

Chem 231A

Fundamentals of Quantum Mechanics

(learning chemistry the hard way!)

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|---------------------------|---|
| Lectures | Monday, Wednesday and Friday @10:00-10:50 AM in PSCB 240 |
| Discussion | Wednesdays @ 12:00-12:50 PM in PSCB 220 |
| Book | <i>Molecular Quantum Mechanics</i> , by P. W. Atkins and R. S. Friedman, 4 th edition, Oxford |
| Chapters | Ch1, Ch2, Ch3, Ch4, Ch6 and Ch7 |
| Grading | 20% homework 30% mid-term exam 50% final exam |
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Topics Covered

- Eigenfunctions and Eigenvalues
- Operators in Quantum Mechanics
- The Schrödinger Equation
- Properties of Wavefunctions
- The Uncertainty Principle
- Boundary Conditions: Particle in a Box, Harmonic Oscillator, Particle on a Sphere
- Coulombic Potential and the Hydrogen Atom
- Angular Momentum Operators
- Combining Angular Momenta
- Perturbation Theory
- Variation Theory
- Spectrum of the Hydrogen Atom
- Structure of the Helium Atom
- Many Electron Systems

Arch-Fathers of Quantum Mechanics

Max Planck



"A scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it."

"No burden is so heavy for a man to bear as a succession of happy days."

Erwin Schrödinger



"I don't like it and I'm sorry I ever had anything to do with it."

Schrödinger on the Schrödinger equation

"Let me say at the outset, that in this discourse, I am opposing not a few special statements of quantum mechanics held today (1950s), I am opposing as it were the whole of it, I am opposing its basic views that have been shaped 25 years ago, when Max Born put forward his probability interpretation, which was accepted by almost everybody."

Werner Heisenberg



"Every word or concept, clear as it may seem to be, has only a limited range of applicability."

"What we observe is not nature itself, but nature exposed to our method of questioning."

"An expert is someone who knows some of the worst mistakes that can be made in his subject, and how to avoid them"

Niels Bohr



"If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet. "

"We are all agreed that your theory is crazy. The question which divides us is whether it is crazy enough to have a chance of being correct. My own feeling is that it is not crazy enough."

Max Born



"It is true that many scientists are not philosophically minded and have hitherto shown much skill and ingenuity but little wisdom."

"I believe there is no philosophical high-road in science, with epistemological signposts. No, we are in a jungle and find our way by trial and error, building our road behind us as we proceed."



Mathematical tools for QM

1. Complex Exponential

A basic understanding of complex calculus will help enormously with grasping the ins and outs of Quantum Mechanics. In particular, the function e^{ix} plays a pivotal role in all of this. Why? Because functions of this form are general solutions of the wave equation, and Quantum Mechanics happens to be based on the Schrödinger's Wave Equation. The complex exponential is defined as follows:

$$e^{ix} = \cos(x) + i \cdot \sin(x) \quad (1)$$

with i , of course, defined as $i^2 = -1$. From (1) the wave-character of the complex exponential is clear. In fact, it consists of two waves, a Real part $Re\{e^{ix}\} = \cos(x)$, and an Imaginary part $Im\{e^{ix}\} = \sin(x)$. Importantly, these waves are always $\pi/2$ 'out-of-phase' with each other (remember that $\cos(x) = \sin(x + \pi/2)$). The Real and Imaginary parts are therefore said to be orthogonal to each other. The complex exponential is often thought of as a 'phase function', with an amplitude of 1 and a phase x as defined by the angle between the Real and Imaginary parts. Below are some useful expressions related to this.

Square modulus

$$\begin{aligned} |e^{ix}|^2 = e^{ix} \cdot e^{-ix} &= \{\cos(x) + i \cdot \sin(x)\} \cdot \{\cos(x) - i \cdot \sin(x)\} \\ &= \cos^2(x) + \sin^2(x) \\ &= 1 \end{aligned} \quad (2)$$

Amplitude

$$|e^{ix}| = \sqrt{|e^{ix}|^2} = 1 \quad (3)$$

Phase

$$\Theta \equiv \text{ArcTan} \left(\frac{\text{Im}\{e^{ix}\}}{\text{Real}\{e^{ix}\}} \right) = \text{ArcTan} \left(\frac{\sin(x)}{\cos(x)} \right) = x \quad (4)$$

Special phase settings (with $n = \pm 0, 1, 2, 3, \dots$)

$$e^{i2n\pi} = 1 \quad (5)$$

$$e^{i(2n+1)\pi} = -1 \quad (6)$$

$$e^{i(2n+1)\frac{\pi}{2}} = (-1)^n i \quad (7)$$

2. Useful Trigonometric Identities

$$\sin^2(x) + \cos^2(x) = 1 \quad (8)$$

$$\sin(2x) = 2 \sin(x) \cos(x) \quad (9)$$

$$\begin{aligned} \cos(2x) &= \cos^2(x) - \sin^2(x) & (10) \\ &= 1 - 2 \sin^2(x) \end{aligned}$$

$$\cos^2(x) = \frac{1}{2} \{1 + \cos(2x)\} \quad (11)$$

$$\sin^2(x) = \frac{1}{2} \{1 - \cos(2x)\} \quad (12)$$

$$\sin^3(x) = \frac{1}{4} \{3 \sin(x) - \sin(3x)\} \quad (13)$$

$$\cos^3(x) = \frac{1}{4} \{3 \cos(x) + \cos(3x)\} \quad (14)$$

$$\sin(x) = \frac{e^{ix} - e^{-ix}}{2i} \quad (15)$$

$$\cos(x) = \frac{e^{ix} + e^{-ix}}{2} \quad (16)$$

3. Table of Useful Integrals

where $a > 0$ and n is an integer

$$\int_0^{2\pi} \sin^2(nx) dx = \pi \quad \{n \neq 0\} \quad (17)$$

$$\int_0^\infty \sin(ax^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{2a}} \quad (18)$$

$$\int_0^\infty \cos(ax^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{2a}} \quad (19)$$

$$\int_0^\infty e^{-ax} dx = \frac{1}{a} \quad (20)$$

$$\int_0^\infty x^n e^{-ax} dx = n!/a^{n+1} \quad (21)$$

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad (22)$$

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a} \quad (23)$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}} \quad (24)$$

4. Rules for Differentiation and Integration

$$\frac{d}{dx}(fg) = f \frac{dg}{dx} + g \frac{df}{dx} \quad (25)$$

$$\frac{d}{dx}(f\{g(x)\}) = \frac{df\{g(x)\}}{dg(x)} \frac{dg(x)}{dx} \quad (26)$$

$$\int f \left(\frac{dg}{dx} \right) dx = fg - \int g \left(\frac{df}{dx} \right) dx \quad (27)$$

Why Quantum Mechanics?

Classical Mechanics Fails

By the turn of the 19th century, classical physics had reached its summit. The nature and motion of particles and matter was properly accounted for. Newtonian mechanics was put in a solid mathematical framework (Lagrange, Hamilton) and the properties of radiation was covered by Maxwell's equations. Classical mechanics, however, failed to describe the inherent properties of matter and radiation, which was evident from a few outstanding problems:

- Matter. Heat capacities (Einstein molar heat capacity) and atomic spectra (Balmer). These observations led to the vision of a quantized form of matter, which was found in the atomic model of Bohr.
- Radiation. Black body radiation (Planck) and photoelectric effect (Einstein). Radiation is quantized as well. The full framework of quantized radiation was developed by Dirac in 1927, and is beyond the scope of this course.

New Theory

Quantum mechanics was developed in the early part of the 20th century to address the shortcomings of classical mechanics. Quantum mechanics is based on the following:

- The state of matter can be described in the form of wavefunctions.
- For particles confined to small scales (atomic, molecular) and with low masses, the wavelike motion results in quantized states.
- Quantized states account for quantized physical properties such as energy and momentum.

Important for Chemistry

Quantum mechanics is important to chemists because, unlike classical mechanics, it describes matter at the atomic and molecular scale. Quantum mechanics explains the energy levels and configuration of the hydrogen atom and provides tools for describing orbitals and molecular bonds.

Elements of Quantum Mechanics

State is Described by a Wavefunction

Quantum Mechanics uses a wavefunction to describe the state of matter. In principle, the wavefunction is not a direct observable. It describes the state in which the matter resides in mathematical terms. From it we can derive physical observables such as energy and momentum indirectly. To find these properties, we have to operate with an 'operator' onto the wavefunction to get the desired information out.

Operators and Wavefunctions

An operator $\hat{\Omega}$ performs a mathematical operation onto a function. An example is $\hat{\Omega} = \frac{d}{dx}$, which means: 'take the derivative to x of the function that follows'. A special case occurs when the operator operates on a function which yields a function proportional to the original:

$$\begin{aligned}\hat{\Omega}f &= \omega f \\ \frac{d}{dx}e^{ax} &= a \cdot e^{ax}\end{aligned}$$

In other words, operating $\hat{\Omega}$ onto f yields the same function f multiplied by a constant ω . We define:

$$\begin{aligned}\hat{\Omega} &= \text{operator} \\ f &= \text{eigenfunction} \\ \omega &= \text{eigenvalue}\end{aligned}$$

Operators may have more than one eigenfunction, each associated with an eigenvalue:

$$\hat{\Omega}f_n = \omega_n f_n$$

So more generally, operators may have a set of eigenfunctions. All the possible eigenfunctions of a given operator together is what we call a *complete set*. These sets play a central role in quantum mechanics, as we will see.

Sets of Eigenfunctions

When an operator operates on one of its eigenfunction, the eigenfunction and the eigenvalue are retrieved. But what if my function of interest, let's say g , is *not* an eigenfunction of the operator I am looking at? We can still work with eigenfunctions. Mathematically, we can expand the complete set of the operator's eigenfunctions f_n in a series to describe any other general function:

$$g = \sum_n c_n f_n$$

What happens when we operate on g with the operator $\hat{\Omega}$?

$$\hat{\Omega}g = \sum_n c_n \hat{\Omega}f_n = \sum_n c_n \omega_n f_n$$

The result is again a series of eigenfunctions that are now each weighted by the coefficients c_n . The following properties of wavefunction sets will be used throughout the rest of the course:

- **Degeneracy.** A wavefunction (sub)set is said to be degenerate if each wavefunction in the set has the same eigenvalue, i.e.

$$\hat{\Omega}f_n^d = \omega f_n^d$$

In this special case any linear combination of f_n^d is again an eigenfunction of $\hat{\Omega}$. Hence, the function $g = \sum_n c_n f_n^d$ is also an eigenfunction of $\hat{\Omega}$:

$$\hat{\Omega}g = \sum_n c_n \omega f_n^d = \omega \sum_n c_n f_n^d = \omega g$$

- **Linear independency.** We can create different sets of functions g_n from the same complete set spanned by f_n . Some of the chosen g_n will actually be linear combinations of other functions $g_{n'}$. A set of functions g_i is linearly independent if for any given set of coefficients C_i :

$$\sum_i C_i g_i \neq 0$$

- **Orthogonality.** Eigenfunctions f_n in the complete set are orthogonal. This implies that the overlap integral of two wavefunctions f_n and f_m taken over whole space is zero:

$$S_{overlap} = \int_{-\infty}^{\infty} f_n f_m^* dV = 0$$

This orthogonality is much similar to the orthogonality of vectors such as the orthogonal vectors (x, y, z) that define Cartesian space. The functions in a complete set are therefore often said to span a complete (multidimensional) space as well. The overlap integral of a (wave)function f_n with itself gives a finite value (see Born postulate for wavefunctions). If the functions are **normalized**, this overlap integral yields 1:

$$\int f_n f_n^* = \int |f_n|^2 = 1$$

Operators

In the previous section we illuminated wavefunctions and sets of wavefunctions. In this section we will be focusing on the other important component of quantum mechanics: operators. We shall see that by studying relations among the different operators we will be able to draw important conclusions concerning observables and the uncertainty in determining observables.

Operator Forms

Important operators are the energy \hat{H} , position \hat{x} , and momentum \hat{p} operators. All these operators yield physical observables when operating onto a wavefunction. What is the mathematical form of the operators? In position (x) space, the operators are taking the following form:

$$\begin{aligned}\hat{x} &= x \cdot \quad (\text{multiply by } x) \\ \hat{p}_x &= \frac{\hbar}{i} \frac{\partial}{\partial x} \\ \hat{H} &= \hat{T} + \hat{V} = \frac{\hat{p}_x^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}\end{aligned}$$

The operator \hat{V} is the operator for the potential energy. For example, for a coulomb potential it is given by:

$$\hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

In three dimensions the Hamiltonian assumes the form:

$$\hat{H} = -\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}$$

Alternatively, we could have expressed the operators in momentum (p) space. The position, momentum and energy operators then assume the forms:

$$\begin{aligned}\hat{x} &= \frac{\hbar}{i} \frac{\partial}{\partial p} \\ \hat{p}_x &= p \cdot \\ \hat{H} &= \hat{T} + \hat{V} = \frac{p^2}{2m} + \hat{V}\end{aligned}$$

Commutation Relations

Operators operate on the function to the right. Hence, a product of two operators should be read as follows:

$$\hat{A}\hat{B}f = \hat{A}(\hat{B}f)$$

where $(\widehat{B}f)$ is the new function for \widehat{A} to operate on. Consequently, the product operator $\widehat{A}\widehat{B}$ is not necessarily the same as the operator $\widehat{B}\widehat{A}$. We now define the commutator of \widehat{A} and \widehat{B} :

$$[\widehat{A}, \widehat{B}] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A}$$

The operators commute if

$$[\widehat{A}, \widehat{B}] = 0$$

If this condition does not hold, the operators are non-commuting. It can be shown quite easily that operators that share the same set of eigenfunctions, commute. We then have:

$$\begin{aligned}\widehat{A}f &= af \\ \widehat{B}f &= bf\end{aligned}$$

and thus

$$\begin{aligned}[\widehat{A}, \widehat{B}]f &= \widehat{A}(\widehat{B}f) - \widehat{B}(\widehat{A}f) \\ &= b\widehat{A}f - a\widehat{B}f \\ &= (ba - ab)f \\ &= 0\end{aligned}$$

Operators do not always share the same set of eigenfunctions. If they don't, the operators are non-commuting. An important example are the position and the momentum operators:

$$\begin{aligned}[\widehat{x}, \widehat{p}]f &= x \cdot \frac{\hbar}{i} \frac{\partial}{\partial x} f - \frac{\hbar}{i} \frac{\partial}{\partial x} \cdot x \cdot f \\ &= \frac{\hbar}{i} x \cdot \frac{\partial f}{\partial x} - \left(\frac{\hbar f}{i} + x \cdot \frac{\hbar}{i} \frac{\partial f}{\partial x} \right) \\ &= i\hbar \cdot f\end{aligned}$$

from which we recognize

$$[\widehat{x}, \widehat{p}] = i\hbar$$

this result is tightly connected to Heisenberg's Uncertainty Principle, and relates to the statement that position and momentum of a small particle cannot be determined with great precision simultaneously. Instead, there is an uncertainty of the order of \hbar between the operators.

Operators and Observables

Operators are needed to extract information out of the wavefunction that leads to observable information and predictions. A physical observable in classical mechanics corresponds to an operation by an operator in quantum mechanics.

Operators are abstract concepts. We have to choose the mathematical form of our operators. As we have seen before, they are commonly chosen to be expressed in terms of the operators for the coordinates $q = (x, y, z)$ and momenta p_q .

- **The basic operators are chosen with the following commutation relations:**

$$\begin{aligned} [\hat{q}, \hat{p}_{q'}] &= i\hbar\delta_{qq'} \\ [\hat{q}, \hat{q}'] &= 0 \\ [\hat{p}_q, \hat{p}_{q'}] &= 0 \end{aligned}$$

- How exactly do we get a physical observable from an operator?

The mean value of an observable is given by the expectation value of the corresponding operator

The expectation value is given by:

$$\langle \hat{\Omega} \rangle = \frac{\int \psi^* \hat{\Omega} \psi dV}{\int \psi^* \psi dV}$$

For normalized wavefunctions this is:

$$\langle \hat{\Omega} \rangle = \int \psi^* \hat{\Omega} \psi dV$$

We can distinguish two situations.

- (1) *The wavefunction is an eigenfunction of the operator.*

Then each measurement of the operator gives an eigenvalue corresponding to the state in which the system resides:

$$\langle \hat{\Omega} \rangle = \int \psi^* \hat{\Omega} \psi dV = \int \psi^* \omega \psi dV = \omega \int \psi^* \psi dV = \omega$$

- (2) *The wavefunction is not an eigenfunction of the operator.*

This is the general situation. We have to write the wavefunction as a series of eigenfunctions of the operator:

$$\psi = \sum_n c_n \phi_n$$

we now get for the expectation value:

$$\langle \hat{\Omega} \rangle = \int \left(\sum_m c_m \phi_m \right)^* \hat{\Omega} \left(\sum_n c_n \phi_n \right) dV$$

$$\begin{aligned}
&= \sum_{n,m} c_m^* c_n \int \phi_m^* \hat{\Omega} \phi_n dV \\
&= \sum_{n,m} c_m^* c_n \omega_n \int \phi_m^* \phi_n dV \\
&= \sum_{n,m} c_m^* c_n \omega_n \delta_{m,n} \\
&= \sum_n c_n^* c_n \omega_n \\
&= \sum_n |c_n|^2 \omega_n
\end{aligned}$$

The latter result underlines a central point in Quantum Mechanics. Every time one does a measurement of an observable, and the system is not in an eigenstate of the corresponding operator, the outcome of the experiment is still an eigenvalue of the operator. In the next measurement, however, the outcome can be a different eigenvalue. The probability of measuring a particular eigenvalue ω is $|c_n|^2$. The expectation value, the 'mean value' of the observable, is a weighted sum of all the eigenvalues.

Wavefunction and Schrödinger Equation

The wavefunction describes all the properties of a quantum mechanical system. It is, however, a mathematical construct. What is its physical meaning? The following section sheds light on the meaning of the wavefunction and the central equation in quantum mechanics: the Schrödinger equation.

The Wavefunction

- **The state of a system is fully described by a wavefunction** $\Psi(r_1, r_2, \dots, t)$

The wavefunction can encompass the state of multiple particles (1, 2...) in a system, such as a nucleus with its many electrons. The **total wavefunction** represents the state of the **whole system**. Remember that a wavefunction can be described as a weighed sum of a complete set of eigenfunctions ϕ_n of an operator:

$$\Psi(r) = \sum_n c_n \phi_n(r)$$

Wavefunctions are often labeled as $\Psi_{a,b,\dots}$ with quantum numbers (a, b, \dots), which denote the different quantized states of the system. What is the meaning of the coefficient c_n ? We gain some insight if we multiply Ψ with an eigenfunction ϕ_i^* :

$$\begin{aligned} \phi_i^* \Psi &= \phi_i^* \sum_n c_n \phi_n \\ &= \sum_n c_n \phi_i^* \phi_n \\ \Rightarrow \int \phi_i^* \Psi dV &= \sum_n c_n \int \phi_i^* \phi_n dV \\ &= \sum_n c_n \delta_{i,n} \\ &= c_i \end{aligned}$$

Hence, c_i is the overlap integral of the eigenfunction ϕ_i^* with the total wavefunction Ψ . In other words, c_i samples 'how much' of ϕ_i is in the total wavefunction. The state of the system does not necessarily have to be in an eigenfunction of an operator. The state can be smeared out over several eigenstates of this operator. The coefficient c_i measures how much of ϕ_i contributes to the series expansion $\sum_n c_n \phi_n$ that describes Ψ .

- The next postulate concerns the interpretation of the wavefunction

The probability that a particle will be found in volume element dV is proportional to $|\Psi(r)|^2$

This postulate is known as the Born interpretation of the wavefunction. In other words, the wavefunction is a probability amplitude and its square modulus a probability density. Born's interpretation of the wavefunction is based on the notion that particle must be somewhere in space, so that the overlap integral of the wavefunction with itself must be finite:

$$\int |\Psi(r)|^2 dV < \infty$$

Hence, the wavefunction should be square integrable. For normalized wavefunctions we get:

$$\int |\Psi(r)|^2 dV = 1$$

which means that if one attempts a measurement over whole space, the chance of finding the particle is one. This postulate also reinforces the meaning of the coefficient c_n . When we write the total wavefunction as $\Psi = \sum_n c_n \phi_n$, we have:

$$\begin{aligned} |\Psi|^2 &= \left(\sum_n c_n \phi_n \right)^* \left(\sum_m c_m \phi_m \right) \\ &= \sum_{n,m} c_n^* c_m \phi_n^* \phi_m \end{aligned}$$

and thus

$$\begin{aligned} \int |\Psi|^2 dV &= \sum_{n,m} c_n^* c_m \int \phi_n^* \phi_m dV \\ &= \sum_{n,m} c_n^* c_m \delta_{n,m} \\ &= \sum_n |c_n|^2 \end{aligned}$$

For normalized wavefunctions we get

$$\sum_n |c_n|^2 = 1$$

In other words, $|c_n|^2$ is the probability that the system is in a particular eigenstate ϕ_n . The probability that the system resides in the collection of all the available eigenstates, which is the sum over all $|c_n|^2$, is 1. This is equivalent to saying that a sampling over the whole of ' ϕ_n -space', must give the probability one, because the system has to be somewhere in this space.

The Schrödinger Equation

The wavefunction $\Psi(r, t)$ fully describes a system in space and time. The full evolution of the wavefunction is found from the **time-dependent Schrödinger Equation**:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

Here \hat{H} is the Hamiltonian, the energy operator:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}_x$$

We can separate the time-dependent Schrödinger equation in a space-dependent and a time-dependent part. Let's write the wavefunction as:

$$\Psi(x, t) = \psi(x)\theta(t)$$

We now plug this into the Schrödinger Equation:

$$\begin{aligned} i\hbar \cdot \psi(x) \frac{\partial \theta(t)}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \cdot \theta(t) + \hat{V}_x \cdot \psi(x)\theta(t) \\ i\hbar \cdot \frac{1}{\theta(t)} \frac{\partial \theta(t)}{\partial t} &= -\frac{\hbar^2}{2m} \cdot \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x \end{aligned}$$

Now comes the trick. Each side depends on a different variable, while they equal each other at all times. Hence, each side equals a constant:

$$\begin{aligned} i\hbar \cdot \frac{1}{\theta(t)} \frac{\partial \theta(t)}{\partial t} &= E \\ -\frac{\hbar^2}{2m} \cdot \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x &= E \end{aligned}$$

which gives

$$\begin{aligned} i\hbar \frac{\partial \theta(t)}{\partial t} &= E\theta(t) \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x &= E\psi(x) \Rightarrow \hat{H}\psi(x) = E\psi(x) \end{aligned}$$

The solution of the first, time-dependent equation is:

$$\theta(t) \propto e^{-iEt/\hbar}$$

The solution of the second, time-independent Schrödinger equation is the stationary wavefunction $\psi(x)$:

$$\hat{H}\psi = E\psi$$

We immediately recognize that this equation is an eigenvalue equation with operator \hat{H} , eigenfunctions Ψ , and eigenvalues E . The values for E thus correspond to the energy of the system. The total wavefunction can now be written as:

$$\Psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}$$

The wavefunction has thus a space-dependent amplitude and time-dependent phase. Note that the phase has no influence on probability density a particle at any time, as

$$|\Psi(x, t)|^2 = \left(\psi(x)e^{-iEt/\hbar}\right) \cdot \left(\psi^*(x)e^{iEt/\hbar}\right) = \psi^*(x)\psi(x) = |\psi(x)|^2$$

Summary

We can find the wavefunction of a system by finding the eigenfunctions of the Hamiltonian. The corresponding eigenvalues give the permissible energy levels of the system. In summary we have:

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H} \Psi(x, t)$$

Time-independent Schrödinger equation

$$\hat{H} \psi(x) = E \psi(x)$$

Wavefunction

$$\Psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}$$

Operators and Uncertainty Principle

Hermitian Operators

The operators that lead to physical observables have real eigenvalues. This is a very important property. In quantum mechanics, operators that share this property are hermitian. Hermitian operators have a couple of interesting features that we should familiarize ourselves with.

We have seen that the expectation value of an operator A (we will drop the hat and use capital letters for operators) can be written as:

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) A \psi_n(x) dx$$

Let us now focus on a more general expression of such an integral, in which the functions to the left and right of the operator are not necessarily the same

$$\int_{-\infty}^{\infty} \psi_n^*(x) A \psi_m(x) dx$$

What is the complex conjugate of this integral?

$$\left\{ \int \psi_n^*(x) [A \psi_m(x)] dx \right\}^* = \int [A \psi_m(x)]^* \psi_n(x) dx$$

We now define the *hermitian conjugate operator* A^\dagger as follows:

$$\int [A \psi_m(x)]^* \psi_n(x) dx = \int \psi_m^*(x) A^\dagger \psi_n(x) dx$$

Consider now the same integral, with the positions of the functions $\psi_{n,m}$ switched before we take the complex conjugate.

$$\left\{ \int \psi_m^*(x) [A \psi_n(x)] dx \right\}^* = \int \psi_n^*(x) A^\dagger \psi_m(x) dx$$

The latter expression shows similarity to the integral we started with. It is equal to the original integral only if $A = A^\dagger$. We then have:

$$\int \psi_n^*(x) A \psi_m(x) dx = \int \psi_n^*(x) A^\dagger \psi_m(x) dx$$

When this holds, the operator is said to be *hermitian*, it is equal to its own hermitian conjugate. For hermitian operators we thus write:

$$\int \psi_n^* A \psi_m dx = \left\{ \int \psi_m^* A \psi_n dx \right\}^*$$

For example, let's find out if the momentum operator is hermitian:

$$\begin{aligned}
 \int \psi_n^* \hat{p}_x \psi_m dx &= \int \psi_n^* \frac{\hbar}{i} \frac{d}{dx} \psi_m dx \\
 &= \frac{\hbar}{i} \psi_n^* \psi_m \Big|_{-\infty}^{\infty} - \frac{\hbar}{i} \int \frac{d\psi_n^*}{dx} \psi_m dx \\
 &= - \int \psi_m \frac{\hbar}{i} \frac{d}{dx} \psi_n^* dx \\
 &= \left\{ \int \psi_m^* \hat{p}_x \psi_n dx \right\}^*
 \end{aligned}$$

Indeed, the momentum operator is hermitian. The hermitian conjugate of \hat{p}_x is similar to the operator itself, i.e. $\hat{p}_x^\dagger = \hat{p}_x$

Dirac Bracket Notation

In order to prevent that we get completely swamped with all these integrals, a different notation is welcome. We find that in the Dirac bracket notation. Here are the definitions, with $\langle m|$ called **bra** and $|n\rangle$ called **ket**:

$$\begin{aligned}
 \langle n|m\rangle &= \int \psi_n^* \psi_m dV = \delta_{nm} \\
 \langle n|A|m\rangle &= \int \psi_n^* A \psi_m dV \\
 \langle n|m\rangle &= \langle m|n\rangle^*
 \end{aligned}$$

Note also that we can write $A|m\rangle$ as a new function $|Am\rangle$, so that:

$$\langle n|A|m\rangle^* = \langle n|Am\rangle^* = \langle Am|n\rangle = \langle m|A^\dagger|n\rangle$$

Hermiticity in bra-ket notation:

$$\langle n|A|m\rangle = \langle m|A|n\rangle^* = \langle n|A^\dagger|m\rangle$$

It is common to use the bra and ket as new functions without 'closing' the integral. For example, it is custom to write an eigenvalue equation as follows:

$$A|m\rangle = m|m\rangle$$

Similarly, the notation for a general wavefunction expressed in the set $\{|m\rangle\}$ is written as:

$$|\Psi\rangle = \sum_m c_m |m\rangle \quad c_m = \langle m|\Psi\rangle$$

Properties of Hermitian Operators

- *Eigenvalues of an hermitian operator are real*

For expectation values, we can write for the condition of hermiticity:

$$\langle m|A|m\rangle = \langle m|A|m\rangle^* = \langle m|A^\dagger|m\rangle$$

We then have

$$\begin{aligned} A|m\rangle &= m|m\rangle \\ \langle m|A|m\rangle &= m\langle m|m\rangle = m \\ \langle m|A|m\rangle^* &= m^* \\ m &= m^* \end{aligned}$$

- *Eigenfunctions of an hermitian operator are orthogonal*
Let's look at two different eigenstates of the operator A :

$$\begin{aligned} A|m\rangle &= m|m\rangle \\ A|n\rangle &= n|n\rangle \end{aligned}$$

We now multiply these equations with the conjugate bra-function:

$$\begin{aligned} \langle n|A|m\rangle &= m\langle n|m\rangle \\ \langle m|A|n\rangle &= n\langle m|n\rangle \end{aligned}$$

We can then write the following:

$$\begin{aligned} \langle n|A|m\rangle - \langle m|A|n\rangle^* &= m\langle n|m\rangle - n\langle m|n\rangle^* \\ 0 &= (m-n)\langle n|m\rangle \end{aligned}$$

Which implies that $\langle n|m\rangle = 0$.

