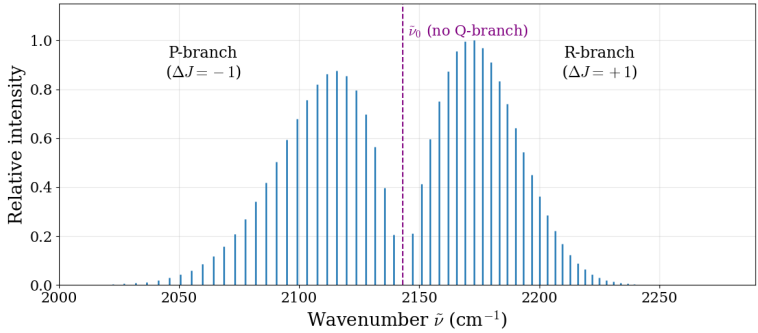


Figure 13.4 Simulated rovibrational spectrum of the fundamental band of carbon monoxide at 298 K. The P-branch is to the left of the band center at 2,143 cm^{-1} (purple dashed line), and the R-branch is to the right.

The simulated spectrum of CO is reported in Fig. 13.4, and the transitions that produce it are shown in Fig. 13.5. Four features of this spectrum are worth noticing:

1. **The missing line**: there is a gap at the band center, where the forbidden Q-branch would be. The gap is $4B$ wide (twice the normal spacing), because the first line of the R-branch is at $\tilde{\nu}_0 + 2B$ and the first line of

the P-branch is at $\tilde{\nu}_0 - 2B$. Even if no line is observed there, the position of the band center can be read directly from the spectrum, and it gives the vibrational energy. For CO, $\tilde{\nu}_0 = 2{,}143\ \mathrm{cm}^{-1}$, and using $\omega_e \approx \tilde{\nu}_0$ we obtain the force constant of the bond: $k = \mu(2\pi c\tilde{\nu}_0)^2 \approx 1{,}860$ N/m, one of the stiffest bonds in chemistry.

2. **The spacing**: the lines in each branch are separated by about $2B$, so the same spectrum also gives the bond length, exactly as in pure rotational spectroscopy. This makes rovibrational spectroscopy useful also for molecules whose rotational spectrum is difficult to measure.

3. **The intensities**: the two branches have the same envelope as the rotational populations of Fig. 13.3, since the intensity of each line depends on the population of its initial rotational level.

4. **The asymmetry**: if you look closely, the lines in the R-branch get slightly closer to each other as J increases, while those in the P-branch get slightly farther apart. This is the effect of B_1 being slightly smaller than B_0, which we neglected in Eq. (13.16).

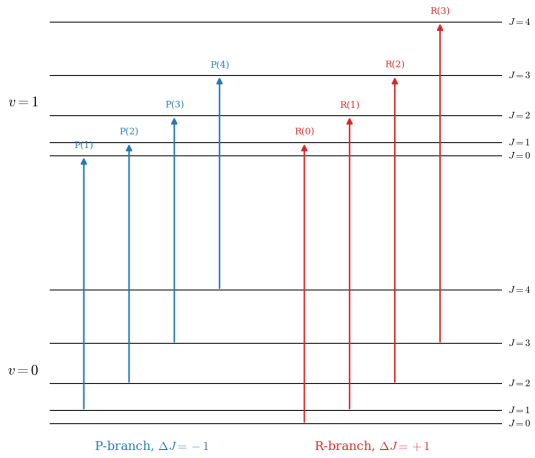


Figure 13.5 Rotational levels of the vibrational states $v = 0$ and $v = 1$ of a diatomic molecule, with the transitions of the P-branch ($\Delta J = -1$, blue) and of the R-branch ($\Delta J = +1$, red) of the fundamental band.

Example 13.1: How stiff is the bond of HCl?

The fundamental vibrational transition of $H^{35}Cl$ is observed at $\tilde{\nu} = 2990\ \mathrm{cm}^{-1}$. What is the force constant of the bond?

Example 13.1: How stiff is the bond of HCl? *(continued)*

Step 1: reduced mass. With masses of 1.008 and 34.969 u:

$$\mu = \frac{(1.008)(34.969)}{1.008 + 34.969}\ \text{u} = 0.980\ \text{u} = 1.627 \times 10^{-27}\ \text{kg}.$$

Step 2: solve for k. From $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ (Chapter 4), we get $k = \mu\,(2\pi c\tilde{\nu})^2$. With c in cm/s:

$$k = (1.627{\times}10^{-27}\ \text{kg})\left[2\pi(2.998 \times 10^{10}\ \text{cm/s})(2990\ \text{cm}^{-1})\right]^2 = 516\ \text{N/m}.$$

This is a typical value for a single bond. Notice that the reduced mass is almost exactly the mass of the hydrogen atom: in a bond to hydrogen, it is essentially only the hydrogen atom that moves.

13.3.2 Vibration of homonuclear diatomic molecules

The energy levels of homonuclear diatomic molecules, such as H_2, N_2, and O_2, are described by the same equations as those of heteronuclear molecules. Their spectra, however, are very different. Because of their symmetry, these molecules have no dipole moment, and stretching the bond does not create one. As a result, they have no rotational spectrum and no IR spectrum. (This is also the reason why the two main components of the atmosphere do not absorb IR radiation, and do not contribute to the greenhouse effect.)

The vibrations of these molecules can still be observed using a different type of vibrational spectroscopy, called **Raman spectroscopy**. In a Raman experiment, the molecule scatters visible light, and a small fraction of the scattered photons comes out with a different energy, having given part of their energy to (or taken it from) the vibration of the molecule. The Raman effect depends on how easily the electron cloud of the molecule can be deformed (its *polarizability*), rather than on its dipole moment, and the selection rules are different. Homonuclear diatomic molecules are Raman active.

