

0.1 The postulates of quantum mechanics

1. The *state* of a system of N particles is represented by a unique *complex-valued wavefunction*, $\psi(\mathbf{x})$, such that

$$\|\psi\|^2 = \langle \psi | \psi \rangle = \int_{\mathbb{R}^{3N}} |\psi(\mathbf{x})|^2 d\mathbf{x} = 1. \quad \text{normalization condition} \quad (1)$$

The wavefunction belongs to a *Hilbert space* - a vector space with an inner product. Here,

$$\langle \psi_1 | \psi_2 \rangle = \int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{x}) \psi_2(\mathbf{x}) d\mathbf{x} \quad (2)$$

is the inner product of two wavefunctions (two states), ψ_1 and ψ_2 .

- (a) The state of a system is *everything* we can know about the system.
 - (b) The wavefunction (uniquely representing a state), $\psi(\mathbf{x})$, is a *smooth, single-valued, bounded* function of \mathbf{x} . Here, $\psi(\mathbf{x})$ is smooth if it, and its first *derivative(s)*, are *continuous* functions of \mathbf{x} .
 - (c) Since $|\psi(\mathbf{x})|^2$ integrates to a finite value, it must decay to zero outside a finite volume of space.
2. Each *observable*, \mathcal{A} , of the system is *represented* by a unique *Hermitian linear operator*, \hat{A} , such that the *eigenvalues* of \hat{A} , $\{a_j\}_{j=1,2,\dots}$, are the *possible outcomes* of a *measurement* of the observable - for all possible system states.

- (a) A *linear operator* satisfies the condition,

$$\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\hat{A}\psi_1 + c_2\hat{A}\psi_2, \quad (3)$$

for any states, ψ_1 and ψ_2 , and any real coefficients, c_1 and c_2 .

- (b) A *Hermitian operator* satisfies the condition,

$$\langle \psi_1 | \hat{A}\psi_2 \rangle = \langle \psi_2 | \hat{A}\psi_1 \rangle^*; \quad \text{matrix representations are Hermitian} \quad (4)$$

i.e.,

$$\int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{x}) \hat{A}\psi_2(\mathbf{x}) d\mathbf{x} = \left(\int_{\mathbb{R}^{3N}} \psi_2^*(\mathbf{x}) \hat{A}\psi_1(\mathbf{x}) d\mathbf{x} \right)^*.$$

or

$$\langle \psi_1 | \hat{A}\psi_2 \rangle = \langle \hat{A}\psi_1 | \psi_2 \rangle \quad (5)$$

- (c) This postulate provides the source of *quantization*. For bound systems (e.g., a stable atom or molecule), the eigenvalues of Hermitian linear operators generally come in discrete sets - they can be labeled by a *quantum number*, $n = 1, 2, \dots$

3. The *expectation value* of an observable (\mathcal{A}), associated with a given state of the system ($\psi(\mathbf{x})$), is given by

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} \psi \rangle = \int_{\mathbb{R}^{3N}} \psi^*(\mathbf{x}) \hat{A} \psi(\mathbf{x}) d\mathbf{x}. \quad (6)$$

The expectation value is the *average* of many measurements of the observable - all starting with the system in state, $\psi(\mathbf{x})$.

- (a) This is where probability enters into quantum mechanics. Quantum mechanics only gives probabilities of outcomes.. In fact, the postulate requires only that quantum mechanics provides the average value of many measurements. Probabilities of outcomes can be derived using this postulate - see below.
- (b) Suppose the state of the system, $\psi(\mathbf{x}) = \psi_j(\mathbf{x})$, the normalized eigenfunction of \hat{A} associated with eigenvalue, a_j ; i.e.,

$$\hat{A} \psi_j(\mathbf{x}) = a_j \psi_j(\mathbf{x}). \quad (7)$$

In this case,

$$\langle \hat{A} \rangle_j = a_j$$

The expectation value of \mathcal{A} for an eigenfunction of \hat{A} is the associated eigenvalue.

- (c) Corollary of this postulate: The *probability* that a_j will be observed upon measurement of observable \mathcal{A} , when the system is in state ψ , equals

$$\begin{aligned} \rho_j &= |\langle \psi_j | \psi \rangle|^2 \\ &= \langle \psi | \psi_j \rangle \langle \psi_j | \psi \rangle. \end{aligned} \quad (8)$$

- i. We know that, if $\psi = \psi_j$, then the outcome of a measurement of \mathcal{A} is certain to be a_j . The above formula gives this result. In this case,

$$\begin{aligned} \rho_j &= |\langle \psi_j | \psi_j \rangle|^2 \\ &= 1. \quad \psi_j \text{ is normalized} \end{aligned}$$

The *eigenfunctions* of \hat{A} thus represent states with *well-defined value* of the observable, \mathcal{A} , and that value is the associated *eigenvalue*.

- ii. $|\psi(\mathbf{x})|^2$ is the *probability density* for observing configuration \mathbf{x} . For a single particle, $|\psi(\mathbf{x})|^2$ is the probability per unit volume for finding the particle at \mathbf{x} .

2'. Operators representing observables:

- (a) The operator that corresponds to position is the multiplication operator, \mathbf{x} . Here, it is best to consider first the case of a single particle in one dimension. In this case, $\mathbf{x} = x$ is a scalar and

$$\hat{x}\psi(x) = x\psi(x); \quad (9)$$

i.e., simply multiply the function $\psi(x)$ by the function x . For one particle in three dimensions,

$$\hat{x}\psi(x, y, z) = x\psi(x, y, z),$$

$$\hat{y}\psi(x, y, z) = y\psi(x, y, z),$$

$$\hat{z}\psi(x, y, z) = z\psi(x, y, z).$$

- i. Any observable which is a function of position is also represented by a multiplication operator - simply multiply by the function of position. The potential energy operator, \hat{V} , is a multiplication operator:

$$\hat{V}\psi(\mathbf{x}) = V(\mathbf{x})\psi(\mathbf{x}). \quad (10)$$

The operator $\hat{A} = \theta_S(\mathbf{x})$, is also a multiplication operator.

- (b) The momentum operator is given by

$$\hat{\mathbf{p}} = -i\hbar \frac{\partial}{\partial \mathbf{x}}.$$

- i. An operator which is a function of momentum is given by the function with $-i\hbar\partial/\partial\mathbf{x}$ inserted as the argument. The kinetic energy operator is

$$\begin{aligned} \hat{T}\psi(\mathbf{x}) &= \frac{\hat{\mathbf{p}}^2}{2m}\psi(\mathbf{x}) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}^2} \psi(\mathbf{x}). \end{aligned} \quad (11)$$

- (c) The Hamiltonian operator:

$$\begin{aligned} \hat{H}\psi(\mathbf{x}) &= \left(\frac{\hat{\mathbf{p}}^2}{2m} + \hat{V} \right) \psi(\mathbf{x}) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}^2} \psi(\mathbf{x}) + V(\mathbf{x})\psi(\mathbf{x}) \end{aligned} \quad (12)$$

The *time independent Schrödinger equation* (TISE) is just the *eigenvalue equation* for the *energy* (Hamiltonian) operator,

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x}). \quad (13)$$

The eigenvalues are the allowed energies of the system. Energy is quantized - in agreement with spectroscopic observations. The special significance of the energy operator in QM arises because of the next postulate.

4. The time evolution of the state of a system is given by the solutions to the *time dependent Schrödinger equation* (TDSE),

$$\hat{H}\Psi(\mathbf{x}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t). \quad (14)$$

Here, we use an upper case psi, $\Psi(\mathbf{x}, t)$, to denote the time dependent state of the system. Given that the system is in the state, $\psi(\mathbf{x})$, at time = 0, the solution to the TDSE consistent with this initial condition provides the state of the system at all later times - it is a function of \mathbf{x} and t .

(a) Solution to TDSE: Let

$$\Psi(\mathbf{x}, t)|_{t=0} = \psi(\mathbf{x}).$$

For a very short time, δt ,

$$\begin{aligned} \Psi(\mathbf{x}, \delta t) &\cong \psi(\mathbf{x}) - \frac{i}{\hbar} \hat{H} \psi(\mathbf{x}) \delta t. \\ &= \left(\hat{1} - \frac{i}{\hbar} \hat{H} \delta t \right) \psi(\mathbf{x}). \end{aligned}$$

$$\begin{aligned} \Psi(\mathbf{x}, t) &= \lim_{n \rightarrow \infty} \left(\hat{1} - \frac{i}{\hbar} \hat{H} \frac{t}{n} \right)^n \psi(\mathbf{x}). \\ &= \exp \left(-\frac{i}{\hbar} \hat{H} t \right) \psi(\mathbf{x}), \end{aligned}$$

where

$$\exp(\hat{A}) = \hat{1} + \hat{A} + \frac{1}{2} \hat{A}^2 + \frac{1}{3!} \hat{A}^3 + \dots$$

is the exponential function of operator \hat{A} .

- (b) Suppose $\Psi(\mathbf{x}, t)|_{t=0} = \psi_n(\mathbf{x})$ where $\psi_n(\mathbf{x})$ is the n th energy eigenstate - i.e., the solution to the TISE,

$$\hat{H}\psi_n(\mathbf{x}) = E_n \psi_n(\mathbf{x}).$$

In this case,

$$\Psi(\mathbf{x}, t) = \exp \left(-\frac{i}{\hbar} E_n t \right) \psi_n(\mathbf{x})$$

i.

$$\begin{aligned} \hat{H} \exp \left(-\frac{i}{\hbar} E_n t \right) \psi_n(\mathbf{x}) &= \exp \left(-\frac{i}{\hbar} E_n t \right) \hat{H} \psi_n(\mathbf{x}) \\ &= E_n \exp \left(-\frac{i}{\hbar} E_n t \right) \psi_n(\mathbf{x}); \end{aligned}$$

i.e., the time evolved energy eigenstate is an equivalent (differs only by a phase factor) eigenstate.