- *When two operators A and B commute, an eigenstate of A is also an eigenstate of B*

When two operators commute, it follows that $AB - BA = 0$. Then, if $|\psi\rangle$ is an eigenstate of A , we can write:

$$\begin{aligned} BA|\psi\rangle &= Ba|\psi\rangle = aB|\psi\rangle \\ AB|\psi\rangle &= aB|\psi\rangle \\ A|B\psi\rangle &= a|B\psi\rangle \end{aligned}$$

In other words, the function $|B\psi\rangle$ behaves as an eigenfunction of A . It yields the same eigenvalue a as $|\psi\rangle$, and so $|B\psi\rangle$ must be proportional to $|\psi\rangle$. We can write this as $B|\psi\rangle = b|\psi\rangle$, which is an eigenvalue equation with the eigenfunction $|\psi\rangle$.

Conversely, if two operators do not commute, they do not share the same eigenfunctions. The observables of two non-commuting operators cannot be determined simultaneously.

Uncertainty Principle

To what extent can we determine the observables of two non-commuting operators? The answer is given by Heisenberg's uncertainty principle. The most general form is given as

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

What does this equation exactly mean? The quantity ΔA can be interpreted as the 'spread' of the operator A , commonly expressed as the root mean square of the deviation from its mean value. The deviation from the mean value is:

$$\delta A = A - \langle A \rangle$$

The root mean square of this is defined as:

$$\Delta A = \langle (\delta A)^2 \rangle$$

We can evaluate this as follows:

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \langle (A - \langle A \rangle)^2 \rangle \\ &= \langle A^2 - 2A \langle A \rangle + \langle A \rangle^2 \rangle \\ &= \langle A^2 \rangle - 2 \langle A \rangle \langle A \rangle + \langle A \rangle^2 \\ &= \langle A^2 \rangle - \langle A \rangle^2 \end{aligned}$$

We can now write:

$$\Delta \hat{A} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$$

Let us test this expression by looking at the non-commuting operators \hat{x} and \hat{p}_x . From the general expression of the uncertainty relation we have:

$$\Delta \hat{x} \Delta \hat{p}_x \geq \frac{1}{2} |\langle [\hat{x}, \hat{p}_x] \rangle| = \frac{1}{2} |i\hbar| = \frac{1}{2} \hbar$$

We can verify this relation by explicitly calculating the uncertainty between the operators \hat{x} and \hat{p}_x for a particular case.

Let $\psi = \sqrt{\frac{2}{L}} \sin(\pi x/L)$ be the wavefunction in the interval $[0, L]$, we can then calculate:

$$\begin{aligned} \langle \hat{x} \rangle &= \frac{2}{L} \int_0^L \sin(\pi x/L) \hat{x} \sin(\pi x/L) dx = \frac{2}{L} \int_0^L x \sin^2(\pi x/L) dx \\ &= \frac{2L}{\pi^2} \int_0^\pi x' \sin^2(x') dx' \\ &= \frac{2L}{\pi^2} x' \left(\frac{1}{2} x' - \frac{1}{4} \sin 2x' \right) \Big|_0^\pi - \frac{2L}{\pi} \int_0^\pi \left(\frac{1}{2} x' - \frac{1}{4} \sin 2x' \right) dx' \\ &= \frac{2L}{\pi^2} \left(\frac{1}{2} \pi^2 - \frac{1}{4} \pi^2 \right) = \frac{L}{2} \end{aligned}$$

and

$$\begin{aligned}
\langle \hat{x}^2 \rangle &= \frac{2}{L} \int_0^L x^2 \sin^2(\pi x/L) dx = \frac{2L^2}{\pi^3} \int_0^\pi (x')^2 \sin^2(x') dx' \\
&= \frac{2L^2}{\pi^3} (x')^2 \left(\frac{1}{2}x' - \frac{1}{4} \sin 2x' \right) \Big|_0^\pi - \frac{4L^2}{\pi^3} \int_0^\pi x' \left(\frac{1}{2}x' - \frac{1}{4} \sin 2x' \right) dx' \\
&= L^2 - \frac{2}{3}L^2 - \frac{L^2}{2\pi^3} x' \cos 2x' \Big|_0^\pi + \frac{L^2}{2\pi^3} \int_0^\pi \cos 2x' dx' \\
&= \frac{1}{3}L^2 - \frac{1}{2\pi^2}L^2
\end{aligned}$$

Similarly:

$$\begin{aligned}
\langle \hat{p}_x \rangle &= \frac{2}{L} \int_0^L \sin(\pi x/L) \frac{\hbar}{i} \frac{d}{dx} \sin(\pi x/L) dx = \frac{2\pi\hbar}{iL^2} \int_0^L \sin(\pi x/L) \cos(\pi x/L) dx \\
&= \frac{\pi\hbar}{iL^2} \int_0^L \sin(2\pi x/L) dx = \frac{\hbar}{2iL} \int_0^{2\pi} \sin(x') dx' \\
&= 0
\end{aligned}$$

and

$$\begin{aligned}
\langle \hat{p}_x^2 \rangle &= -\frac{2\hbar^2}{L} \int_0^L \sin(\pi x/L) \frac{d^2}{dx^2} \sin(\pi x/L) dx = \frac{2\pi^2\hbar^2}{L^3} \int_0^L \sin^2(\pi x/L) dx \\
&= \frac{2\pi\hbar^2}{L^2} \int_0^\pi \sin^2(x') dx' \\
&= \frac{2\pi\hbar^2}{L^2} \frac{1}{2}\pi
\end{aligned}$$

This gives for the uncertainty relation:

$$\begin{aligned}
\Delta \hat{x} &= \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} = \sqrt{\frac{1}{3}L^2 - \frac{1}{2\pi^2}L^2 - \frac{1}{4}L^2} \\
\Delta \hat{p}_x &= \sqrt{\langle \hat{p}_x^2 \rangle - \langle \hat{p}_x \rangle^2} = \sqrt{\frac{\pi^2\hbar^2}{L^2}} \\
\Delta \hat{x} \Delta \hat{p}_x &= \frac{\hbar}{2\sqrt{3}} \sqrt{\pi^2 - 6} = 0.568\hbar > \frac{1}{2}\hbar
\end{aligned}$$

Matrices and Time Evolution

Matrices

We have already seen that integrals of the type $\int \psi_m^* \hat{\Omega} \psi_n dV$ play a very important role in quantum mechanics. We have written this shorthand as:

$$\langle m | \hat{\Omega} | n \rangle = \int \psi_m^* \hat{\Omega} \psi_n dV$$

we can write this even shorter as follows:

$$\Omega_{mn} = \langle m | \hat{\Omega} | n \rangle$$

This is the matrix notation in quantum mechanics, first introduced by Heisenberg. These matrices are composed of diagonal Ω_{nn} and off-diagonal Ω_{mn} matrix elements, and thus contain a lot of information.

$$\Omega = \begin{bmatrix} \Omega_{nn} & \Omega_{nm} & \Omega_{nk} & \cdot \\ \Omega_{mn} & \Omega_{mm} & \Omega_{mk} & \cdot \\ \Omega_{kn} & \Omega_{km} & \Omega_{kk} & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

The good thing is that we can make use of all the matrix calculus tools available to us. From matrix multiplication we know that:

$$P_{mk} = \sum_n A_{mn} B_{nk} = (AB)_{mk}$$

In Dirac notation this would be:

$$\langle m | P | k \rangle = \sum_n \langle m | A | n \rangle \langle n | B | k \rangle = \langle m | AB | k \rangle$$

from which we can deduce the very important relation:

$$\sum_n |n\rangle \langle n| = 1$$

Hermiticity in matrix language is defined as:

$$\begin{aligned} \langle m | \hat{\Omega} | n \rangle &= \langle n | \hat{\Omega} | m \rangle^* \\ \Omega_{mn} &= \Omega_{nm}^* \\ \Omega_{mn} &= \Omega_{mn}^\dagger \end{aligned}$$

The matrix representation is very useful when finding a complete set of eigenfunctions of an operator, in particular the Hamiltonian. In general, we can write a wavefunction as a linear combination of a complete set of states $|n\rangle$:

$$|\psi\rangle = \sum_n c_n |n\rangle$$

We want to solve the Schrödinger equation, i.e. $\hat{H}\psi = E\psi$, but the functions in the set $|n\rangle$ are not necessarily eigenfunctions of the Hamiltonian. When evaluating the Schrödinger equation we find:

$$\begin{aligned}\hat{H}\psi &= E\psi \\ \hat{H} \sum_n c_n |n\rangle &= E \sum_n c_n |n\rangle \\ \sum_n c_n \langle m | \hat{H} | n \rangle &= E \sum_n c_n \langle m | n \rangle \\ \sum_n H_{mn} c_n &= E c_m\end{aligned}$$

This is not an eigenvalue equation. The last expression becomes an eigenvalue relation if all the non-diagonal elements of the matrix \mathbf{H} vanish and only the diagonal elements remain. Because then the only remaining equation is:

$$H_{mm}c_m = E c_m$$

Hence, eigenfunctions and eigenvalues can be found by diagonalizing the Hamiltonian matrix. This is an important finding that is used extensively in molecular quantum mechanics.

Time Evolution

We have already learned that classical physical observables correspond to expectation values in quantum mechanics. We have found expressions for the position, momentum and energy.

$$\begin{aligned}x &= \langle \hat{x} \rangle \\ p &= \langle \hat{p} \rangle \\ E &= \frac{\langle \hat{p}^2 \rangle}{2m} = \langle \hat{H} \rangle\end{aligned}$$

So far, we have only considered the operators in the steady state. Limiting our discussion to operators that are time-independent, i.e. $dA/dt = 0$, what can we say about the time dependence of their expectation values?

Let us try to answer this question by starting to look at general wavefunctions that are solutions of the Schrödinger wave equation. In this case, the wavefunction is written as:

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

The time dependence of the expectation value of an operator is now:

$$\frac{d}{dt} \langle A \rangle = \frac{d}{dt} \langle \psi(r)e^{-iEt/\hbar} | A | \psi(r)e^{-iEt/\hbar} \rangle$$

$$\begin{aligned}
&= \frac{d}{dt} \langle \psi(r) | A e^{+iEt/\hbar} e^{-iEt/\hbar} | \psi(r) \rangle \\
&= \frac{d}{dt} \langle \psi(r) | A | \psi(r) \rangle \\
&= \left\langle \psi(r) \left| \frac{d}{dt} A \right| \psi(r) \right\rangle = 0
\end{aligned}$$

Hence, in the special case of eigenfunctions of the Hamiltonian, the expectation values of operators are time-independent. Let us now look at the general case in which the wavefunction is not necessarily an eigenfunction of the Hamiltonian. We know that in general the time dependence of wavefunctions can be found from the time-dependent Schrödinger equation:

$$\frac{d\psi(x, t)}{dt} = -\frac{i}{\hbar} H\psi(x, t)$$

A general solution to this equation is found by solving only the time-dependent part:

$$\psi(x, t) = e^{-iHt/\hbar} \psi(x, 0)$$

Note that the operator H is still in the exponential. Using this general expression for the wavefunction, we can write for the expectation value of a time-independent operator A :

$$\begin{aligned}
\langle A \rangle &= \langle \psi(x, t) | A | \psi(x, t) \rangle \\
&= \langle e^{-iHt/\hbar} \psi(x, 0) | A e^{-iHt/\hbar} \psi(x, 0) \rangle \\
&= \langle \psi(x, 0) | e^{iHt/\hbar} A e^{-iHt/\hbar} \psi(x, 0) \rangle \\
&= \langle \psi(x, 0) | A(t) | \psi(x, 0) \rangle \\
&= \langle A(t) \rangle
\end{aligned}$$

we have now defined a time-varying operator in the following way:

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar}$$

This way of writing the time dependence of an operator, in terms of a time-independent operator that is sandwiched between the time-dependent operators $e^{iHt/\hbar}$, is called the *Heisenberg picture*. In this picture, the states are time independent and the observables evolve according to the time-varying operator. When we keep the operator time-independent, the states have to become time-dependent. The latter is called the *Schrödinger picture*. The two are equivalent, and it is a matter of choice of how to evaluate the time-dependence of observables. In the Heisenberg picture we can calculate:

$$\begin{aligned}
\frac{d}{dt} A(t) &= \frac{i}{\hbar} H e^{iHt/\hbar} A e^{-iHt/\hbar} - \frac{i}{\hbar} e^{iHt/\hbar} A H e^{-iHt/\hbar} \\
&= \frac{i}{\hbar} H A(t) - \frac{i}{\hbar} A(t) H \\
&= \frac{i}{\hbar} [H, A(t)]
\end{aligned}$$

In this general case, the expectation value of the observable is thus obtained as:

$$\frac{d}{dt}\langle A(t) \rangle = \frac{i}{\hbar} \langle [H, \hat{A}(t)] \rangle$$

A similar result can be obtained in the Schrödinger picture. The physical interpretation is as follows. If the operator commutes with the Hamiltonian, its observable does not vary in time. These observables are a constant of motion. Hence, every time we do a measurement, we will measure the same value as long as the system retains the same wavefunction. This does not imply that the system is not evolving. The wavefunction (or the operator) might change as a function of time, however, the measured expectation value does not.

What is the time-dependence of the momentum? We can find this by calculating the commutator with the Hamiltonian:

$$\begin{aligned} \frac{d}{dt} \langle p \rangle_x &= \frac{i}{\hbar} [\hat{H}, \hat{p}_x] \\ &= \frac{i}{\hbar} \left[\frac{\hat{p}_x^2}{2m} + \hat{V}, \hat{p}_x \right] \\ &= \frac{i}{\hbar} [\hat{V}, \hat{p}_x] \\ &= \left[\hat{V}, \frac{d}{dx} \right] \end{aligned}$$

The latter can be shown to satisfy:

$$\left[\hat{V}, \frac{d}{dx} \right] \psi = \left\{ \hat{V} \frac{d\psi}{dx} - \hat{V} \frac{d\psi}{dx} - \frac{d\hat{V}}{dx} \psi \right\} = -\frac{d\hat{V}}{dx} \psi$$

In other words, the time dependence of the momentum observable depends on whether the expectation value for the potential energy changes with x :

$$\frac{d}{dt} \langle \hat{p}_x \rangle = - \left\langle \frac{d\hat{V}}{dx} \right\rangle = \langle \hat{F} \rangle$$

Here \hat{F} is the operator corresponding to the observable force. The latter relation is part of *Ehrenfest's theorem* which connects classical mechanics to quantum mechanics. Classical mechanics only deals with expectation values whereas quantum mechanics tells more about the system through the wavefunction description.

More on Wavefunctions

Good Wavefunction, Bad Wavefunction

We have learned that the wavefunction

- gives a full description of the system
- physical observables can be extracted from the wavefunction
- is *not* a physical observable itself
- the probability distribution of finding the particle within volume element dV is given by $|\psi(r)|^2 dV$, postulated by Born

Not any given wavefunction is a good wavefunction. Born's interpretation of the wavefunction imposes some constraints onto what is an acceptable wavefunction. Second, because the wavefunction is a solution of the Schrödinger equation, which is a second order differential equation, there are further constraints on what is an acceptable wavefunction.

1. The square modulus of the wavefunction must be single valued in order to fulfill Born's postulate that $|\psi(r)|^2$ is the probability density.

Because the probability of finding a particle at dV can only be one value, it follows that $|\psi(r)|^2$ and thus $\psi(r)$ must be single valued.

2. The wavefunction must not be infinite over a finite region. If it were, it would violate Born's postulate in the sense that the probability of finding the particle somewhere must be a finite number. The wavefunction can be come infinite only over an infinitesimal region, because then the integral can still yield a finite value. The delta function is a good example of such a case:

$$\int \delta(x - a) dx = 1$$

3. The wavefunction must be continuous everywhere. Discontinuous wavefunctions have ill-behaved second order derivatives, which violates the fact that the wavefunction needs to be a solution of a second order differential equation.
4. The wavefunction must have a continuous first order derivative. No sudden kinks are allowed. This does not hold in regions of ill-behaved potential energy

Curvature

We can learn a lot about the wavefunction by considering its curvature. The curvature is understood as the shape of the wavefunction, whether it is curved positively or negatively. The curvature depends on the second order derivative:

$$\begin{aligned}\hat{H}\psi &= E\psi \\ \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} \psi &= E\psi \\ \frac{d^2}{dx^2} \psi &= \frac{2m}{\hbar^2} \{V(x) - E\} \psi\end{aligned}$$

The curvature depends on:

- the sign and value of ψ
- the sign and value of $\{V(x) - E\}$

The higher the value, the more curved the wavefunction. The sign determines whether the curvature is positive or negative. For regions in space where $V(x)$ is a constant, we can rewrite the equation above with $k^2 = 2m/\hbar^2 (E - V)$ as:

$$\frac{d^2}{dx^2} \psi = -k^2 \psi$$

The difference between the potential energy and the total energy greatly influences the curvature. We can identify three important cases:

1. $E - V > 0$, $k > 0$ and $\psi \propto e^{\pm ikx}$.
The potential energy is smaller than the total energy, i.e. the kinetic energy is positive and nonzero. This is the common situation, the particle has enough kinetic energy to move around inside the region with this potential.
2. $E - V = 0$, $k = 0$ and $\psi \propto e^{ikx} = e^{0 \cdot x} = 1$.
the potential energy equals the total energy, i.e. the kinetic energy is zero. The curvature is zero, and thus the wavefunction is 'flat'.
3. $E - V < 0$, $k < 0$ and $\psi \propto e^{-\kappa x}$ with $\kappa = -ik$.
the potential energy is larger than the total available energy. The particle is now in a classically forbidden zone, because it implies that the kinetic energy is negative. As we will see, in quantum mechanics, the particle can still reside in these regions, but the wavefunction amplitude must quickly approach zero in this region: $e^{-\kappa x}$, a decaying function.

Non-classical Regimes

In quantum mechanics the wavefunction can have an amplitude in regions where the total available energy is less than the potential barrier. In classical mechanics the particle would be rejected from these regions. A ball bounces off a wall

when its kinetic energy is too low to go through. There's no chance of finding the ball in or on the other side of the wall when the kinetic energy is not available. In quantum mechanics, this is possible. Hence, we may find a particle on the other side of a barrier even though it did not have enough kinetic energy to make it classically through.

This phenomenon is often referred to as tunneling, which represents a clear difference between classical and quantum mechanics.

Quantization

Not every wavefunction is acceptable. In a region bound by a potential, the wavefunction needs to be well-behaved at the boundary points. The curvature needs to comply with the conditions we identified above. Only certain values of $E - V$ give rise to a correct and acceptable wavefunction. Thus, only certain energy values E are allowed for the system to be described by an acceptable wavefunction. This is the principle of quantization: the system can only be described by certain forms of the wavefunction.

Quantization is a result of the particle being bound by regions where $E - V < 0$, regions where the potential energy is larger than the energy available to the particle. The confinement of the particle leads to only certain wavefunctions to be allowed. The particle can now reside only in certain states, as defined by the quantized wavefunctions.

Motion in Free Space

Previously we have learned that the potential energy $V(x)$ can confine a particle in space. In that case, the wavefunctions take on only certain forms and thus the behavior of the particle becomes quantized. We now focus on a much simpler case: the potential energy is zero everywhere. For this special situation, a particle in free space, we expect no quantization.

A General Solution

With $V(x) = 0$ the Hamiltonian becomes:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

The Schrödinger equation becomes:

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

and

$$k = \sqrt{2mE}/\hbar$$

A solution to this equation is

$$\psi(x) = Ae^{ikx}$$

Another solution is:

$$\psi(x) = Be^{-ikx}$$

So we may write as a general solution to the Schrödinger equation in free space:

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

Note that because $e^{ikx} = \cos(kx) + i \sin(kx)$, the oscillatory functions $\cos(kx)$ and $\sin(kx)$ are also solutions of the Schrödinger equation. The free space wavefunction thus has the properties of an oscillatory wave.

Flux

How do we interpret this wavefunction? We can get some physical sense if we try to retrieve the momentum of this general wavefunction. Suppose that we set $B = 0$, we can calculate the momentum with the momentum operator:

$$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} \psi = \frac{\hbar}{i} \frac{d}{dx} Ae^{ikx} = Ak\hbar e^{ikx} = k\hbar \psi$$

The result is a particle that moves in the $+x$ with momentum $k\hbar$. Now we set $A = 0$ and calculate the momentum operator again:

$$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} Be^{-ikx} = -k\hbar \psi$$

However, the expectation value of the momentum operator, $\langle \hat{p}_x \rangle$, is ill-defined, because the functions $e^{\pm ikx}$ are not square-integrable. An alternative quantity that sheds light on the nature of the behavior of the wavefunction is the flux. The observable for the flux is defined as:

$$J_x = \frac{\hbar}{2mi} \left(\psi^* \frac{d}{dx} \psi - \psi \frac{d}{dx} \psi^* \right)$$

Note that, unlike with $\langle \hat{p}_x \rangle$, an integration over whole space is omitted here. For the wavefunction with $B = 0$, we find for the flux:

$$\begin{aligned} J_x &= \frac{\hbar |A|^2}{2mi} \left\{ e^{-ikx} \frac{d}{dx} e^{ikx} - e^{ikx} \frac{d}{dx} e^{-ikx} \right\} \\ &= \frac{k\hbar |A|^2}{m} \end{aligned}$$

For the wavefunction with $A = 0$ we find:

$$J_x = -\frac{k\hbar |B|^2}{m}$$

We can interpret this result as follows. For particles traveling to the left the flux is $p|A|^2/m = v|A|^2$, where v is the (classical) velocity, multiplied by the probability ($|A|^2$) that the particle is in that state. For a particle traveling to the right, the flux is $-v|B|^2$.

Motion for Non-eigenfunctions

In the discussion above, we assumed that the wavefunction was an eigenfunction of the energy operator. Each individual function was also an eigenfunction of the momentum operator, yielding real eigenvalues for the momentum. However, what if our particle was prepared in a general state that is not an eigenfunction of the momentum operator?

The function

$$\psi = C \cos(kx)$$

is an eigenfunction of the Hamiltonian, yet it is not an eigenfunction of the momentum operator:

$$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} C \cos(kx) = iCk\hbar \sin(kx)$$

In other words, the momentum of this wavefunction is ill-defined. However, we can get a physical picture of this condition if we realize that

$$C \cos(kx) = \frac{C}{2} (e^{ikx} + e^{-ikx})$$

Which suggests that we are dealing with a particle that is traveling to the right with a momentum $k\hbar$ with probability $|C|^2$, and to the left with a momentum of similar magnitude and probability. The average linear momentum is thus zero, as we can also verify through taking the expectation value of the momentum operator:

$$\begin{aligned} \langle \psi | \hat{p}_x | \psi \rangle &= -\frac{\hbar C^2}{4i} \int (e^{-ikx} + e^{ikx}) \frac{d}{dx} (e^{ikx} + e^{-ikx}) dx \\ &= -\frac{\hbar C^2}{4i} \left\{ \int ik (1 - e^{2ikx} + e^{-2ikx} - 1) dx \right\} \\ &= -\frac{\hbar k C^2}{4} \left\{ -\int e^{2ikx} dx + \int e^{-2ikx} dx \right\} \\ &= -\frac{\hbar k C^2}{4} \left\{ -\int e^{2ikx} dx + \int e^{2ikx} dx \right\} \\ &= 0 \end{aligned}$$

So, the expectation value of the momentum operator is still well-defined.

Potential Barriers in Free Space

A Semi-infinite Potential Wall

A semi-infinite wall divides space up in two zones. Zone I where the potential energy is zero and zone II where the potential energy is V . We can think of this as a step function centered at $x = 0$. We consider the wavefunction in each of the zones:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \\ \psi_{x<0} &= e^{ikx} + Re^{-ikx} \quad \rightarrow \quad k = \frac{\sqrt{2mE}}{\hbar}\end{aligned}$$

This is an oscillating function in free space. From the flux we learn that it involves a wave traveling to the right with a reflected portion $|R|^2$:

$$\begin{aligned}J &= \frac{\hbar}{2im} [(e^{-ikx} + R^*e^{ikx})(ike^{ikx} - ikRe^{-ikx}) - c.c.] \\ &= \frac{\hbar k}{m} (1 - |R|^2)\end{aligned}$$

For zone II we find:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \\ \psi_{x>0} &= Se^{ikx} + Te^{-ikx} \quad \rightarrow \quad k = \frac{\sqrt{2m(E-V)}}{\hbar}\end{aligned}$$

In zone II the total energy of the system is less than the potential energy of the barrier, hence $E - V < 0$. This implies that we are taking the square root of a negative number, which yields an imaginary number in return. We thus write:

$$\begin{aligned}k &= \frac{\sqrt{2m(E-V)}}{\hbar} = i \frac{\sqrt{2m(V-E)}}{\hbar} = i\kappa \\ \kappa &= \frac{\sqrt{2m(V-E)}}{\hbar} = -ik\end{aligned}$$

We can now write the wavefunction as follows:

$$\psi_{x>0} = Te^{-\kappa x}$$

We see that in zone II the wavefunction is not an oscillating function anymore but a decaying function instead. We can solve for R and T by applying the conditions of a well-behaved wavefunction near the boundary of the potential wall at $x = 0$. Amplitude continuity:

$$1 + R = T$$

Slope continuity:

$$ik(1 - R) = -\kappa T$$

We thus find for R and T :

$$\begin{aligned} R &= \frac{ik+\kappa}{ik-\kappa} \rightarrow |R|^2 = \frac{k^2 + \kappa^2}{k^2 + \kappa^2} = 1 \\ T &= \frac{2ik}{ik-\kappa} \rightarrow |T|^2 = \frac{4k^2}{k^2 + \kappa^2} \end{aligned}$$

Because there is no time dependence, the flux on the right must equal the flux on the left:

$$\begin{aligned} J_{x<0} &= J_{x>0} \\ \frac{\hbar k}{m}(1 - |R|^2) &= J_{x>0} \end{aligned}$$

Because $|R|^2 = 1$, $J_{x>0}$ must be zero. We can verify this by calculating $J_{x>0}$ explicitly:

$$J_{x>0} = \frac{-\hbar\kappa|T|^2}{im} [e^{-2\kappa x} - e^{-2\kappa x}] = 0$$

Hence, there is no net flux in the wall. When $V > E$, all of the wave is reflected at the wall, similar to classical mechanics. However, there is still a finite transmission into the wall, because $|\psi_{x>0}|^2 = |T|^2 e^{-2\kappa x} = \frac{4k^2}{k^2 + \kappa^2} e^{-2\kappa x}$ is finite. This is very much unlike classical mechanics.

We can define $1/\kappa$ as the penetration depth. Let's now consider a particle with kinetic energy $1.6 \cdot 10^{-19}$ and a potential barrier of $3.2 \cdot 10^{-19}$. We then find for the penetration depth for particles of different mass:

$$\begin{aligned} 1/\kappa &= \frac{\hbar}{\sqrt{2m(V - E)}} = \frac{1.054 \cdot 10^{-34}}{\sqrt{3.2 \cdot 10^{-19} \cdot m}} \\ &= 0.2 \cdot 10^{-17} \text{ nm} \rightarrow m = 1 \text{ kg} \\ &= 0.2 \text{ nm} \rightarrow m = 9.109 \cdot 10^{-31} \text{ kg} \end{aligned}$$

Barrier of Finite Width

For a barrier width finite width, we can identify three zones: zone I with $V(x) = 0$, zone II with $V(x) = V$ for $0 \leq x \leq L$, and zone III with $V(x) = 0$. The wavefunctions in each of these zones are thus found as:

$$\begin{aligned} \psi_I &= e^{ikx} + Re^{-ikx} \\ \psi_{II} &= Ae^{-\kappa x} + Be^{\kappa x} \\ \psi_{III} &= Te^{ikx} \end{aligned}$$

We set $E - V < 0$ and consider what happens to a particle traveling to the right. What is the chance of the particle making it through? Similar to the previous

example, we must solve for the coefficients at the boundaries. In this case, the calculation is a little more tedious but we can find for the transmission:

$$\begin{aligned} |T|^2 &= \frac{(4k\kappa)^2}{(k^2 + \kappa^2)^2(e^{-\kappa L} - e^{\kappa L})^2 + (4k\kappa)^2} \\ &= \left(1 + \frac{(e^{-\kappa L} - e^{\kappa L})^2}{16E(1 - E/V)/V}\right)^{-1} \end{aligned}$$

This number can be interpreted as the *tunneling probability*. Tunneling is a very important quantum mechanical property that has no classical analog. The following aspects should be recognized:

- The probability of transmission is larger for shorter L
- The probability is larger when the particle has more energy E
- The probability is larger for smaller potential energy V
- The probability is larger for particles with low mass m

We now set $E - V > 0$. This situation is quite different. The particle has now enough energy to overcome the barrier. Classically, the particle would simply make it over the barrier. In quantum mechanics, however, there is still a finite probability that the particle will be reflected. This phenomenon is called *anti-tunneling* or *nonclassical reflection*. The probability of transmission is:

$$|T|^2 = \left(1 + \frac{\sin^2(kL)}{4E(1 - E/V)/V}\right)^{-1}$$

Note the following:

- The probability is an oscillating function, reflecting the wave-like character of the particle.
- The probability of transmission is less for barriers with larger V and/or longer L
- The probability of transmission approaches 1 for larger kinetic energy E

Wavepackets

We have looked at functions of the form e^{ikx} that were solutions of the Schrödinger equation and eigenfunctions of the momentum operator. What if our particle is was prepared by a rather undefined energy, i.e. the wavefunction cannot be described as a single eigenfunction of the Hamiltonian? We now must make a combination of Hamiltonian eigenfunctions to describe the particle's state. A linear superposition gives:

$$\Psi = \sum_k g_k \psi_k$$

Where each wavefunction is given as $\psi_k = e^{ikx}$ and g_k is the coefficient for each ψ_k . In case we need many functions to describe the particle's state, we may replace the summation by an integration:

$$\Psi(x) = \int g(k)\psi_k dk = \int g(k)e^{ikx} dk$$

This looks like a *Fourier Transformation* of the function $g(k)$. The result is a superposition of many waves, leading to a *wavepacket*. Instead of a single wave, the particle is now described by a wavepacket that peaks at a given x' . The peak location corresponds to the point where all the waves constructively interfere. The functions also move as a function of time, and consequently, the wavepacket moves along x , peaking at $x'(t)$. Making use of Fourier transformation techniques, we can find a reverse connection between the shape of the wavefunction and the shape of $g(k)$:

$$g(k) = \frac{1}{2\pi} \int \Psi(x)e^{-ikx} dx$$

The 'width' of $\Psi(x)$ and of $g(k)$ are related. This is yet another expression of the uncertainty in the dimensions x (space) and k ($\hbar k$ is momentum).