13.3.3 Vibrations of polyatomic molecules

A molecule with N atoms needs $3N$ coordinates to describe the positions of its nuclei. Three of them describe the translation of the whole molecule, and three describe its rotation (only two for a linear molecule, since rotation around the molecular axis does not move any nucleus). The remaining $3N-6$ coordinates ($3N-5$ for linear molecules) describe vibrations. For water, $3\times 3-6=3$ vibrations; for carbon dioxide, which is linear, $3\times 3-5=4$.

In a polyatomic molecule, the atoms do not vibrate independently. If we

treat the potential energy surface as a multi-dimensional parabola around its minimum (Chapter 10), the vibrational motion can be separated into independent **normal modes**: collective motions in which all atoms move in phase, with the same frequency, each along its own direction. Each normal mode behaves like an independent harmonic oscillator, with its own frequency and its own ladder of equally spaced levels. The normal modes of water and carbon dioxide are shown in Fig. 13.6.

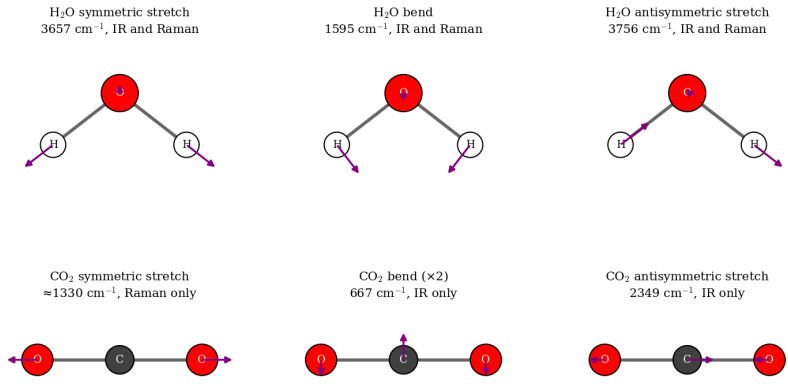


Figure 13.6 Normal modes of water (top) and carbon dioxide (bottom), with experimental wavenumbers and their activity in IR and Raman spectroscopy. The arrows show the directions in which the atoms move (not to scale). The bending mode of CO_2 is doubly degenerate: the molecule can bend in the plane of the page or perpendicular to it.

The normal modes tell us which vibrations we can observe, and how:

1. **IR activity.** As we saw at the beginning of this chapter, a vibration absorbs IR light only if the dipole moment of the molecule changes during the motion. All three modes of water change its dipole moment, so all three are IR active. In CO_2, the symmetric stretch keeps the molecule symmetric, and its dipole moment stays zero: this mode is IR inactive. The bend and the antisymmetric stretch, instead, create a dipole moment, and they are IR active. The antisymmetric stretch of CO_2 at 2,349 cm^{-1} and its bend at 667 cm^{-1} are the absorptions responsible for the greenhouse effect of carbon dioxide.

2. **Raman activity.** A vibration is Raman active if the *polarizability* of the molecule (how easily its electron cloud is deformed by an electric field) changes during the motion. The symmetric stretch of CO_2 changes the

size of the electron cloud, and it is Raman active, while the other two modes are not. For molecules with a center of inversion, such as CO_2, no mode can be both IR and Raman active: this is called the **rule of mutual exclusion**. IR and Raman spectroscopy are therefore complementary.

3. **Group frequencies.** In larger molecules, many normal modes are dominated by the motion of a few atoms, and their frequencies are almost the same in different molecules: for example, O–H stretches appear around 3,600 cm^{-1}, C–H stretches around 3,000 cm^{-1}, and C=O stretches around 1,700 cm^{-1}. This is why IR spectroscopy is so useful to identify functional groups in organic chemistry.

13.4 Electronic Spectroscopy

Electronic spectroscopy measures the energies of transitions between different electronic states of molecules, for example when the description of one electron changes from a bonding to an antibonding orbital. These energies are much larger than vibrational energies, and electronic transitions are typically observed in the visible and ultraviolet regions, at wavelengths of approximately $200-700$ nm ($50{,}000-14{,}000$ cm^{-1}). This is the type of spectroscopy responsible for the colors that we see around us.

Since electrons move much faster than nuclei, we can use the Born–Oppenheimer approximation of Chapter 10: each electronic state has its own potential energy curve, with its own vibrational and rotational levels, and the total energy of the molecule is approximately the sum of the electronic, vibrational, and rotational energies. An electronic transition, therefore, is always accompanied by changes in the vibrational state (giving the spectrum a *coarse structure*) and, in the gas phase, in the rotational state (giving a *fine structure*). Transitions that involve both an electronic and a vibrational change are called *vibronic* transitions. Notice that, unlike pure rotational and vibrational spectra, electronic spectra can be observed for any molecule, including homonuclear diatomics, since an electronic transition can always change the distribution of the charges. To keep track of the two electronic states, it is conventional to label the quantum numbers of the lower state with a double prime (v'', J''), and those of the upper state with a single prime (v', J').

In absorption, the molecule usually starts from the lowest vibrational level of the ground electronic state, $v'' = 0$, since at room temperature the vibrational energy is large compared to kT. It can end up in many different vibrational levels of the excited state, $v' = 0, 1, 2, 3, \ldots$, giving a series of bands called a *progression*. In emission, the molecule can start from different vibrational levels of the excited state, and end up in many vibrational levels of the ground state, so emission spectra are usually more complicated than absorption spectra.