- ii. Probability density in position space is *independent of time*, when the system state is an energy eigenstate.

$$\begin{aligned} |\Psi(\mathbf{x}, t)|^2 &= \left| \exp\left(-\frac{i}{\hbar} E_n t\right) \psi_n(\mathbf{x}) \right|^2 \\ &= |\Psi(\mathbf{x}, 0)|^2 \end{aligned}$$

- iii. Moreover, the probability of measuring *any* observable, \mathcal{A} , to have value, a_j , does not change in time, when the system state is an energy eigenstate.

$$\begin{aligned} \rho_j(t) &= |\langle \psi_j | \Psi(\mathbf{x}, t) \rangle|^2 \\ &= |\langle \psi_j | \psi_n \rangle|^2 \end{aligned}$$

- (c) Energy eigenstates are also called *stationary states* - for the above reasons.
- (d) The TDSE determines the time dependence of any state, $\Psi(x, t)$, given the state at any time (usually $t = 0$). Expand the initial state, $\psi(x)$, in terms of the energy eigenstates,

$$\psi(x) = \sum_n c_n \psi_n(x).$$

The state is given at any time, t , by

$$\begin{aligned} \Psi(x, t) &= \exp\left(-\frac{i}{\hbar} \hat{H} t\right) \psi(x) \\ &= \sum_n c_n \exp\left(-\frac{i}{\hbar} E_n t\right) \psi_n(x). \end{aligned} \tag{15}$$

The coefficients, c_n , are given by

$$c_n = \langle \psi_n | \psi \rangle.$$

0.2 Fundamental theorems of quantum mechanics

0.2.1 The eigenvalues and eigenfunctions of Hermitian operators

Theorem 1. The eigenvalues of a Hermitian operator are real.

Proof: Let $\{a_j\}$ be the eigenvalues of Hermitian operator, \hat{A} , with $\{\psi_j\}$ the corresponding eigenfunctions - i.e.,

$$\hat{A}\psi_j = a_j\psi_j.$$

The Hermitian property of \hat{A} gives

$$\langle \psi | \hat{A} \varphi \rangle = \langle \varphi | \hat{A} \psi \rangle^*,$$

for any ψ and φ . If we let $\psi = \varphi = \psi_j$, then

$$\begin{aligned} \langle \psi_j | \hat{A} \psi_j \rangle &= \langle \psi_j | \hat{A} \psi_j \rangle^* \\ \langle \psi_j | a_j \psi_j \rangle &= \langle \psi_j | a_j \psi_j \rangle^* \\ a_j \langle \psi_j | \psi_j \rangle &= a_j^* \langle \psi_j | \psi_j \rangle \\ a_j &= a_j^* \quad \text{i.e., } a_j \text{ is real} \end{aligned}$$

Theorem 2. Eigenfunctions associated with distinct eigenvalues of a Hermitian operator are orthogonal.

Proof: The Hermitian property of \hat{A} gives

$$\langle \psi | \hat{A} \varphi \rangle = \langle \varphi | \hat{A} \psi \rangle^*,$$

for any ψ and φ . If we let $\psi = \psi_j$ and $\varphi = \psi_{j'}$, such that $a_j \neq a_{j'}$, then

$$\begin{aligned} \langle \psi_j | \hat{A} \psi_{j'} \rangle &= \langle \psi_{j'} | \hat{A} \psi_j \rangle^* \\ \langle \psi_j | a_{j'} \psi_{j'} \rangle &= \langle \psi_{j'} | a_j \psi_j \rangle^* \\ a_{j'} \langle \psi_j | \psi_{j'} \rangle &= a_j^* \langle \psi_{j'} | \psi_j \rangle^* \\ a_{j'} \langle \psi_j | \psi_{j'} \rangle &= a_j \langle \psi_j | \psi_{j'} \rangle \quad a_j \text{ is real} \end{aligned}$$

or

$$(a_{j'} - a_j) \langle \psi_j | \psi_{j'} \rangle = 0.$$

Since, $a_j \neq a_{j'}$, we must have

$$\langle \psi_j | \psi_{j'} \rangle = 0;$$

i.e., ψ_j and $\psi_{j'}$ are orthogonal.

0.2.2 Commutators

Operators can be added or multiplied. Operator multiplication is like (exactly like) matrix multiplication (matrices are just operators that act on vectors). In particular, operators do not necessarily commute - specifically, in general,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}.$$

When $\hat{A}\hat{B}$ does equal $\hat{B}\hat{A}$, we say that \hat{A} and \hat{B} *commute*. Now we consider another fundamental theorem of quantum mechanics.

Theorem 3. \hat{A} and \hat{B} commute iff they have a common set of eigenfunctions, $\{\psi_j\}$.

Proof (if): Suppose \hat{A} and \hat{B} have a common set of eigenfunctions, $\{\psi_j\}$. For physical observables, the set of eigenfunctions is always a complete set - i.e., any function, $\psi(x)$, can be written as a linear combination of the eigenfunctions:

$$\psi(x) = \sum_j c_j \psi_j(x).$$

$$\begin{aligned} \hat{A}\hat{B}\psi &= \hat{A}\hat{B} \sum_j c_j \psi_j(x) \\ &= \sum_j c_j \hat{A}\hat{B}\psi_j(x) \\ &= \sum_j c_j a_j b_j \psi_j(x) \\ &= \sum_j c_j \hat{B}\hat{A}\psi_j(x) \\ &= \hat{B}\hat{A}\psi(x) \end{aligned}$$

\hat{A} and \hat{B} commute.

Proof (only if): Suppose that \hat{A} and \hat{B} commute. Let $\{\psi_j\}$ be the set of eigenfunctions of \hat{A} ; i.e.,

$$\hat{A}\psi_j = a_j \psi_j.$$

Now apply $\hat{A}\hat{B}$ to any ψ_j .

$$\begin{aligned} \hat{A}\hat{B}\psi_j &= \hat{B}\hat{A}\psi_j && \hat{A} \text{ and } \hat{B} \text{ commute} \\ &= \hat{B}a_j\psi_j && \psi_j \text{ is an eigenfunction of } \hat{A} \\ &= a_j\hat{B}\psi_j && \hat{B} \text{ is linear} \end{aligned}$$

This means that $\hat{B}\psi_j$ is an eigenfunction of \hat{A} , associated with eigenvalue, a_j . However, ψ_j is the eigenfunction of \hat{A} , associated with eigenvalue, a_j . If there is only one eigenfunction associated with eigenvalue, a_j , the eigenvalue is said to be *non-degenerate*. In this case, $\hat{B}\psi_j$ must be a multiple of ψ_j ; i.e.,

$$\hat{B}\psi_j = b_j \psi_j.$$

The multiple is denoted by b_j and is seen here to be the eigenvalue of \hat{B} associated with eigenfunction, ψ_j . Specifically, we see that ψ_j is an eigenfunction of \hat{B} and b_j is the associated eigenvalue. Thus, the eigenfunctions of \hat{A} are also eigenfunctions of \hat{B} . Degenerate case works too.

We see that commuting operators have a *common set of eigenfunctions*. This means that the associated observables have well-defined values for exactly the same states. For example, if a state has well-defined value of observable, A , then it also has well-defined value of any other observable, B , for which the operators representing A and B commute.

The commutator of two operators is simply defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

If two operators commute, their commutator is zero. To evaluate commutators, consider the operators acting on some wavefunction, $\psi(x)$. $\hat{A}\hat{B}\psi$ is given by first applying \hat{B} to ψ , then applying \hat{A} to the result.

0.2.3 The commutator of position and momentum

For position and momentum operators, we consider the action of the position and momentum commutator on an arbitrary wavefunction, $\psi(x)$.

$$\begin{aligned} [\hat{p}, x] \psi(x) &= \left[-i\hbar \frac{d}{dx}, x \right] \psi(x) && \text{definition of } \hat{p} \\ &= -i\hbar \frac{d}{dx} x \psi(x) - x \left(-i\hbar \frac{d}{dx} \right) \psi(x) && \text{definition of commutator} \\ &= -i\hbar \left(\frac{d}{dx} x \psi(x) - x \frac{d\psi(x)}{dx} \right) \\ &= -i\hbar \left(\psi(x) + x \frac{d\psi(x)}{dx} - x \frac{d\psi(x)}{dx} \right) && \text{product rule} \\ &= -i\hbar \psi(x). \end{aligned}$$

Since the above is true for all wavefunctions, $\psi(x)$, we must have

$$[\hat{p}, x] = -i\hbar \tag{16}$$

This means that $[\hat{p}, x]$ is just $-i\hbar \times$ the identity operator. Note that since

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

for all \hat{A} and \hat{B} , we also have

$$[x, \hat{p}] = i\hbar. \tag{17}$$

Position and momentum do not have a common set of eigenfunctions. Position and momentum cannot have well-defined values for the same system state.

0.3 Uncertainty principles

0.3.1 The Heisenberg uncertainty principle

The relationship between uncertainty in position and uncertainty in momentum is quantified by the *Heisenberg uncertainty principle*. To understand this principle, we must first define *uncertainty*. In quantum mechanics, the outcomes of measurements are, in general, uncertain. The mean of such outcomes is given by the expectation value of the associated operator. In statistics, the *standard deviation*, σ , gives the spread in a distribution. It is the square root of the variance,

$$\begin{aligned}
 \sigma^2 &= \langle \psi | \left(\hat{A} - \langle \hat{A} \rangle \right)^2 | \psi \rangle \\
 &= \langle \psi | \left(\hat{A}^2 - 2 \langle \hat{A} \rangle \hat{A} + \langle \hat{A} \rangle^2 \right) | \psi \rangle \\
 &= \langle \psi | \hat{A}^2 | \psi \rangle - 2 \langle \hat{A} \rangle \langle \psi | \hat{A} | \psi \rangle + \langle \hat{A} \rangle^2 \langle \psi | \psi \rangle \quad \langle \hat{A} \rangle \text{ is a constant} \\
 &= \langle \psi | \hat{A}^2 | \psi \rangle - 2 \langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2 \\
 &= \langle \psi | \hat{A}^2 | \psi \rangle - \langle \psi | \hat{A} | \psi \rangle^2,
 \end{aligned} \tag{18}$$

where

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle.$$

If ψ were an eigenfunction of \hat{A} , then $\langle \psi | \hat{A}^2 | \psi \rangle = \langle \psi | \hat{A} | \psi \rangle^2$ and $\sigma = 0$; i.e., there is no uncertainty in the value of \mathcal{A} .