Connection with De Broglie

We have used the number k to label different solutions of the Schrödinger wave equation. These numbers appear in the form $\cos(kx)$ or $\sin(kx)$, in other words, they have a relation to the wavelength of the oscillating eigenfunction. The wavelength is usually defined as the length λ in which a full oscillation of the form $\sin(ax)$ has been completed:

$$a\lambda = 2\pi \quad \rightarrow \quad a = \frac{2\pi}{\lambda}$$

Comparing this general expression with the specific solutions of the wave equation:

$$\sin(2\pi x/\lambda) \quad \rightarrow \quad \sin(kx)$$

indicates that $k = 2\pi/\lambda$. The number k is often referred to as the *wavevector* of the wavefunction. We also recognize that for eigenfunctions of the Hamiltonian, the momentum is found in the form $p = k\hbar$. Therefore we can find:

$$p = k\hbar = \frac{2\pi}{\lambda} \cdot \hbar = \frac{h}{\lambda}$$

which is the well-known de Broglie relation. We see that this relation follows quite naturally from the quantum mechanical analysis. The reason is that in quantum mechanics, motion is expressed in terms of wavefunctions which have a characteristic wavelength λ . This is a determining factor in the total energy of the system, and thus also in the momentum of the system. Wavelike properties show up in observables like the momentum. In classical mechanics, this relation is less clear, because motion is not generally expressed as wavelike.

Special Potentials

In this section we examine two very important potential wells: a particle in a box and a particle in a parabolic potential. These are two model potentials that we will find very useful in applications of quantum mechanics to atomic and molecular systems.

Particle in One-dimensional Box

The 'box' potential is defined as:

$$\begin{aligned} V &= \infty & \rightarrow & x < 0 \\ V &= 0 & \rightarrow & 0 \leq x \leq L \\ V &= \infty & \rightarrow & x > L \end{aligned}$$

We know that for the part where $V = 0$ we can solve for the wavefunction:

$$\psi = Ae^{ikx} + Be^{-ikx}, \quad k = \sqrt{2mE}/\hbar$$

At the boundaries $x = 0$ and $x = L$, the potential is infinite. A potential solution of the form $Ce^{-\kappa x}$ would yield zero because $\kappa \rightarrow \infty$ for an infinite barrier. The boundary conditions are thus:

$$\begin{aligned} \psi(0) &= 0 \\ \psi(L) &= 0 \end{aligned}$$

From the first condition we find:

$$\psi(0) = A + B = 0 \quad \rightarrow \quad B = -A$$

From the second condition we get, using $B = -A$:

$$\psi(L) = A(e^{ikL} - e^{-ikL}) = 2Ai \sin(kL) = 0 \quad \rightarrow \quad k = n\pi/L \quad n = 1, 2, \dots$$

We can thus write for the wavefunction and the energy E :

$$\begin{aligned} \psi(x) &= C \sin\left(\frac{n\pi x}{L}\right) \\ E &= \frac{k^2 \hbar^2}{2m} = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, \dots \end{aligned}$$

Note the following:

- Both the wavefunction and the energy are *quantized*. The quantum number is n , which labels different possible solutions of the wave equation under the current boundary conditions. Quantization is a direct result of the boundary conditions, as we did not see this for free space solutions without boundaries.
- The separation of the different wave functions and energy levels depends on length L of the box. For shorter L , the energy levels are farther apart. More confinement leads to stronger quantization.
- The separation of the energy levels also depends on the mass m . Quantization is stronger for lighter particles. Hence, heavy objects are less likely to have sharply separated energy levels.
- The lowest energy is $E = h^2/8mL^2$. This is the zero-point energy. The lowest possible energy is thus a finite number. This is related to the fact that the wavefunction always exhibits curvature in order to fit in the box, and curvature is related to the kinetic energy.

Particle in Two-dimensional Box

We can expand this problem to more dimensions. The two-dimensional Hamiltonian for the particle in a two-dimensional box is given as:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right)$$

We can make use of the technique of separation of variables for writing two separate equations for x and y . The result is:

$$\begin{aligned} \psi(x, y) &= \psi_x \psi_y = A_x A_y \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \\ E(n_x, n_y) &= E(n_x) + E(n_y) = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \end{aligned}$$

Note that there are now two quantum numbers (n_x, n_y) that define the wavefunctions and energies. We may encounter the situation in which two different wavefunctions have the same energy. The wavefunctions are then said to have degenerate energies. This is especially the case if the system exhibits symmetry, such as when the 2D box is square and $L_x = L_y$. The following wavefunctions have different quantum labels but exhibit the same energy:

$$\begin{aligned} \psi_{31} &= A_3 A_1 \sin\left(\frac{3\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right), & E &= \frac{h^2}{8mL^2}(3^2 + 1) \\ \psi_{13} &= A_1 A_3 \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{3\pi y}{L}\right), & E &= \frac{h^2}{8mL^2}(1 + 3^2) \end{aligned}$$

Particle in a Parabolic Well

We now turn to a parabolic potential. This potential is intimately related to the harmonic oscillator and is a model for vibrational motion in general. The potential is a function of the force constant k and has the following form:

$$V = \frac{1}{2}kx^2$$

and the Schrödinger equation is written as:

$$\hat{H}\psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi + \frac{1}{2}kx^2 \psi = E\psi$$

Despite its simplicity, solving this equation is rather burdensome. Instead, we turn directly to the solutions. The energies in the parabolic potential are given by:

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega \quad \omega = \left(\frac{k}{m}\right)^{1/2} \quad \nu = 0, 1, 2, \dots$$

The corresponding wavefunctions are found as:

$$\psi_\nu = N_\nu H_\nu(y) e^{-y^2/2} \quad y = \frac{x}{\alpha} \quad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

where

- $H_\nu(y)$ are the Hermite polynomials. We obtain the exact expression from a table. For example, $H_0 = 1$ and $H_1 = 2y$
- N_ν is a normalization constant. It is given by $N_\nu = (2^\nu \nu! \pi^{1/2} \alpha)^{-1/2}$

The wavefunctions describe the motion of a quantum mechanical harmonic oscillator. Let's have a closer look at the properties of this harmonic oscillator.

- The separation between energy levels is $E_{\nu+1} - E_\nu = \hbar\omega$. This result is intimately linked to the parabolic well: all the energy levels are equidistant.
- The level spacing increases for larger force constants k . This implies that for steeper wells, the quantization is stronger. This is yet another manifestation of larger quantization for more confined potentials, a general trend in quantum mechanics.
- The wavefunctions can penetrate the 'wall' to a certain extent because the wall is not of infinite potential. This is different from the particle in a box.

- The particle has both kinetic and potential energy in a parabolic well. The kinetic and potential contributions are linked through the *virial theorem* which states that if the potential energy is of the form $V = ax^s$ then

$$2 \langle T \rangle = s \langle V \rangle$$

For the harmonic oscillator $s = 2$ and thus $\langle T \rangle = \langle V \rangle$: the *average* kinetic and potential energy are of similar magnitude.

- For higher energetic wavefunctions, the probability density of the wave gets larger near the walls of the potential well. This complies with approaching the classical limit, in which a pendulum spends relatively more time at its turning points.
- Similar to the particle in a box, there is a zero-point energy. When $\nu = 0$, the energy is $E = \frac{1}{2} \hbar \omega$.

Particle on a Ring

We previously discussed the behavior of particles in confined potentials such as the box potential and the parabolic potential. We now turn to another important class of systems: systems with rotational symmetry. We now move one step closer to the world of atoms, as atomic systems exhibit a great deal of rotational symmetry. Here we will find out what wavefunctions confined to circular motion look like.

Hamiltonian and Schrödinger Equation

Consider a particle moving on a ring. Important parameters are the radius r and the angle ϕ . From classical physics we know that:

| unit | translational | rotational |
|-------------|------------------------------------|---|
| 'mass' | m | $I = mr^2$ |
| momentum | $p = m \cdot v$ | $l = I \cdot \omega$ |
| kin. energy | $\frac{p^2}{2m} = \frac{1}{2}mv^2$ | $\frac{l^2}{2I} = \frac{1}{2}I\omega^2$ |

It is helpful to use the polar coordinates (r, ϕ) instead of the cartesian coordinates (x, y) . They are related through $x = r \cos \phi$ and $y = r \sin \phi$. With $V = 0$ anywhere on the ring, the two-dimensional Hamiltonian can now be written as:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + \frac{1}{r^2} \frac{d^2}{d\phi^2} \right)$$

As long as we are dealing with a perfect circular motion, r will be constant and all derivatives to r will be zero. The Hamiltonian then simply becomes:

$$\hat{H} = -\frac{\hbar^2}{2mr^2} \frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2}$$

The Schrödinger equation takes then on the form, writing the angular wavefunction as $\Phi(\phi)$ which depends only on ϕ :

$$\begin{aligned} \hat{H}\Phi(\phi) &= -\frac{\hbar^2}{2I} \frac{d^2\Phi(\phi)}{d\phi^2} = E\Phi(\phi) \\ \frac{d^2\Phi(\phi)}{d\phi^2} &= -\frac{2IE}{\hbar^2}\Phi(\phi) \end{aligned}$$

The general solutions of this equation take on the familiar form:

$$\Phi(\phi) = Ae^{im_l\phi} + Be^{-im_l\phi} \quad m = \left(\frac{2IE}{\hbar^2} \right)$$

where m_l plays a similar role as the label k we encountered for non-circular translational motion.

The Wavefunctions and Energies

The wavefunctions are again oscillatory functions, this time along a ring. The real part behaves like a cosine whereas the imaginary part is a sine wave:

$$e^{im_l\phi} = \cos(m_l\phi) + i\sin(m_l\phi)$$

We can find the specific form of the wavefunction from the general solution by taking into consideration the boundary conditions for motion on a ring. One boundary condition is that at any given point along the ring the wave needs to have same amplitude after it completes a full rotation of 2π . If this condition is not fulfilled, the wavefunction would not be single-valued, which is not allowed. We thus need to fulfill:

$$\begin{aligned} e^{im_l(\phi+2\pi)} &= e^{im_l\phi} \\ e^{i2\pi m_l} &= 1 \\ \rightarrow m &= 0, \pm 1, \pm 2, \dots \end{aligned}$$

This confines the values of m_l to integers. The normalized wavefunction takes on the form:

$$\Phi(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} e^{im_l\phi}$$

We can leave the $e^{-im_l\phi}$ function out here because m_l can take on both positive and negative values. It is important to remember that the resulting wavefunction is complex, it has real and imaginary parts. We may represent it in the form of sine and cosines to get a better physical picture, but the full wavefunction is given as above. From this we see that the probability distribution is uniform along the ring:

$$|\Phi|^2 = \frac{1}{2\pi} e^{-im_l\phi} e^{im_l\phi} = \frac{1}{2\pi}$$

Note that we would not have obtained this result if we would have written the solution in the cosine or sine form. The uniform distribution implies that the average location of the particle is ill-defined. This, in turn, means that we can specify the momentum very precisely.

The energy is expressed as:

$$E = \frac{m_l^2 \hbar^2}{2I}$$

The energy is quantized because m_l takes on only discrete values. Note that we can have a zero-point energy of 0, because m_l is allowed to be zero. This is different from the particle in the box and harmonic potential where we have a nonzero lowest point energy. The reason is that we can give up the precise location of the particle on a ring so that we are allowed to precisely determine the angular momentum, which is related to the energy. We can allow the momentum to be precisely zero, which is the reason why the system can have 0 zero-point energy.

Angular Momentum

We finally turn to another crucial variable for rotational motion: the angular momentum. Classically the angular momentum is defined as a vector that is the vector product of the distance vector \mathbf{r} and the momentum vector \mathbf{p} :

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

Here we will be concerned with the z-component of the angular momentum, which is given as:

$$l_z = xp_y - yp_x$$

Plugging in the operator forms of x and p :

$$\hat{l}_z = x \frac{\hbar}{i} \frac{d}{dy} - y \frac{\hbar}{i} \frac{d}{dx}$$

we can make use of the following relations to write this equation in polar coordinates:

$$\begin{aligned} dx &= \cos(\phi)dr - r \sin(\phi)d\phi \\ dy &= \sin(\phi)dr + r \cos(\phi)d\phi \\ dr &= \sin(\phi)dy + \cos(\phi)dx \\ d\phi &= \frac{1}{r} (-\sin(\phi)dx + \cos(\phi)dy) \\ \frac{d}{dx} &= \frac{dr}{dx} \frac{d}{dr} + \frac{d\phi}{dx} \frac{d}{d\phi} = \cos(\phi) \frac{d}{dr} - \frac{\sin(\phi)}{r} \frac{d}{d\phi} \\ \frac{d}{dy} &= \frac{dr}{dy} \frac{d}{dr} + \frac{d\phi}{dy} \frac{d}{d\phi} = \sin(\phi) \frac{d}{dr} + \frac{\cos(\phi)}{r} \frac{d}{d\phi} \end{aligned}$$

Finally:

$$x \frac{d}{dy} - y \frac{d}{dx} = r \frac{d}{dr} (\sin(\phi) \cos(\phi) - \cos(\phi) \sin(\phi)) + \frac{d}{d\phi} (\sin^2(\phi) + \cos^2(\phi)) = \frac{d}{d\phi}$$

Hence, we find for the angular momentum operator in terms of polar coordinates:

$$\hat{l}_z = \frac{\hbar}{i} \frac{d}{d\phi}$$

Operating on the wavefunction gives for the momentum:

$$\hat{l}_z \Phi(\phi) = \left(\frac{1}{2\pi} \right)^{1/2} \frac{\hbar}{i} \frac{d}{d\phi} e^{im_l \phi} = m_l \hbar \left(\frac{1}{2\pi} \right)^{1/2} e^{im_l \phi} = m_l \hbar \Phi(\phi)$$

The wavefunction is thus an eigenfunction and the z-angular momentum is quantized as $m_l \hbar$.

Particle on a Sphere

We have seen that particles (or waves) in a box potential, a harmonic potential and on a ring are all quantized (for small mass m and confinement in space to small dimensions). We next turn to a particle on a sphere, and excellent model for the electron around the nucleus of the hydrogen atom. From the previous discussions we may anticipate quantization in this system as well.

Hamiltonian and Schrödinger Equation

A particle on a sphere is a 3-dimensional problem best described by the spherical coordinates (r, ϕ, θ) .

$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$

With $V(r, \phi, \theta) = 0$ we can write the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} r + \frac{1}{r^2} \Lambda^2 \right)$$

where Λ^2 is an operator called Legendrian that depends only on the angles (ϕ, θ) and is given by:

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta}$$

For a particle on a sphere, r is constant, so that all derivatives to r disappear and we need only be concerned with the angular part of the Hamiltonian. The Schrödinger equation can be recast as:

$$\begin{aligned}\hat{H}\Psi(\theta, \phi) &= -\frac{\hbar^2}{2mr^2} \Lambda^2 \Psi(\theta, \phi) = E\Psi(\theta, \phi) \\ \Lambda^2 \Psi(\theta, \phi) &= -\left(\frac{2IE}{\hbar^2} \right) \Psi(\theta, \phi)\end{aligned}$$

The wavefunctions and energies follow from solving the latter differential equations.

The Wavefunctions and Energies

Solving the angular Schrödinger equation is cumbersome. Fortunately, the outcome is well-known. The solutions are called the *spherical harmonics*. The spherical harmonics are the product the following functions

- $\Theta(\theta)$ is called the associated Legendre function, it depends only on the azimuth angle θ
- $\Phi(\phi)$ is the 'particle on a ring' function, which depends only on the polar angle ϕ

The spherical harmonics are thus written as:

$$Y_{l,m_l}(\theta, \phi) = \Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$$

The spherical harmonics are quantized and their quantum numbers are l and m_l . They label different solutions of the Schrödinger equation. The allowed values are:

$$l = 0, 1, 2, \dots \quad m_l = l, (l-1), (l-2), \dots, -l$$

The definition of the spherical harmonics are:

$$Y_{l,m_l}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m_l)!}{(l+m_l)!}} P_{l,m_l}(\cos \theta) e^{im_l \phi}$$

where $P_{l,m_l}(x)$ is the associated Legendre polynomial. The associated and the ordinary Legendre polynomials $P_l(x)$ are related through:

$$P_{l,m_l}(x) = (-1)^{m_l} (1-x^2)^{m_l/2} \frac{d^{m_l}}{dx^{m_l}} P_l(x)$$

The P_{l,m_l} polynomials are well tabulated. We find, therefore, the spherical harmonics from tables. The first few spherical harmonics are given as

| l | m_l | $Y_{l,m_l}(\theta, \phi)$ |
|-----|---------|---|
| 0 | 0 | $(2\pi)^{-1/2}$ |
| 1 | 0 | $\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \cos \theta$ |
| 1 | ± 1 | $\mp \frac{1}{2} \left(\frac{3}{2\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$ |

The spherical harmonics form an orthonormal set:

$$\int_0^{2\pi} \int_0^\pi Y_{l,m_l}(\theta, \phi) Y_{l',m_l'}^*(\theta, \phi) \sin \theta d\theta d\phi = \delta_{m_l, m_l'} \delta_{l, l'}$$

The complex conjugate of the spherical harmonic is:

$$Y_{l,m_l}^* = (-1)^{m_l} Y_{l,-m_l}$$

Note the following:

- The quantum numbers l and m_l are linked. They both are a measure of the angular momentum. The magnitude of the momentum is quantized by l , whereas m_l labels the corresponding values for the momentum along the z-axis.
- Similar to the particle on a ring, the probability density $|Y_{l,m_l}|^2$ is uniform along the polar angle, meaning that its location on ϕ is not well-defined.

The energies of this system can be found by realizing that the spherical harmonics satisfy the equation:

$$\Lambda^2 Y_{l,m_l}(\theta, \phi) = -l(l+1)Y_{l,m_l}(\theta, \phi)$$

we then find for the energy:

$$E = l(l+1) \left(\frac{\hbar^2}{2I} \right)$$

The energy does not depend on m_l . For each energy labeled by l , there are $2l+1$ values of m_l . Each energy level is thus $2l+1$ fold degenerate. Note also that there is no zero-point energy, for reasons similar to the ones of the particle on a ring system.

Angular Momentum

In three dimensions, we can think of the angular momentum as a vector with a magnitude and projections onto the x , y and z axes. Both the magnitude and the projections are quantized. The magnitude of the angular momentum depends solely on l and is given by:

$$\{l(l+1)\}^{1/2} \hbar$$

Its projection on the z-axis is labeled by m_l . The magnitude for the z-component of the angular momentum can be found by operating with the \hat{l}_z operator onto the spherical harmonics.

$$\hat{l}_z Y_{l,m_l} = \hat{l}_z \Theta_{l,m_l} \Phi_{m_l} = \Theta_{l,m_l} \hat{l}_z \Phi_{m_l} = m_l \hbar \Theta_{l,m_l} \Phi_{m_l} = m_l \hbar Y_{l,m_l}$$

The projection of the angular momentum onto the z-axis thus takes on the values $m_l \hbar$. It is restricted to only $2l+1$ values for a given l . When the projection on the z-axis is well-determined, we lose information on the x and y -components of the angular momentum. This is a consequence of the fact that the \hat{l}_z does not commute with \hat{l}_x or \hat{l}_y , as we will see in the next chapter.

Rigid Rotor

We can expand our analysis to a two-particle system with masses m_1 and m_2 that rotate with a fixed distance R between them. We can separate out the

translational motion of the system as a whole and their motion relative to one another. Instead of using the separate masses m_1 and m_2 , we can define the joint mass M and the reduced mass μ as follows:

$$\begin{aligned} M &= m_1 + m_2 \\ \frac{1}{\mu} &= \frac{1}{m_1} + \frac{1}{m_2} \end{aligned}$$

Using the technique of the separation of variables, the Schrödinger equation can be split into an equation that depends on the center coordinates and the joint mass M , and an equation that depends on the relative coordinates of the system with reduced mass μ :

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla_M^2 \Psi_M &= E_M \Psi_M \\ -\frac{\hbar^2}{2\mu} \nabla_\mu^2 \Psi_\mu &= E_\mu \Psi_\mu \end{aligned}$$

The total wavefunction is written as $\Psi = \Psi_M \Psi_\mu$ and the total energy is $E = E_M + E_\mu$. We are only concerned with the relative motion of the system. For constant r we then have for the Schrödinger equation:

$$-\frac{\hbar^2}{2I} \Lambda^2 \Psi_\mu = E \Psi_\mu$$

This is the same problem as the particle on a sphere. The solutions are the spherical harmonics and the energies are:

$$E = J(J+1) \frac{\hbar^2}{2I}$$

where the labels J and M_J are used for labeling the states of the rigid rotor.

The Radial Wavefunctions

In the previous section we learned about the wavefunctions and energy levels of a particle on a sphere. This model comes very close to the description of an electron circling around a proton nucleus, i.e. the hydrogen atom. However, we have assumed that the potential energy is zero everywhere. This is certainly not true for the hydrogen atom. The electron experiences a potential which is defined by the Coulombic interaction with the nucleus. In this section we focus on taking this potential into account so that we can solve the wavefunctions for the hydrogen atom system.

The Radial Schrödinger Equation

The Coulombic potential energy is:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The full Hamiltonian of the electron-nucleus system is therefore:

$$\hat{H} = -\frac{\hbar^2}{2m_n} \nabla_{r_n}^2 - \frac{\hbar^2}{2m_e} \nabla_{r_e}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

In order to solve the Schrödinger equation using this Hamiltonian, we need to consider the following points:

1. Separating the degrees of freedom of the electron from those of the nucleus, so that we are only dealing with electronic wavefunctions.
2. Separating the angular motion from the motion in the radial direction. The Coulombic potential only depends on r and is independent of (θ, ϕ) . This suggests that we might be able to solve the problem considering only the radial coordinate.

The first point is readily achieved by writing the Hamiltonian in terms of the center-of-mass coordinates and the relative distance between the nucleus and the electron. For the kinetic energy part it is found that:

$$\begin{aligned} M &= m_n + m_e, & \frac{1}{\mu} &= \frac{1}{m_n} + \frac{1}{m_e} \\ R &= \frac{m_e r_e + m_n r_n}{M}, & r &= r_n - r_e \\ -\frac{\hbar^2}{2m_n} \nabla_{r_n}^2 - \frac{\hbar^2}{2m_e} \nabla_{r_e}^2 &= -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 \end{aligned}$$

The potential energy contribution is only dependent on relative distance r . We then only solve for the relative distance and ignore the overall translational

motion of the atom in space, in which case the Schrödinger equation becomes:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$

$$\frac{1}{r}\frac{d^2}{dr^2}r\psi + \frac{1}{r^2}\Lambda^2\psi + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}\psi = -\left(\frac{2\mu E}{\hbar^2}\right)\psi$$

To achieve the second point, we will write the wavefunction as $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, where $Y(\theta, \phi)$ are the spherical harmonics that are the solutions in the angular dimension. If we substitute these functions into the Schrödinger equation we get:

$$\frac{1}{r}\frac{d^2}{dr^2}rRY - \frac{l(l+1)}{r^2}RY + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}RY = -\left(\frac{2\mu E}{\hbar^2}\right)RY$$

$$\frac{1}{r}\frac{d^2(rR)}{dr^2} + \left\{\frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r} - \frac{l(l+1)}{r^2}\right\}R = -\left(\frac{2\mu E}{\hbar^2}\right)R$$

We first multiply this equation with r , and then define the function $\Pi = rR$. We then can write the Schrödinger equation, which depends only on the radial coordinate r , as:

$$\frac{d^2\Pi}{dr^2} - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}\Pi = -\left(\frac{2\mu E}{\hbar^2}\right)\Pi$$

where the effective potential is defined as:

$$V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Note the following:

- The angular part has been divided out in the Schrödinger equation. The contribution from the angular dimension is implicitly present in the effective potential through the $l(l+1)\hbar^2$ term.
- The coulombic part provides an attractive (negative) potential. The angular term, however, provides a repulsive (positive) potential. These two effects will counterbalance depending on the quantum number l and the distance from the nucleus r .
- The angular centrifugal force is zero for $l = 0$. This implies that the potential is purely attractive and thus that there is a finite chance of finding the electron at the nucleus.
- Close to the nucleus, the angular centrifugal force for $l \neq 0$ is larger than the attractive coulombic force. Consequently, the electron is expelled from the nucleus and the probability of finding the electron at the nucleus is zero.

The Radial Wavefunctions

Solving the radial Schrödinger equation is nontrivial and we therefore rely on specific mathematical tricks for finding the wavefunctions. Fortunately, the outcome to this differential equation is well-known. The wavefunctions take on the form of *associated Laguerre functions* multiplied by a decaying exponential. The radial functions $R_{n,l}$ are labeled by two quantum numbers: the principal quantum number $n = 1, 2, \dots$ and the momentum quantum number $l = 0, 1, \dots, (n - 1)$:

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\} \rho^l L_{n+l}^{2l+1} e^{-\rho/2}$$

where the associated Laguerre function L_n^k is a polynomial given by:

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+k}) = (-1)^k \frac{d^k}{dx^k} [L_{n+k}(x)]$$

We now define:

$$\rho = \left(\frac{2Z}{na} \right) r, \quad a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Then the first few radial wavefunctions $R_{n,l}$ are given by:

| n | l | $\mathbf{R}_{n,l}(\rho)$ |
|----------|----------|---|
| 1 | 0 (1s) | $\left(\frac{Z}{a}\right)^{3/2} 2e^{-\rho/2}$ |
| 2 | 0 (2s) | $\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{2}}(2-\rho)e^{-\rho/2}$ |
| 2 | 1 (2p) | $\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{6}}\rho e^{-\rho/2}$ |

Note the following:

- The radial wavefunction is 0 for $l \neq 0$ and nonzero for $l = 0$
- The number of nodes is $n - l - 1$

The Hydrogen Atomic Orbitals

We are now in a position to construct the atomic orbitals of the hydrogen atom. We will look at their energies, degeneracies and probability distribution in space.

Organization of Atomic Orbitals

The total hydrogenic wavefunction is:

$$\Psi_{n,l,m_l} = R_{n,l,m_l} Y_{l,m_l}$$

The quantum numbers are:

$$\begin{aligned} n &= 1, 2, \dots \\ l &= 0, 1, 2, \dots, n-1 \quad (n-1) \text{ levels} \\ m_l &= 0, \pm 1, \pm 2, \dots, \pm l \quad (2l+1) \text{ levels} \end{aligned}$$

The energies are:

$$E_n = - \left(\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \right) \frac{1}{n^2}$$

Each of these n -levels has $n-1$ different l states, which in turn have $2l+1$ different m_l states. Note the following:

- The energy only depends on the principal quantum number n . The quantum number for the momentum l does not influence the energy.
- Each level n has $(n-1)$ sub-levels of the same energy with $l = 0, 1, \dots, n-1$
- The total number of levels for a given level labeled with l , is $2l+1$, which results from the possible allowed values of the quantum number m_l .
- The energy level spacing decreases quadratically.