13.4.1 Electronic spectroscopy of diatomic molecules

Each vibronic band of a diatomic molecule in the gas phase shows a rotational fine structure, with P- and R-branches as in the IR spectrum. For some electronic transitions, a Q-branch ($\Delta J = 0$) is also allowed. The positions of the lines of a vibronic band are given (in wavenumbers) by:

$$\tilde{\nu}(J', J'') = \tilde{\nu}_{v'-v''} + B'J'(J'+1) - B''J''(J''+1), \tag{13.17}$$

where $\tilde{\nu}_{v'-v''}$ is the position of the band center. The main difference with the IR case is that now the rotational constants of the two states, B' and B'', can be very different, since the two electronic states can have very different bond lengths. Since $B \propto 1/d^2$, and since an electronic excitation often changes the description of one electron from a bonding to an antibonding orbital, making the bond longer, usually $B' < B''$.

Each branch is obtained by replacing the selection rule in Eq. (13.17): $J' = J'' - 1$ for the P-branch, and $J' = J'' + 1$ for the R-branch. The two branches can then be combined into a single formula by introducing an index m:

$$\tilde{\nu}_{P,R} = \tilde{\nu}_{v'-v''} + (B' + B'')m + (B' - B'')m^2, \quad m = \pm 1, \pm 2 \ldots, \tag{13.18}$$

where positive values of m give the R-branch ($m = J' = J'' + 1$) and negative values give the P-branch ($m = -J''$). If $B' = B''$, the quadratic term disappears, and we recover the equally spaced lines of the IR spectrum. When $B' < B''$, the quadratic term is negative, and the lines of the R-branch get closer and closer as m increases, until they turn around and start moving back towards lower wavenumbers. The point where this happens is called the *band head*, and it is one of the most recognizable features of electronic spectra of diatomic molecules.

Derivation: the P- and R-branch formulas

To find the lines of the P-branch, we replace $J' = J'' - 1$ in Eq. (13.17):

$$\begin{aligned} \tilde{\nu}_P &= \tilde{\nu}_{v'-v''} + B'(J''-1)J'' - B''J''(J''+1) \\ &= \tilde{\nu}_{v'-v''} - (B' + B'')J'' + (B' - B'')J''^2. \end{aligned} \tag{13.19}$$

Similarly, for the R-branch we replace $J'' = J' - 1$:

$$\begin{aligned} \tilde{\nu}_R &= \tilde{\nu}_{v'-v''} + B'J'(J'+1) - B''J'(J'-1) \\ &= \tilde{\nu}_{v'-v''} + (B' + B'')J' + (B' - B'')J'^2. \end{aligned} \tag{13.20}$$

Writing $m = -J''$ in Eq. (13.19) and $m = J'$ in Eq. (13.20) gives the same expression, Eq. (13.18).

The intensities of the different vibronic bands are explained by the **Franck–Condon principle**. Since the electronic transition is much faster than the

motion of the nuclei, the nuclei do not have time to move while the electron jumps from one state to the other. In a potential energy diagram, the transition is therefore a vertical line, as shown in Fig. 13.7. The most intense transitions are those to the vibrational levels of the excited state whose wave functions overlap the most with the initial vibrational wave function. If the two states have similar bond lengths, the strongest band is $v' = 0 \leftarrow v'' = 0$. If the excited state has a much longer bond, the strongest bands are those to higher vibrational levels, whose wave functions have large amplitude near their classical turning points (recall the harmonic oscillator wave functions of Chapter 4).

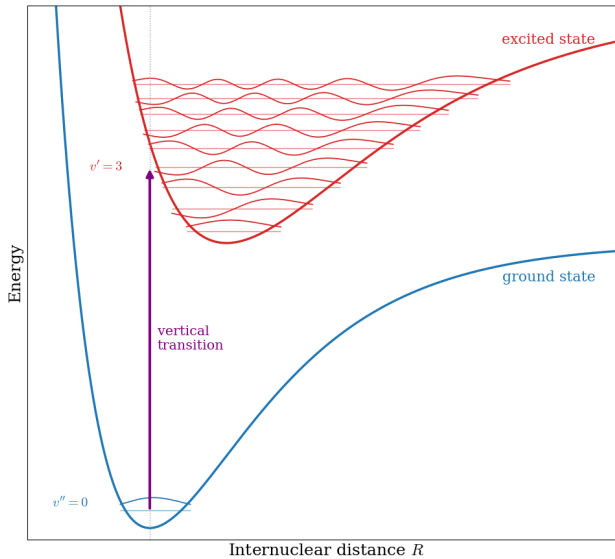


Figure 13.7 The Franck–Condon principle. The excited electronic state (red) has a longer bond than the ground state (blue). Starting from $v'' = 0$, the electronic transition is vertical (purple arrow), and the most intense band is the one to the excited vibrational level whose wave function overlaps most with the initial one (here $v' = 3$).

13.4.2 Fluorescence and phosphorescence

What happens to a molecule after it absorbs a photon and reaches an excited electronic state? The possible processes are usually summarized in a **Jablonski diagram**, such as the one in Fig. 13.8. Following the notation of Chapter 9, the electronic states are labeled by their multiplicity: most stable molecules have a singlet ground state (S_0), with all electron spins paired, and the excited states can be singlets (S_1, S_2, ...) or triplets (T_1, ...). As for atoms, the lowest triplet is lower in energy than the corresponding singlet, because electrons with parallel spins avoid each other and repel each other less (Sec. 9.4).