For position, we have

$$\sigma_x^2 = \langle \psi | (\Delta x)^2 | \psi \rangle$$

where

$$\Delta x = x - \langle x \rangle.$$

Similarly, for momentum,

$$\sigma_p^2 = \langle \psi | (\Delta p)^2 | \psi \rangle$$

where

$$\Delta p = \hat{p} - \langle \hat{p} \rangle.$$

The *Heisenberg uncertainty principle*:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \tag{19}$$

The uncertainty in the position and momentum of a particle are reciprocally related. If one of position and momentum is precisely known, the other is less precisely known - and vice versa. $\hbar/2$ sets the scale on which the uncertainty

principle plays a role. It is not relevant to the macroscopic objects normally treated using classical mechanics. It is very important for electrons on the atomic scale.

0.3.2 Angular momentum

Angular momentum is a vector observable for particles in three dimensional space. The three components of angular momentum are given by

$$\begin{aligned}\hat{L}_x &= y\hat{p}_z - z\hat{p}_y \\ \hat{L}_y &= z\hat{p}_x - x\hat{p}_z \\ \hat{L}_z &= x\hat{p}_y - y\hat{p}_x.\end{aligned}\tag{20}$$

The angular momentum vector is the cross product of the position and momentum vectors,

$$\hat{\mathbf{L}} = \mathbf{x} \times \hat{\mathbf{p}}.$$

The order of the position and momentum factors in the terms on the right sides of the above equations does not matter because each position component is paired with a different momentum component - these operators commute. However, the different components of $\hat{\mathbf{L}}$ do not commute.

$$\begin{aligned}\left[\hat{L}_x, \hat{L}_y\right] &= -i\hbar y\hat{p}_x + i\hbar x\hat{p}_y \\ &= i\hbar (x\hat{p}_y - y\hat{p}_x) \\ &= i\hbar \hat{L}_z.\end{aligned}\tag{21}$$

Similarly,

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar \hat{L}_x$$

and

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar \hat{L}_y.$$

The latter two equations are obtained by substituting x for y , y for z and z for x . The components of angular momentum advance in the same fashion.

0.4 Since no two of the components of $\hat{\mathbf{L}}$ commute, there is no common set of eigenfunctions. However, each component of $\hat{\mathbf{L}}$ commutes with the (square) magnitude of $\hat{\mathbf{L}}$.

$$\left[\hat{L}_z, \hat{\mathbf{L}}^2\right] = 0.\tag{22}$$

0.4. SINCE NO TWO OF THE COMPONENTS OF $\hat{\mathbf{L}}$ COMMUTE, THERE IS NO COMMON SET OF EIGENFUN

We also have

$$\left[\hat{L}_x, \hat{\mathbf{L}}^2 \right] = 0$$

and

$$\left[\hat{L}_y, \hat{\mathbf{L}}^2 \right] = 0.$$

Uncertainty principles for angular momentum components:

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} \left| \left\langle \hat{L}_z \right\rangle \right|,$$

$$\sigma_{L_y} \sigma_{L_z} \geq \frac{\hbar}{2} \left| \left\langle \hat{L}_x \right\rangle \right|$$

and

$$\sigma_{L_z} \sigma_{L_x} \geq \frac{\hbar}{2} \left| \left\langle \hat{L}_y \right\rangle \right|.$$

Model systems:

0.5 Particle in a one dimensional box

Consider a mass, m , particle constrained to move in one dimension with rigid boundaries. The position of the particle is specified by one variable, x . The state of the system is represented by a function, $\psi(x)$ - the *wavefunction*. The allowed wavefunctions must be zero on the boundaries of the box, at $x = 0$ and $x = L$. Otherwise, the wave function must be continuous. Normally we would also impose the condition that the derivative of the wavefunction is continuous at the boundary. However, in this case, the derivative of the wavefunction is not continuous at the boundary. This arises because the potential of the particle in a box has infinite discontinuities. The potential is zero within the box, but infinite outside. Specifically,

$$V(x) = \begin{cases} \infty, & x \leq 0 \\ 0, & 0 < x < L \\ \infty, & L \leq x \end{cases}, \quad (23)$$

as shown in the Figure.

The infinite potential walls are accounted for by *boundary conditions*,

$$\psi(x) = 0 \quad x = 0 \text{ or } x = L$$

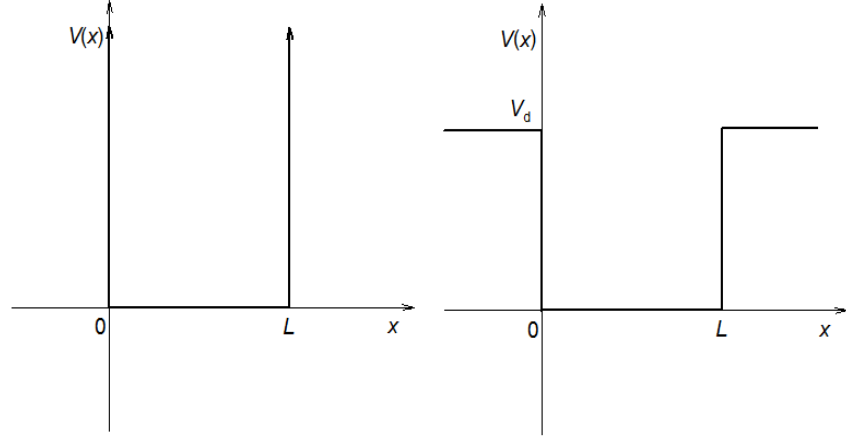


Figure 1: The particle in a one dimensional box potential (left), and particle in a finite one dimensional well (right). L is the width of the box and well. V_d is the depth of the well. The particle in a box potential is the $V_d \rightarrow \infty$ limit of the particle in a well potential.

With the above boundary conditions, we solve the TISE for the energy eigenstates. For the particle in a one dimensional box, the TISE takes the form,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \quad (24)$$

or

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

We need the *eigenfunctions* of d^2/dx^2 .

The *exponential function* is an eigenfunction of the d^2/dx^2 operator;

$$\frac{d^2}{dx^2} \exp(ax) = a^2 \exp(ax).$$

For positive energy ($E > 0$), setting

$$a^2 = -\frac{2mE}{\hbar^2}$$

gives

$$a = \pm i \frac{\sqrt{2mE}}{\hbar}$$

There are thus two solutions to Eq. 24:

$$\exp\left(i \frac{\sqrt{2mE}}{\hbar} x\right) \quad \text{and} \quad \exp\left(-i \frac{\sqrt{2mE}}{\hbar} x\right).$$

Any combination of these two functions also solves Eq. 24 . The most general solution takes the form,

$$\psi(x) = A \exp\left(i \frac{\sqrt{2mE}}{\hbar} x\right) + B \exp\left(-i \frac{\sqrt{2mE}}{\hbar} x\right).$$

Now, we impose the *boundary conditions*.

1. At $x = 0$, $\psi(x) = 0$ gives

$$0 = A + B$$

or

$$B = -A$$

and

$$\begin{aligned} \psi(x) &= A \left[\exp\left(i \frac{\sqrt{2mE}}{\hbar} x\right) - \exp\left(-i \frac{\sqrt{2mE}}{\hbar} x\right) \right] \\ &= C \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right) \end{aligned}$$

2. At $x = L$, $\psi(x) = 0$ gives

$$\begin{aligned} 0 &= C \sin\left(\frac{\sqrt{2mE}}{\hbar} L\right), \\ \sin\left(\frac{\sqrt{2mE}}{\hbar} L\right) &= 0 \end{aligned}$$

and

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \quad n = 1, 2, 3, \dots \quad \text{the zeros of the sine function} \quad (25)$$

The *energy eigenvalues* - the solutions to Eq. 25 - are given by

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (26)$$

These eigenvalues, also known as *energy levels* are depicted in Fig. 3.2. They are the possible outcomes of an energy measurement for a mass, m , particle in a one dimensional box of width, L .

The *energy eigenstates* are associated with a *discrete* set of energies. *Energy level*, E_n , is associated with energy eigenstate,

$$\psi_n(x) = C \sin\left(\frac{n\pi x}{L}\right) \quad \text{inside box, zero outside.} \quad (27)$$

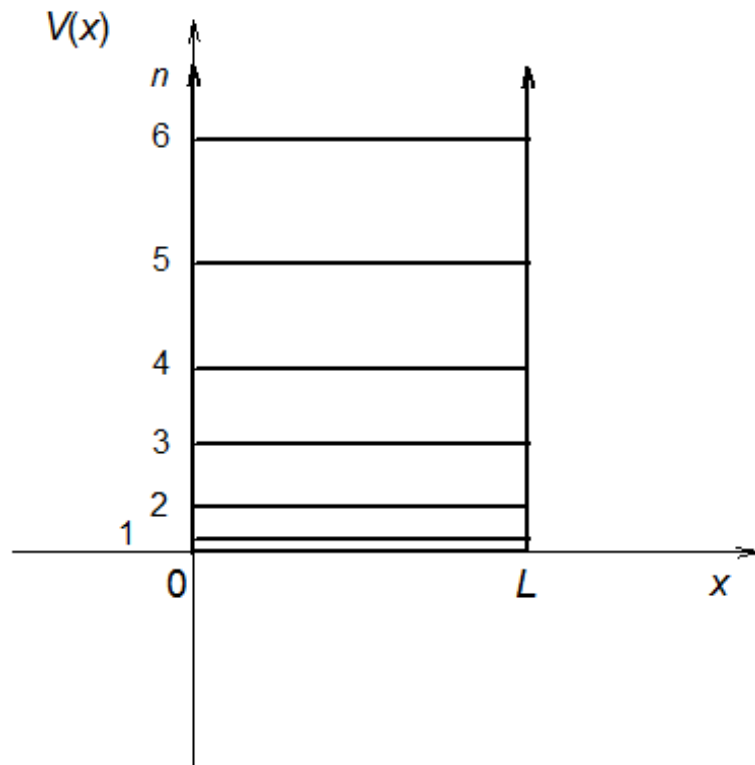


Figure 2: The first six energy levels of a particle in a one dimensional box.
 $E_n = n^2 E_1 = E_1, 4E_1, 9E_1, 16E_1, \dots$

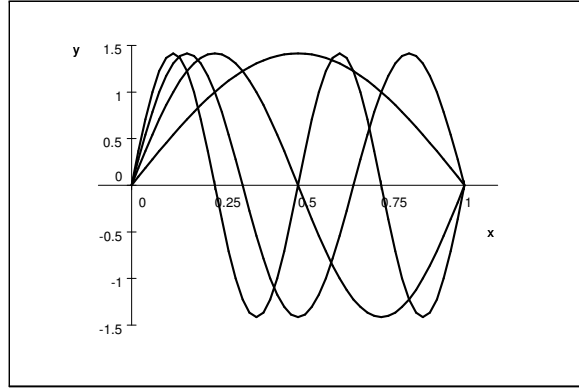


Figure 3: The first four energy eigenstates of a particle in a one dimensional box.