The total degeneracy for each level n is:

$$g = \sum_{l=0}^{n-1} 2l+1 = n^2$$

We can visualize the levels schematically as:

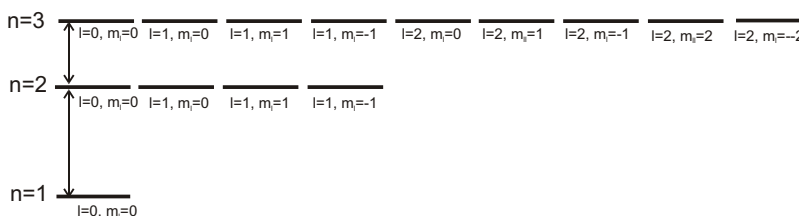


Figure 1: energy diagram

The Probability Distribution

The Hydrogen wavefunctions are normalized over whole space, i.e. the chance of finding the electron wavefunction somewhere must be 1. The normalization condition is:

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi \Psi_{n,l,m_l}^* \Psi_{n',l',m_l'} dV = \delta_{n,n'} \delta_{l,l'} \delta_{m_l,m_l'}$$

where the incremental volume element is defined as:

$$dV = r^2 \sin \theta dr d\theta d\phi$$

The probability density of finding the electron in volume element $dV = r^2 \sin \theta d\theta d\phi dr$ is:

$$|\Psi_{n,l,m_l}|^2 dV$$

What is the probability of finding the electron between the distance r and $r + dr$ from the nucleus? We find this by integrating out the angular part as follows:

$$\begin{aligned} P(r)dr &= \int_\Omega |\Psi_{n,l,m_l}|^2 dV = \int_0^\pi \int_0^{2\pi} R^2 |Y|^2 r^2 \sin \theta dr d\theta d\phi \\ &= R^2 r^2 dr \int_0^\pi \int_0^{2\pi} |Y|^2 \sin \theta d\theta d\phi \\ &= R^2 r^2 dr \end{aligned}$$

We call $P(r) = R^2 r^2$ the radial distribution function. The r^2 takes care of the fact that a surface at distance r from the nucleus expands like r^2 . Hence, for larger r , we are dealing with a larger segment of space, which in turn increases the chance of finding the electron there. Without the r^2 we are not considering the true three-dimensional geometry of the problem.

The most probable distance to find the electron at is obtained by finding r for which $dP/dr = 0$. For the wavefunction $\Psi_{1,0,0}$ this is:

$$\begin{aligned}\frac{dP}{dr} &= \frac{d}{dr} R_{1,0,0}^2 r^2 = 4 \left(\frac{Z}{a}\right)^3 \frac{d}{dr} r^2 e^{-2Zr/a} \\ &= 4 \left(\frac{Z}{a}\right)^3 (2 - 2Zr/a) r e^{-2Zr/a} = 0 \\ &\rightarrow r_{max} = a/Z\end{aligned}$$

with

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \approx \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 = 0.529\text{\AA}$$

where a_0 is known as the Bohr radius.

s-Orbitals

s-Orbitals have zero angular momentum and thus $l = 0$ and $m_l = 0$. The first two levels (1s) and (2s) are given as:

$$\begin{aligned}\Psi_{n,l,m_l} &= R_{n,l,m_l} Y_{l,m_l} \quad l = 0, \quad m_l = 0 \\ \Psi_{1,0,0} &= R_{1,0,0} \left(\frac{1}{2\pi}\right)^{1/2} = \left(\frac{1}{2\pi}\right)^{1/2} \left(\frac{Z}{a}\right)^{3/2} 2e^{-Zr/a} \\ \Psi_{2,0,0} &= R_{2,0,0} \left(\frac{1}{2\pi}\right)^{1/2} = \left(\frac{1}{2\pi}\right)^{1/2} \left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{2}}(2 - Zr/a)e^{-Zr/2a}\end{aligned}$$

Note that:

- Because s-orbitals have no angular dependence, they are spherically symmetric.
- There is a finite chance to find the electron at the nucleus. This chance, however, has to be put in the proper perspective by realizing that at the nucleus the wavefunction has maximum curvature and thus maximum kinetic energy. The electron will therefore 'shoot through' the nucleus instead of sitting permanently at the origin.

p-Orbitals

p-Orbitals are orbitals with $l = 1$. For every n there are 3 p-levels, labeled with $m_l = 0, m_l = 1, m_l = -1$. These three levels are given by:

$$\begin{aligned}p_z &= \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \cos \theta \\ p_+ &= -\left(\frac{3}{8\pi}\right)^{1/2} R_{n,l}(r) \sin \theta e^{i\phi} \\ p_- &= \left(\frac{3}{8\pi}\right)^{1/2} R_{n,l}(r) \sin \theta e^{-i\phi}\end{aligned}$$

It is more custom to combine the last two orbitals and rewrite them as real and imaginary parts. These new combined orbitals align with the x - and y -axis and are therefore easier to visualize. They are given by:

$$p_x = \frac{1}{\sqrt{2}}(p_- - p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \sin\theta \cos\phi$$

$$p_y = \frac{i}{\sqrt{2}}(p_- + p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \sin\theta \sin\phi$$

If we now remember that $x = r \sin\theta \cos\phi$ and that $y = r \sin\theta \sin\phi$, we see that the p_x orbital has 'x'-character and the p_y orbital has 'y'-character. Indeed, these composite orbitals are aligned along the respective axes. Note also that:

- Because of the nonzero angular momentum, p-orbitals have a zero radial probability distribution at the origin.
- The p_x and p_y functions are also valid wavefunctions. In general we can write a linear combination of eigenstates $\psi = A|n\rangle + B|m\rangle$ as a new solution of the Schrödinger equation by choosing the right constants A and B . The p_x and p_y function fulfill this condition.

d-Orbitals

d-Orbitals have angular momentum $l = 2$ and thus occur for levels with $n \geq 3$. There are 5 d-orbitals for every quantum number $n \geq 3$. It is custom to compose linear combinations of these five solutions to end up with wavefunctions with intuitive symmetries:

$$d_{z^2} = d_0 = \left(\frac{5}{16\pi}\right)^{1/2} R_{n2}(r)(3z^2 - r^2)/r^2$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(d_{+2} + d_{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} R_{n2}(r)(x^2 - y^2)/r^2$$

$$d_{xy} = \frac{1}{i\sqrt{2}}(d_{+2} - d_{-2}) = \left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)xy/r^2$$

$$d_{yz} = \frac{1}{i\sqrt{2}}(d_{+1} + d_{-1}) = -\left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)yz/r^2$$

$$d_{zx} = \frac{1}{\sqrt{2}}(d_{+1} - d_{-1}) = -\left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)zx/r^2$$

Mean Radius

The mean radius is defined as the expectation value of r , not to be confused with the most probable radius (found through $d(R_{nl}^2 r^2)/dr = 0$). We can calculate

the mean radius as:

$$\begin{aligned}\langle r \rangle &= \int_V \Psi_{n,l,m_l}^* r \Psi_{n,l,m_l} dV = \int_0^\infty R_{nl}^* r R_{nl} r^2 dr \int_0^{2\pi} \int_0^\pi Y_{l,m_l}^* Y_{l,m_l} \sin \theta d\theta d\phi \\ &= \int_0^\infty R_{nl}^* r R_{nl} r^2 dr = \left(\frac{2Z}{na} \right)^2 \left[\frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^2 \int_0^\infty e^{-\rho} \rho^{2l+3} [L_{n+l}^{2l+1}(\rho)]^2 d\rho\end{aligned}$$

This integral can be solved using standard Laguerre identities (see <http://mathworld.wolfram.com/LaguerrePolynomial.html>). The outcome of this integral is:

$$\langle r \rangle = \frac{n^2 a_0}{Z} \left\{ \frac{3}{2} - \frac{l(l+1)}{2n^2} \right\}$$

Note that the mean radius of an s-orbital is greater than that of a p-orbital for the same principal quantum number (shell), due to the presence of an additional node in the s-orbital ($n - 1$ for s, $n - 2$ for p-orbitals).

Angular Momentum Operators

The angular momentum and its operators play a central role in quantum mechanics. The reason for this is that with the set of angular momentum operator properties we can investigate quantum mechanical systems very thoroughly without turning to the Schrödinger equation, the explicit form of the wavefunctions or even the explicit form of the operators. All we shall use are the operators and their commutation relations, and with it we will be able to draw important conclusions about the corresponding observables.

Magnitude and Projections

We are already familiar with the angular momentum and its projection along the z-axis. Here we will have a closer look at the underlying structure of the classical angular momentum and its quantum mechanical analog.

Classically, the angular momentum is a vector with components along the x, y, z axes:

$$\mathbf{l} = l_x \hat{\mathbf{i}} + l_y \hat{\mathbf{j}} + l_z \hat{\mathbf{k}}$$

It is defined by the vector product of the position vector $\mathbf{r} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}}$ and the linear momentum vector $\mathbf{p} = p_x\hat{\mathbf{i}} + p_y\hat{\mathbf{j}} + p_z\hat{\mathbf{k}}$:

$$\begin{aligned} \mathbf{l} = \mathbf{r} \times \mathbf{p} &= \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\hat{\mathbf{i}} + (zp_x - xp_z)\hat{\mathbf{j}} + (xp_y - yp_x)\hat{\mathbf{k}} \end{aligned}$$

We thus find for the projections of the angular momentum:

$$\begin{aligned} l_x &= (yp_z - zp_y) \\ l_y &= (zp_x - xp_z) \\ l_z &= (xp_y - yp_x) \end{aligned}$$

The magnitude of the angular momentum is:

$$\begin{aligned} l^2 &= (l_x \hat{\mathbf{i}} + l_y \hat{\mathbf{j}} + l_z \hat{\mathbf{k}})^2 \\ &= l_x^2 \hat{\mathbf{i}}^2 + l_y^2 \hat{\mathbf{j}}^2 + l_z^2 \hat{\mathbf{k}}^2 + 2l_x l_y \hat{\mathbf{i}}\hat{\mathbf{j}} + 2l_x l_z \hat{\mathbf{i}}\hat{\mathbf{k}} + 2l_y l_z \hat{\mathbf{j}}\hat{\mathbf{k}} \\ &= l_x^2 + l_y^2 + l_z^2 \end{aligned}$$

In quantum mechanics, we replace the classical expression for position and momentum with the corresponding operator forms. For example:

$$\begin{aligned} \hat{l}_z &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{l}^2 &= \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \end{aligned}$$

We are now in a position to evaluate the commutation relations among the angular momentum operators.

Representations

In this Chapter we will not frequently use the explicit representations of the angular momentum operators in x-space or p-space. However, to draw a parallel with previous chapters, we briefly summarize the explicit forms of the operators. The \hat{l}_z operator, expressed as a function of polar angle ϕ , is given as:

$$\hat{l}_z = \frac{\hbar}{i} \frac{d}{d\phi}$$

Operators of the type \hat{l}_x^2 are written as:

$$\hat{l}_x^2 = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)^2 = -\hbar^2 \left\{ y^2 \frac{d^2}{dz^2} - y \frac{d}{dy} - z \frac{d}{z} + z^2 \frac{d^2}{dy^2} \right\}$$

The angular momentum magnitude operator \hat{l}^2 is the sum of \hat{l}_x^2 , \hat{l}_y^2 and \hat{l}_z^2 . Its form in spherical coordinates is:

$$\hat{l}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} + \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} \right\}$$

We also note that the magnitude of the angular momentum is related to the kinetic energy operator, from which we can directly write down the corresponding eigenvalue equation:

$$\begin{aligned} \hat{T} &= \frac{\hat{l}^2}{2I} \\ \hat{T} |l\rangle &= \frac{l(l+1)\hbar^2}{2I} |l\rangle \\ \hat{l}^2 |l\rangle &= l(l+1)\hbar^2 |l\rangle \end{aligned}$$

Commutation Relations

Recall the following fundamental commutation relations (from here on we will assume that all symbols indicate operators):

$$\begin{aligned} [q, p_{q'}] &= i\hbar \delta_{qq'} \\ [q, q'] &= 0 \\ [p_q, p_{q'}] &= 0 \end{aligned}$$

Another useful relation that we will use frequently is:

$$[A, BC] = B[A, C] + [A, B]C$$

Let us start with evaluating $[l_x, l_y]$:

$$[l_x, l_y] = [yp_z - zp_y, zp_x - xp_z]$$

$$\begin{aligned}
&= [yp_z, zp_x] - [y, x] p_z^2 - z^2 [p_y, p_x] + [zp_y, xp_z] \\
&= [yp_z, zp_x] + [zp_y, xp_z] \\
&= y [p_z, z] p_x + x [z, p_z] p_y \\
&= -yp_x i\hbar + xp_y i\hbar \\
&= i\hbar(xp_y - yp_x) = i\hbar l_z
\end{aligned}$$

By permutation we find the important relations:

$$\begin{aligned}
[l_x, l_y] &= i\hbar l_z \\
[l_y, l_z] &= i\hbar l_x \\
[l_z, l_x] &= i\hbar l_y
\end{aligned}$$

Using these relations we can calculate the commutation relation between the angular momentum magnitude operator l^2 and the components l_x, l_y, l_z :

$$\begin{aligned}
[l^2, l_x] &= [l_x^2 + l_y^2 + l_z^2, l_x] \\
&= [l_y^2, l_x] + [l_z^2, l_x]
\end{aligned}$$

We can evaluate the resulting commutators as:

$$\begin{aligned}
[l_y^2, l_x] &= l_y [l_y, l_x] + [l_y, l_x] l_y \\
&= -i\hbar l_y l_z - i\hbar l_z l_y \\
[l_z^2, l_x] &= l_z [l_z, l_x] + [l_z, l_x] l_z \\
&= i\hbar l_z l_y + i\hbar l_y l_z
\end{aligned}$$

Consequently,

$$[l^2, l_x] = 0$$

Similarly,

$$[l^2, l_y] = 0 \quad [l^2, l_z] = 0$$

From these relations we can conclude the following:

- We cannot simultaneously determine the observables of two components of the angular momentum, as these components do not commute.
- We can determine the magnitude of the angular momentum and one of its components simultaneously. We will use this fact frequently when dealing with atomic and molecular orbitals.

Shift Operators

We can construct linear combinations of the angular momentum operators. Useful combinations are the following:

$$l_+ = l_x + il_y \quad l_- = l_x - il_y$$

These operators are known as the raising and lowering operators, respectively. It is easy to find the following commutation relations for the shift operators:

$$\begin{aligned} [l_z, l_+] &= [l_z, l_x + il_y] = i\hbar l_y + \hbar l_x = \hbar l_+ \\ [l_z, l_-] &= [l_z, l_x - il_y] = i\hbar l_y - \hbar l_x = -\hbar l_- \\ [l_+, l_-] &= [l_x + il_y, l_x - il_y] = -i[l_x, l_y] + i[l_y, l_x] = 2\hbar l_z \end{aligned}$$

The product of the shift operators is written as:

$$l_+ l_- = (l_x + il_y)(l_x - il_y) = l_x^2 + l_y^2 - i[l_x, l_y]$$

From this we write for the operator for the angular momentum magnitude:

$$l^2 = l_x^2 + l_y^2 + l_z^2 = l_+ l_- + l_z^2 + i[l_x, l_y] = l_+ l_- + l_z^2 - \hbar l_z$$

This operator can also be written in the alternative forms:

$$\begin{aligned} l^2 &= l_- l_+ + l_z^2 + \hbar l_z \\ l^2 &= \frac{1}{2}(l_+ l_- + l_- l_+) + l_z^2 \end{aligned}$$

From the commutation relation $[l^2, l_i] = 0$ we can immediately write down the following commutators:

$$\begin{aligned} [l^2, l_+] &= 0 \\ [l^2, l_-] &= 0 \end{aligned}$$

The usefulness of the shift operators will become apparent when we operate on an angular momentum eigenfunction, which we will discuss in the next section.

Eigenvalues of the Angular Momentum

Angular Momentum Relations

We will write the states on which the operators operate as a function of the angular momentum magnitude quantum number l and the z-projection quantum number m_l in the form $|l, m_l\rangle$. From previous sections we know that:

- l_z operating on an eigenstate yields eigenvalue $m_l\hbar$.
- l^2 operating on an eigenstate yields the magnitude of angular momentum $l(l+1)\hbar^2$, which is only dependent on l and not on m_l .
- l_z and l^2 commute and thus share similar eigenstates.

We thus expect the following:

$$\begin{aligned}l_z |l, m_l\rangle &= m_l\hbar |l, m_l\rangle \\l^2 |l, m_l\rangle &= l(l+1)\hbar^2 |l, m_l\rangle\end{aligned}$$

In the following we will show that these relations can be proved from the properties of the angular momentum operators alone without adopting any specific form for the functions $|l, m_l\rangle$. To do this, we shall make extensively use of the shift operators. Before we start we shall examine the effect of the shift operators on the functions $|l, m_l\rangle$.

Effect of Shift Operators

To study the effect of the shift operators, we first consider the operator $l_z l_+$. From the commutation relations we know that:

$$l_z l_+ = l_+ l_z + \hbar l_+$$

When this operator is operating in a function $|l, m_l\rangle$ we thus have:

$$l_z l_+ |l, m_l\rangle = (l_+ l_z + \hbar l_+) |l, m_l\rangle = (m_l + 1)\hbar l_+ |l, m_l\rangle$$

Compare this with:

$$l_z |l, m_l\rangle = m_l\hbar |l, m_l\rangle$$

and we see that the function $l_+ |l, m_l\rangle$ must be proportional to $|l, m_l + 1\rangle$:

$$l_+ |l, m_l\rangle = c_{l, m_l}^+ \hbar |l, m_l + 1\rangle$$

Hence, the l_+ operator raises the z-projection quantum number by 1 when it operates on the function $|l, m_l\rangle$. Similarly we find:

$$l_- |l, m_l\rangle = c_{l, m_l}^- \hbar |l, m_l - 1\rangle$$

The l_- lowers the z-projection quantum number by 1 when it operates on $|l, m_l\rangle$. In both cases, $|l, m_l\rangle$ is not an eigenfunction of l_+ or l_- . What are the values of

the constants c^+ and c^- ? By multiplying the equations above with $\langle l, m_l \pm 1 |$ we get a formal definition of these coefficients:

$$\begin{aligned}\langle l, m_l + 1 | l_+ | l, m_l \rangle &= c_{l, m_l}^+ \hbar \\ \langle l, m_l - 1 | l_- | l, m_l \rangle &= c_{l, m_l}^- \hbar\end{aligned}$$

It is helpful to study first what the complex conjugate of these coefficients are. We have:

$$\begin{aligned}(c_{l, m_l}^+ \hbar)^* &= \langle l, m_l + 1 | l_+ | l, m_l \rangle^* \\ &= \{\langle l, m_l + 1 | l_x | l, m_l \rangle + i \langle l, m_l + 1 | l_- | l, m_l \rangle\}^* \\ &= \langle l, m_l | l_x | l, m_l + 1 \rangle - i \langle l, m_l | l_- | l, m_l + 1 \rangle \\ &= \langle l, m_l | l_- | l, m_l + 1 \rangle \\ &= c_{l, m_l + 1}^- \hbar\end{aligned}$$

From these relations we also see that l_+ and l_- are each others hermitian conjugate, even though each operator is not hermitian by itself (no physical observable is associated with l_+ and l_-). From the above we can conclude that:

$$\begin{aligned}(c_{l, m_l}^+)^* &= c_{l, m_l + 1}^- \\ c_{l, m_l}^- &= (c_{l, m_l - 1}^+)^*\end{aligned}$$

We next consider the effect of the operator $l_- l_+$ on the function $|l, m_l\rangle$:

$$l_- l_+ |l, m_l\rangle = l_- c_{l, m_l}^+ |l, m_l + 1\rangle = c_{l, m_l + 1}^- c_{l, m_l}^+ |l, m_l\rangle = |c_{l, m_l}^+|^2 |l, m_l\rangle$$

We also have:

$$l_- l_+ |l, m_l\rangle = (l^2 - l_z^2 - \hbar l_z) |l, m_l\rangle = [l(l+1) - m_l(m_l+1)] \hbar^2 |l, m_l\rangle$$

And thus it must follow that

$$|c_{l, m_l}^+|^2 = [l(l+1) - m_l(m_l+1)]$$

Which gives

$$\begin{aligned}c_{l, m_l}^+ &= [l(l+1) - m_l(m_l+1)]^{1/2} \\ c_{l, m_l}^- = (c_{l, m_l - 1}^+)^* &= [l(l+1) - m_l(m_l-1)]^{1/2}\end{aligned}$$

We now know the effect of the shift operator in terms of changing the quantum number of the z-projection of the angular momentum. The shift operators do not change the magnitude of the angular momentum, so the quantum number l is unaffected. The reason for this difference is that l_+, l_- commute with l^2 but do not commute with l_z :

$$l^2 l_+ |l, m_l\rangle = l_+ l^2 |l, m_l\rangle = l_+ l(l+1) \hbar^2 |l, m_l\rangle = l(l+1) \hbar^2 l_+ |l, m_l\rangle$$

Derivation Based on Operator Properties Alone

We now try to find the form of the eigenvalues of the magnitude of the angular momentum. We can write the relation as:

$$l^2 |l, m_l\rangle = f(l, m_l) \hbar^2 |l, m_l\rangle$$

where we would like to find $f(l, m_l)$. The observable of l^2 is real and must be non-negative because of the square. We can also conclude that each of its elements (l_x^2, l_y^2, l_z^2), which are hermitian, must have real and non-negative eigenvalues. It follows that:

$$\begin{aligned} (l^2 - l_z^2) |l, m_l\rangle &= l_x^2 + l_y^2 |l, m_l\rangle \geq 0 \\ [f(l, m_l) - m_l^2] \hbar^2 |l, m_l\rangle &\geq 0 \\ \Rightarrow f(l, m_l) &\geq m_l^2 \end{aligned}$$

We start by examining the maximum values of m_l . We know that the projection cannot be larger than the total magnitude of the momentum. We set the maximum value to $m_l = l'$. For the function $|l, l'\rangle$ we thus require:

$$l_+ |l, l'\rangle = 0$$

which also implies that:

$$l_- l_+ |l, l'\rangle = 0$$

And thus

$$\begin{aligned} l_- l_+ |l, l'\rangle &= l^2 - l_z^2 - \hbar l_z |l, l'\rangle = 0 \\ \Rightarrow l^2 |l, l'\rangle &= l_z^2 + \hbar l_z |l, l'\rangle \\ l^2 |l, l'\rangle &= (l'^2 + l') \hbar^2 |l, l'\rangle \end{aligned}$$

Which implies that $f(l, l') = l'(l' + 1)$. This holds for the highest value of m_l only (l'). However, if we step down with the operator l_- on $|l, l'\rangle$ we know that the magnitude of the momentum will not change, only its z-component. Because $l_- l^2 |l, l'\rangle = l'(l' + 1) l_- |l, l'\rangle$ we can write

$$f(l, m_l) = l'(l' + 1) \quad \text{for } m_l = l', l' - 1, \dots$$

How low can we go with m_l ? We have to set the lowest m_l value to $-l'$ so that

$$f(l, m_l) = l'(l' + 1) \quad \text{for } m_l = l', l' - 1, \dots, -l'$$

It is easily shown that indeed the magnitude of the angular momentum has not changed by stepping down the ladder from l' to $-l'$:

$$\begin{aligned} l_+ l_- |l, -l'\rangle &= l^2 - l_z^2 + \hbar l_z |l, -l'\rangle = 0 \\ \Rightarrow l^2 |l, -l'\rangle &= l_z^2 - \hbar l_z |l, -l'\rangle \\ l^2 |l, -l'\rangle &= (-l')^2 \hbar^2 - (-l') \hbar^2 |l, -l'\rangle = l'(l' + 1) \hbar^2 |l, -l'\rangle \end{aligned}$$

It is also clear that $l' = l$, because when we change the magnitude of the angular momentum, the quantum number l' has to change. We thus have

$$l^2 |l, m_l\rangle = l(l+1)\hbar^2 |l, m_l\rangle$$

What are the allowed values for l ? We know that we have to form a symmetrical ladder when stepping down the value for m_l from l to $-l$ in integer steps. Only two types of numbers comply with this demand: integers and half-integers. Consequently, both are allowed. It depends on the characteristics of the system we study whether we can allow l to take on integer or half-integer values. For the orbital angular momentum these were integers because of the cyclic boundary conditions.

Generalization of Momentum: Spin

Because orbital angular momentum is only one form of angular momentum, we will reserve the symbol l for orbital angular momentum and generalize angular momentum as the symbol j , for both the operators and the quantum numbers. As a quantum number j can be an integer or a half-integer. Whereas orbital angular momentum is an example of j an integer, the spin angular momentum has half-integer quantum numbers. We shall write the quantum number as s . It has only one allowed value, which is $s = 1/2$:

$$s = \frac{1}{2} \quad m_s = -\frac{1}{2}, +\frac{1}{2}$$

Consequently, only two eigenstates are possible for the operators s^2 and s_z , which we can write as $\alpha = |\frac{1}{2}, +\frac{1}{2}\rangle$ and $\beta = |\frac{1}{2}, -\frac{1}{2}\rangle$. The actions of the operators on these states are as follows:

$$\begin{aligned} s^2\alpha &= s(s+1)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha \\ s^2\beta &= \frac{3}{4}\hbar^2\beta \\ s_z\alpha &= m_s\hbar\alpha = \frac{1}{2}\hbar\alpha \\ s_z\beta &= -\frac{1}{2}\hbar\beta \end{aligned}$$

For the shift operators we find:

$$\begin{aligned} s_+\alpha &= 0 & s_-\alpha &= \hbar\beta \\ s_+\beta &= \hbar\alpha & s_-\beta &= 0 \end{aligned}$$

Composite Angular Momenta

Combined Angular Momenta

We have seen that for a particle with angular momentum j , we can specify the magnitude and the z component of the angular momentum. The x and y projections are indeterminate once the z component is known. This was the result of the non-commuting properties among the operators \hat{j}_x , \hat{j}_y and \hat{j}_z :

$$[\hat{j}_x, \hat{j}_y] = i\hbar\hat{j}_z \quad [\hat{j}_y, \hat{j}_z] = i\hbar\hat{j}_x \quad [\hat{j}_z, \hat{j}_x] = i\hbar\hat{j}_y$$

What happens now if we have two particles? In the case of two particles with angular momentum we have

- particle 1 with angular momentum j_1 and projections m_{j_1} : $|j_1, m_{j_1}\rangle$
- particle 2 with angular momentum j_2 and projections m_{j_2} : $|j_2, m_{j_2}\rangle$

The angular momenta can be any form of angular momentum such as orbital or spin angular momenta. The permitted values for j are, as before, either integers or half integers. What are we allowed to specify? For this we have to investigate the commutation relations. We know that:

$$\begin{aligned} [\hat{j}_1^2, \hat{j}_2^2] &= 0 \\ [\hat{j}_{z1}, \hat{j}_{z2}] &= 0 \end{aligned}$$

As operators from different particles commute, we may fully specify the angular momentum magnitudes and projections of each particle individually. Hence the eigenvalues of \hat{j}_1^2 , \hat{j}_2^2 , \hat{j}_{z1} and \hat{j}_{z2} ($j_1, j_2, m_{j_1}, m_{j_2}$) can all be specified simultaneously. We can write the total state as $|j_1, m_{j_1}; j_2, m_{j_2}\rangle$

The question now is what happens if we *combine* the momenta of the particles. The combined angular momentum is:

$$\hat{j}_c = \hat{j}_1 + \hat{j}_2$$

The combined angular momentum behaves according to the commutation relations of angular momentum. For example, we can look at the commutation relation between its x projection and its y projection:

$$\begin{aligned} [\hat{j}_{c,x}, \hat{j}_{c,y}] &= [\hat{j}_{1x} + \hat{j}_{2x}, \hat{j}_{1y} + \hat{j}_{2y}] \\ &= [\hat{j}_{1x}, \hat{j}_{1y}] + [\hat{j}_{2x}, \hat{j}_{2y}] + [\hat{j}_{1x}, \hat{j}_{2y}] + [\hat{j}_{2x}, \hat{j}_{1y}] \\ &= i\hbar\hat{j}_{1z} + i\hbar\hat{j}_{2z} + 0 + 0 = i\hbar\hat{j}_{c,z} \end{aligned}$$

We see indeed that the combined angular momentum \hat{j}_c has the same properties as any other type of angular momentum. We can thus immediately conclude that:

- magnitude of the combined angular momentum is $\sqrt{j_c(j_c + 1)\hbar^2}$
- it has $2j_c + 1$ z-projections with values $m_{j_c}\hbar$ and $m_{j_c} = j_c, j_c - 1, \dots, -j_c$

The total number of angular momentum observables has now increased. We have the magnitude and projection of each particle individually and the magnitude and projection of their combination. The available quantum number are thus:

$$j_c, m_{j_c}, j_1, m_{j_1}, j_2, m_{j_2}$$

Can these all be determined simultaneously? Let us see if \hat{j}_c^2 commutes with both the magnitude and projection operators of the individual particles.

- Combined and individual magnitudes:

$$[\hat{j}_c^2, \hat{j}_1^2] = [(\hat{j}_1 + \hat{j}_2)^2, \hat{j}_1^2] = 0$$

And also $[\hat{j}_c^2, \hat{j}_2^2] = 0$. The magnitude of the combined angular momentum commutes with each individual angular momentum magnitude. Hence we can specify j_c, m_{j_c}, j_1 and j_2 all at the same time.