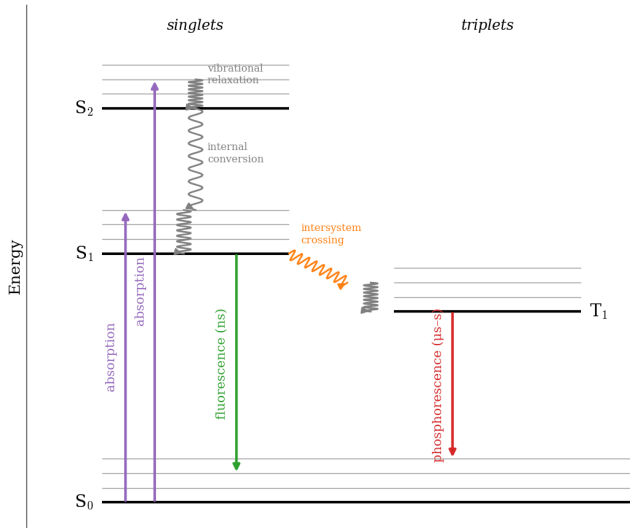


Figure 13.8 Jablonski diagram. Straight arrows are radiative processes (absorption and emission of light), and wavy arrows are non-radiative processes, in which the energy is transferred to the surroundings as heat. Thin lines are vibrational levels.

1. **Absorption** takes the molecule from S_0 to an excited singlet ($\Delta S = 0$), usually to an excited vibrational level, following the Franck–Condon principle.
2. **Vibrational relaxation and internal conversion.** The excess vibrational energy is quickly lost to the surrounding molecules as heat, in about 10^{-12} s, and higher excited states quickly convert to S_1. As a consequence, emission almost always starts from the lowest vibrational level of S_1, no matter which state was initially excited (this is known as *Kasha's rule*).
3. **Fluorescence** is the emission of light from S_1 to S_0. Since it is spin-allowed ($\Delta S = 0$), it is fast, with lifetimes of about 10^{-9} s, and it stops as soon as the light source is turned off. Since part of the energy was lost before the emission, fluorescence occurs at longer wavelengths than absorption (the *Stokes shift*). This is why fluorescent markers absorb UV or blue light and emit green or red light.
4. **Intersystem crossing.** Thanks to the small mixing of singlet and triplet states caused by spin–orbit coupling, the molecule can occasionally cross from S_1 to T_1 without emitting light. This process is spin-forbidden, but it can compete with fluorescence, especially in molecules that contain heavy atoms, where spin–orbit coupling is stronger.
5. **Phosphorescence** is the emission from T_1 to S_0. It is also spin-forbidden ($\Delta S \neq 0$), so it is very slow, with lifetimes from microseconds

to seconds or even minutes. This is the light emitted by glow-in-the-dark materials, which keep shining long after the lights have been turned off.

13.5 Magnetic Resonance Spectroscopy

All the spectroscopies that we have discussed so far use the electric field of light to drive transitions between energy levels that exist even without the light. In **magnetic resonance** spectroscopies, instead, the energy levels are *created* by placing the sample in a strong magnetic field, and the transitions are driven by the magnetic field of radio waves or microwaves. Both techniques are a direct application of the spin that we discussed in Chapter 7.

13.5.1 The energy of a spin in a magnetic field

A particle with spin has a magnetic moment proportional to its spin. In a magnetic field B_0 along the z axis, the energy of the particle depends on the orientation of its spin, that is, on its quantum number m:

$$E_m = -\gamma \hbar m B_0, \tag{13.21}$$

where γ is a constant, called the *gyromagnetic ratio*, which is characteristic of each type of particle. For a particle with spin $\frac{1}{2}$, the field splits the two spin states, $m = +\frac{1}{2}$ and $m = -\frac{1}{2}$, by an amount that grows linearly with the field, as shown in Fig. 13.9a. This splitting is called the **Zeeman effect**. A photon can drive a transition between the two states (the selection rule is $\Delta m = \pm 1$) if its energy matches the splitting:

$$\Delta E = h\nu = \gamma \hbar B_0, \qquad \nu = \frac{\gamma B_0}{2\pi}. \tag{13.22}$$

13.5.2 Nuclear magnetic resonance (NMR)

Many nuclei have a spin, called *nuclear spin*, with quantum number I. The most important for chemistry are ^{1}H and ^{13}C, both with $I = \frac{1}{2}$, so their behavior in a magnetic field is exactly the one in Fig. 13.9a. For protons, $\gamma = 2.675 \times 10^8$ rad s^{-1} T^{-1}, so, in the field of a typical superconducting magnet ($B_0 = 9.4$ T), Eq. (13.22) gives a frequency of 400 MHz, in the radio-frequency region. This is why NMR spectrometers are named by the proton frequency at which they operate ("a 400 MHz NMR").

The energy splitting is tiny: $h\nu$ at 400 MHz is only about 0.16 J/mol, thousands of times smaller than the thermal energy at room temperature. As a consequence, the two spin states are almost equally populated (Eq. (13.10)), with an excess of only about 3 nuclei per hundred thousand in the lower state.

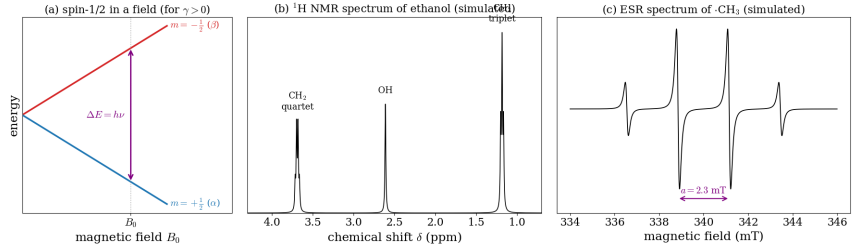


Figure 13.9 (a) Energy of the two states of a spin-$\frac{1}{2}$ particle as a function of the magnetic field. (b) Simulated ^{1}H NMR spectrum of ethanol, CH_3CH_2OH, at 400 MHz, showing three groups of signals with intensities 3:2:1, split by spin–spin coupling. (c) Simulated ESR spectrum of the methyl radical, $\cdot CH_3$, plotted as the first derivative of the absorption, as is customary in ESR.