Discrete energy levels is a hallmark of quantum mechanics. The energy levels of any bound particle are discrete. Here, the particle is bound within a one dimensional box. The spacing between energy levels increases with increasing n , because of the n^2 energy level dependence. The spacing is reciprocal to the mass of the particle, and the square of the width of the box. A heavier particle, or a larger box, produces smaller energy level spacings.

0.5.1 Normalization of energy eigenstates

The overall multiplicative constant, C , is determined by imposing *normalization*. Specifically, we impose the condition that the probability of finding the particle somewhere inside the box is one; i.e.,

$$\int_0^L |\psi_n(x)|^2 dx = 1. \quad \text{the particle is definitely inside the box } (\psi_n(x) = 0 \text{ for } x < 0 \text{ or } L < x)$$

gives

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{inside box, zero outside.}$$

The four lowest energy eigenstates, $\psi_n(x)$ ($n = 1$ to 4), are depicted in the Figure.

0.5.2 Properties of a particle in a box

Momentum:

The expectation value of momentum for a particle in a box, in state $\psi_n(x)$:

$$\begin{aligned}
 \langle \hat{p} \rangle_n &= \langle \psi_n | \hat{p} \psi_n \rangle = \langle \hat{p} \psi_n | \psi_n \rangle \quad \hat{p} \text{ is Hermitian} \\
 &= \int_0^L \left[-i\hbar \frac{d}{dx} \psi_n(x) \right]^* \psi_n(x) dx \\
 &= \int_0^L \left[+i\hbar \frac{d}{dx} \psi_n(x) \right] \psi_n(x) dx \quad \psi_n(x) \text{ is real} \\
 &= - \int_0^L \left[-i\hbar \frac{d}{dx} \psi_n(x) \right] \psi_n(x) dx \\
 &= - \langle \hat{p} \rangle_n = 0
 \end{aligned}$$

The energy eigenstates of the particle in a box are standing waves - superpositions of *equal* amounts of *left-going* and *right-going* wavefunctions.

Position

The expectation value of position for a particle in a box, in state $\psi_n(x)$:

$$\begin{aligned}
 \langle \hat{x} \rangle_n &= \langle \psi_n | \hat{x} \psi_n \rangle = \int_0^L \psi_n^*(x) x \psi_n(x) dx \\
 &= \frac{L}{2}
 \end{aligned} \tag{28}$$

The distribution of position is spread out within the box, symmetrically about the middle, $x = L/2$. The average of many position measurements would be $L/2$, for any energy eigenstate, ψ_n .

0.5.3 Spectroscopic transitions

The *probability* P_{n_f, n_i} that the electron absorbs the light (per unit time squared, given a constant intensity of light) is proportional to the light intensity, and to the square of the expectation of the electron dipole moment, $\hat{\mu}_e = -ex$, ($-e$ is the charge on an electron).

$$P_{n_f, n_i} \propto \left| \langle \hat{\mu}_e \rangle_{n_f, n_i} \right|^2 = e^2 \left| \int_0^L x \psi_{n_f}(x) \psi_{n_i}(x) dx \right|^2.$$

For example, in the case of $n_i = 1$ and $n_f = 2$, the *transition integral* (the probability is proportional to the square of this integral) takes the form,

$$I_{2,1} = \frac{2}{L} \int_0^L x \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) dx = -\frac{16L}{9\pi^2}. \tag{29}$$

The associated transition probability is proportional to

$$P_{2,1} \propto |I_{2,1}|^2 = \frac{256L^2}{81\pi^4}.$$

$$P_{3,1} = P_{5,1} = \dots = 0$$

Transitions from odd to odd (and even to even) are forbidden

0.6 A well with finite binding energy

Bound particles are everywhere. However, for real systems, the particles have a finite *binding energy*. Particles can be ejected from a well by absorbing energy - most often by absorbing light. The lowest that can eject the particle is called the binding energy of the particle in the well. Here, we consider a one-sided well with finite depth, V_d ;

$$V(x) = \begin{cases} \infty, & x \leq 0 \\ 0, & 0 < x < L \\ V_d, & L < x \end{cases}.$$

For this potential, the particle can only escape the well to the right. The well depth is larger than the binding energy because the particle has energy in its ground state - c.f., the case of a one dimensional box.

Just like the particle in the box, we solve the Schrödinger equation inside the well and apply the boundary condition, $\psi(0) = 0$ (there is still a hard wall at $x = 0$) to get

$$\psi(x) = C_1 \sin\left(\frac{\sqrt{2mEx}}{\hbar}\right).$$

For $x > L$, the Schrödinger equation takes the form,

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V_d\right) \psi(x) = E\psi(x),$$

which rearranges to

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\frac{2m(E - V_d)}{\hbar^2} \psi \\ &= \frac{2m(V_d - E)}{\hbar^2} \psi. \end{aligned}$$

If $E < V_d$ (the states of the particle bound to the well), $V_d - E > 0$ and the general solution to this equation is

$$\begin{aligned} \psi(x) &= A \exp\left(\frac{\sqrt{2m(V_d - E)}x}{\hbar}\right) + B \exp\left(-\frac{\sqrt{2m(V_d - E)}x}{\hbar}\right) \\ &= B \exp\left(-\frac{\sqrt{2m(V_d - E)}x}{\hbar}\right) \quad \text{the other function blows up} \end{aligned}$$

This is a boundary condition at infinity - solutions which blow up are discarded. This leaves

$$\psi(x) = \begin{cases} C_1 \sin\left(\frac{\sqrt{2mE}x}{\hbar}\right), & 0 < x < L \\ C_2 \exp\left(-\frac{\sqrt{2m(V_d - E)}(x - L)}{\hbar}\right), & L < x \end{cases},$$

The exponential decay portion of the wavefunction is called *barrier penetration*. In quantum mechanics, particles penetrate into regions where they are *classically forbidden*. In classical mechanics, a particle cannot be in a place, x , where $E < V(x)$. This is because kinetic energy cannot be negative. When wavefunctions penetrate into classically forbidden regions, they decay exponentially. A larger difference between the barrier and particle energy, or larger mass of particle, produces a faster exponential decay.

0.6.1 Energy levels

Since the wavefunction must be smooth, it is subject to boundary conditions at $x = L$.

First, the values of $\psi^{(1)}(x)$ and $\psi^{(2)}(x)$ must match at $x = L$;

$$\psi^{(1)}(L) = \psi^{(2)}(L),$$

or

$$C_1 \sin\left(\frac{\sqrt{2mEL}}{\hbar}\right) = C_2. \quad (30)$$

This reduces the number of arbitrary constants back to one.

Next, the derivatives of $\psi^{(1)}(x)$ and $\psi^{(2)}(x)$ must match at $x = L$. This gives the smoothest possible wavefunction at a discontinuity in the potential.

$$\left.\frac{d\psi^{(1)}}{dx}\right|_{x=L} = \left.\frac{d\psi^{(2)}}{dx}\right|_{x=L},$$

or

$$\frac{\sqrt{2mE}}{\hbar} C_1 \cos\left(\frac{\sqrt{2mEL}}{\hbar}\right) = -\frac{\sqrt{2m(V_d - E)}}{\hbar} C_2. \quad (31)$$

or

$$\tan\left(\frac{\sqrt{2mEL}}{\hbar}\right) = -\sqrt{\frac{E}{V_d - E}}. \quad (32)$$

This is an equation only for the energy. It is the *quantization condition* for the particle in a (one-sided) well.

ϵ_1 is the ground state energy of the particle in the same width box - i.e.,

$$\epsilon_1 = \frac{\pi^2 \hbar^2}{2mL^2}.$$

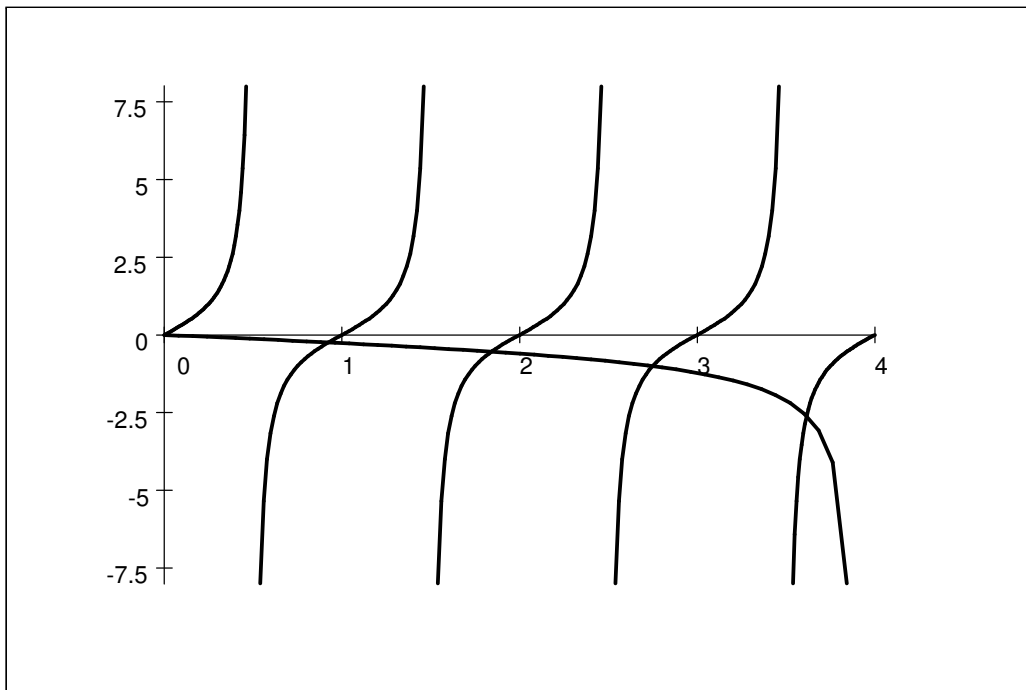


Figure 4: The quantization condition for a particle in a well. The intersections of the tangent function (solid) and the square root function (dashed) determine the energy levels. The well depth, $V_0 = 15\epsilon_1$, where $\epsilon_1 = \pi^2\hbar^2/(2mL^2)$ is the ground state the particle in a box with the same width. The horizontal axis here is $(E/\epsilon_1)^{1/2}$.