- Combined magnitude with individual projections:

$$\begin{aligned} [\hat{j}_c^2, \hat{j}_{1z}] &= [\hat{j}_{c,x}^2, \hat{j}_{1z}] + [\hat{j}_{c,y}^2, \hat{j}_{1z}] + [\hat{j}_{c,z}^2, \hat{j}_{1z}] \\ &= [(\hat{j}_{1x}^2 + 2\hat{j}_{1x}\hat{j}_{2x}), \hat{j}_{1z}] + [(\hat{j}_{1y}^2 + 2\hat{j}_{1y}\hat{j}_{2y}), \hat{j}_{1z}] \\ &= [(\hat{j}_{1x}^2 + \hat{j}_{1y}^2), \hat{j}_{1z}] + 2[\hat{j}_{1x}, \hat{j}_{1z}]\hat{j}_{2x} + 2[\hat{j}_{1y}, \hat{j}_{1z}]\hat{j}_{2y} \\ &= [(\hat{j}^2 - \hat{j}_{1z}^2), \hat{j}_{1z}] - 2i\hbar\hat{j}_{1y}\hat{j}_{2x} + 2i\hbar\hat{j}_{1x}\hat{j}_{2y} \\ &= 2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x}) \end{aligned}$$

The magnitude of the combined angular momentum does not commute with the z-projections of the individual momenta. We cannot both specify the quantum number j_c and z-projections m_{j_1} and m_{j_2} of the individual momenta.

Coupled and Uncoupled Picture

We can now distinguish two pictures in which we either specify j_c or the z-projections of the individual momenta.

1. Coupled picture

The combined angular momentum is specified, whereas the z-projections j_{1z} and j_{2z} are indeterminate.

Known: $j_c, m_{j_c}(= m_{j_1} + m_{j_2}), j_1, j_2$

Unknown: m_{j_1}, m_{j_2}

In the coupled picture the total state can be written as $|j_c, m_{j_c}; j_1, j_2\rangle$

2. Uncoupled picture

The individual angular momenta j_1, j_2 and their z-projections j_{1z}, j_{2z} are fully specified. The combined z-projection is $m_j = m_{j_1} + m_{j_2}$, but the magnitude of the combined angular momentum j is unspecified.

Known: $j_1, m_{j_1}, j_2, m_{j_2}, m_{j_c}(= m_{j_1} + m_{j_2})$

Unknown: j_c

In the uncoupled picture the total state can be written as $|j_1, m_{j_1}; j_2, m_{j_2}\rangle$

Each picture is valid, but we can only adopt one at the time. It is a direct result from the commutation relations.

Clebsch-Gordan Series

In the uncoupled picture, a particle with angular momentum j_1 has $2j_1 + 1$ possible angular eigenstates, characterized by the sublabels $m_{j_1} = j_1, j_1 - 1, \dots, -j_1$. If we combine angular momenta of two particles, we thus create

$$(2j_1 + 1)(2j_2 + 1) = 4j_1j_2 + 2j_1 + 2j_2 + 1$$

possible states. In the coupled picture, how many values of j_c does this correspond to? The answer is found in the Clebsch-Gordan series, which predicts the allowed values of j_c as follows:

$$j_c = (j_1 + j_2), (j_1 + j_2) - 1, \dots, |j_1 - j_2|$$

In the coupled picture, we thus have the following structure:

| j_c | number | m_{j_c} |
|-----------------|--------------------------------------|-----------------|
| $j_1 + j_2$ | $2(j_1 + j_2) + 1$ | $m_{j_1+j_2}$ |
| $j_1 + j_2 - 1$ | $2(j_1 + j_2 - 1) + 1$ | $m_{j_1+j_2-1}$ |
| $j_1 + j_2 - 2$ | $2(j_1 + j_2 - 2) + 1$ | $m_{j_1+j_2-2}$ |
| ⋮ | ⋮ | ⋮ |
| ⋮ | ⋮ | ⋮ |
| $ j_1 - j_2 $ | $2 j_1 + j_2 + 1$ | $m_{ j_1+j_2 }$ |
| total | ----- $4j_1j_2 + 2j_1 + 2j_2 + 1$ | |

The coupled and the uncoupled picture thus predict the same number of states, as required. We use the Clebsch-Gordan series only in the coupled picture.

Vector Visualization

The coupled and uncoupled pictures can be schematically depicted.

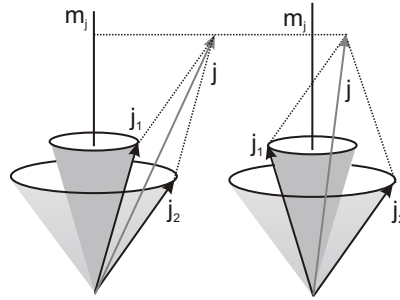


Figure 2: Uncoupled representation. The individual momenta j_1 and j_2 , plus their projections m_{j_1} and m_{j_2} can be specified. The z-projection of the combined momentum (m_j) can be specified, but the magnitude of the combined momentum j remains unspecified. This is a result of the fact that the x and y projections of the individual momenta are indeterminate

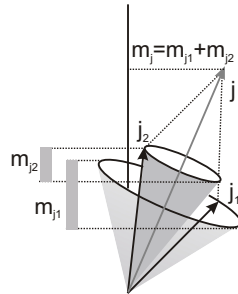


Figure 3: Coupled representation. The individual momenta j_1 and j_2 , the combined angular momentum j and its z-projection m_j can be specified. The z-projection of the individual momenta cannot be specified (j_{1z}, j_{2z}).

Spin coupling

Types of Angular Momentum Coupling

- **Orbital-Orbital Coupling**

The orbital angular momenta l_1 and l_2 of two particles are combined to form a total angular momentum L . Clebsch-Gordan is used to find the allowed values for L . Hence, for two d -electrons ($l_1 = l_2 = 2$) we find $L = 4, 3, 2, 1, 0$. The value for L is usually indicated with capital roman letter as follows:

$$\begin{array}{cccccc} & S & P & D & F & G \\ L = 0 & 1 & 2 & 3 & 4 & \end{array}$$

- **Spin-Spin Coupling**

Because spin is also angular momentum, two spins s_1 and s_2 can also couple. In the coupled picture we define the magnitude of the combined spin as $S = s_1 + s_2$ with projections $M_S = S, S - 1, \dots - S$. In the case of two coupled spins ($s_{1,2} = \frac{1}{2}$), S takes on the values $S = 1, 0$

- **Spin-Orbital Coupling**

The orbital and spin angular momentum may also couple. This is in fact a very important coupling that explains the nature of atomic and molecular spectra. Spin-orbital coupled states are indicated by *term symbols*, the details of which will be discussed in Chapter 7.

Spin-Spin coupling

The combined angular momentum of two spins plays a very important role in quantum chemistry. As mentioned above, two spins can combine. Let us now focus on what the combined states look like in the coupled and the uncoupled picture. Each particle has $s = \frac{1}{2}$ and can adopt the α state or the β state with $m_s = -\frac{1}{2}, \frac{1}{2}$, respectively. The total number of combinations is $(2s+1)(2s+1) = 4$.

- In the uncoupled picture we can write these states as follows:

$$\alpha_1\alpha_2 \quad \alpha_1\beta_2 \quad \beta_1\alpha_2 \quad \beta_1\beta_2$$

- In the coupled picture we have the combined angular momentum $S = s_1 + s_2$ with z-projections $M_S = S, S - 1, \dots, -S$. The maximum value for S is $\frac{1}{2} + \frac{1}{2} = 1$. The possible realizations for S and M_S are thus:

$$S = 1, M_S = 1 \quad S = 1, M_S = 0 \quad S = 1, M_S = -1 \quad S = 0, M_S = 0$$

The $S = 1$ state, with its three realizations $M_S = -1, 0, 1$ is called a **triplet** state. The $S = 0$ state is called a **singlet** state.

Relation between Coupled and Uncoupled States

In the coupled picture we know:

$$j_1, j_2, j = j_1 + j_2, m_j = m_{j_1} + m_{j_2} \rightarrow |j_1 j_2; j m_j\rangle$$

We only know m_j and not the individual values of m_{j_1}, m_{j_2} . In the uncoupled picture we can specify:

$$j_1, m_{j_1}, j_2, m_{j_2}, m_j = m_{j_1} + m_{j_2} \rightarrow |j_1 m_{j_1}; j_2 m_{j_2}\rangle$$

Both wavefunction sets, coupled or uncoupled, are complete sets in which the wavefunctions are orthonormal. The coupled states $|j_1 j_2; j m_j\rangle$ can be related to the uncoupled states $|j_1 m_{j_1}; j_2 m_{j_2}\rangle$ in a linear fashion. Making use of the property of a complete set, we may write the coupled states as a linear combination of the uncoupled states:

$$|j_1 j_2; j m_j\rangle = \sum_{m_{j_1}, m_{j_2}} C_{m_{j_1}, m_{j_2}} |j_1 m_{j_1}; j_2 m_{j_2}\rangle$$

The coefficients represent the overlap integrals between functions of the coupled and the uncoupled sets.

$$\begin{aligned} \langle j_1 m_{j_1}; j_2 m_{j_2} | j_1 j_2; j m_j \rangle &= \sum_{m'_{j_1}, m'_{j_2}} C_{m'_{j_1}, m'_{j_2}} \langle j_1 m_{j_1}; j_2 m_{j_2} | j_1 m'_{j_1}; j_2 m'_{j_2} \rangle \\ \langle j_1 m_{j_1}; j_2 m_{j_2} | j_1 j_2; j m_j \rangle &= C_{m_{j_1}, m_{j_2}} \end{aligned}$$

Let us examine the case of two coupled spins. The complete set consists of four uncoupled states. Our challenge is to find the four coupled states

$$|S, M_S\rangle = |1, 1\rangle, |1, 0\rangle, |1, -1\rangle, |0, 0\rangle$$

as linear combinations of the uncoupled functions

$$\alpha_1 \alpha_2 \quad \alpha_1 \beta_2 \quad \beta_1 \alpha_2 \quad \beta_1 \beta_2$$

We start with observing that the only way we can form the $|1, 1\rangle$ state is by having two spins up ($\frac{1}{2} + \frac{1}{2} = 1$). This is the state $\alpha_1 \alpha_2$:

$$|1, 1\rangle = \alpha_1 \alpha_2$$

Using the same kind of reasoning, we can quickly conclude that

$$|1, -1\rangle = \beta_1 \beta_2$$

We can now use the lowering operator S_- defined in the coupled representation by

$$S_- |S, M_S\rangle = \{S(S+1) - M_S(M_S - 1)\}^{1/2} \hbar |S, M_S - 1\rangle$$

to find $|1, 0\rangle$ by operating on $|1, +1\rangle$:

$$S_- |1, +1\rangle = \sqrt{2}\hbar |1, 0\rangle$$

In the uncoupled representation, the operator S_- is $S_- = s_{1-} + s_{2-}$. We now find for the state $|1, 0\rangle$

$$\begin{aligned} S_- |1, +1\rangle &= (s_{1-} + s_{2-})\alpha_1\alpha_2 \\ &= \left\{ \frac{1}{2}\left(\frac{1}{2} + 1\right) - \frac{1}{2}\left(\frac{1}{2} - 1\right) \right\}^{1/2} \hbar(\alpha_1\beta_2 + \beta_1\alpha_2) \\ &= \hbar(\alpha_1\beta_2 + \beta_1\alpha_2) \end{aligned}$$

Combining the two expressions gives:

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$$

This state has $M_S = 0$. The other state with $M_S = 0$ is the state $|0, 0\rangle$. We can assume a similar form of this wavefunction, because it requires one spin up and one spin down to achieve $M_S = 0$. We thus have:

$$|0, 0\rangle = A\alpha_1\beta_2 + B\beta_1\alpha_2$$

It has, however, to be orthonormal to $|1, 0\rangle$, and thus

$$\begin{aligned} \langle 1, 0|0, 0\rangle &= \left\{ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \right\}^* \{A\alpha_1\beta_2 + B\beta_1\alpha_2\} \\ &= A\frac{1}{\sqrt{2}}\langle\alpha_1\beta_2|\alpha_1\beta_2\rangle + B\frac{1}{\sqrt{2}}\langle\beta_1\alpha_2|\beta_1\alpha_2\rangle \\ &= \frac{1}{\sqrt{2}}(A + B) = 0 \end{aligned}$$

And so, $A = -B$. Normalization of the function then yields:

$$\begin{aligned} \langle 0, 0|0, 0\rangle &= A^2(\alpha_1\beta_2 - \beta_1\alpha_2)^2 \\ &= A^2(\langle\beta_1\alpha_2|\beta_1\alpha_2\rangle + \langle\alpha_1\beta_2|\alpha_1\beta_2\rangle) \\ &= A^2(1 + 1) = 1 \end{aligned}$$

And so, $A = \frac{1}{\sqrt{2}}$. The relation between the coupled spin states and the uncoupled spin states is thus written:

$$\begin{aligned} |1, +1\rangle &= \alpha_1\alpha_2 & |1, 0\rangle &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ |1, -1\rangle &= \beta_1\beta_2 & |0, 0\rangle &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \end{aligned}$$

Perturbation Theory I

Many problems in quantum mechanics cannot be solved with exact methods. We have to turn to approximate methods. Perturbation theory is a widely used approach to find the energies and wavefunctions of more complicated systems.

Notation

In perturbation theory we will make extensive use of the matrix notation. Let us briefly review this notation form. Assume we have a system described by a Hamiltonian with two eigenstates $|n\rangle$ and $|m\rangle$. We can then write:

$$\begin{aligned} H |n\rangle &= E_n |n\rangle \\ H |m\rangle &= E_m |m\rangle \end{aligned}$$

We can multiply each equation with $\langle n|$ or $\langle m|$ from the left and obtain the following terms:

$$\begin{aligned} \langle n| H |n\rangle &= E_n \langle n|n\rangle = E_n \\ \langle n| H |m\rangle &= E_m \langle n|m\rangle = 0 \\ \langle m| H |n\rangle &= E_n \langle m|n\rangle = 0 \\ \langle m| H |m\rangle &= E_m \langle m|m\rangle = E_m \end{aligned}$$

In matrix notation this would be:

$$\begin{aligned} H_{nn} &= E_n & H_{nm} &= 0 \\ H_{mn} &= 0 & H_{mm} &= E_m \end{aligned}$$

And thus the Hamiltonian matrix looks like:

$$\mathbf{H} = \begin{bmatrix} H_{nn} & H_{nm} \\ H_{mn} & H_{mm} \end{bmatrix} = \begin{bmatrix} E_n & 0 \\ 0 & E_m \end{bmatrix}$$

In perturbation theory we will be concerned with Hamiltonians of the form:

$$H = H^{(0)} + H^{pet}$$

where $H^{(0)}$ is our original Hamiltonian with well-defined eigenstates, and H^{pet} is a perturbing term. The matrix elements now become:

$$\mathbf{H} = \begin{bmatrix} H_{nn}^{(0)} + H_{nn}^{pet} & H_{nm}^{(0)} + H_{nm}^{pet} \\ H_{mn}^{(0)} + H_{mn}^{pet} & H_{mm}^{(0)} + H_{mm}^{pet} \end{bmatrix} = \begin{bmatrix} E_n + H_{nn}^{pet} & H_{nm}^{pet} \\ H_{mn}^{pet} & E_m + H_{mm}^{pet} \end{bmatrix}$$

We see that the off-diagonal elements are no longer zero for this new Hamiltonian. Note that the total Hamiltonian is still hermitian, which implies that H^{pet} must be hermitian as well. We thus have:

$$(H_{nm}^{pet})^* = (H^{pet})_{mn}^\dagger = H_{mn}^{pet}$$

We will use these matrix elements throughout the remainder of the Chapter.

Idea Behind Perturbation Theory

Perturbation theory assumes that the solution is close to an exact solution. It describes the system in terms of a simplified Hamiltonian to which we know the wavefunctions and energies, with a small correction to account for the actual complexity of the system. We can therefore write the total Hamiltonian as:

$$H = H^{(0)} + H^{pet}$$

Here $H^{(0)}$ is the Hamiltonian with known energies and wavefunctions, and H^{pet} is the correction, or perturbation to the simplified Hamiltonian. The total Hamiltonian now gives a full description of the system. How do we find the wavefunctions? Generally, we can use the known solutions $|n\rangle$ as a basis set and composing the new solutions from a linear combinations of $|n\rangle$:

$$\Psi = \sum_n c_n |n\rangle$$

This always holds, but it is generally not so straightforward to find the wavefunctions in this fashion. It is more convenient to proceed in steps and find solutions of converging accuracy to the actual wavefunction. Perturbation theory therefore assumes the following. The perturbation Hamiltonian can be written as an expansion, with each element giving a slight correction to the former:

$$\begin{aligned} H &= H^{(0)} + H^{pet} \\ H^{pet} &= \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \end{aligned}$$

where λ is a parameter that indicates the order of the correction. We assume that the energy can be written accordingly:

$$\begin{aligned} E &= E_n + E_n^{pet} \\ E_n^{pet} &= \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned}$$

with $E_n^{(1)}$ the first order correction to the unperturbed energy and $E_n^{(2)}$ the second order correction to the unperturbed energy. The energy is thus close to the unperturbed energy E_0 and we add subsequent orders to arrive at a better approximation for the actual energy. Similarly, we can approach the actual wavefunction step by step as:

$$\begin{aligned} \Psi &= \Psi_n + \Psi^{pet} \\ \Psi^{pet} &= \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots \end{aligned}$$

here, the correction to a state $|n\rangle$ can be written as

$$\begin{aligned} \Psi_n &= |n\rangle \\ \Psi_n^{(1)} &= \sum_n a_n^{(1)} |n\rangle \\ \Psi_n^{(2)} &= \sum_{n'} a_{n'}^{(2)} |n'\rangle \end{aligned}$$

Subsequent orders give a better description of the actual wavefunction Ψ . Most commonly, we will truncate the expansion after one or two corrections if we are satisfied with the result, as higher orders give only incremental improvements of the actual wavefunction.

Two-level Model: Exact Calculation

In the simple case of a two-level system, it is possible to find an exact solution of Ψ with perturbation theory. We have states $|n\rangle, |m\rangle$ defined by:

$$\begin{aligned} H_0 |n\rangle &= E_n |n\rangle \\ H_0 |m\rangle &= E_m |m\rangle \end{aligned}$$

The total Hamiltonian is however perturbed and we thus write:

$$H = H_0 + H^{pet}$$

We are looking for corrections to the wavefunctions to incorporate the effect of the perturbation:

$$\begin{aligned} \Psi(n) &= |n\rangle + \sum_n a_n^{pet} |n\rangle \\ &= |n\rangle + a_n^{pet} |n\rangle + a_m^{pet} |m\rangle \\ &= (1 + a_n^{pet}) |n\rangle + a_m^{pet} |m\rangle \end{aligned}$$

And similarly for $|m\rangle$. We can solve the corrections to the energies E_n and E_m at once by writing the total wavefunction as:

$$\begin{aligned} \Psi(n, m) &= c_n \Psi(n) + c_m \Psi(m) \\ &= c_n \{(1 + a_n^{pet}) |n\rangle + a_m^{pet} |m\rangle\} + c_m \{(1 + a_m^{pet}) |m\rangle + a_n^{pet} |n\rangle\} \\ &= (c_n(1 + a_n^{pet}) + c_m a_n^{pet}) |n\rangle + (c_m(1 + a_m^{pet}) + c_n a_m^{pet}) |m\rangle \\ &= c'_n |n\rangle + c'_m |m\rangle \end{aligned}$$

Renaming the coefficients as c_n and c_m , we can now solve for the Schrödinger equation:

$$\begin{aligned} H\Psi(n, m) &= E\Psi(n, m) \\ c_n(H - E) |n\rangle + c_m(H - E) |m\rangle &= 0 \end{aligned}$$

multiplying by $\langle n|$ and $\langle m|$ yields the two equations:

$$\Rightarrow \begin{cases} c_n(\langle n|H|n\rangle - E) + c_m \langle n|H|m\rangle = 0 \\ c_n \langle m|H|n\rangle + c_m(\langle m|H|m\rangle - E) = 0 \end{cases}$$

solving for c_n and c_m yields the following condition for nontrivial solutions:

$$c_n = -\frac{H_{nm}}{(H_{nn} - E)} c_m$$

$$\begin{aligned}
&\Rightarrow -\frac{H_{nm}H_{mn}}{(H_{nn} - E)}c_m + H_{mm}c_m = 0 \\
&\Rightarrow c_m \left\{ -\frac{H_{nm}H_{mn}}{(H_{nn} - E)} + (H_{mm} - E) \right\} = 0 \\
&\Rightarrow H_{nm}H_{mn} - (H_{nn} - E)(H_{mm} - E) = 0
\end{aligned}$$

we can write this condition also as:

$$\begin{vmatrix} H_{nn} - E & H_{nm} \\ H_{mn} & H_{mm} - E \end{vmatrix} = 0$$

We can solve for the energy E and find the two possible solutions to this quadratic equation:

$$\begin{aligned}
E_+ &= \frac{1}{2}(H_{nn} + H_{mm}) + \frac{1}{2} \{ (H_{nn} - H_{mm})^2 + 4H_{nm}H_{mn} \}^{1/2} \\
E_- &= \frac{1}{2}(H_{nn} + H_{mm}) - \frac{1}{2} \{ (H_{nn} - H_{mm})^2 + 4H_{nm}H_{mn} \}^{1/2}
\end{aligned}$$

A closer look at the diagonal Hamiltonian matrix elements reveals:

$$H_{mm} = H_{mm}^{(0)} + H_{mm}^{pet} = E_m + H_{mm}^{pet}$$

Our discussion will be limited to perturbations with H_{mm}^{pet} (we consider only perturbing Hamiltonians that 'mix' the states, and thus have only nondiagonal elements). We then find for the energies:

$$E_{\pm} = \frac{1}{2}(E_n + E_m) \pm \frac{1}{2} \{ (E_n - E_m)^2 + 4\epsilon^2 \}^{1/2}$$

with $\epsilon^2 = |H_{nm}^{pet}|^2$. This expression is exact. We can, however get more insight into the result by rewriting it under a simple approximation. For small perturbations, i.e. $\epsilon^2 \ll (E_n - E_m)$, the second term can be expanded according to $(1+x)^{1/2} = 1 + \frac{1}{2}x + \dots$, to obtain:

$$E_{\pm} = \frac{1}{2}(E_n + E_m) \pm \frac{1}{2}\Delta E \left(1 + \frac{2\epsilon^2}{\Delta E^2} + \dots \right)$$

with $\Delta E = E_n - E_m$ (we will assume that $|n\rangle$ is of higher energy than $|m\rangle$ so ΔE is positive). We can now observe the following:

- The energy levels are changing because of the perturbation. When the perturbation is zero, i.e. $\epsilon = 0$, the unperturbed energy levels E_n and E_m are retrieved.
- The levels can be written as (to second order in ϵ):

$$\begin{aligned}
E_+ &= E_n + \frac{\epsilon^2}{\Delta E} \\
E_- &= E_m - \frac{\epsilon^2}{\Delta E}
\end{aligned}$$

In other words, one level is lowered in energy, the other is raised.

- A perturbation tends to increase the spacing between the (unperturbed) levels.
- In the case of degenerate levels, i.e. $E_n = E_m$, the splitting is 2ϵ .

Perturbation Theory II

We learned that perturbation theory can be used to calculate the energy and wavefunction for systems that are somewhat different from simple case scenarios. With perturbation theory we can calculate the effect of a small perturbation to the Hamiltonian on the energies and wavefunctions, to arrive at a better description of the system. By looking at a two level system, we saw that:

- A perturbation tends to increase the energy splitting of two levels; the lower level goes down while the higher level goes up.
- A perturbation will mix the unperturbed states to arrive at a new wavefunction which gives a better description of the new system.

Wavefunction and Energies in Two Level Systems

In the case of only two levels $|n\rangle$ and $|m\rangle$, we found that the original energy levels were pulled apart in the presence of the perturbation. We obtained exact expressions for the two (perturbed) energy levels:

$$E_{\pm} = \frac{1}{2}(E_n + E_m) \pm \frac{1}{2} \{\Delta E_{nm}^2 + 4\epsilon^2\}^{1/2}$$

with $\Delta E_{nm} = E_n - E_m$ and $\epsilon^2 = |H_{nm}^{pet}|^2$. In the case of a perturbation small relative to the energy separation ΔE between the levels, we approximated this as follows:

$$E_+ \approx E_n + \frac{\epsilon^2}{\Delta E_{nm}}$$
$$E_- \approx E_m - \frac{\epsilon^2}{\Delta E_{nm}}$$

Once the energies are known, we can solve for the wavefunctions one by one by substituting E_+ or E_- into the Schrödinger equation. Without further proof, we list the perturbed wavefunctions as follows (see Atkins and Friedman, p166):

$$\psi_+ \approx |n\rangle - \frac{\epsilon}{\Delta E} |m\rangle$$
$$\psi_- \approx |m\rangle + \frac{\epsilon}{\Delta E} |n\rangle$$

We see that the perturbation mixes some of the one state into the other. The coefficient of the mixed in state depends on the strength of the perturbation ϵ and the energy separation of the states. The closer in energy, the more mixing takes place.

Multiple Levels: Expansions

We now turn to the more general case of multiple levels. In a multi-level system it is harder to find exact solutions. We will, therefore, make use of the expansion

property in perturbation theory and select the applied perturbation by order. To this end we have for the Hamiltonian, energies and wavefunctions for some arbitrary level m the following:

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \\ E &= E_m + \lambda E_m^{(1)} + \lambda^2 E_m^{(2)} + \dots \\ \Psi &= \Psi_m + \lambda \Psi_m^{(1)} + \lambda^2 \Psi_m^{(2)} + \dots \end{aligned}$$

where λ is the perturbation order parameter. We find solutions, as always, by solving the Schrödinger equation:

$$H\Psi = E\Psi$$

Upon substitution of the expanded Hamiltonian, energy and wavefunction, we obtain a infinite equation. We may sort this equation in terms of λ , and writing λ^0 for the 'zeroth' order:

$$\begin{aligned} &\lambda^0 \left\{ H^{(0)}\Psi_m - E_m\Psi_m \right\} \\ + &\lambda^1 \left\{ H^{(0)}\Psi_m^{(1)} + H^{(1)}\Psi_m - E_m\Psi_m^{(1)} - E_m^{(1)}\Psi_m \right\} \\ + &\lambda^2 \left\{ H^{(0)}\Psi_m^{(2)} + H^{(1)}\Psi_m^{(1)} + H^{(2)}\Psi_m - E_m\Psi_m^{(2)} - E_m^{(1)}\Psi_m^{(1)} - E_m^{(2)}\Psi_m \right\} \\ + &\dots \\ = &0 \end{aligned}$$

Each term in a given order of λ must equal zero individually because λ is an arbitrary parameter. We can then specify the equations for each order separately:

$$\begin{aligned} 0^{th} \quad &H^{(0)}\Psi_m = E_m\Psi_m \\ 1^{st} \quad &\left\{ H^{(0)} - E_m \right\} \Psi_m^{(1)} = \left\{ E_m^{(1)} - H^{(1)} \right\} \Psi_m \\ 2^{nd} \quad &\left\{ H^{(0)} - E_m \right\} \Psi_m^{(2)} = \left\{ E_m^{(2)} - H^{(2)} \right\} \Psi_m + \left\{ E_m^{(1)} - H^{(1)} \right\} \Psi_m^{(1)} \end{aligned}$$

We can now solve the energies and wavefunctions order by order. Lower orders are easier to calculate, and depending on the nature of the problem, we add higher orders to it to improve the result.

Energies

We learned that we may write the higher order corrections to the wavefunction as linear superpositions of the unperturbed wavefunctions:

$$\left| \Psi^{(p)} \right\rangle = \sum_n a_n^{(p)} |n\rangle$$

For solving the first order correction to the energy, we insert the wavefunction with $p = 1$ into the Schrödinger equation first order in the perturbation.