Since absorption and stimulated emission cancel each other for equally populated levels, only this small excess contributes to the signal, which is why NMR requires strong magnets and relatively concentrated samples.

What makes NMR so powerful for chemistry are two small effects that make the frequency of each nucleus depend on its chemical environment:

1. **Chemical shift.** The electrons around a nucleus respond to the external field and create a small opposing field, so each nucleus feels a slightly different field, $B_{\text{eff}} = (1 - \sigma)B_0$, where σ is called the shielding constant. Nuclei in different chemical environments resonate at slightly different frequencies. These differences, of a few parts per million (ppm), are reported as the *chemical shift*, δ, measured from a reference compound. In the spectrum of ethanol (Fig. 13.9b), the protons of the CH_2 group, close to the electronegative oxygen, are less shielded, and they appear at a larger chemical shift than those of the CH_3 group. The area of each signal is proportional to the number of equivalent protons (3:2:1 for CH_3, CH_2, and OH).
2. **Spin–spin coupling.** The magnetic moments of neighboring nuclei interact through the bonding electrons, and each signal is split according to the spin states of the nearby nuclei. A group of protons with n equivalent neighbors is split into $n + 1$ lines: in ethanol, the CH_3 signal is a triplet (split by the two CH_2 protons), and the CH_2 signal is a quartet (split by the three CH_3 protons).

13.5.3 Electron spin resonance (ESR)

Electrons also have spin $\frac{1}{2}$, and the same experiment can be done with electron spins. This technique is called **electron spin resonance** (ESR), or electron paramagnetic resonance (EPR). For electrons, the energy splitting is usually

written as $\Delta E = g\mu_B B_0$, where $\mu_B = 9.274 \times 10^{-24}$ J/T is the *Bohr magneton* and $g \approx 2.0023$ for a free electron. Since the magnetic moment of the electron is much larger than that of a nucleus, the resonance frequencies are much higher: in a field of 0.34 T, the resonance occurs at about 9.5 GHz, in the microwave region.

The most important difference with NMR is that ESR is only possible for molecules with **unpaired electrons**. In a molecule in which all electrons are paired in singlet states, the spins of each pair cancel each other, and there is no signal. ESR is therefore the technique of choice to study radicals, transition-metal complexes, and paramagnetic molecules such as O_2 (Chapter 11). As in NMR, the unpaired electron interacts with nearby magnetic nuclei, which splits the ESR signal into several lines, a pattern called *hyperfine structure*. For the methyl radical (Fig. 13.9c), the unpaired electron interacts with three equivalent protons, and the spectrum shows four equally spaced lines with intensities 1:3:3:1, separated by the *hyperfine coupling constant*, $a = 2.3$ mT. The hyperfine pattern tells us how many magnetic nuclei the unpaired electron "sees," and how strongly, which is a direct map of the orbital that describes the unpaired electron.

13.6 Chapter Review

13.6.1 Key Ideas

- Spectra are maps of energy levels: line positions come from energy differences, intensities from populations, and selection rules from the transition dipole integral.
- Rotational spectra require a permanent dipole moment. Their lines are spaced by $2B$, which gives the bond length.
- Vibrations absorb IR light only if the dipole moment changes. Rovibrational spectra show P- and R-branches, and the vibrational frequency gives the force constant.
- A molecule with N atoms has $3N - 6$ normal modes ($3N - 5$ if linear). Raman spectroscopy observes vibrations that change the polarizability.
- Electronic transitions are vertical (Franck–Condon). After absorption, molecules relax by fluorescence or, through triplet states, by slow phosphorescence.
- NMR and ESR measure the energies of nuclear and electron spins in a magnetic field; the chemical shift reflects the electronic environment of each nucleus.

13.6.2 Study Questions

1. A transition between two states is forbidden when:

a. the two states have different energies

b. the light is too intense
c. the transition dipole moment integral between the two states is zero
d. the molecule has a dipole moment
e. the upper state is degenerate

2. Which of the following molecules has a pure rotational (microwave) spectrum?

a. N_2
b. H_2
c. O_2
d. CO_2
e. CO

3. The lines of the rotational spectrum of a rigid diatomic molecule are:

a. equally spaced by $2B$
b. equally spaced by B
c. closer together as J increases
d. all at the same frequency
e. farther apart as J increases

4. At room temperature, why are many rotational levels populated, with a maximum at $J > 0$?

a. because the energy levels are degenerate in J
b. because only $J = 0$ is populated
c. because rotational energies are larger than kT
d. because of the Pauli principle
e. because the degeneracy $2J + 1$ grows with J, while the Boltzmann factor decreases

5. A vibration absorbs infrared light only if:

a. the molecule has a permanent dipole moment
b. the molecule is homonuclear
c. the dipole moment of the molecule changes during the vibration
d. the vibration is very fast
e. the polarizability of the molecule is zero

6. The fundamental band of the infrared spectrum of CO shows:

a. a single line
b. a P-branch, a Q-branch, and an R-branch
c. only an R-branch
d. a P-branch and an R-branch separated by a gap at the band center
e. a continuous absorption