The number of intersections is finite because the square root function on the right of Eq. 32 is real only if $E < V_d$. There are no bound states with energy above the well depth. This is the biggest contrast with the particle in a box. A finite well depth produces a finite number of bound states. The figure shows that the number of bound states is just $(V_d/\epsilon_1)^{1/2}$, rounded to the nearest whole number. The energy levels of the *particle in a well* are lower than the corresponding particle in a box levels.

$$\begin{aligned} E_n &= \eta_n^2 \epsilon_1 \\ &\cong (n - \delta_n)^2 \epsilon_1 \\ &= n^2 \left(\frac{\eta_d}{\eta_d + 1/\pi} \right)^2 \epsilon_1. \end{aligned} \tag{33}$$

0.6.2 Bound state energy eigenfunctions

$$\psi_n(x) \cong \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{\eta_d}{\eta_d + 1/\pi} \frac{n\pi x}{L}\right), & 0 < x < L \\ \sqrt{\frac{2}{L}} \frac{(-1)^{n+1} n}{\eta_d + 1/\pi} \exp\left(-\left(\eta_d^2 - n^2 \left(\frac{\eta_d}{\eta_d + 1/\pi}\right)^2\right)^{1/2} \frac{\pi(x-L)}{L}\right), & L < x \end{cases} \tag{34}$$

These wavefunctions are depicted in the Figure.

0.6.3 State with energy above binding energy

For energy greater than the binding energy, the particle is not bound to the box. If $E > V_d$, $E - V_d > 0$ and the general solution to the Schrödinger equation for $x > L$ is

$$\psi(x) = A \exp\left(i \frac{\sqrt{2m(E - V_d)}x}{\hbar}\right) + B \exp\left(-i \frac{\sqrt{2m(E - V_d)}x}{\hbar}\right),$$

or

$$\psi(x) = C_2 \exp\left(i \frac{\sqrt{2m(E - V_d)}(x - L)}{\hbar}\right) + C_3 \exp\left(-i \frac{\sqrt{2m(E - V_d)}(x - L)}{\hbar}\right),$$

Neither of the two solutions blows up as $x \rightarrow \infty$. They describe *beams* of particles. These *beam states* are spread over an infinite distance, and they have infinite norm. However, they are *beam-normalized*: $|\psi(x)|^2$ gives the number of particles per unit distance, at x .

Because neither of the two arbitrary constants, C_2 and C_3 , is eliminated by the boundary condition at $x = \infty$, there is one less constraint on the coefficients than there were in the case of bound states. Energy is not quantized for states above the binding energy - it varies continuously, just as in classical mechanics.

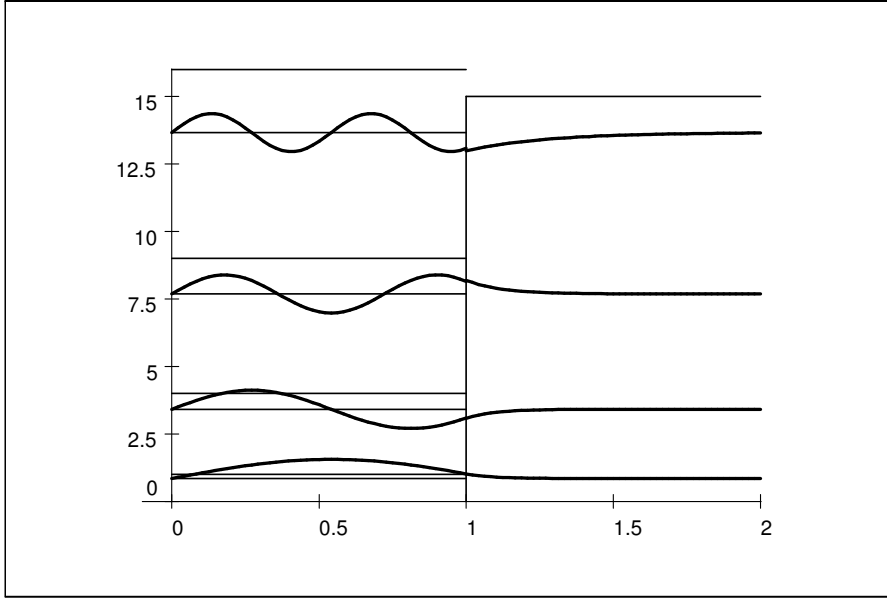


Figure 5: The four bound energy eigenstates of a particle in a one dimensional well. The wavefunctions (solid) are show superimposed on a potential energy plot (dashed). There is separate vertical axis for each wavefunction - the wavefunction zero is translated vertically to match the associated energy eigenvalue. The wavefunctions are scaled by $1/2$, so they do not overlap. The energy levels are depicted with thin dashed lines, while the corresponding particle in a box energy levels are shown as dotted lines. Eigenfunctions and eigenvalues are computed using Eqs. 34 and 33 , respectively.

The boundary conditions at $x = L$ relate unknown coefficient C_1 to unknown coefficients, C_2 and C_3 . Specifically,

$$\psi^{(1)}(L) = \psi^{(2)}(L),$$

gives

$$C_1 \sin(kL) = C_2 + C_3, \quad (35)$$

where

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

is the wavenumber that corresponds with energy, E . Also,

$$\left. \frac{d\psi^{(1)}}{dx} \right|_{x=L} = \left. \frac{d\psi^{(2)}}{dx} \right|_{x=L},$$

gives

$$kC_1 \cos(kL) = i\sqrt{k^2 - k_d^2} (C_2 - C_3), \quad (36)$$

where

$$k_d = \frac{\sqrt{2mV_d}}{\hbar}$$

is the well-depth wavenumber.

For a unit intensity incoming beam, $C_3 = 1$. In this case,

$$C_1 \sin(kL) = C_2 + 1$$

and

$$kC_1 \cos(kL) = i\sqrt{k^2 - k_d^2} (C_2 - 1),$$

or

$$\frac{1}{k} \tan(kL) = -i \frac{1}{\sqrt{k^2 - k_d^2}} \left(\frac{C_2 + 1}{C_2 - 1} \right)$$

which gives

$$C_2 = -\frac{\kappa + i\sigma}{\kappa - i\sigma} \quad (37)$$

where

$$\kappa = k \cos(kL)$$

and

$$\sigma = \sqrt{k^2 - k_d^2} \sin(kL).$$

$|C_2|^2 = 1$; i.e., the intensity of the outgoing beam equals that of the incoming beam. This corresponds to particle conservation - there is an outgoing particle for every incoming particle.

Determining C_1 completes specification of the wavefunction.

$$\begin{aligned} C_1 &= -\frac{2i\sigma}{(\kappa - i\sigma) \sin(kL)} \\ &= -2i \frac{\sqrt{k^2 - k_d^2}}{\kappa - i\sigma} \end{aligned}$$

and

$$\psi_E(x) = \begin{cases} 2i \frac{\sqrt{k^2 - k_d^2}}{\kappa - i\sigma} \sin(kx), & 0 < x < L \\ -\frac{\kappa + i\sigma}{\kappa - i\sigma} \exp\left(i\sqrt{k^2 - k_d^2}(x - L)\right) \\ \quad + \exp\left(-i\sqrt{k^2 - k_d^2}(x - L)\right), & L < x \end{cases} \quad (38)$$

The the mean particle density within the well is

$$\begin{aligned} |C_1|^2 / 2 &= 2 \frac{k^2 - k_d^2}{\kappa^2 + \sigma^2} \\ &= 2 \frac{k^2 - k_d^2}{k^2 \cos^2(kL) + (k^2 - k_d^2) \sin^2(kL)} \\ &= 2 \frac{k^2 - k_d^2}{k^2 - k_d^2 \sin^2(kL)} \end{aligned}$$

It has a maximum of 2, when $\sin(kL) = \pm 1$, or $kL = (n + 1/2)\pi$. Corresponding energies are called *resonances*.

If the well were *two-sided* - i.e., the infinite barrier on the left is replaced by a V_d barrier, as on the right - then the resonance condition reverts back to the particle in a box quantization condition, $kL = n\pi$. At the particle in a box energies, a wave incoming from the right passes through the barrier with 100% likelihood - i.e., 100% transmission probability. At other energies, there is some reflection. Reflection is a maximum at half integral multiples of π , in this case.

0.6.4 Tunneling

We now suppose that the barrier on the right side of the well just described has a finite width, w . Here, there is a second boundary at $x = L + w$, beyond which $V(x) = V_e < V_d$, the particle escape potential. Specifically,

$$V(x) = \begin{cases} \infty, & x \leq 0 \\ 0, & 0 < x < L \\ V_d, & L < x < L + w \\ V_e, & L + w < x \end{cases} \quad .$$

We consider the below barrier - but above escape potential - case with $V_e < E < V_d$. In this case, were it not for the escape channel on right, the eigenstates would be the particle in a well bound states found in Sec. 3.2.2 above. To find