Remember that we can write the function $|\Psi_0\rangle$ simply as $|m\rangle$.

$$\begin{aligned}
\sum_n a_n^{(1)} \{H^{(0)} - E_m\} |n\rangle &= \{E_m^{(1)} - H^{(1)}\} |m\rangle \\
\Rightarrow \sum_n a_n^{(1)} \{E_n - E_m\} |n\rangle &= \{E_m^{(1)} - H^{(1)}\} |m\rangle \\
(\langle m| \times) \Rightarrow \sum_n a_n^{(1)} \{E_n - E_m\} \delta_{mn} &= E_m^{(1)} - \langle m| H^{(1)} |m\rangle \\
&\Rightarrow 0 = E_m^{(1)} - \langle m| H^{(1)} |m\rangle
\end{aligned}$$

We can now solve for $E_m^{(1)}$, the first order correction to the energy:

$$E_m^{(1)} = H_{mm}^{(1)}$$

which is the expectation value of the first order perturbation Hamiltonian. We can apply a similar strategy for the second order correction. We now take $p = 2$ and focus on the Schrödinger equation second order in λ . This gives:

$$\begin{aligned}
\sum_n a_n^{(2)} \{E_n - E_m\} |n\rangle &= \{E_m^{(2)} - H^{(2)}\} |m\rangle + \sum_n a_n^{(1)} \{E_m^{(1)} - H^{(1)}\} |n\rangle \\
\Rightarrow \sum_n a_n^{(2)} \{E_n - E_m\} \delta_{mn} &= E_m^{(2)} - H_{mm}^{(2)} + \sum_n a_n^{(1)} \{E_m^{(1)} \delta_{mn} - H_{mn}^{(1)}\} \\
&\Rightarrow 0 = E_m^{(2)} - H_{mm}^{(2)} + \sum_n a_n^{(1)} \{E_m^{(1)} \delta_{mn} - H_{mn}^{(1)}\}
\end{aligned}$$

Let us look at the last term in this expression. If $n = m$ it is zero because $E_m^{(1)} - H_{mm}^{(1)} = 0$. If $n \neq m$ it equals $-\sum_{n \neq m} a_n^{(1)} H_{mn}^{(1)}$. We thus have:

$$E_0^{(2)} = H_{mm}^{(2)} - \sum_n \{E_m^{(1)} \delta_{mn} - H_{mn}^{(1)}\} = H_{mm}^{(2)} + \sum_{n \neq m} a_n^{(1)} H_{mn}^{(1)}$$

We can obtain an expression for the coefficient $a_n^{(1)}$ by focusing on the Schrödinger equation first order in the perturbation and multiplying it with an arbitrary state $\langle k|$:

$$\begin{aligned}
\sum_n a_n^{(1)} \{E_n - E_m\} \delta_{kn} &= E_0^{(1)} \delta_{km} - H_{km}^{(1)} \\
\Rightarrow a_k^{(1)} \{E_k - E_m\} &= -H_{km}^{(1)} \quad (k \neq m) \\
\Rightarrow a_k^{(1)} &= \frac{H_{km}^{(1)}}{E_m - E_k}
\end{aligned}$$

We thus have

$$E_m^{(2)} = H_{mm}^{(2)} + \sum_{n \neq m} \frac{H_{mn}^{(1)} H_{nm}^{(1)}}{E_m - E_n} = H_{mm}^{(2)} + \sum_{n \neq m} \frac{|H_{mn}^{(1)}|^2}{\Delta E_{mn}}$$

In summary,

$$\begin{aligned} E &= E_m + E_m^{(1)} + E_m^{(2)} + \dots \\ E_m^{(1)} &= H_{mm}^{(1)} \\ E_m^{(2)} &= H_{mm}^{(2)} + \sum_{n \neq m} \frac{|H_{mn}^{(1)}|^2}{\Delta E_{mn}} \end{aligned}$$

Note that we have set the parameter λ to 1.

Wavefunctions

We can write for the wavefunction:

$$\begin{aligned} \Psi &= \Psi_m + \Psi_m^{(1)} + \dots \\ \Psi_m^{(1)} &= \sum_k a_k^{(1)} \Psi_k \\ &= \sum_{k \neq m} \left\{ \frac{H_{km}^{(1)}}{E_m - E_k} \right\} \Psi_k \end{aligned}$$

We see that, indeed, the perturbation mixes other states, weighed by a coefficient, into the original wavefunction. States that are closer to the original level in energy, have a higher coefficient than states that are far away in energy.

Interpretation

From the expressions found for the first and second order correction to the energy and the first order correction to the wavefunction we can conclude the following:

- When a perturbation is present, both the energies and wavefunctions may change.
- When a perturbation is present, the character of a state is mostly affected by states that are nearby in energy. We see that the energy difference ΔE_{mn} is key. States farther away from the original state have a limited effect, whereas states close in energy to the original state will mix in most efficiently.
- The off-diagonal terms of the perturbed Hamiltonian are important. We can see that the new wavefunction to the first order contains corrections by mixing in other states, and that the weight of each depends on the off-diagonal elements $H_{km}^{(1)}$. Mixing of states happens generally through off-diagonal elements of the perturbed Hamiltonian.
- Even though the perturbed Hamiltonian is hermitian, the unperturbed wavefunctions are *not* necessarily eigenfunctions of the corrections $H^{(1)}$,

$H^{(2)}$ etc. From the above we see for instance that $H_{mm}^{(2)} \neq E_m^{(2)}$. Hence, in general, we cannot say that $H_{mm}^{(p)} = E_m^{(p)}$.

Methods of Approximation

From our previous discussion we know that the perturbation corrections to the ground state energy and wavefunctions are calculated as:

$$E = E_0 + H_{00}^{(1)} + \left\{ H_{00}^{(2)} + \sum_{n \neq 0} \frac{H_{0n}^{(1)} H_{n0}^{(1)}}{E_0 - E_n} \right\} + \dots$$

$$\Psi = \Psi_0 + \sum_{k \neq m} \left\{ \frac{H_{km}^{(1)}}{E_m - E_k} \right\} + \dots$$

We will now try to simplify the sum in the second order correction term using the closure approximation, and we will look at the case of degenerate energy levels in which case the denominator of the second order term becomes ill- defined.

Closure Approximation

In certain cases it is useful to make some rough approximations to get a better insight into the effect of perturbations on energy levels. We shall assume the following:

- We will set the level $|m\rangle$ as the ground state level. This is the lowest energy level which we can now write as $|0\rangle$. The energy differences $E_0 - E_n$ are now the energy differences between the ground state and a higher lying state.
- The separation between higher lying levels $|n\rangle$ and $|0\rangle$ is large whereas the difference among the states $|n\rangle$ is small. The higher lying states are thus 'clustered' together, away from the groundstate, a situation that is often encountered in electronic spectroscopic transitions. We can now assume that for all n the energy difference is $E_n - E_0 \approx \Delta E$.

Under these conditions we may write

$$\begin{aligned} E^{(2)} &\approx H_{00}^{(2)} - \frac{1}{\Delta E} \sum_{n \neq 0} H_{0n}^{(1)} H_{n0}^{(1)} \\ &= H_{00}^{(2)} - \frac{1}{\Delta E} \sum_n H_{0n}^{(1)} H_{n0}^{(1)} + \frac{1}{\Delta E} H_{00}^{(1)} H_{00}^{(1)} \\ &= H_{00}^{(2)} - \frac{1}{\Delta E} \left\{ \langle 0 | H^{(1)} H^{(1)} | 0 \rangle - \langle 0 | H^{(1)} | 0 \rangle^2 \right\} \\ &= H_{00}^{(2)} - \frac{\epsilon^2}{\Delta E} \end{aligned}$$

This is called the closure approximation, which gives a useful expression for $E^{(2)}$ without the sum over all the n states.

Perturbation Theory for Degenerate States

For degenerate states the expressions for the perturbation corrections to the energy and wavefunction we derived are nontrivial because the denominator $E_0 - E_m$ may be zero. We can, however, still calculate the effect of perturbations on degenerate states $|0, l\rangle$ using an approach quite similar to the recipe we applied in the case of a two-level system. We focus here on the first order correction and we will write the energies and wavefunctions as:

$$\begin{aligned} E_i &= E_0 + \lambda E_{0i}^{(1)} + \dots \\ \Psi_i &= \phi_{0i} + \lambda \phi_{0i}^{(1)} + \dots \end{aligned}$$

Here is the important difference with our previous case: the wavefunctions ψ_{0i} and $\psi_{0i}^{(1)}$ are written as:

$$\begin{aligned} \phi_{0i} &= \sum_l c_{il} |0, l\rangle \\ \phi_{0i}^{(1)} &= \sum_l a_l |0, l\rangle + \sum_n a_n |n\rangle \end{aligned}$$

That is, the zeroth order wavefunction is a linear combination of the unperturbed degenerate levels $|0, l\rangle$. The label l runs over all the degenerate states with energy E_0 . After the perturbation, however, these energies may be spread out and thus we label the energies and wavefunctions with a new label i . The first order correction is now a combination of the ground state levels (a linear combination instead of a single wavefunction) and all the other levels in the system (which can be nondegenerate). The first order condition from the Schrödinger equation is now:

$$\begin{aligned} &\sum_l a_l \{E_0 - E_0\} |0, l\rangle + \sum_n a_n \{E_n - E_0\} |n\rangle = \sum_l c_{il} \{E_{0i}^{(1)} - H^{(1)}\} |0, l\rangle \\ \Rightarrow &\sum_n a_n \{E_n - E_0\} \langle 0, k|n\rangle = \langle 0, k| \sum_l c_{il} \{E_{0i}^{(1)} - H^{(1)}\} |0, l\rangle \\ \Rightarrow &0 = \sum_l c_{il} \{E_{0i}^{(1)} \langle 0, k|0, l\rangle - \langle 0, k| H^{(1)} |0, l\rangle\} \end{aligned}$$

With $S_{kl} = \langle 0, k|0, l\rangle$ and $H_{kl}^{(1)} = \langle 0, k| H^{(1)} |0, l\rangle$, the last equation can be written as:

$$\begin{aligned} \sum_l c_{il} \{E_{0i}^{(1)} S_{kl} - H_{kl}^{(1)}\} &= 0 \\ \Rightarrow \mathbf{det} |H_{kl}^{(1)} - E_{0i}^{(1)} S_{kl}| &= 0 \end{aligned}$$

These last equations are called the secular equations. Equating the secular determinant to zero allow us to find solutions to the sought after $E_{0i}^{(1)}$.

Variation Theory

Variation theory is another powerful method for finding wavefunctions and energies in systems that do not lend themselves for a direct analytical solution. Variation theory is a trial-and-error method in which we vary a trial wavefunction so that it minimizes the ground state energy. We make use of the following condition:

$$E = \frac{\int \psi_{trial}^* H \psi_{trial} dV}{\int \psi_{trial}^* \psi_{trial} dV} \geq E_0$$

That is, the expectation value of the energy using an arbitrary wavefunction is equal or larger than the ground state energy. This condition is easily verified by writing the (normalized) trial wavefunction in terms of the linear combination of the Hamiltonian's basis set $\psi_{trial} = \sum_n c_n |n\rangle$ and calculating the integral $\langle H \rangle$:

$$\begin{aligned} \langle H \rangle &= \sum_{n,n'} c_n^* c_{n'} \langle n | (H) | n' \rangle \\ &= \sum_{n,n'} c_n^* c_{n'} E_{n'} \delta_{nn'} \\ &= \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 \\ \Rightarrow \langle H \rangle &\geq E_0 \sum_n |c_n|^2 \\ \Rightarrow \langle H \rangle &\geq E_0 \end{aligned}$$

We can parameterize the wavefunctions in various ways. One way is to include an adjustable parameter in the functional form of the wavefunction itself. For instance, if we consider the Hamiltonian for the harmonic oscillator, i.e. $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$, and the trial function of the form $\psi_a = e^{-ax^2}$, we get through variation theory:

$$\begin{aligned} \int \psi_a H \psi_a dV &= \int e^{-ax^2} \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right\} e^{-ax^2} dx \\ &= \frac{\hbar^2}{2m} \int e^{-ax^2} (-2axe^{-ax^2} + 4a^2 x^2 e^{-ax^2}) dx \\ &\quad + \frac{1}{2} k \int x^2 e^{-2ax^2} dx \\ &= -\frac{a\hbar^2}{m} \int x e^{-2ax^2} dx + \left(\frac{2a^2\hbar^2}{m} + \frac{1}{2} k \right) \int x^2 e^{-2ax^2} dx \\ &= 0 + \left(\frac{2a^2\hbar^2}{m} + \frac{1}{2} k \right) \frac{1}{4a} \sqrt{\frac{\pi}{2a}} \\ \int e^{-ax^2} \cdot e^{-ax^2} dx &= \sqrt{\frac{\pi}{2a}} \end{aligned}$$

We thus have

$$E = \frac{\left(\frac{2a^2\hbar^2}{m} + \frac{1}{2}k\right)\frac{1}{4a}\sqrt{\frac{\pi}{2a}}}{\sqrt{\frac{\pi}{2a}}} = \frac{a\hbar^2}{2m} + \frac{k}{8a}$$

Minimizing for a implies $dE/da = 0$:

$$\begin{aligned}\frac{dE}{da} &= \frac{\hbar^2}{2m} - \frac{k}{8a^2} = 0 \\ \Rightarrow a^2 &= \frac{km}{4\hbar^2} \\ \Rightarrow a &= \frac{1}{2}\sqrt{\frac{km}{\hbar^2}}\end{aligned}$$

We thus have for the energy and wavefunction:

$$\begin{aligned}E &= \frac{1}{4}\sqrt{\frac{k}{m}}\hbar + \frac{1}{4}\sqrt{\frac{k}{m}}\hbar = \frac{1}{2}\sqrt{\frac{k}{m}}\hbar \\ \psi_a &= e^{-\frac{1}{2}\sqrt{\frac{km}{\hbar^2}}x^2}\end{aligned}$$

Which are the ground state wavefunction and energy of the harmonic oscillator.

Rayleigh-Ritz Method

Another way to parameterize the wavefunction is to write the trial function as a linear combination of a certain basis set, and vary the coefficients while keeping the functional form of the wavefunctions intact. We thus have

$$\psi_{trail} = \sum_i c_i \psi_i$$

We then get

$$E = \frac{\int \psi_{trail}^* H \psi_{trail} dV}{\int \psi_{trail}^* \psi_{trail} dV} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{i,j} c_i c_j S_{ij}}$$

In the Rayleigh-Ritz method we take the derivative with respect to the coefficients $c_{i,j}$ and set the derivative to zero. Using the chain rule and deriving with respect to each c_i and c_j in the equation above, one can show that:

$$\frac{dE}{dc_k} = \frac{\sum_i c_i (H_{ik} - ES_{ik}) + \sum_i c_i (H_{ki} - ES_{ki})}{\sum_{i,j} c_i c_j S_{ij}} = 0$$

We will assume that the wavefunctions are real functions. In this case, $H_{ik} = H_{ki}$ and $S_{ik} = S_{ki}$. We see that both terms of the nominator become equal. The following condition is then obtained:

$$\sum_i c_i (H_{ik} - ES_{ik}) = 0$$

This is a secular equation for each k , which can be generally solved through:

$$\mathbf{det} |H_{ik} - ES_{ik}| = 0$$

from which we can solve the lowest energy E . The wavefunction coefficients c_i are then found by using the lowest energy in the secular equations.

Hellmann-Feynman Theorem

Above we have seen that we can parameterize the wavefunction and look at the derivative of the expectation value of the energy. Within the variation principle, we look for the minimum energy by equating the derivative of energy to zero. A related problem is how the energy changes when we change the Hamiltonian instead of the wavefunction. This question is answered by the Hellmann-Feynman theorem, which states that :

$$\frac{dE}{dp} = \left\langle \frac{dH}{dp} \right\rangle$$

The usefulness of this relation lies in the fact that we can take the derivative of the Hamiltonian *before* we take its expectation value. This significantly facilitates the calculation in the case that the Hamiltonian is a simple function of p . Nonetheless, this only holds if the wavefunctions used (bra and ket) are already eigenfunctions of the Hamiltonian. This fact requires an independent method of finding the eigenfunctions to the Hamiltonian, after which we can quickly study the change of energy with p .

Time-dependent Perturbation Theory

Time-dependent Schrödinger Equation and Wavefunctions

The time-dependent Schrödinger equation is given by:

$$i\hbar \frac{d\Psi(r,t)}{dt} = H\Psi(r,t)$$

The time-dependent wavefunctions are generally written as:

$$\Psi(r,t) = \psi(r)e^{-iEt/\hbar}$$

If we substitute this wavefunction in the time-dependent Schrödinger equation we see that the time-independent part obeys the time-independent Schrödinger equation:

$$\begin{aligned} i\hbar\psi(r)\frac{de^{-iEt/\hbar}}{dt} &= e^{-iEt/\hbar}H\psi(r) \\ -i\hbar(iE/\hbar)\psi(r)e^{-iEt/\hbar} &= e^{-iEt/\hbar}H\psi(r) \\ \Rightarrow H\psi(r) &= E\psi(r) \end{aligned}$$

Time-dependent Perturbations

We can introduce a perturbation to the Hamiltonian. We will only consider perturbations up to the first order in λ :

$$H = H_0 + \lambda H^{(1)}(t)$$

Similar to time-independent perturbation theory, we can expand the wavefunction in powers of λ :

$$\Psi(r,t) = \Psi^{(0)}(r,t) + \lambda\Psi^{(1)}(r,t) + \lambda^2\Psi^{(2)}(r,t) + \dots$$

The unperturbed wavefunction is again given by

$$\left| \Psi_n^{(0)}(r,t) \right\rangle = |\psi_n(r)\rangle e^{-iE_n t/\hbar} = |n\rangle e^{-iE_n t/\hbar}$$

The higher order wavefunctions are written as an expansion of the unperturbed wavefunctions, using time-dependent coefficients $a_l^{(N)}(t)$.

$$\begin{aligned} \left| \Psi^{(N)}(r,t) \right\rangle &= \sum_l a_l^{(N)}(t) \left| \Psi_l^{(0)}(r,t) \right\rangle \\ &= \sum_l a_l^{(N)}(t) |l\rangle e^{-iE_l t/\hbar} \end{aligned}$$

As before, we substitute the perturbed Hamiltonian and the wavefunctions in the (time-dependent) Schrödinger equation and collect equations in powers of

λ . We get for the lowest orders:

$$\begin{aligned}\lambda = 0 : \quad i\hbar \frac{d\Psi^{(0)}}{dt} &= H_0 \Psi^{(0)} \\ \lambda = 1 : \quad i\hbar \frac{d\Psi^{(1)}}{dt} &= H_0 \Psi^{(1)} + H^{(1)} \Psi^{(0)} \\ \lambda = N : \quad i\hbar \frac{d\Psi^{(N)}}{dt} &= H_0 \Psi^{(N)} + H^{(1)} \Psi^{(N-1)}\end{aligned}$$

The last, most general equation is evaluated as:

$$\begin{aligned}i\hbar \left\{ \sum_l \frac{da_l^{(N)}}{dt} |l\rangle e^{-iE_l t/\hbar} - iE_l/\hbar \sum_l a_l^{(N)} |l\rangle e^{-iE_l t/\hbar} \right\} &= E_l \sum_l a_l^{(N)} |l\rangle e^{-iE_l t/\hbar} \\ &+ H^{(1)} \sum_l a_l^{(N-1)} |l\rangle e^{-iE_l t/\hbar} \\ i\hbar \sum_l \frac{da_l^{(N)}}{dt} |l\rangle e^{-iE_l t/\hbar} &= H^{(1)} \sum_l a_l^{(N-1)} |l\rangle e^{-iE_l t/\hbar}\end{aligned}$$

Multiplying the last equation with $\langle k|$ and using $E_l/\hbar = \omega_l$ yields:

$$\begin{aligned}i\hbar \sum_l \frac{da_l^{(N)}}{dt} \langle k|l\rangle e^{-i\omega_l t} &= \sum_l a_l^{(N-1)} \langle k|H^{(1)}|l\rangle e^{-i\omega_l t} \\ \dot{a}_k^{(N)}(t) &= (i\hbar)^{-1} \sum_l a_l^{(N-1)} H_{kl}^{(1)} e^{-i(\omega_l - \omega_k)t}\end{aligned}$$

We can integrate the derivative out to arrive at the general expression:

$$a_k^{(N)}(t) - a_k^{(N)}(0) = (i\hbar)^{-1} \sum_l \int_0^t a_l^{(N-1)} H_{kl}^{(1)} e^{-i\omega_l \tau} d\tau$$

This expression can be further evaluated with the following boundary conditions:

- It is assumed that the system resides in the ground state $|g\rangle$ before the perturbation occurs.
- The coefficient $a_g^{(0)}(0)$ of the unperturbed state is 1 at $t = 0$, while the coefficients of all the other states are $a_k^{(N)}(0) = 0$
- It is assumed that the perturbation is small and that $a_g^{(0)}$ stays close to its initial value, i.e. $a_g^{(0)}(t) \approx 1$

We can then write for the time dependent coefficient of the state $|k\rangle$ to the first order in N :

$$a_k^{(1)}(t) = (i\hbar)^{-1} \int_0^t H_{kg}^{(1)} e^{-i\omega_{gk} \tau} d\tau$$

Coefficients with higher values of N can be found by substituting the lower order coefficients into the expression for $a_k^{(N)}(t)$. The time-dependent corrections to the wavefunctions are thus expressed through the coefficients $a^{(N)}(t)$. For example, to the first order we have for the ground state wavefunction:

$$|\Psi_g(r, t)\rangle = |g\rangle e^{-i\omega_g t} + (i\hbar)^{-1} \sum_l |l\rangle \int_0^t H_{lg}^{(1)} e^{-i\omega_g t}$$

Two Level Problem

For a two level system, we do not have to write the wavefunction as a complete expansion of multiple unperturbed states. Because the two levels span a complete basis set, we can simply write the perturbed wavefunction in terms of the sum the two functions, with the coefficients to be determined:

$$\Psi = a_1(t) |1\rangle e^{-iE_1 t/\hbar} + a_2(t) |2\rangle e^{-iE_2 t/\hbar}$$

We insert this into the time-dependent Schrödinger equation using $H = H_0 + H^{(1)}$. This yields:

$$\begin{aligned} a_1(t) H^{(1)} |1\rangle e^{-iE_1 t/\hbar} + a_2(t) H^{(1)} |2\rangle e^{-iE_2 t/\hbar} \\ = i\hbar \dot{a}_1(t) |1\rangle e^{-iE_1 t/\hbar} + i\hbar \dot{a}_2(t) |2\rangle e^{-iE_2 t/\hbar} \end{aligned}$$

We now multiply this equation with either $\langle 1|$ or $\langle 2|$ and assume that the perturbation $H^{(1)}$ only has nondiagonal elements, i.e. $H_{11}^{(1)} = H_{22}^{(1)} = 0$. We then get the following time-dependent differential equations for the coefficients a_1 and a_2 :

$$\begin{aligned} \dot{a}_1 &= (i\hbar)^{-1} a_2 H_{12}^{(1)} e^{-i\omega_{21} t} \\ \dot{a}_2 &= (i\hbar)^{-1} a_1 H_{21}^{(1)} e^{-i\omega_{12} t} \end{aligned}$$

We shall assume the following:

- The perturbation is a constant potential energy $H^{(1)} = \hbar V$
- The system is initially ($t = 0$) in state $|1\rangle$, so that $a_1(0) = 1$ and $a_2(0) = 0$.

The coupled differential equations can now be solved by differentiation and substitution. The result is:

$$\begin{aligned} a_1(t) &= \left\{ \cos \Omega t + \frac{i\omega_{21}}{2\Omega} \sin \Omega t \right\} e^{-i\omega_{21} t/2} \\ a_2(t) &= - \left(\frac{i|V|}{\Omega} \right) \sin \Omega t e^{-i\omega_{12} t/2} \end{aligned}$$

with Ω called the Rabi frequency, defined by

$$\Omega = \frac{1}{2}(\omega_{21}^2 + 4|V|^2)^{1/2}$$

The meaning of the time-dependent coefficients will become apparent when we consider the probability of finding the system in a particular state.

Probabilities

Our system started out in $|1\rangle$ before the perturbation was switched on. After the perturbation, the system gains more $|2\rangle$ -character". What is the probability of finding the time-varying system in the state $\Psi_2 = a_2(t) |2\rangle e^{-iE_2t/\hbar}$? We can find this by calculating the overlap integral of Ψ_{tot} with Ψ_2 :

$$\begin{aligned}\langle \Psi_2 | \Psi_{tot} \rangle &= a_2^*(t) \langle 2 | \left\{ a_1(t) |1\rangle e^{-iE_1t/\hbar} + a_2(t) |2\rangle e^{-iE_2t/\hbar} \right\} e^{iE_2t/\hbar} \\ &= |a_2(t)|^2 \langle 2 | 2 \rangle = |a_2(t)|^2\end{aligned}$$

Hence, the square moduli of the time-dependent coefficients give the probability of finding the system in the corresponding state. We can find for the probability of finding the system in $|2\rangle$:

$$P_2(t) = |a_2(t)|^2 = \left(\frac{|V|}{\Omega} \right)^2 \sin^2 \Omega t$$

We see that this is an oscillating function of time, oscillating with frequency Ω , the Rabi frequency. Now consider two limiting cases.

1. The energy separation between the levels is large relative to the strength of the perturbation. The Rabi frequency is now $\Omega \approx \frac{1}{2}\omega_{21}$, and the probability becomes:

$$P_2(t) = |a_2(t)|^2 = \left(\frac{2|V|}{\omega_{21}} \right)^2 \sin^2 \frac{1}{2}\omega_{21}t$$

The system oscillates with a frequency $\frac{1}{2}\omega_{21}$, but never reaches the value 1 because $\frac{2|V|}{\omega_{21}}$ is smaller than 1. The perturbation is not strong enough to push the system from $|1\rangle$ into $|2\rangle$.

2. The energy separation between $|1\rangle$ and $|2\rangle$ is small compared to the strength of the perturbation. The Rabi frequency can now be approximated as $\Omega \approx |V|$. We then find for the probability of finding the system in $|2\rangle$:

$$P_2(t) = |a_2(t)|^2 = \sin^2 |V|t$$

Now the system does reside periodically in $|2\rangle$ because the probability reaches 1 with a frequency $|V|$. The system oscillates back and forth between $|1\rangle$ and $|2\rangle$. The stronger the perturbation, the more rapid the oscillation. The perturbation has "coupled" the two states and, integrated over time, there is an equal chance of finding the system in $|1\rangle$ as in $|2\rangle$.

Effect of Time-dependent Perturbations

Previously we found that the perturbed time-dependent wavefunction is written as:

$$\begin{aligned}\Psi(r, t) &= \Psi^{(0)}(r, t) + \lambda\Psi^{(1)}(r, t) + \dots \\ \rightarrow \Psi_n^{(0)}(r, t) &= |n\rangle e^{-iE_n t/\hbar} \\ \rightarrow \Psi_n^{(1)}(r, t) &= \sum_l a_l^{(1)}(t) |l\rangle e^{-iE_l t/\hbar}\end{aligned}$$

The time-dependent probability of finding the system in a certain state is given by the square modulus of the time-dependent coefficients $|a_n^{(1)}(t)|^2$. From the previous section we know:

$$a_l^{(1)}(t) = (i\hbar)^{-1} \int_0^t H_{lg}^{(1)} e^{-i\omega_{gl}t}$$

Our task is thus to find the behavior of the coefficients to an applied time-varying perturbation $H^{(1)}(t)$.

A Special Form of the Perturbation Hamiltonian

Before we turn to time-dependent perturbations, let us consider a special form of the perturbing Hamiltonian $H^{(1)}$. We have seen that mixing among states occurs through the non-diagonal elements of the perturbation Hamiltonian matrix. It is convenient to express the operator form of the perturbing Hamiltonian in the following way:

$$H^{(1)}(t) = f(t) \{|l\rangle\langle g| + |g\rangle\langle l|\}$$

We then have as the matrix elements in terms of the states $|g\rangle$ and $|l\rangle$:

$$\begin{aligned}H_{gg}^{(1)} &= f(t) \langle g| \{|l\rangle\langle g| + |g\rangle\langle l|\} |g\rangle = 0 \\ H_{ll}^{(1)} &= f(t) \langle l| \{|l\rangle\langle g| + |g\rangle\langle l|\} |l\rangle = 0 \\ H_{gl}^{(1)} &= f(t) \langle g| \{|l\rangle\langle g| + |g\rangle\langle l|\} |l\rangle = f(t) \langle g|g\rangle \langle l|l\rangle = f(t) \\ H_{lg}^{(1)} &= f(t) \langle l|l\rangle \langle g|g\rangle = f(t)\end{aligned}$$

We thus see that this form of the Hamiltonian leads to nonzero non-diagonal elements, while the diagonal elements vanish. This form will be useful in our discussion of time-dependent perturbations.

A Slowly Switched-on Perturbation

Let us consider the following perturbation, which describes a slowly rising function that saturates to a constant value V :

$$H^{(1)}(t) = \begin{cases} 0 & \text{for } t < 0 \\ \hbar V [|l\rangle\langle g| + |g\rangle\langle l|] (1 - e^{-kt}) & \text{for } t \geq 0 \end{cases}$$

where k is a parameter that controls how 'fast' the perturbation is switched on, a larger k means that the constant value V is reached sooner. As we have seen, this perturbation 'couples' two states $|g\rangle$ and $|l\rangle$ and has the zero diagonal elements:

$$\begin{aligned} H_{gl}^{(1)} = H_{lg}^{(1)} &= \hbar V(1 - e^{-kt}) \\ H_{gg}^{(1)} = H_{ll}^{(1)} &= 0 \end{aligned}$$

We thus find for the time-dependent coefficient:

$$\begin{aligned} a_l^{(1)}(t) &= -iV \int_0^t (1 - e^{-kt}) e^{-i\omega_{gl}t} dt \\ &= -iV \left\{ \frac{e^{-i\omega_{gl}t} - 1}{-i\omega_{gl}} + \frac{e^{-(k+i\omega_{gl})t} - 1}{k + i\omega_{gl}} \right\} \end{aligned}$$

This is an oscillating function of frequency ω_{gl} around a median that changes over time. The probability of finding the system in the state $|l\rangle$ after the perturbation is switched on is again given by:

$$P_l(t) = |a_l^{(1)}|^2 = V^2 \left\{ \frac{4k^2 \sin^2(\frac{1}{2}\omega_{gl}t) + \omega_{gl}^2(1 - e^{-kt})^2}{\omega_{gl}^2(k^2 + \omega_{gl}^2)} \right\}$$

$P_l(t)$ is a rather complicated function, and more insight is obtained if we study the behavior of $P_l(t)$ for certain conditions. The first condition we are interested in is its behavior at long times after the perturbation has come very close to its limiting value, i.e. $t \gg 1/k$. In this case, the probability of finding the system in $|l\rangle$ is:

$$P_l(t) = V^2 \frac{1}{k^2 + \omega_{gl}^2} \left\{ \frac{k^2}{\omega_{gl}^2} 4 \sin^2(\frac{1}{2}\omega_{gl}t) + 1 \right\}$$

Which consists of a oscillating function around a constant value. We can further simplify this expression by considering a perturbation that is switched on much slower than the characteristic oscillations of the system, i.e. $k^2 \ll \omega_{gl}^2$. We then have:

$$P_l(t) = \frac{V^2}{\omega_{gl}^2}$$

A constant value, equal to the probability found in case we would have used time-independent perturbation theory ($H^{(1)} = \hbar V$). This limit is relevant because we usually are interested in the effects of a perturbation in the long time limit. Also, many perturbations in chemistry occur on time scales much larger than the relevant motional frequencies of molecules, which justifies the assumption $k^2 \ll \omega_{gl}^2$. This is, however, not the case for rapidly oscillating perturbations, such as a perturbation of a light wave of frequency ω_{gl} to the molecule.