7. How many vibrational normal modes does the linear molecule CO_2 have?

a. 3

b. 4
c. 5
d. 6
e. 9

8. According to the Franck–Condon principle, an electronic transition:

a. is vertical, since the nuclei do not move while the electron changes state
b. always ends in the lowest vibrational level of the excited state
c. changes the bond length during the absorption
d. is forbidden if the bond lengths of the two states differ
e. happens only between states with the same vibrational quantum number

9. Why is phosphorescence much slower than fluorescence?

a. because triplet states have higher energy
b. because the emission from T_1 to S_0 is spin-forbidden
c. because the molecule must first rotate
d. because phosphorescence involves only vibrational levels
e. because fluorescence is spin-forbidden

10. In NMR, the chemical shift arises because:

a. nuclei have different masses
b. the nuclei vibrate
c. neighboring nuclei transfer electrons
d. the electrons around each nucleus partially shield it from the external magnetic field
e. the magnetic field is not uniform

Answers

1.c, 2.e, 3.a, 4.e, 5.c, 6.d, 7.b, 8.a, 9.b, 10.d

APPENDIX A

Mathematical Toolkit

This appendix collects the mathematical tools used throughout the book, with the minimum of theory needed to use them. Each section points to the chapters where the tool is first needed. For a more complete treatment, see the mathematics references in Appendix C.

A.1 Complex Numbers

A complex number has a real part and an imaginary part:

$$z = a + ib, \qquad i^2 = -1, \tag{A.1}$$

where a and b are real numbers. Its **complex conjugate**, z^*, is obtained by replacing i with $-i$ everywhere:

$$z^* = a - ib. \tag{A.2}$$

The product of a complex number with its conjugate is always real and non-negative, and it is called the **squared modulus**:

$$|z|^2 = z^* z = (a - ib)(a + ib) = a^2 + b^2. \tag{A.3}$$

This is the reason why wave functions, which can be complex, are always combined as $\psi^*\psi = |\psi|^2$ when we compute probabilities (Sec. 3.2): the result is guaranteed to be a real, non-negative number.

Euler's formula connects complex exponentials with sines and cosines:

$$e^{i\theta} = \cos\theta + i \sin\theta, \tag{A.4}$$

and, combining it with its conjugate, $e^{-i\theta} = \cos\theta - i\sin\theta$:

$$\cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2}, \qquad \sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}. \tag{A.5}$$

Two consequences are used often. First, $|e^{i\theta}|^2 = e^{-i\theta}e^{i\theta} = 1$ for any real θ, so a complex exponential is a "pure phase" that does not change probabilities. Second, any complex number can be written in *polar form*, $z = |z|\, e^{i\theta}$, with a modulus $|z|$ and a phase θ. Complex numbers first appear with the classical waves of chapter 1 (Eq. (1.19)), and they are used for plane waves (Chapter 3), the particle on a ring (Chapter 4), and the spherical harmonics (Chapter 5).

A.2 Derivatives

The derivatives that appear most often in quantum mechanics are:

$$\frac{d}{dx}e^{ax} = a\,e^{ax}, \qquad \frac{d}{dx}\sin(kx) = k\cos(kx), \qquad \frac{d}{dx}\cos(kx) = -k\sin(kx), \tag{A.6}$$

together with the **product rule**, $\frac{d}{dx}\left[f(x)g(x)\right] = f'(x)g(x) + f(x)g'(x)$, and the **chain rule**, $\frac{d}{dx}f\left(g(x)\right) = f'\left(g(x)\right)g'(x)$. Taking the derivative of Eq. (A.6) twice gives:

$$\frac{d^2}{dx^2}\sin(kx) = -k^2\sin(kx), \qquad \frac{d^2}{dx^2}e^{ikx} = -k^2e^{ikx}. \tag{A.7}$$

In both cases, the second derivative returns the same function multiplied by a constant. This is exactly why sines, cosines, and complex exponentials are the solutions of the Schrödinger equation for a free particle and for the particle in a box (Chapter 4): they are eigenfunctions of the kinetic energy operator (Sec. A.6).

A.2.1 Partial derivatives

When a function depends on more than one variable, such as a wave function $\psi(x, y, z)$, a **partial derivative** is the derivative with respect to one variable, while all the others are kept constant. For example, for $f(x, y) = x^2y$:

$$\frac{\partial f}{\partial x} = 2xy, \qquad \frac{\partial f}{\partial y} = x^2. \tag{A.8}$$

The most important combination of partial derivatives in this book is the **Laplacian**, which appears in the kinetic energy operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{A.9}$$

A.3 Integrals

Normalization, expectation values, and overlap integrals all require integrals. The following ones cover almost every case in the book.

Sines and cosines (particle in a box, Chapter 4), with n and m positive integers:

$$\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{a}{2}, \qquad \int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx = 0 \quad (n \neq m). \tag{A.10}$$

The first integral gives the normalization constant $\sqrt{2/a}$; the second one shows that different eigenfunctions are orthogonal.

Exponentials times powers (hydrogen atom, Chapter 5), with $a > 0$ and $n = 0, 1, 2, \ldots$:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}. \tag{A.11}$$

Gaussians (harmonic oscillator, Chapter 4; also the Gaussian basis functions used in the calculations of Chapter 11 and Chapter 12), with $a > 0$:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \qquad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}. \tag{A.12}$$

Symmetry shortcut. If a function is *odd*, $f(-x) = -f(x)$, its integral over a symmetric interval, such as $-\infty$ to ∞, is zero. For example, $\int_{-\infty}^{\infty} x\, e^{-ax^2} dx = 0$ without any calculation. This shortcut is the origin of many selection rules (Chapter 13).