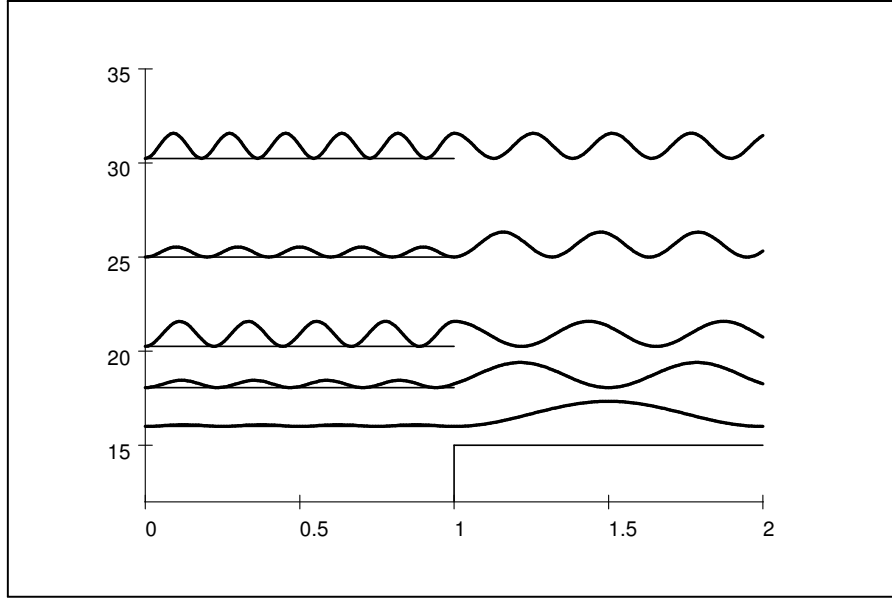


Figure 6: Some unbound energy eigenstates of a beam of particles encountering a one dimensional well. The wavefunctions (solid) are show superimposed on a potential energy plot (dashed). Here, the top of the well is just visible. There is separate vertical axis for each wavefunction - the wavefunction zero is translated vertically to match the associated energy eigenvalue. Since all energies above V_d are eigenvalues, only a few examples are shown. The wavefunctions are scaled by $1/3$, so they do not overlap. The energy levels are depicted with thin dashed lines. Eigenfunctions are computed using Eq. 38 .

the new energy eigenstates requires introducing two new constants, and satisfying two new boundary conditions. Anticipating that there will be resonances at the well energy eigenvalues between V_e and V_d , we consider the beam states of the particle only at these energies. In addition, rather than imposing a unit intensity incoming (or outgoing) beam from the left, we normalize by imposing that there be one particle in well. The resulting outgoing beam intensity is related to probability (per unit time) with which the particle tunnels from the well. Consequently, we adopt the following wavefunction - expressed in terms of four unknown coefficients - with the coefficient in the well specified by the one particle normalization - the wavefunction integrates to (close to) 1 within the well.

$$\psi_{E_n}(x) \cong \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{\eta_n \pi x}{L}\right), & 0 < x < L \\ C_1 \exp\left(-(\eta_d^2 - \eta_n^2)^{1/2} \frac{\pi(x-L)}{L}\right) \\ + C_2 \exp\left((\eta_d^2 - \eta_n^2)^{1/2} \frac{\pi(x-L)}{L}\right) & L < x < L + w \\ C_3 \exp\left(i(\eta_n^2 - \eta_e^2)^{1/2} \frac{\pi(x-L-w)}{L}\right) \\ + C_4 \exp\left(-i(\eta_n^2 - \eta_e^2)^{1/2} \frac{\pi(x-L-w)}{L}\right) & L + w < x \end{cases} \quad (39)$$

where

$$\eta_n = n \frac{\eta_d}{\eta_d + 1/\pi}$$

and

$$\eta_e = \frac{\sqrt{2mV_e}}{\pi\hbar} L.$$

The boundary conditions at $x = L$ are the continuity equation,

$$\sqrt{\frac{2}{L}} \sin(\eta_n \pi) = C_1 + C_2,$$

and the continuity of derivative equation,

$$\sqrt{\frac{2}{L}} \eta_n \frac{\pi}{L} \cos(\eta_n \pi) = -(\eta_d^2 - \eta_n^2)^{1/2} \frac{\pi}{L} (C_1 - C_2)$$

which give

$$\frac{C_1 + C_2}{C_1 - C_2} = -\frac{(\eta_d^2 - \eta_n^2)^{1/2}}{\eta_n} \tan(\eta_n \pi) = -\tau$$

or

$$C_2 = -\frac{\tau + 1}{\tau - 1} C_1.$$

Substituting this back into the first equation gives,

$$\begin{aligned} \sqrt{\frac{2}{L}} \sin(\eta_n \pi) &= \left(1 - \frac{\tau + 1}{\tau - 1}\right) C_1 \\ &= -\frac{2}{\tau - 1} C_1 \end{aligned}$$

or

$$C_1 = -\frac{\tau-1}{2}\sqrt{\frac{2}{L}}\sin(\eta_n\pi)$$

and

$$C_2 = \frac{\tau+1}{2}\sqrt{\frac{2}{L}}\sin(\eta_n\pi).$$

At the resonance energies, $\tau = -1$. In this case,

$$C_1 = \sqrt{\frac{2}{L}}\sin(\eta_n\pi)$$

and

$$C_2 = 0.$$

The energy eigenstate reduces to the form of the well bound state, at resonance energies.

The boundary conditions at $x = L + w$ are the continuity equation,

$$C_1\gamma + C_2\gamma^{-1} = C_3 + C_4$$

where

$$\gamma = \exp\left(-(\eta_d^2 - \eta_n^2)^{1/2} \frac{\pi w}{L}\right)$$

and the continuity of derivative equation,

$$-(\eta_d^2 - \eta_n^2)^{1/2} \frac{\pi}{L} (C_1\gamma - C_2\gamma^{-1}) = i(\eta_n^2 - \eta_e^2)^{1/2} \frac{\pi}{L} (C_3 - C_4).$$

Under resonance conditions, these two equations become

$$\gamma\sqrt{\frac{2}{L}}\sin(\eta_n\pi) = C_3 + C_4$$

and

$$i\left(\frac{\eta_d^2 - \eta_n^2}{\eta_n^2 - \eta_e^2}\right)^{1/2} \gamma\sin(\eta_n\pi) = C_3 - C_4.$$

These lead to

$$\frac{C_3 - C_4}{C_3 + C_4} = i\left(\frac{\eta_d^2 - \eta_n^2}{\eta_n^2 - \eta_e^2}\right)^{1/2} = i\beta$$

or

$$C_3 = \frac{1+i\beta}{2}\gamma\sqrt{\frac{2}{L}}\sin(\eta_n\pi)$$

and

$$C_4 = \frac{1-i\beta}{2}\gamma\sqrt{\frac{2}{L}}\sin(\eta_n\pi).$$

The intensity of the outgoing beam - i.e., the probability, per unit distance, of finding a particle in the beam - is just

$$\begin{aligned} |C_3|^2 &= \frac{1 + \beta^2}{2L} \gamma^2 \sin(\eta_n \pi) \\ &= \frac{V_d - V_e}{2L(E_n - V_e)} \exp\left(-2(2m(V_d - E_n))^{1/2} \frac{w}{\hbar}\right) \sin\left((2mE_n)^{1/2} \frac{L}{\hbar}\right). \end{aligned}$$

$|C_4|^2 = |C_3|^2$ gives the intensity of the associated incoming beam that maintains one particle in the well. If we multiply $|C_3|^2$ by the velocity of the outgoing particles, $(2(E_n - V_e)/m)^{1/2}$, we get the outgoing flux - the probability per unit time of a particle *tunneling* from the n th state of the well,

$$\begin{aligned} P_{\text{tunnel}} &= (2(E_n - V_e)/m)^{1/2} |C_3|^2 \\ &= \frac{V_d - V_e}{L(2m(E_n - V_e))^{1/2}} \exp\left(-2(2m(V_d - E_n))^{1/2} \frac{w}{\hbar}\right) \sin\left((2mE_n)^{1/2} \frac{L}{\hbar}\right) \end{aligned} \quad (40)$$

The tunneling probability (flux) decreases exponentially with increasing barrier width, and the square root of the energy difference to the top of the barrier.

A simple model for *scanning tunneling microscopy (STM)*. In STM, a very sharp metal tip (represented above by the escape region to the right) is brought very close to the surface of another metal. Atoms on the surface are like wells for electrons. Tunneling current, $-eP_{\text{tunnel}}$, is measured as the tip is scanned across the metal surface. The distance between the tip and an atom on the surface is represented here by w . Because the exponential function is so sensitive to w , a distinctly larger current is measured when the tip is directly over an atom, than when it is over the space between atoms. The exponential sensitivity of STM gives it *atomic level resolution*. Individual atoms can be seen on the surface when the tunneling current, as a function of tip position over the surface, is itself rendered as a surface.

0.7 Particle in a three dimensional box

The particle in a three dimensional box has three coordinates, and state represented by a wavefunction, $\psi(x, y, z)$. The Hamiltonian for this problem is pure kinetic energy, with three components,

$$\begin{aligned} \hat{H} &= \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) \\ &= \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). \end{aligned}$$

The potential energy is zero inside the box.

The TISE for this problem,

$$\begin{aligned} \hat{H}\psi(x, y, z) &= E\psi(x, y, z) \\ &= \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z), \end{aligned} \quad (41)$$

is solved by the product state,

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z).$$

Substitute this *ansatz* into the TISE, and divide both sides by $\psi(x, y, z)$, to get

$$E = E_x + E_y + E_z,$$

where

$$\begin{aligned} \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi_x(x) &= E_x \psi_x(x), \\ \frac{-\hbar^2}{2m} \frac{d^2}{dy^2} \psi_y(y) &= E_y \psi_y(y) \end{aligned}$$

and

$$\frac{-\hbar^2}{2m} \frac{d^2}{dz^2} \psi_z(z) = E_z \psi_z(z).$$

This is called *separation of variables*.

The total energy is the sum of three energy eigenvalues - one for each degree of freedom:

$$E = E_x + E_y + E_z.$$

Each of the individual energies is an eigenvalue of a particle in a one dimensional box. The energy eigenvalues are labeled by three quantum numbers, n_x , n_y and n_z , each varying from 1 to ∞ in unit steps (1, 2, 3, ...). If the box has length a in the x direction, b in the y direction and c in the z direction, the energy eigenvalues are

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right). \quad (42)$$

If $a = b = c$, then

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2),$$

and there are many degeneracies. First, any distinct permutation of the three quantum numbers produces the same energy. If all three quantum numbers are different, then there are six such permutations. There are even more degeneracies. For example, since $36 + 49 = 4 + 81$, the quantum numbers $(6, 7, n)$ (or any permutation) produce the same energy as $(2, 9, n)$ (or any permutation).