An Oscillating Perturbation

A very important perturbation is the interaction of a molecule with electromagnetic field of frequency ω . We can write the perturbation as:

$$H^{(1)} = 2\hbar V [|l\rangle \langle g| + |g\rangle \langle l|] \cos \omega t = \hbar V [|l\rangle \langle g| + |g\rangle \langle l|] (e^{i\omega t} + e^{-i\omega t})$$

We then have $H_{lg}^{(1)} = \hbar V (e^{i\omega t} + e^{-i\omega t})$ and we can write the time-dependent coefficient as:

$$\begin{aligned} a_l^{(1)}(t) &= -i\hbar V \int_0^t (e^{i\omega t} + e^{-i\omega t}) e^{-i\omega_{gl}t} dt \\ &= -i\hbar V \left\{ \frac{e^{-i(\omega_{gl}-\omega)t} - 1}{i(\omega - \omega_{gl})} + \frac{e^{-i(\omega_{gl}+\omega)t} - 1}{-i(\omega + \omega_{gl})} \right\} \end{aligned}$$

Again, the coefficient is an oscillating function of time. Note, however, that the amplitude of the first term becomes very large when the frequency of the field approaches the characteristic frequency of the molecule, $\omega \rightarrow \omega_{gl}$. The probability of finding the system in state $|l\rangle$ is then only determined by the first term and is written as:

$$P_l(t) = |a_l^{(1)}(t)|^2 = \frac{4V^2}{(\omega - \omega_{gl})^2} \sin^2 \frac{1}{2}(\omega - \omega_{gl})t$$

The probability becomes large in the limit $\omega \rightarrow \omega_{gl}$. We call this the *resonance* condition, which implies that a state can be very efficiently transferred from $|g\rangle$ to $|l\rangle$ when the frequency of the electromagnetic wave approaches the characteristic quantum mechanical frequency of the system. We call $P_l(t)$ therefore the transition probability from the groundstate g to state final state l .

Fermi's Golden Rule

Sometimes the final state l is part of a manifold of other states with energies very close to one another. When this manifold is very dense, we can speak of a continuum of states. In this case, it is useful to use the quantity $\rho(E)$, the density of states, defined as the number of states between E and $E + dE$. The transition probability to states in the vicinity (range) of $|l\rangle$ is now:

$$\begin{aligned} P(t) &= \int_{range} P_l(t) \rho(E) dE \\ &= \int_{range} 4V^2 \frac{\sin^2 \frac{1}{2}(\omega - E_{gl}/\hbar)t}{(\omega - E_{gl}/\hbar)^2} \rho(E) dE \end{aligned}$$

We shall now make the following assumptions:

- The density of states is about constant near our range of interest, i.e. $\rho(E)_{range} \approx \rho_l$.

- The strength of the perturbation V is not dependent on the energy in our range of interest.
- The function under the integrand peaks sharply around level l because the applied field frequency is resonant with ω_{gl} . Consequently, the most significant contribution stems from the range around l and the role of other energy levels is relatively minor. We may now extend the integration boundaries over the entire energy 'space', i.e. we integrate over $[-\infty, \infty]$.

Under these assumptions, the transition probability is:

$$P(t) = 4V^2 \rho_l \int_{-\infty}^{\infty} \frac{\sin^2 \frac{1}{2}(\omega - E_{gl}/\hbar)t}{(\omega - E_{gl}/\hbar)^2} dE$$

To solve this integral we set $x = \frac{1}{2}(E_{gl}/\hbar - \omega)$, so that $dE = (2\hbar/t)dx$. The integral can then be written as:

$$P(t) = \frac{2\hbar}{t} V^2 \rho_l t^2 \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = 2\pi\hbar t V^2 \rho_l$$

The transition rate between these states, written as $W = \frac{dP(t)}{dt}$ is now:

$$W = 2\pi\hbar V^2 \rho_l$$

This is Fermi's Golden Rule for the transition rates between states. It tells us that the rate is proportional to the square of the perturbation strength times the density around the final state l , the state to which the resonance condition applies.

Transitions Between States

We have learned that the transition rate W between eigenstates of a system can be described by Fermi's golden rule. The general expression of Fermi's golden rule is:

$$W_{2\leftarrow 1} = \frac{2\pi}{\hbar} |H_{21}^{(1)}|^2 \rho(E_2 - E_1)$$

which gives $W = 2\pi\hbar V^2 \rho$ for $H_{21}^{(1)} = \hbar V$ and $\rho(E_2 - E_1) = \rho$. The transition rate describes how fast the system can transfer from the ground state $|1\rangle$ to an excited state $|2\rangle$ under the influence of a perturbation $H^{(1)}$. This expression is used extensively to describe the efficiency of molecular excitation by light. The electromagnetic field acts then as the perturbation that couples the two states efficiently under resonance conditions. In the case of the interaction with an electromagnetic field, the perturbation takes on the following form:

$$H_{21}^{(1)} = -\langle 2|\hat{\mu}|1\rangle \cdot E = e\langle 2|\hat{\mathbf{r}}|1\rangle \cdot E$$

where $\hat{\mu}$ is the operator for the transition dipole moment and E is the electric field strength. The transition rate between states in the presence of the radiation becomes:

$$W_{2\leftarrow 1} = \frac{2\pi}{\hbar} |\mu_{21}|^2 E^2 \rho(E_{21})$$

We next want to consider the orientational average of the transition dipole, which implies that $|\mu_{21}|^2 \rightarrow \frac{1}{3}|\mu_{21}|^2$. We also want to rewrite the $E^2\rho(E_{21})$ in terms of the mean energy density of the radiation $\rho_{rad}(E)$. The result of these conversions is:

$$\begin{aligned} W_{2\leftarrow 1} &= \frac{\pi|\mu_{21}|^2}{3\epsilon_0\hbar^2} \rho_{rad}(E_{21}) \\ &= B_{12}\rho_{rad}(E_{21}) \\ B_{12} &= \frac{\pi|\mu_{21}|^2}{3\epsilon_0\hbar^2} \end{aligned}$$

Where we have defined the Einstein coefficient B_{12} . This coefficient is a measure for the rate of absorption of light for the transition $|2\rangle \leftarrow |1\rangle$. This process is, however, not the only mechanism that governs the overall transition rate between two quantum mechanical states. In addition to absorption, there are important relaxation mechanisms that affect the transition rate. We will have a look at these processes next.

Einstein Probability Coefficients

Consider again the levels $|1\rangle$ and $|2\rangle$. The energy separation is

$$\hbar\omega = E_1 - E_2$$

and their relative populations are N_1 and N_2 , respectively. Population here means how much of the state is likely to be occupied. At thermal equilibrium, the relative population is given by Boltzmann's distribution:

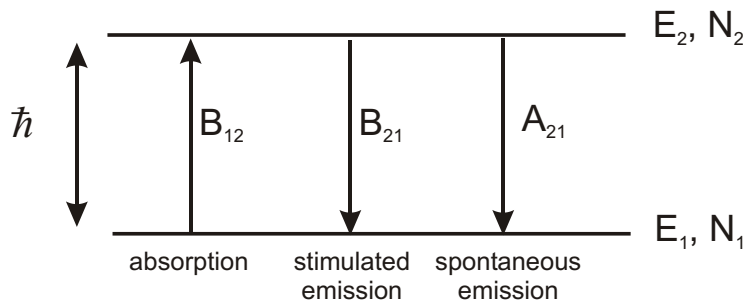
$$\frac{N_2}{N_1} = e^{\hbar\omega/kT}$$

with k the Boltzmann constant and T the temperature. In the presence of electromagnetic fields, this distribution is going to change because of possible transitions between the levels. We thus have to consider all the possible sources of radiation that will affect the population distribution. We can write the total density of radiation at frequency ω as $\rho(\omega)$. The total radiation density is a sum of the thermal radiation $\rho_T(\omega)$ and the electromagnetic field radiation $\rho_E(\omega)$

$$\rho(\omega) = \rho_T(\omega) + \rho_E(\omega)$$

We next need to consider the possible mechanisms for transition between the states. Einstein identified three processes:

- Transition from 1 to 2 due to the radiation density. The probability depends on how much radiation is available. We can write this contribution as $B_{12}\rho(\omega)$, also known as the absorption rate.
- Transition from 2 to 1 due to the radiation density. There is no reason why the radiation can only induce upward transitions, as the backward transition is equally likely to occur. We write this as $B_{21}\rho(\omega)$, also known as the rate of spontaneous emission.
- Transition from 2 to 1 due to spontaneous relaxation to the lowest level. When the system is out of thermal equilibrium, the system will tend to relax spontaneously back to its equilibrium. This may happen under the emission of a photon. We call this process spontaneous emission, and its probability is given by A_{21}



We can write the rate of change in the population as:

$$\frac{N_1}{dt} = -\frac{N_2}{dt} = N_2A_{21} - N_1B_{12}\rho(\omega) + N_2B_{21}\rho(\omega)$$

In the steady state situation, the derivatives are zero and thus

$$N_2A_{21} - N_1B_{12}\rho(\omega) + N_2B_{21}\rho(\omega) = 0$$

Ignoring for the moment the influence of external fields, we can calculate for the thermally excited radiation:

$$\rho_T(\omega) = \frac{A_{21}}{e^{-\hbar\omega/kT}B_{12} - B_{21}}$$

However, it is well-known that Planck's law for the thermally excited radiation is:

$$\rho_T(\omega) = \frac{\hbar\omega^3}{\pi^2c^3} \frac{1}{e^{-\hbar\omega/kT} - 1}$$

These two equations are equal if

$$B_{12} = B_{21} \quad A_{21} = \frac{\hbar\omega^3}{\pi^2c^3}B_{21}$$

We thus see that the Einstein coefficients are interrelated. Note the following:

- The coefficients for absorption and stimulated emission are the same. In practice, however, the probability of absorption will be larger because the population of the ground state is much larger than the higher lying level. The total transfer of population from $1 \rightarrow 2$ due to absorption, for instance, is proportional to $N_1B_{12}\rho(\omega)$, which is generally larger than $N_2B_{21}\rho(\omega)$
- The probability for spontaneous emission increases rapidly for higher lying levels (because of the ω^3 dependence). Higher lying levels will therefore more rapidly lose their population than lower lying levels.

Lifetimes and Uncertainties

The energy of a system is well-defined if the system resides in one of its eigenstates. Conversely, the energy is ill-defined if the system does not reside in one of its eigenstates. The wavefunction can then be expressed as a linear combination of eigenstates, which adds to the uncertainty in energy. This discussion holds for the time-independent picture.

If we consider the time-evolution of a system, another uncertainty creeps in. Even if the system initially resides in an eigenstate, relaxation mechanisms may blur the energy certainty. Consider an eigenstate of the system $\Psi = \psi e^{-i\omega t}$. At any time, the probability is $|\Psi|^2 = |\psi|^2$, which is time-independent, and the

energy stays well-defined. In practice, however, the system may relax to other states, as we learned above. We can write the probability now as:

$$|\Psi|^2 = |\psi|^2 e^{-t/\tau}$$

which results in the following expression for the wavefunction itself:

$$\Psi = \psi e^{-i\omega t - t/2\tau}$$

The wavefunction 'loses' amplitude because of the decaying exponential. This corresponds to a loss of certainty regarding the energy. This uncertainty is dependent on the characteristic lifetime τ , which is related to the Einstein A coefficient. We now need to find a relation between time and energy. The relation between τ and the energy uncertainty can be found by using Fourier transform techniques. A time-dependent function $f(t)$ can be expressed as a Fourier transform of a frequency dependent function $g(\omega)$, as follows

$$f(t) = F\{g(\omega)\} = \int_{-\infty}^{\infty} g(\omega) e^{-i\omega t} d\omega$$

If we find the form of function $g(\omega)$, we know how a temporal change translates into an energy (frequency) change. We thus write:

$$e^{-i\omega t - t/2\tau} = \int_{-\infty}^{\infty} g(\omega') e^{-i\omega' t} d\omega'$$

Using standard Fourier tables, the frequency dependent function reads:

$$g(\omega') = \frac{(1/2\tau)}{(\omega - \omega')^2 + (1/2\tau)^2}$$

This function is called the *spectral density function*. In case the lifetime is long, i.e. the system resides for a long time in a well-defined state, the spectral density function is a sharp peak at frequency ω . This implies that the frequency (and thus energy through $\hbar\omega$) is well defined. For shorter lifetimes, the spectral density function broadens, and the uncertainty in energy is increased. The width of $g(\omega')$ is proportional to $1/2\tau$, and thus $\delta\omega \approx 1/2\tau$. We can write this as:

$$\tau \hbar \delta\omega \approx \frac{1}{2} \hbar \quad \rightarrow \quad \tau \delta E \approx \frac{1}{2} \hbar$$

This relation can be considered as an uncertainty relation for energy, analogous to Heisenberg's uncertainty relations. The take-home message here is: the finite lifetime of states gives rise to a spread in energy.

Spectroscopic Transitions

Electromagnetic radiation can induce transitions between quantum mechanical states. The electromagnetic field has two components: an oscillating electric field and an oscillating magnetic field. In the absence of a strong external magnetic field, the transitions induced by the electric field by far exceed the strength of the transitions induced by the magnetic field, and we will, therefore, mainly focus on the electric-field induced transitions. The interaction Hamiltonian matrix element of the electric dipole transitions is:

$$H_{gl} = -\mu_{gl} \cdot E$$

where E is the electric field of the electromagnetic radiation. The quantity that describes the efficiency of the transition is the electric transition dipole moment:

$$\mu_{gl} = \langle g | \mu | l \rangle = -e \langle g | \hat{\mathbf{r}} | l \rangle$$

Transitions are only allowed if the corresponding dipole moment integral above does not vanish. It turns out that, due to the symmetry of the operator and the wavefunctions, only certain transitions are allowed. Allowed transitions are specified by spectroscopic selection rules.

Selection Rules

The symmetry of the quantum mechanical hydrogen-like states are governed by the angular momenta of the states. In a transition, the angular momentum of the initial state can be different than that of the final state. There will thus be an overall change in angular momentum. The electromagnetic field, interpreted in terms of photons, also carries angular momentum. The orbital angular momentum of a photon is $l = 1$. Because there must be a conservation of momentum upon the light-matter interaction, the orbital momentum change in our quantum mechanical system also needs to be 1. The selection rule for the orbital angular momentum is thus:

$$\Delta l = \pm 1$$

The positive and negative sign correspond to absorption and emission of a photon, respectively. Each level l corresponds to $2l + 1$ states labeled with the quantum number m_l . Is there a selection rule for m_l as well? Yes there is. These states correspond to rotational motion around the polar angle of a symmetry axis through the system. Again, the change in rotational motion due to the transition needs to match the rotational character of the photon. If the photon is left-circularly polarized it is said to have a helicity of $\sigma = 1$, and a helicity of $\sigma = -1$ for right-circularly polarized light. These correspond to a change of $\Delta m_l = \pm 1$ in case the symmetry axis of our system is lined up with the propagation direction of the photon. If it is not lined up, we also have to allow intermediate values (combinations) of m_l . We then arrive at the following selection rules for m_l :

$$\Delta m_l = \pm 1, 0$$

There is a deeper philosophy behind the derivation of the selection rules in term of symmetry. This, however, lies outside the scope of this course.

Orbital and Spin Magnetic Moments

The quantum number m_l labels the projection of the orbital momentum onto an (z -)axis of our system. In our hydrogen-like model, the electron rotates around this axis. Because an electron is charged, it generates a magnetic moment upon circling around the nucleus. The quantum number m_l is, therefore, called the magnetic moment quantum number. Classically, the magnitude of the orbital angular momentum is:

$$|\mathbf{L}| = m_e v r = m \left(\frac{2\pi r}{T} \right) r = \frac{2m_e \pi r^2}{T} = 2m_e \frac{A}{T}$$

where A is the area enclosed by the circular motion and T is the roundtrip time. The magnetic dipole moment is defined as the current generated by the circular motion times the area:

$$|\mu_{\mathbf{m}}^l| = IA = \frac{q}{T} A = \frac{q}{2m_e} |\mathbf{L}| = -\frac{e}{2m_e} |\mathbf{L}|$$

We next focus on the z -component of the magnetic moment, and make the jump to its quantum mechanical representation:

$$\mu_{m,z}^l = -\frac{e}{2m_e} l_z = \gamma_e l_z = \gamma_e m_l \hbar = -\mu_B m_l$$

where we have defined the magnetogyric ration as $\gamma_e = -e/2m_e$ and the Bohr magneton as $\mu_B = e\hbar/2m_e$. The value of the Bohr magneton is $9.274 \cdot 10^{-24} \text{JT}^{-1}$. The orbital angular momentum is not the only source of the magnetic moment. Also the spin angular momentum contributes. The total magnetic moment is:

$$\mu_{\mathbf{m}} = -\frac{e}{2m_e} (\mathbf{L} + g_e \mathbf{S})$$

The second term arises because of spin angular momentum. The so-called g_e factor of the electron is given by:

$$g_e = 2 \left(1 + \frac{1}{2\pi} \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)$$

The second factor is very small and corrects for relativistic effects. A good approximation is $g_e \approx 2$. We thus have for the spin magnetic moment:

$$\mu_{\mathbf{m}}^s = g_e \gamma_e \mathbf{S} \quad \mu_{m,z}^s = -g_e \mu_B m_s$$

The magnetic dipole moment plays a role similar to the electric dipole moment. In the presence of the magnetic field, the interaction Hamiltonian is:

$$H = -\mu_{\mathbf{m}} \cdot \mathbf{B}$$

The electron generates a very small but finite magnetic field because of its orbital angular momentum. This implies that the magnetic field can couple with the spin magnetic moment and shift the energy levels of our system. We will look at this spin-orbit coupling effect in the following section.

Spin-Orbit Coupling

The magnetic field experienced by the electron because of its orbital motion, is given by:

$$\mathbf{B} = \frac{\mathbf{E} \times \mathbf{v}}{c^2}$$

Here the electric field \mathbf{E} can be expressed in terms of the electric potential:

$$\mathbf{E} = -\mathbf{n}_r \frac{V(r)}{dr} = -\frac{\mathbf{r}}{r} \frac{V(r)}{dr}$$

where \mathbf{n}_r is the unit vector in the direction of r . In our hydrogen-like system, the electric potential arises because of the coulomb potential between the electron and the nucleus. We can thus write:

$$\mathbf{E} = -\frac{\mathbf{r}}{r} \frac{d}{dr} \left(\frac{Ze}{4\pi\epsilon_0 r} \right) = \frac{Ze}{4\pi\epsilon_0 r^3} \mathbf{r}$$

In the frame of the electron, the nucleus circles around the electron, generating the magnetic field experienced by the electron. We have to take into account a relativistic factor of $\frac{1}{2}$ to account for this motion. The magnetic field seen by the electron is then:

$$\mathbf{B} = \frac{1}{2} \frac{Ze}{4\pi\epsilon_0 r^3 c^2} \mathbf{r} \times \mathbf{v} = \frac{Ze}{8\pi\epsilon_0 m_e r^3 c^2} \mathbf{L}$$

The interaction Hamiltonian now becomes:

$$H_{so} = -\boldsymbol{\mu}_m^s \cdot \mathbf{B} = -g_e \gamma_e \frac{Ze}{8\pi\epsilon_0 m_e r^3 c^2} \mathbf{L} \cdot \mathbf{S} = \xi(r) \mathbf{L} \cdot \mathbf{S}$$

with

$$\xi(r) = -\frac{Zeg_e\gamma_e}{8\pi\epsilon_0 m_e r^3 c^2}$$

Note that ξ behaves as an operator in the sense that it multiplies a wavefunction $\psi(r)$ with a factor proportional to $1/r^3$. We will now study what the effect of the spin-orbit coupling Hamiltonian is on the existing levels in our hydrogen-like system.

Fine-structure of Spectra

The expectation value of the spin-orbit coupling Hamiltonian corresponds to an energy. These energies are corrections to the previously considered energy levels of the hydrogen-like system, due to the presence of spin-orbit coupling. Because

spin-orbit coupling is a weak effect, we use the formalism of perturbation theory to find the corrections. We have for a one-electron system circling around the nucleus:

$$H_{so}^{(1)} = \xi(r)\mathbf{l} \cdot \mathbf{s}$$

We will write the states in terms of their angular momenta l and s in the coupled representation: $|j, m_j; l, s\rangle$. The first order correction to the energy is then:

$$E_{so}^{(1)} = \langle j, m_j; l, s | H^{(1)} | j, m_j; l, s \rangle = \langle j, m_j; l, s | \xi(r) \hat{l} \cdot \hat{s} | j, m_j; l, s \rangle$$

We will make use of the relation

$$\hat{j}^2 = |\hat{l} + \hat{s}|^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{l} \cdot \hat{s}$$

and write the operator as

$$\xi(r) \hat{l} \cdot \hat{s} = \frac{1}{2} \xi(r) (\hat{j}^2 - \hat{l}^2 - \hat{s}^2)$$

Operating on the wavefunction $|j, m_j; l, s\rangle$ gives:

$$\frac{1}{2} \xi(r) (\hat{j}^2 - \hat{l}^2 - \hat{s}^2) |j, m_j; l, s\rangle = \frac{1}{2} \hbar^2 \{j(j+1) - l(l+1) - s(s+1)\} \xi(r) |j, m_j; l, s\rangle$$

The correction to the energy is therefore:

$$E_{so}^{(1)} = \frac{1}{2} \hbar^2 \{j(j+1) - l(l+1) - s(s+1)\} \langle j, m_j; l, s | \xi(r) | j, m_j; l, s \rangle$$

The matrix $\langle j, m_j; l, s | \xi(r) | j, m_j; l, s \rangle$ element only depends on r , which implies that it is dependent on the radial part of the wavefunction R_{nl} . It depends on the quantum numbers n and l , and can be rewritten as:

$$\langle n, l | \xi(r) | n, l \rangle = -\frac{Zeg_e\gamma_e}{8\pi\epsilon_0 m_e c^2} \langle n, l | r^{-3} | n, l \rangle = -\frac{Zeg_e\gamma_e}{8\pi\epsilon_0 m_e c^2} \frac{Z^3}{n^3 a_0^3 l(l + \frac{1}{2})(l + 1)}$$

We will now define the spin-orbit coupling ζ_{nl} constant as:

$$hc\zeta_{nl} = \hbar^2 \langle n, l | \xi(r) | n, l \rangle$$

Introducing the fine-structure constant α and the Rydberg constant R

$$\begin{aligned} \alpha &= \frac{e^2}{4\pi\epsilon_0 \hbar c} \\ R &= \frac{m_e e^4}{8\epsilon_0^2 \hbar^3 c} \end{aligned}$$

we get the following for the spin-orbit coupling constant:

$$\zeta_{nl} = \frac{\alpha^2 R Z^4}{n^3 l(l + \frac{1}{2})(l + 1)}$$

The energy becomes:

$$E_{so}^{(1)} = \frac{1}{2}hc\zeta_{nl} \{j(j+1) - l(l+1) - s(s+1)\}$$

Note the following:

- Spin-orbit coupling gives rise to shifting of the energy levels.
- This correction is small: for a 2p-electron in the hydrogen system the coupling energy is $hc\alpha^2 R/24$, which is about $2.22 \cdot 10^{-6} \times hcR$. The energy level separation of the unperturbed levels in hydrogen is on the order of hcR . Hence, the effect is very small relative to the unperturbed energy levels.
- The spin-orbit coupling grows to the fourth power with Z . For heavier atoms, the effect becomes steadily more important.

Hydrogen and Helium

Spin-Orbit Coupling and Term Symbols

In hydrogen, the state of the single electron is characterized by two quantum numbers for angular momentum: the orbital angular momentum l and the spin angular momentum s . We have also seen that the coupling between these two angular momenta gives rise to corrections to the energy levels in hydrogen:

$$E_n = E_n^{(0)} + E_{so}^{(1)}$$

with

$$E_n^{(0)} = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -hcR \frac{1}{n^2}$$

$$E_{so}^{(1)} = \frac{1}{2} hc\zeta_{nl} \{j(j+1) - l(l+1) - s(s+1)\}$$

What is the effect of spin-orbit coupling? Let us look at the 2p levels. Ignoring spin-orbit coupling, the 2p ($n=2, l=1$) levels in hydrogen ($2p_z, 2p_+, 2p_-$) are degenerate. Because there are three orbital states and two spin states, the total number of states of the electron is 6. When spin-orbit coupling is present these levels split. We have $l=1$ and $s=\frac{1}{2}$ and thus $j=\frac{3}{2}$ and $j=\frac{1}{2}$. There are $2 \cdot \frac{3}{2} + 1 = 4$ states with $j=\frac{3}{2}$ and $2 \cdot \frac{1}{2} + 1 = 2$ states for $j=\frac{1}{2}$. Their energy corrections are:

$$E_{so, (j=\frac{3}{2})}^{(1)} = +\frac{1}{2} hc\zeta_{nl}$$

$$E_{so, (j=\frac{1}{2})}^{(1)} = -hc\zeta_{nl}$$

We can label these levels by use of a new notation called term symbols, defined as follows:

$$\text{multiplicity} \rightarrow 2S+1 \{L\}_{J \text{ level}}$$

Here L , S and J , indicate the total orbital, spin and combined momentum. We use numbers for S and J and letters for L (S,P,D,F...). For hydrogen we have $L=l$, $S=s$ and $J=j$. We thus get for our 2p levels: ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$.

Note that the $j=\frac{3}{2}$ level, in which the spin and orbital angular momentum are 'parallel', is higher in energy than the $j=\frac{1}{2}$ level, in which the momenta are 'anti-parallel'.

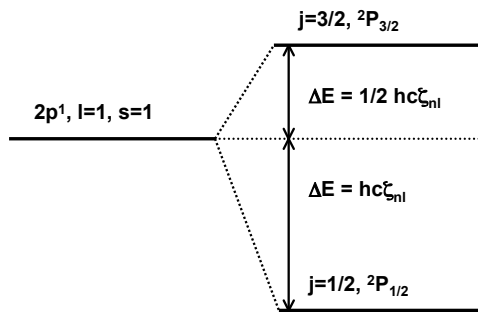


Figure 5: splitting of the 2p level due to spin-orbit coupling in hydrogen

Spectrum of Hydrogen

Taking into account the spin-orbit couplings, we can now draw the energy level diagram for hydrogen and study the transitions between the levels. Because there is only 1 electron in hydrogen with $s = \frac{1}{2}$, the multiplicity of each level is 2, and hence all the levels with $l > 0$ are doublets (for the 1s state, $l = 0$ and there is no splitting because j is single-valued).