As an example, consider the normalization of the hydrogen 1*s* orbital, $\psi = Ne^{-r/a_0}$. Using the volume element of spherical coordinates (Sec. A.4) and Eq. (A.11) with $n = 2$ and $a = 2/a_0$:

$$1 = N^2 \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-2r/a_0}\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = N^2\,(4\pi)\,\frac{2!}{(2/a_0)^3} = N^2 \pi a_0^3, \tag{A.13}$$

which gives $N = 1/\sqrt{\pi a_0^3}$.

A.4 Spherical Polar Coordinates

Atoms are spherical, and their wave functions are much simpler to write in **spherical polar coordinates** (r, θ, φ) than in Cartesian coordinates (x, y, z). The two sets are related by:

$$x = r\sin\theta\cos\varphi, \qquad y = r\sin\theta\sin\varphi, \qquad z = r\cos\theta, \tag{A.14}$$

where r is the distance from the origin ($0 \le r < \infty$), θ is the angle from the z axis ($0 \le \theta \le \pi$), and φ is the angle around the z axis ($0 \le \varphi < 2\pi$). The volume of a small box in these coordinates is *not* simply $dr\, d\theta\, d\varphi$, but:

$$d\tau = r^2 \sin\theta\, dr\, d\theta\, d\varphi. \tag{A.15}$$

The factor r^2 is the reason why the radial probability of hydrogen is $r^2R(r)^2$ and not just $R(r)^2$ (Chapter 5): there is more volume in a thin shell far from the nucleus than in a thin shell close to it. Integrating the angular part alone gives

$\int_0^{2\pi}\int_0^{\pi}\sin\theta\,d\theta\,d\varphi = 4\pi$, the solid angle of a full sphere. Finally, the Laplacian of Eq. (A.9) becomes:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}. \tag{A.16}$$

It looks complicated, but each term depends on one variable only, and this is what allows the separation of variables for the particle on a sphere (Chapter 4), the rigid rotor (Chapter 6), and the hydrogen atom (Chapter 5).

A.5 Determinants and Secular Equations

A **determinant** is a single number computed from a square array of numbers. For a 2×2 array:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc, \tag{A.17}$$

and for a 3×3 array we expand along the first row, multiplying each element by the 2×2 determinant left after removing its row and column, with alternating signs:

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & k \end{vmatrix} = a\begin{vmatrix} e & f \\ h & k \end{vmatrix} - b\begin{vmatrix} d & f \\ g & k \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix}. \tag{A.18}$$

Two properties are important for this book. Exchanging two rows (or two columns) changes the sign of the determinant, and a determinant with two identical rows (or columns) is zero. These are exactly the properties that make Slater determinants antisymmetric and enforce the Pauli exclusion principle (Chapter 9).

A.5.1 Secular equations

When a molecular orbital is written as a combination of two basis functions, $\psi = c_a\phi_a + c_b\phi_b$, the variational method leads to two equations for the two unknown coefficients (Chapter 11):

$$\begin{aligned} (H_{aa} - E)\,c_a + (H_{ab} - ES)\,c_b &= 0 \\ (H_{ab} - ES)\,c_a + (H_{bb} - E)\,c_b &= 0. \end{aligned} \tag{A.19}$$

This system always has the useless solution $c_a = c_b = 0$. It has other solutions only if the determinant of the coefficients is zero:

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{vmatrix} = 0. \tag{A.20}$$

This is the **secular determinant**. Expanding it with Eq. (A.17) gives an equation for E whose solutions are the orbital energies. For a homonuclear diatomic, $H_{aa} = H_{bb}$, and the two solutions are:

$$E_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S}. \tag{A.21}$$

Once E is known, each value is substituted back into Eq. (A.19) to find the ratio c_b/c_a, and normalization fixes the remaining constant. With n basis functions, the determinant is $n \times n$ and gives n orbital energies; this is what the computer solves at each step of the SCF procedure (Chapter 10) and what we solve by hand in Hückel theory (Chapter 12).

A.6 Eigenvalue Problems

An **eigenvalue problem** asks: which functions are left unchanged by an operator, apart from a multiplicative constant? In symbols:

$$\hat{A} f = a f, \tag{A.22}$$

where f is an **eigenfunction** of the operator $\hat{A}$ and the number a is the corresponding **eigenvalue**. We have already seen an example in Eq. (A.7): $\sin(kx)$ is an eigenfunction of $\frac{d^2}{dx^2}$ with eigenvalue $-k^2$. A counterexample is x^2: its second derivative is 2, which is not a constant times x^2, so x^2 is not an eigenfunction of $\frac{d^2}{dx^2}$. The time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, is an eigenvalue problem in which the operator is the Hamiltonian, the eigenfunctions are the wave functions of the stationary states, and the eigenvalues are their energies (Chapter 3 and Chapter 6).

When the wave function is expanded in a basis set, the operator becomes a matrix, the eigenfunction becomes a column of coefficients, and the eigenvalue problem becomes a matrix equation, $\mathbf{Ac} = a\,\mathbf{c}$. For example, the 2×2 matrix below has two eigenvectors:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (\alpha + \beta) \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (\alpha - \beta) \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{A.23}$$

The eigenvalues $\alpha \pm \beta$ are the roots of the secular determinant $\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$. This is the Hückel treatment of ethylene (Chapter 12): the in-phase combination is the bonding π orbital, and the out-of-phase combination is the antibonding π^* orbital. Solving a secular determinant and finding the eigenvalues of a matrix are the same problem.

Appendix B

Physical Constants and Unit Conversions

The values below are rounded to six significant figures, which is more than enough for every calculation in this book. Exact values (marked with *) are fixed by the definition of the SI units. For the full list with all digits, see the NIST reference on constants (National Institute of Standards and Technology, n.d.-c).