The eigenfunctions associated with the above energy eigenvalues are given by

$$\begin{aligned} \psi_{n_x, n_y, n_z}(x, y, z) &= \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \\ &= \frac{2^{3/2}}{\sqrt{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right). \end{aligned}$$

0.7.1 Properties of a particle in three dimensional box

The inner product for states of a particle in three dimensions is an integral over all three coordinates, x , y and z . For example, the *expectation value* of x for a particle in the above state, $\psi_{n_x, n_y, n_z}(x, y, z)$, is

$$\begin{aligned}\langle x \rangle_{n_x, n_y, n_z} &= \int_0^a \int_0^b \int_0^c \psi_{n_x, n_y, n_z}^*(x, y, z) x \psi_{n_x, n_y, n_z}(x, y, z) dx dy dz \\ &= \frac{2}{a} \int_0^a x \sin^2\left(\frac{n_x \pi x}{a}\right) dx \frac{2}{b} \int_0^b \sin^2\left(\frac{n_y \pi y}{b}\right) dy \frac{2}{c} \int_0^c \sin^2\left(\frac{n_z \pi z}{c}\right) dz \\ &= \frac{a}{2} \times 1 \times 1 = \frac{a}{2}. \quad \text{see Eq. 28}\end{aligned}$$

0.8 Many independent electron systems

When we treat a multiparticle system, the wavefunction is a function of the coordinates of all the particles. However, if the particle-particle interaction is negligible, or can be approximated by a *mean field*, the energy eigenstates are products of one-particle states. In this case, the energy eigenvalues are sums of one-particle eigenvalues. When the particles are electrons, the energy eigenstates must satisfy the *Pauli principle*. This means that only two electrons - one with spin up, the other with spin down - can occupy each one-particle state. This limits the number of energy levels of an n electron system. These points are illustrated by considering many electrons in one and three dimensional boxes, and in a one dimensional well.

0.8.1 Many electrons in a one dimensional box

For example, four electrons in a box produces the ground state energy,

$$\begin{aligned}E_{\text{g.s.}} &= 2E_1 + 2E_2 \\ &= (2 + 2 \times 2^2) E_1 \\ &= 10E_1\end{aligned}$$

because the two lowest energy one-particle states accomodate the four electrons. The first excited state energy for this system corresponds to one of the $n = 2$ electrons excited to the $n = 3$ level, and its energy is given by

$$\begin{aligned}E_{1\text{st e.s.}} &= 2E_1 + E_2 + E_3 \\ &= (2 + 2^2 + 3^2) E_1 \\ &= 15E_1.\end{aligned}$$

The transition energy, $5E_1$, is just the difference in energy between the $n = 3$ and $n = 2$ levels. It is an even to odd transition that is *dipole-allowed*.

The next three excited states of the four electron system have energy,

$$\begin{aligned} E_{2\text{nd e.s.}} &= E_1 + 2E_2 + E_3 \\ &= (1 + 2 \times 2^2 + 3^2) E_1 \\ &= 18E_1, \end{aligned}$$

$$\begin{aligned} E_{3\text{rd e.s.}} &= 2E_1 + 2E_3 \\ &= (2 + 2 \times 3^2) E_1 \\ &= 20E_1 \end{aligned}$$

and

$$\begin{aligned} E_{4\text{th e.s.}} &= 2E_1 + E_2 + E_4 \\ &= (2 + 2^2 + 4^2) E_1 \\ &= 22E_1. \end{aligned}$$

However, transitions to these levels are *dipole-forbidden*. The first of these requires a 1 to 3 transition - an odd to odd - while the last requires a 2 to 4 transition - an even to even. The third excited state is also dipole-forbidden - it requires two electrons to make transitions simultaneously. This is dipole-forbidden for independent electron systems.

0.8.2 Many electrons in a three dimensional box

Now, we let the box be three dimensional - in particular a cubic box; $a = b = c$. In this case, the first three one-particle energy levels are

$$\begin{aligned} E_1 &= E_{1,1,1} = (1^2 + 1^2 + 1^2) \epsilon_1 \\ &= 3\epsilon_1, \end{aligned}$$

$$\begin{aligned} E_2 &= E_{1,1,2} = (1^2 + 1^2 + 2^2) \epsilon_1 \\ &= 6\epsilon_1 \end{aligned}$$

and

$$\begin{aligned} E_3 &= E_{1,2,2} = (1^2 + 2^2 + 2^2) \epsilon_1 \\ &= 9\epsilon_1 \end{aligned}$$

where

$$\epsilon_1 = \frac{\hbar^2 \pi^2}{2ma^2}.$$

The second and third energy levels are triply degenerate. The three distinct permutations of the indices 1,1,2 and 1,2,2 produce the same energy. Thus, the

first two energy levels can accomodate eight electrons. The ground and first excited state energies of eight electron in this box are

$$\begin{aligned} E_{\text{g.s.}} &= 2E_1 + 6E_2 \\ &= (2 \times 3 + 6 \times 6) \epsilon_1 \\ &= 42\epsilon_1 \end{aligned}$$

and

$$\begin{aligned} E_{\text{1st e.s.}} &= 2E_1 + 5E_2 + E_3 \\ &= (2 \times 3 + 5 \times 6 + 9) E_1 \\ &= 45\epsilon_1. \end{aligned}$$

Transitions to the first excited state are dipole-allowed, involving an $n_x = 1$ to 2 (or, for n_y or n_z) transition of one electron from the E_2 to the E_3 level. The energy difference is $3\epsilon_1$.

0.8.3 Many electrons in a one dimensional well

We return to electrons in one dimension - this time in a well with finite depth. The finite well depth allows the system to model ionization processes - the electrons can escape. We determine the ionization energy and electron affinity for a system of four independent electrons in the well depicted in Figure 3.6. These electrons occupy the bottom two one-electron levels - two electrons in each. The ground state energy is

$$\begin{aligned} E_{\text{g.s.}} &= 2E_1 + 2E_2 \\ &= 2(\eta_1^2 + \eta_2^2) \epsilon_1 \\ &= 2(1^2 + 2^2) \left(\frac{\eta_d}{\eta_d + 1/\pi} \right)^2 \epsilon_1 \\ &= 10E_1 \end{aligned}$$

Suppose the four electron system is neutral - i.e., the well has a net charge of $+4e$ that binds the electrons. The (first) ionization energy, I_1 , is the difference in energy between the cation ground state plus one electron at the ionization threshold, and the ground state of the neutral system. Here, the ionization threshold is $V_d = \eta_d^2 \epsilon_1 (= 15\epsilon_1$ for the well depicted in Fig. 3.6).

$$\begin{aligned} I_1 &= E_{\text{cation g.s.}} + V_d - E_{\text{g.s.}} \\ &= 2E_1 + E_2 + V_d - 10E_1 \\ &= 6E_1 + V_d - 10E_1 \\ &= \eta_d^2 \epsilon_1 - 4 \left(\frac{\eta_d}{\eta_d + 1/\pi} \right)^2 \epsilon_1 \\ &= \left(15 - 4 \frac{15}{(\sqrt{15} + 1/\pi)^2} \right) \epsilon_1 \\ &= 11.584\epsilon_1 \end{aligned}$$

The (first) electron affinity, A_1 , is the difference in energy between the anion ground state, and the neutral system plus one electron at the ionization threshold.

$$\begin{aligned}
A_1 &= E_{\text{anion g.s.}} - (E_{\text{g.s.}} + V_d) \\
&= 2E_1 + 2E_2 + E_3 - 10E_1 - V_d \\
&= 19E_1 - 10E_1 - V_d \\
&= 9 \left(\frac{\eta_d}{\eta_d + 1/\pi} \right)^2 \epsilon_1 - \eta_d^2 \epsilon_1 \\
&= \left(9 \frac{15}{(\sqrt{15} + 1/\pi)^2} - 15 \right) \epsilon_1 \\
&= -7.3151 \epsilon_1
\end{aligned}$$

Many electrons in boxes or wells provide models for *quantum dots* - nanocrystals of a semiconductor.

Chapter 1

Vibrations of a diatomic molecule

Diatomic molecules vibrate and rotate, while their center of mass travels freely. The diatomic molecule is well-modeled by first solving the Schrödinger equation for the electrons in the diatomic molecule, for all distances between the nuclei. The resulting electronic ground state energy, as a function of distance between the nuclei, becomes the potential energy that binds the nuclei together. We suppose that the electronic portion of the Schrödinger equation has been solved, and the Schrödinger equation for two nuclei has a potential energy that depends only on the distance between the nuclei. Since we have two particles in three dimensional space, there are six degrees of freedom in total - three coordinates for each nucleus. The TISE is a partial differential equation in six coordinates. However, it is subject to *separation of variables*.

1.1 Relative and center of mass motion

The Hamiltonian has the form,

$$\hat{H} = \frac{1}{2m_1}\hat{\mathbf{p}}_1^2 + \frac{1}{2m_2}\hat{\mathbf{p}}_2^2 + V(r),$$

where $\hat{\mathbf{p}}_1$ and $\hat{\mathbf{p}}_2$ are the momentum operators (each a three component vector) for nucleus 1 and nucleus 2. These momentum operators are conjugate to the position vectors, \mathbf{x}_1 and \mathbf{x}_2 of the two nuclei;

$$\hat{\mathbf{p}}_j = -i\hbar \frac{\partial}{\partial \mathbf{x}_j}$$

is the gradient with respect to the coordinates of the j th atom (nucleus). Since the potential depends only on

$$r = \|\mathbf{x}_2 - \mathbf{x}_1\|,$$

we change variables to *relative* and *center of mass* variables,

$$\mathbf{x} = \mathbf{x}_2 - \mathbf{x}_1$$

and

$$\mathbf{X} = \frac{m_1 \mathbf{x}_1 + m_2 \mathbf{x}_2}{M},$$

respectively. $M = m_1 + m_2$ is the total mass. The result is

$$\psi(\mathbf{x}, \mathbf{X}) = \psi_{\text{rel}}(\mathbf{x}) \psi_{\text{cen}}(\mathbf{X})$$

and note that the TISE separates into

$$\left(\frac{1}{2m} \hat{\mathbf{p}}^2 + V(\|\mathbf{x}\|) \right) \psi_{\text{rel}}(\mathbf{x}) = E_{\text{rel}} \psi_{\text{rel}}(\mathbf{x}) \quad (1.1)$$

and

$$\frac{1}{2M} \hat{\mathbf{P}}^2 \psi_{\text{cen}}(\mathbf{X}) = E_{\text{cen}} \psi_{\text{cen}}(\mathbf{X}). \quad (1.2)$$

The total energy is the sum of relative and center of mass energies,

$$E = E_{\text{cen}} + E_{\text{rel}}.$$

Here,

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

is the reduced mass.