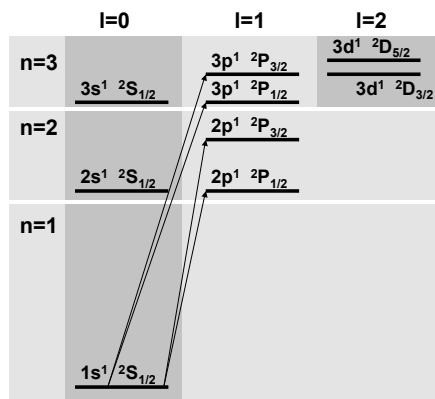


Figure 6: energy levels in hydrogen and transitions from $2S_{1/2}$ state

Hamiltonian and Energies of Helium

Whereas the solution to the energy levels of the hydrogen system was obtained with a great deal of accuracy, determining the energy levels for the next atom of the periodic table, helium, imposes some problems. Because the helium atom constitutes a three-body problem, one nucleus and two electrons, we cannot find analytical solutions to their respective motions. Consequently, we have to make some stiff approximations to obtain insight into the structure of the helium atom. The first step we take is to separate the motion of the electrons from those of the nucleus and consider only the relative motion of the electrons. The Hamiltonian then becomes:

$$\begin{aligned} H &= H_{kin}(r_1) + H_{kin}(r_2) + V(r_1) + V(r_2) + V_{ee}(r_1 - r_2) \\ &= -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned}$$

The last term is an additional coulombic interaction between the electrons that manifests itself as electron-electron repulsion. We will assume that this last term is relatively small (which is not completely justified!) and consider it as a perturbation to the Hamiltonian without the electron-electron repulsion.

$$\begin{aligned} H &= H^{(0)} + H^{(1)} \\ H^{(0)} &= H_1 + H_2 = \left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}\right) \\ H^{(1)} &= \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned}$$

The unperturbed Hamiltonian is easy to solve. It consists of two *independent* terms. We therefore write the groundstate wavefunction (both electrons in the 1s orbital, which we will call $a(r)$) as

$$\Psi(r_1, r_2) = a_1(r_1)a_2(r_2)$$

And substitute this into the Schrödinger equation with $H^{(0)}$:

$$\begin{aligned} H^{(0)}a_1(r_1)a_2(r_2) &= E a_1(r_1)a_2(r_2) \\ a_2(r_2)H_1a_1(r_1) + a_1(r_1)H_2a_2(r_2) &= E a_1(r_1)a_2(r_2) \\ (E_1 + E_2)a_1(r_1)a_2(r_2) &= E a_1(r_1)a_2(r_2) \end{aligned}$$

which gives for the energy:

$$E = E_1 + E_2 = -4hcR \left(\frac{1}{n^2} + \frac{1}{n^2} \right)$$

The first order correction to the energy due to the electron repulsion is

$$\begin{aligned} E^{(1)} &= \langle \Psi | H^{(1)} | \Psi \rangle = \frac{e^2}{4\pi\epsilon_0} \langle a_1 a_2 | \frac{1}{r_{12}} | a_1 a_2 \rangle \\ &= \frac{e^2}{4\pi\epsilon_0} \int \frac{|a_1|^2 |a_2|^2}{r_{12}} dV_1 dV_2 = J \end{aligned}$$

We call J the Coulomb integral. Its value is $2.5hcR$, which gives for the groundstate energy of helium $E = (-4 - 4 + 2.5)hcR = -5.5hcR$. We also see that the coulomb integral is not particularly small and that the perturbation approach does not give a very accurate description of our system. Nonetheless, we can get a good sense of the forces at play in this three-body system, and a reasonable estimate of their contributions.

The Exchange Interaction

The groundstate configuration of helium is $1s^2$. Upon excitation of the helium atom, one of the electrons can occupy a different level, for instance $1s^12p^1$. We now have two orbitals $a(r)$ and $b(r)$ and two permutations for occupying them: electron 1 in orbital a and electron 2 in b [$\phi_1 = a(1)b(2)$], or electron 1 in b and electron 2 in a [$\phi_2 = a(2)b(1)$]. Note that

$$\begin{aligned}\langle \phi_1 | \phi_1 \rangle &= \langle a(1) | a(1) \rangle \langle b(2) | b(2) \rangle = 1 \\ \langle \phi_1 | \phi_2 \rangle &= \langle a(1) | b(1) \rangle \langle b(2) | a(2) \rangle = 0\end{aligned}$$

and the energies are:

$$\begin{aligned}\langle \phi_1 | H^{(0)} | \phi_1 \rangle &= \langle a(1) | H_1 | a(1) \rangle \langle b(2) | b(2) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | H_2 | b(2) \rangle = E_a + E_b \\ \langle \phi_2 | H^{(0)} | \phi_2 \rangle &= \langle a(2) | a(2) \rangle \langle b(1) | H_1 | b(1) \rangle + \langle a(2) | H_2 | a(2) \rangle \langle b(1) | b(1) \rangle = E_a + E_b\end{aligned}$$

Hence, without the electron repulsion contribution, these states are degenerate. However, with the perturbing term, this degeneracy can be removed, and we need to apply perturbation theory for degenerate states to study the result of this perturbation. We need to solve:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

The matrix elements are:

$$\begin{aligned}H_{11} &= \langle \phi_1 | (H_1 + H_2 + V_{ee}) | \phi_1 \rangle = \langle a(1)b(2) | (H_1 + H_2 + V_{ee}) | a(1)b(2) \rangle \\ &= E_a + E_b + J \\ H_{22} &= E_a + E_b + J \\ H_{12} &= \langle a(1)b(2) | H_1 + H_2 + V_{ee} | a(2)b(1) \rangle = \langle a(1)b(2) | V_{ee} | a(2)b(1) \rangle = K \\ H_{21} &= K \\ S_{11} &= S_{22} = 1 \\ S_{12} &= S_{21} = 0\end{aligned}$$

where we have defined K as the exchange integral:

$$K = \frac{e^2}{4\pi\epsilon_0} \int \frac{a(1)b(2) \cdot a(2)b(1)}{r_{12}} dV_1 dV_2$$

The secular determinant takes on the form:

$$\begin{vmatrix} E_a + E_b + J - E & K \\ K & E_a + E_b + J - E \end{vmatrix} = 0$$

which gives for the energy

$$E = E_a + E_b + J \pm K$$

And for the wavefunctions we find:

$$\begin{aligned} \psi_+ &= \frac{1}{\sqrt{2}} \{a(1)b(2) + a(2)b(1)\} \\ \psi_- &= \frac{1}{\sqrt{2}} \{a(1)b(2) - a(2)b(1)\} \end{aligned}$$

We see that the perturbation has removed the degeneracy and split the two levels with an energy difference $\Delta E = 2K$. The resulting wavefunctions have different spatial properties. In particular, when the electrons are occupying the same region in space, i.e. $r_1 = r_2 = r$, $\psi_-(r_1, r_2)$ goes to zero while $\psi_+(r_1, r_2)$ does not:

$$\begin{aligned} |\psi_-(r)|^2 &= \frac{1}{2} |a(r)b(r) - a(r)b(r)|^2 = 0 \\ |\psi_+(r)|^2 &= \frac{1}{2} |a(r)b(r) + a(r)b(r)|^2 = 2|a(r)b(r)|^2 \end{aligned}$$

In ψ_- electrons seem to be avoiding each other, which leads to a lower overall energy. In ψ_+ the probability of finding the electrons in the same place is actually enhanced, which is a high energy situation. This effect is purely quantum mechanical and has no classical analogue. It is also a purely space correlation effect, independent of the charge of the particles. We will see that the properties of ψ_- and ψ_+ have profound implications for the electron distribution in atoms and molecules.

Multiple Electron Wavefunctions

The total wavefunction for a two-electron system such as helium consists of two parts: an orbital part ψ and a spin part σ :

$$\Psi(r_1, r_2) = \psi(r_1, r_2)\sigma(1, 2)$$

In the previous discussion we learned that the orbital wavefunction of helium can take on several forms, depending on whether the electrons occupy similar or different orbitals:

$$\begin{aligned}\psi(r_1, r_2) &= a(1)a(2) && \text{(same orbitals)} \\ \psi_-(r_1, r_2) &= \frac{1}{\sqrt{2}} \{a(1)b(2) - a(2)b(1)\} && \text{(different orbitals)} \\ \psi_+(r_1, r_2) &= \frac{1}{\sqrt{2}} \{a(1)b(2) + a(2)b(1)\} && \text{(different orbitals)}\end{aligned}$$

For the spin states we previously found:

$$\begin{aligned}\sigma_+^{(1)}(1, 2) &= \alpha(1)\alpha(2) \\ \sigma_+^{(0)}(1, 2) &= \frac{1}{\sqrt{2}} \{\alpha(1)\beta(2) + \alpha(2)\beta(1)\} \\ \sigma_+^{(-1)}(1, 2) &= \beta(1)\beta(2) \\ \sigma_-(1, 2) &= \frac{1}{\sqrt{2}} \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}\end{aligned}$$

In the section that follows we will see that not every combination of orbital and spin wavefunction is allowed.

The Pauli Principle

How do the spin and orbital wavefunctions behave when we interchange the states of the electrons? We find that the wavefunctions are either symmetric or anti-symmetric under particle exchange. We find for the symmetric functions:

$$\psi(1, 2) = \psi(2, 1) \quad \psi_+(1, 2) = \psi_+(2, 1)$$

and

$$\sigma_+^{(1)}(1, 2) = \sigma_+^{(1)}(2, 1) \quad \sigma_+^{(0)}(1, 2) = \sigma_+^{(0)}(2, 1) \quad \sigma_+^{(-1)}(1, 2) = \sigma_+^{(-1)}(2, 1)$$

For the anti-symmetric functions we have:

$$\psi_-(1, 2) = -\psi_-(2, 1) \quad \sigma_-(1, 2) = -\sigma_-(2, 1)$$

The Pauli principle states that *the total wavefunctions must be anti-symmetric under the interchange of any pair of fermions*. Given that electrons are fermions,

the total wavefunction in our atomic system thus has to be antisymmetric. This implies that the wavefunction $\psi_{-\sigma_+^{(0)}}$ is allowed but that the function $\psi_{-\sigma_-}$ is not. We can write the total wavefunction more compact in the form of a determinant composed of *spinorbitals*:

$$\psi_a^\alpha(1) = \psi_a(r_1)\alpha(1) \quad \psi_a^\beta(1) = \psi_a(r_1)\beta(1)$$

The determinant form of allowed wavefunctions is then:

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) \end{vmatrix}$$

This determinant is called the Slater determinant. It ensures that the wavefunction $\Psi(1, 2)$ is anti-symmetric. For instance, for the two electrons that occupy the 1s orbital, the total wavefunction is expressed as:

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}^\alpha(1) & \psi_{1s}^\beta(1) \\ \psi_{1s}^\alpha(2) & \psi_{1s}^\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \psi_{1s}(r_1)\psi_{1s}(r_2) \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

The Slater determinant is not limited to two electrons and generally we can write for an N-particle system:

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_z(2) \\ \vdots & \vdots & \dots & \vdots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_z(N) \end{vmatrix}$$

The Slater determinant is N by N , because one electron can occupy only one spinorbital. Another realization of the electron distribution in which the electrons occupy different spinorbitals, leads to another Slater determinant. Hence, every arrangement is characterized by its own Slater determinant. The only non-vanishing Slater determinants are the ones that lead to an anti-symmetric overall wavefunction.

From the Pauli principle follows that if two electrons have the same spin state, they cannot occupy the same orbital. An identical spin state implies that the spin wavefunction is symmetric, which means that the orbital wavefunction must be anti-symmetric and hence of the form $a(1)b(2) - a(2)b(1)$. This can only be realized if the electrons occupy different orbitals otherwise the wavefunction would be zero for all locations. If the electrons do occupy the same orbital (symmetric), their spin part must be anti-symmetric to satisfy the Pauli principle. This corresponds to the following principles:

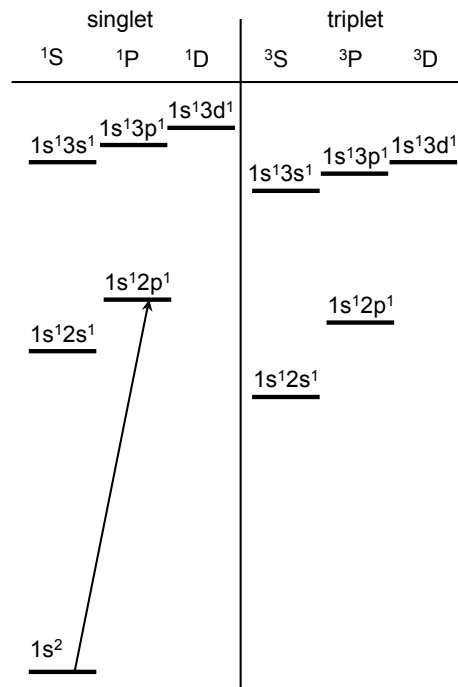
- No two electrons can occupy the same state (Pauli exclusion principle)
- When two electrons occupy the same orbital, their spins must pair, i.e. the spin wavefunction is $\sigma_-(1, 2)$

It follows from these principles that when the spatial part of the two-electron wavefunction is antisymmetric, the spin part must be symmetric, i.e. $S = 1$. Triplet states are thus associated with anti-symmetric spatial wavefunctions, which implies that the electrons are avoiding each other. This is called spin correlation. It leads to a lower overall energy, and the observation that triplet states lie generally lower in energy than the corresponding singlet states (associated with symmetric spatial wavefunction).

Spectrum of Helium

We are now in a position to study the excited states of helium. For transitions we are using the following spectroscopic rules:

- The symmetry of the spatial part of the wavefunction does not change upon excitation.
- The change in orbital angular momentum is $\Delta l = \pm 1$



Helium has two electrons, which gives rise to singlet $S = 0$ and triplet $S = 1$ states. The ground state is $1s^2$, which is a singlet state 1S . Upon excitation to the first excited states, we can have either $1s^12s^1$ or $1s^12p^1$. Only transitions

with $\Delta l = \pm 1$ are allowed, which means that we excite the system to the $1s^1 2p^1$ state. This corresponds to the 1P_1 term symbol. We cannot excite it into the 3P states because that would mean a change in the spatial symmetry of the wavefunction.

Many-Electron Atoms

Penetration and Shielding

For many electrons atoms, the method that we have used to arrive at the estimated energy levels for helium becomes increasingly more difficult because of the electron-electron interactions. Instead of going through a complicated calculation, the energies of many-electron systems are commonly approached in a very qualitative way. The following approximations are made:

- The orbitals of many electron atoms take the form of the hydrogenic orbitals. This is called the orbital approximation. The orbitals are filled using Pauli's principle, which implies that an orbital can only be occupied by a maximum of two electrons.
- The electron-electron interaction is approximated by assuming that each electron sees an effective nuclear charge $Z_{eff} = Z - \sigma$. Here σ is the nuclear screening constant, which takes into consideration shielding of the nuclear charge due to the presence of the other electrons.

The shielding approximation allows us to write the electrostatic contribution to the Hamiltonian for each electron as:

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r_1} + \sum_{i \neq 1} \frac{e^2}{4\pi\epsilon_0 r_{1i}} \approx -\frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{\sigma e^2}{4\pi\epsilon_0 r_1} = -\frac{(Z - \sigma)e^2}{4\pi\epsilon_0 r_1}$$

The result is that we find energy levels that follow the same trend as the hydrogen energy levels. We will name the levels as follows:

- The n -levels (principle quantum number) are called shells. They are labeled as K, L, M, \dots for $n = 1, 2, 3, \dots$
- Each shell has n subshells, the familiar s, p, d, f, \dots levels. Electrons in each of the subshells see a different Z_{eff} , which means that the subshells commonly have different energies within a main shell. Generally, $s < p < d < f$, but there are deviations.
- Each subshell has $2l + 1$ orbitals. Each orbital has two states for accommodating a total of two electrons.

Generally, s -electrons within a shell are closer to the nucleus and see a smaller σ than the electrons in the p and d subshells. The electrons in the s -orbital have, therefore, a lower energy than the electrons in the p and d orbitals. We say that the ns -electrons penetrate the atom to a larger extent than a np -electron and are less shielded.

Aufbau Principle

With the above approximations we can find the *ground-state electron configurations* of many-electron atoms. The orbitals are filled using the Aufbau-principle

which states that the shells and subshells are filled according to their energies: lower lying levels are filled first before higher lying states are being filled. We will also use the Pauli-exclusion principle for allowing only two electrons per orbital, and for demanding that if the orbital is filled, the electron spins must be paired. In addition, the following features should be noted:

- When more than one orbital is available for occupation, electrons will occupy different orbitals before pairing up. This leads to a lower energy.
- When two electrons occupy different orbitals they do so with parallel spins. This is Hund's rule, which is related to spin correlation.

For example:

P(15): $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
 Ti(22): $1s^2 2s^2 2p^6 3s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

Russell-Saunders Spin-Orbit Coupling

Similar to the hydrogen atom, the levels found from the unperturbed Schrödinger equation for many-electron atoms are affected by spin-orbit coupling. These levels can be labeled with term symbols. Other than in hydrogen, we have many more electrons to take into consideration. As a consequence, coupling schemes might get quite entangled. There are two schemes of spin-orbit coupling that are used for many electron atoms:

- jj-coupling. In this scheme we form combined orbital and spin momentum $j = l + s$ for each electron before the total angular momentum J is found through combining j_1, j_2, j_3, \dots through Clebsch Gordan series. This coupling scheme is used for the heavier atoms of the periodic table.
- Russell Saunders coupling. In the RS-scheme, we first find the total spin and orbital angular S and L , and combine them to find the total angular momentum J . We can only use this scheme if spin-orbit coupling is weak, which does not hold for the heavier atoms.

The RS scheme is somewhat easier to deal with, and is usually associated with the term symbols for spectroscopic transitions. In the RS scheme, we have for two electrons:

$$\begin{aligned} S &= s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2| \\ L &= l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2| \\ J &= L + S, L + S - 1, \dots, |L - S| \end{aligned}$$

With RS-coupling we find all the possible levels, but care must be taken to make sure that the Pauli-principle is still fulfilled for each of the term symbols found.

Let us look at the configuration $3d^2$. We have:

$$\begin{aligned} S &= 1, 0 \\ L &= 4, 3, 2, 1, 0 \\ J &= 5(1), 4(3), 3(4), 2(4), 1(4), 0(2) \end{aligned}$$

This leads to the term symbols:

$${}^3G_J, {}^1G_J, {}^3F_J, {}^1F_J, {}^3D_J, {}^1D_J, {}^3P_J, {}^1P_J, {}^1S_J, {}^3S_J$$

In comparing the terms with the *microstates* of this configuration, we can find which of these term symbols correspond to a configuration supported by the Pauli principle. We will write the states in terms of the m_l quantum numbers of the electrons as microstates in the form (m_{l1}, \bar{m}_{l2}) . A bar indicates a β spin state, no bar means an α state. The microstates of this configuration can be listed in the following table:

| $\mathbf{M_L}$ | $M_S = +1$ | $M_S = 0$ | $M_S = -1$ |
|----------------|------------------|---|--|
| +4 | | (2, 2) | |
| +3 | (2, 1) | ($\bar{2}$, 1); (2, $\bar{1}$) | ($\bar{2}$, $\bar{1}$) |
| +2 | (2, 0) | ($\bar{2}$, 0); (2, $\bar{0}$); (1, $\bar{1}$) | ($\bar{2}$, $\bar{0}$) |
| +1 | (1, 0); (2, -1) | ($\bar{1}$, 0); (1, $\bar{0}$); ($\bar{2}$, -1); (2, - $\bar{1}$) | ($\bar{1}$, $\bar{0}$); ($\bar{2}$, - $\bar{1}$) |
| 0 | (2, -2); (1, -1) | ($\bar{2}$, -2); (2, - $\bar{2}$); ($\bar{1}$, -1); (1, - $\bar{1}$); (0, $\bar{0}$) | ($\bar{2}$, - $\bar{2}$); ($\bar{1}$, - $\bar{1}$) |
| -1 | (-1, 0); (-2, 1) | (- $\bar{1}$, 0); (-1, $\bar{0}$); (- $\bar{2}$, 1); (-2, $\bar{1}$) | (- $\bar{1}$, $\bar{0}$); (- $\bar{2}$, $\bar{1}$) |
| -2 | (-2, 0) | (- $\bar{2}$, 0); (-2, $\bar{0}$); (-1, - $\bar{1}$) | (- $\bar{2}$, $\bar{0}$) |
| -3 | (-2, -1) | (- $\bar{2}$, -1); (-2, - $\bar{1}$) | (- $\bar{2}$, - $\bar{1}$) |
| -4 | | (-2, - $\bar{2}$) | |

We check to which terms symbols these states belong by:

1. Identify the first element in the first row and find L and S for this state.
2. There are $(2L+1)(2S+1)$ states with the same term symbol (same L and S). We may strike out this amount of states from the columns and rows spanned by M_L and M_S .
3. Move on the next element and repeat till there are no states left. We now have selected only the term symbols that comply with Pauli's principle.

For the $3d^2$ configuration we find:

$${}^1G, {}^3F, {}^1D, {}^3P, {}^1S$$

For lighter atoms we use the RS-scheme, but for heavier atoms we have to use jj -coupling scheme because the coupling is too strong to ensure that RS-coupling still holds. In the jj -scheme the L and S are not well-defined because

we focus on $j = l + s$ instead. However, J is well-defined in both schemes. We can correlate the J -levels of the heavier atoms to the term symbols of the lighter atoms given that states of similar symmetry will not cross. Based on the location of the energy levels, we can connect the J -levels across a group of the periodic table between light elements and heavy elements. To be able to construct such a correlation diagram, we need to know the relative energies of the levels.

Hund's Rules and Transitions

Hund's rules help us to find the lowest energy level of the term symbols:

1. The term with the highest multiplicity lies lowest in energy.
2. For a given multiplicity, the highest value of L lies lowest.
3. Atoms with their shells half-filled, the lowest value of J lies lowest.

For example, for our $3d^2$ configuration, the lowest level is 3F . These rules work reasonably well but break down if there is, for instance, *configuration interaction* in the atom. This is the case if there are configurations of close energy in which the atom can reside. For example, the atom with configuration $3s^13d^1$ can partially reside in the nearby configuration $3p^2$. Levels of similar symmetry will now mix, which leads to splitting and shifting of energy levels. Hund's rules cannot take account of this.

Now that we have identified the energy levels and included spin-orbit coupling, it is time to look at transitions between the states. Which transitions are allowed? The following selection rules apply to many-electron atoms:

$$\begin{aligned}\Delta J &= 0, \pm 1 \quad (J = 0 \rightarrow J = 0 \text{ forbidden}) \\ \Delta L &= 0, \pm 1 \quad \Delta l = \pm 1 \quad \Delta S = 0\end{aligned}$$

The $\Delta l = \pm 1$ remains valid to account for the character of the actual electron being excited. The ΔS rule relates to the fact that the symmetry of the spatial wavefunction cannot change upon excitation. Note that there's no need to specify the rules for M_L for transitions between term symbols because the term symbols do not specify M_L ; there is always a state covered by the term symbol that fulfills the selection rule for the magnetic quantum number as long as $\Delta L = 0, \pm 1$ is met.

Atoms in Electric and Magnetic Fields

Electric and magnetic fields can exert influence on the electrons (and nuclei) in our quantum mechanical system. The electric or magnetic field communicates with our system because the system has a *moment*: a handle for the field to grab onto and modify the system to a certain extent. The lowest non-vanishing moment is the dipole moment, which is the most significant as higher order moments are usually much smaller. As we have seen, a quantum mechanical system such as the hydrogen atom has an electric and a magnetic dipole moment. Both the electric and magnetic field can, therefore, perturb our atom system. In this section we will see how external fields can give rise to additional splitting of otherwise degenerate levels.

Splitting by Magnetic Field

The 'handle' for the magnetic field is the magnetic dipole moment. We have already seen that it has the form:

$$\bar{\mu} = -\frac{e}{2m_e}(\bar{L} + g_e\bar{S}) = \gamma_e(\bar{L} + g_e\bar{S}) \approx \gamma_e(\bar{L} + 2\bar{S})$$

The bar indicates that these quantities are vectors. When the magnetic field grabs onto the magnetic moment, it perturbs the system with an energy:

$$H^{(1)} = -\bar{\mu} \cdot \bar{B}$$

We have learned that the magnetic moment arises because of angular momentum. In case spin-orbit coupling is significant, and the magnetic field is not too strong, the angular momentum the \bar{B} field sees is the total angular momentum \bar{J} , instead of the individual sources of angular momentum (\bar{L} and \bar{S}). We therefore look for the extent of the magnetic moment collinear with the total angular momentum \bar{J} :

$$\bar{\mu}_J = |\mu_J|\bar{n}_J = |\mu_J|\frac{\bar{J}}{|\bar{J}|}$$

We now need to find the magnitude of $|\mu_J|$. This is given by projecting \bar{L} and \bar{S} onto \bar{n}_J :

$$|\mu_J| = \gamma_e(\bar{L} \cdot \bar{n}_J + 2\bar{S} \cdot \bar{n}_J) = \gamma_e\left(\bar{L} \cdot \frac{\bar{J}}{|\bar{J}|} + 2\bar{S} \cdot \frac{\bar{J}}{|\bar{J}|}\right)$$

The contribution to the energy is now:

$$H^{(1)} = -\bar{\mu}_J \cdot \bar{B} = \gamma_e(\bar{L} \cdot \bar{J} + 2\bar{S} \cdot \bar{J})\frac{\bar{J} \cdot \bar{B}}{|\bar{J}|^2}$$

To evaluate this expression we make use of $\bar{J} = \bar{L} + \bar{S}$ and derive the following relations:

$$\begin{aligned} \bar{J} - \bar{L} = \bar{S} &\Rightarrow (\bar{J} - \bar{L})^2 = (\bar{S})^2 &\Rightarrow 2\bar{L} \cdot \bar{J} = J^2 + L^2 - S^2 \\ \bar{J} - \bar{S} = \bar{L} &\Rightarrow (\bar{J} - \bar{S})^2 = (\bar{L})^2 &\Rightarrow 2\bar{S} \cdot \bar{J} = J^2 + S^2 - L^2 \end{aligned}$$

We get for the energy:

$$H^{(1)} = -\gamma_e \left\{ \frac{\frac{1}{2}(J^2 + L^2 - S^2) + J^2 + S^2 - L^2}{J^2} \right\} \bar{J} \cdot \bar{B} = -\gamma_e \left\{ 1 + \frac{J^2 + S^2 - L^2}{2J^2} \right\} \bar{J} \cdot \bar{B}$$

Plugging in the quantum mechanical values for the magnitude of the angular momenta ($\hbar^2 J^2(J+1)$) finally yields:

$$H^{(1)} = -\gamma_e \left\{ 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right\} \bar{J} \cdot \bar{B} = -\gamma_e g_J(L, S) \bar{J} \cdot \bar{B}$$

where we have defined the Landé g-factor, which depends on the details of the angular momenta. Let us next look at what effect this has on the energy levels.

Zeeman Effects

Consider a field that is aligned with the z -axis of our system. We can then write the perturbing Hamiltonian as:

$$H^{(1)} = -\gamma_e g_J J_z \cdot B_z$$

The first order energy correction is found by solving the secular determinant used for calculating splittings of degenerate systems. Because the wavefunctions $\langle M_J |$ are eigenfunctions of J_z , the only non-vanishing matrix elements are the diagonal elements. We then get for the energy:

$$E^{(1)} = \langle M_J | H^{(1)} | M_J \rangle = -\gamma_e g_J M_J \hbar \cdot B_z = g_J \mu_B M_J \cdot B_z$$

Let us consider two important cases.

- The total spin angular momentum is zero, i.e. $S=0$ (singlet levels). We see that the Landé factor is 1. Furthermore, the angular momentum is equal to orbital angular momentum $J = L$ and thus the energy splitting of singlet levels is:

$$E^{(1)} = \mu_B M_L B_z$$

For a 1P level, this implies that the three otherwise degenerate M_L orbitals ($M_L = 1, 0, -1$) are equi-distantly separated in energy by $\Delta E = \mu_B B_z$. Similarly, a 1D level is split into 5 different M_L states. This effect is called the *normal Zeeman effect*.

A singlet-singlet transition that would otherwise have given rise to a single line in the spectrum, now has three lines due to energy splitting by the magnetic field.

- The total spin angular momentum is not zero. This is called the *anomalous Zeeman effect*. This pertains, for instance, to doublets and triplets. As a result, many more lines may arise. The splittings now depend on the term symbols. For instance, a $^2D_{3/2}$ level will be split with a Landé factor of $g_{3/2}(2, \frac{1}{2}) = \frac{4}{5}$, whereas a $^2D_{5/2}$ level will be split with a factor $g_{5/2}(2, \frac{1}{2}) = \frac{1}{5}$

Exceptions

If the applied magnetic field is many times stronger than the spin-orbit coupling strength, the combined angular momentum J is no longer a good quantum number for interpreting the splitting. Instead, the magnetic field grabs onto the orbital angular momentum individually. The spin angular momentum has no longer an influence on the energies because the field couples to the spatial distribution of the electrons only. The anomalous effect changes then to the normal Zeeman effect, a transition which is called the Paschen-Back effect.

Splitting by Electric Field

We have already seen that the electric field can perturb the states in our atoms. The perturbing Hamiltonian is:

$$H^{(1)} = -\bar{\mu}_e \bar{E}$$

Instead of an oscillating electromagnetic field, we now apply a constant electric field. For an external, steady state electric field along the z -symmetry axis of our system, the perturbation becomes:

$$H^{(1)} = -\mu_z E_z = ezE_z$$

Similar to the magnetic field, the constant electric field can overturn degeneracies in our system. For instance, for the otherwise degenerate levels $2s$ and $2p_z$ in hydrogen, the presence of an electric field will lift the degeneracy. We know that diagonal matrix elements of the electric dipole operator μ are zero, so only the off-diagonal elements are important. Using perturbation theory for degenerate states, we find for the correction to the energy:

$$E^{(1)} = \frac{1}{2}(4H_{2s,2p_z}^{(1)} H_{2p_z,2s}^{(1)})^{1/2} = \sqrt{|H_{2p_z,2s}^{(1)}|^2} = \langle 2p_z | H^{(1)} | 2s \rangle$$

Making use of the hydrogen wavefunctions, this matrix element can be shown to be

$$\langle 2p_z | H^{(1)} | 2s \rangle = 3ea_0 E_z$$

The level splitting due to the electric field is thus $\Delta E = 6ea_0 E$. This effect is called the *Stark effect*. The splitting is generally very small for typical field strengths. Only for very high electric fields are the hydrogen levels significantly altered.