Table B.1 Physical constants used in this book.

Constant	Symbol	Value
Planck constant*	h	6.62607×10^{-34} J s
Reduced Planck constant	$\hbar = h/2\pi$	1.05457×10^{-34} J s
Speed of light in vacuum*	c	2.99792×10^{8} m s^{-1}
Elementary charge*	e	1.60218×10^{-19} C
Electron mass	m_e	9.10938×10^{-31} kg
Proton mass	m_p	1.67262×10^{-27} kg
Atomic mass unit	u	1.66054×10^{-27} kg
Vacuum permittivity	ε_0	8.85419×10^{-12} C^2 J^{-1} m^{-1}
Avogadro constant*	N_A	6.02214×10^{23} mol^{-1}
Boltzmann constant*	k_B	1.38065×10^{-23} J K^{-1}
Bohr radius	a_0	5.29177×10^{-11} m = 0.529177 Å
Hartree energy	E_h	4.35974×10^{-18} J
Rydberg constant	R_∞	1.09737×10^{5} cm^{-1}

Spectroscopists, chemists, and computational chemists all use different energy units. Table B.2 converts between the ones used in this book. To use it, read across a row: for example, 1 eV = 96.4853 kJ/mol.

Table B.2 Conversion factors between energy units (per molecule for E_h, eV, and cm^{-1}; per mole for kJ/mol).

	E_h	eV	kJ/mol	cm^{-1}
1 E_h	1	27.2114	2625.50	219475
1 eV	0.0367493	1	96.4853	8065.54
1 kJ/mol	$3.80880 \cdot 10^{-4}$	0.0103643	1	83.5935
1 cm^{-1}	$4.55634 \cdot 10^{-6}$	$1.23984 \cdot 10^{-4}$	0.0119627	1

A few more relations that are useful in practice:

- **Photon energy and wavelength:** $E = hc/\lambda$, with $hc = 1239.84$ eV nm. A photon of 500 nm therefore carries 2.48 eV.
- **Wavenumbers:** $\tilde{\nu} = 1/\lambda$, so a wavelength of 1 μm corresponds to 10,000 cm^{-1}.
- **Thermal energy at room temperature (**298 **K):** $k_B T = 0.0257$ eV $=$ 207 cm^{-1}, and $RT = 2.48$ kJ/mol.
- **Lengths:** 1 Å $= 10^{-10}$ m $= 100$ pm, and 1 $a_0 = 0.529177$ Å.

Appendix C

Further Reading and References

This book covers the essentials at a level suitable for a first course. When you want a second explanation, more detail, or the derivations that we skipped, these are good places to look. They are grouped by purpose, roughly from the most accessible to the most advanced. Resources marked *free* are available online at no cost.

C.1 A second explanation, at the same level

- **McQuarrie (2008)** and **McQuarrie and Simon (1997)**: the classic chemistry texts for this course, with very clear derivations and many worked problems. Most topics in this book have a matching chapter in either one.
- **LibreTexts (n.d.)** (*free*): open textbooks and course notes covering the same material, written by many different instructors. Useful when you want the same topic explained in different words.
- **MIT OpenCourseWare (2017)** (*free*): lecture notes, problem sets, and exams from MIT's quantum chemistry course.
- **Peverati (n.d.)** (*free*): the companion volume, on thermodynamics and kinetics.

C.2 More depth on quantum mechanics

- **Levine (2014)**: the standard graduate-level quantum chemistry text, more mathematical, with complete derivations for atoms, molecules, and the variational method.
- **Atkins and Friedman (2011)**: a more formal treatment, including angular momentum, group theory, and molecular properties.
- **Griffiths and Schroeter (2018)**: the most widely used physics text on the subject, excellent for the postulates, operators, spin, and the meaning of the theory (Chapter 8).
- **Feynman et al. (2013)** (*free*): Feynman's famous lectures, which start from the two-slit experiment and build the theory around probability

amplitudes. Good reading for anyone curious about *why* quantum mechanics works the way it does.

C.3 Electronic structure and computational chemistry (chapters 9–12)

- **Szabo and Ostlund (1996)**: the reference text for the Hartree–Fock method, basis sets, and the SCF procedure, with all the details of Chapter 10.
- **Cramer (2004)** and **Jensen (2017)**: modern introductions to computational chemistry, from Hartree–Fock to density functional theory, with practical advice on choosing methods and basis sets.
- **Sherrill (n.d.)** (*free*): short, clear notes on Hartree–Fock theory, electron correlation, and many other topics, written for students.

C.4 Spectroscopy and symmetry (chapter 13)

- **Harris and Bertolucci (1989)**: an affordable and readable introduction to molecular symmetry, group theory, and vibrational and electronic spectroscopy.
- **Hollas (2004)**: a comprehensive spectroscopy text covering rotational, vibrational, electronic, and magnetic resonance spectroscopy.

C.5 Mathematics (Appendix A)

- **McQuarrie (2003)**: written by a chemist for chemists, covering everything in the math appendix and much more.
- **Boas (2006)**: the standard reference for mathematical methods in the physical sciences.

C.6 Data

- **National Institute of Standards and Technology (n.d.-c)** (*free*): the recommended values of the fundamental constants (Appendix B).
- **Kramida et al. (n.d.)** (*free*): experimental energy levels and spectral lines of atoms and ions (Chapter 9).
- **National Institute of Standards and Technology (n.d.-a)** (*free*): experimental spectroscopic and thermochemical data for molecules, including vibrational frequencies and bond lengths.
- **National Institute of Standards and Technology (n.d.-b)** (*free*): experimental and computed properties of small molecules, useful to compare the results of different computational methods with experiment.

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