1.1.1 Center of mass motion

The center of mass TISE - Eq. 1.2 above - in turn separates into three independent TISE's - one for each dimension of space;

$$\begin{aligned} \psi_{\text{cen}}(\mathbf{X}) &= \psi_{\text{cen}, X}(X) \psi_{\text{cen}, Y}(Y) \psi_{\text{cen}, Z}(Z), \\ \frac{1}{2M} \hat{P}_X^2 \psi_{\text{cen}, X}(X) &= E_{\text{cen}, X} \psi_{\text{cen}, X}(X), \quad \text{etc.} \end{aligned} \quad (1.3)$$

and

$$E_{\text{cen}} = E_{\text{cen}, X} + E_{\text{cen}, Y} + E_{\text{cen}, Z}.$$

Center of mass motion is *unbound* - it is the motion of a free particle in three dimensions. For each coordinate, there are two states - plane waves corresponding to forward and backward motion - for each energy eigenvalue, $E_{\text{cen}, X, Y \text{ or } Z} > 0$. For energy greater than or equal to zero, the *plane wave solutions* are

$$\psi_{\text{cen}}(\mathbf{X}) = \exp\left(i \frac{\sqrt{2ME_{\text{cen}, X}}}{\hbar} X\right) \exp\left(i \frac{\sqrt{2ME_{\text{cen}, Y}}}{\hbar} Y\right) \exp\left(i \frac{\sqrt{2ME_{\text{cen}, Z}}}{\hbar} Z\right).$$

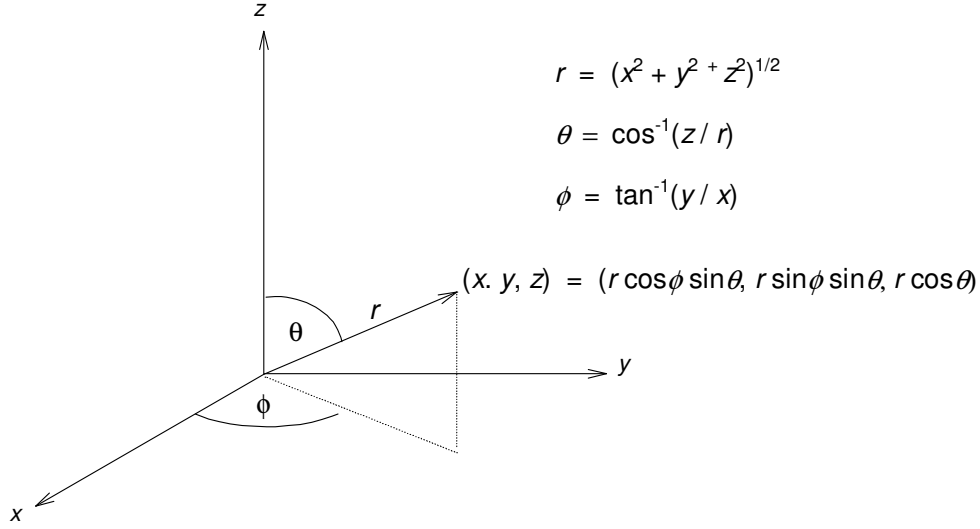


Figure 1.1: Cartesian coordinates in terms of spherical coordinates - and vice versa.

1.2 Relative motion - angular and radial

The relative TISE - Eq. 1.1 above - also further separates. Here, we must change variables - this time from Cartesian (x , y and z) to *spherical coordinates*, (r , θ and ϕ) defined in Figure 4.1.

$$\psi(r, \theta, \phi) = \psi_r(r) Y(\theta, \phi).$$

Substituting this form into the TISE for the relative motion gives

$$\left(-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + V(r) + \frac{1}{2mr^2} \hat{\mathbf{L}}^2 \right) \psi_r(r) Y(\theta, \phi) = E \psi_r(r) Y(\theta, \phi).$$

If $Y(\theta, \phi)$ is an eigenfunction of $\hat{\mathbf{L}}^2$, i.e.,

$$\hat{\mathbf{L}}^2 Y(\theta, \phi) = L^2 Y(\theta, \phi),$$

then we can divide the above equation by $Y(\theta, \phi)$ to get

$$\left[-\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + V(r) + \frac{L^2}{2mr^2} \right] \psi_r(r) = E \psi_r(r)$$

The kinetic energy portion of the above radial TISE can be simplified by making the substitution,

$$\psi_r(r) = \frac{1}{r} \varphi(r),$$

to get

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) + \frac{L^2}{2mr^2}\right) \varphi(r) = E\varphi(r)$$

the *TISE* for a mass, m , particle in one dimension subject to the potential, $V(r) + L^2/(2mr^2)$.

1.3 The quantum harmonic oscillator

The radial relative motion of the diatomic molecule is the *molecular vibration*. Typically, the binding potential, $V(r)$, consists of a narrow well restricting r to a narrow range about the mean bond distance between the two atoms, and

$$\frac{L^2}{2mr^2} \cong \frac{L^2}{2mr_0^2} = \frac{L^2}{2I_0},$$

For r close to r_0 ,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{1}{2} V''(r_0) (r - r_0)^2\right) \varphi(r) = E_{\text{vib}} \varphi(r).$$

or, the TISE for the *harmonic oscillator*,

$$\hat{H}_{\text{vib}} \psi_{\text{vib}}(x) = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{k}{2} x^2\right) \psi_{\text{vib}}(x) = E_{\text{vib}} \psi_{\text{vib}}(x), \quad (1.4)$$

where

$$\begin{aligned} x &= r - r_0, \\ k &= V''(r_0) \end{aligned}$$

is the *force constant* of the harmonic oscillator, and

$$\psi_{\text{vib}}(x) = \varphi(r_0 + x)$$

is just the wavefunction expressed in terms of displacement from equilibrium.

Multiplying Eq. 1.4 by $m^{1/2}/(\hbar k^{1/2})$ gives

$$\frac{1}{2} \left(-\frac{\hbar}{(mk)^{1/2}} \frac{d^2}{dx^2} + \frac{(mk)^{1/2}}{\hbar} x^2\right) \psi_{\text{vib}}(x) = \frac{E_{\text{vib}}}{\hbar\omega} \psi_{\text{vib}}(x)$$

or

$$\hat{H}\psi(y) = \frac{1}{2} \left(-\frac{d^2}{dy^2} + y^2\right) \psi(y) = \epsilon \psi(y) \quad (1.5)$$

where

$$\begin{aligned} y &= \frac{x}{\alpha}, \\ \alpha &= \frac{\hbar^{1/2}}{(mk)^{1/4}}, \end{aligned}$$

$$\epsilon = \frac{E_{\text{vib}}}{\hbar\omega}$$

and

$$\omega = \left(\frac{k}{m}\right)^{1/2}.$$

Equation 1.5 is the scaled TISE for the harmonic oscillator. It corresponds to solving Eq. 1.4 with displacement from equilibrium measured in units of α , and energy measured in units of $\hbar\omega$.

1.3.1 Raising and lowering operators

We solve the vibrational TISE using *raising and lowering operators*, \hat{a}^\dagger and \hat{a} , respectively:

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(-\frac{d}{dy} + y \right)$$

and

$$\hat{a} = \frac{1}{\sqrt{2}} \left(\frac{d}{dy} + y \right).$$

Since

$$\begin{aligned} \hat{a}^\dagger \hat{a} \varphi(y) &= \frac{1}{\sqrt{2}} \left(-\frac{d}{dy} + y \right) \frac{1}{\sqrt{2}} \left(\frac{d}{dy} + y \right) \varphi(y) \\ &= \frac{1}{2} \left(-\frac{d^2}{dy^2} + y \frac{d}{dy} - \frac{d}{dy} y + y^2 \right) \varphi(y) \\ &= \frac{1}{2} \left(\left(-\frac{d^2}{dy^2} + y^2 \right) \varphi(y) + y \frac{d}{dy} \varphi(y) - \frac{d}{dy} y \varphi(y) \right) \\ &= \frac{1}{2} \left(\left(-\frac{d^2}{dy^2} + y^2 \right) \varphi(y) + y \frac{d}{dy} \varphi(y) - y \frac{d}{dy} \varphi(y) - \varphi(y) \right) \\ &= \hat{H} \varphi(y) - \frac{1}{2} \varphi(y), \end{aligned}$$

$$\hat{a}^\dagger \hat{a} = \hat{H} - \frac{1}{2}$$

or

$$\hat{H} = \hat{a}^\dagger \hat{a} + \frac{1}{2}.$$

To use the raising and lowering operators to solve the TISE associated with \hat{H} , we need the commutation relations of \hat{a}^\dagger and \hat{a} with each other and with the Hamiltonian.

Commutators:

$$[\hat{a}^\dagger, \hat{a}] = -1$$

$$[\hat{H}, \hat{a}] = -\hat{a}$$

$$[\hat{H}, \hat{a}^\dagger] = \hat{a}^\dagger$$

Suppose $\psi(y)$ is an eigenstate of \hat{H} associated with eigenvalue, ϵ ; i.e.,

$$\hat{H}\psi(y) = \epsilon\psi(y).$$

Now consider \hat{H} acting on $\hat{a}\psi(y)$:

$$\hat{H}\hat{a}\psi(y) = (\epsilon - 1)\hat{a}\psi(y)$$

implies $\hat{a}\psi(y)$ is also an eigenstate of the Hamiltonian, with lowered eigenvalue, $\epsilon - 1$.

$$\hat{H}\hat{a}^\dagger\psi(y) = (\epsilon + 1)\hat{a}^\dagger\psi(y);$$

i.e., \hat{a}^\dagger is a *raising operator*.

1.3.2 The ground state

The ground state cannot be lowered. Instead, it is zeroed:

$$\hat{a}\psi(y) = 0 \tag{1.6}$$

or

$$\frac{1}{\sqrt{2}} \left(\frac{d}{dy} + y \right) \psi(y) = 0$$

or

$$\frac{d}{dy}\psi(y) = -y\psi(y)$$

which gives

$$\frac{d\psi}{\psi} = -ydy.$$

Integrating both sides of this equation (from $y = 0$) gives

$$\begin{aligned} \int_{\psi(0)}^{\psi(y)} \frac{d\psi}{\psi} &= - \int_0^y y' dy' \\ [\ln \psi]_{\psi(0)}^{\psi(y)} &= - \left[\frac{1}{2} y'^2 \right]_0^y \\ \ln \psi(y) - \ln \psi(0) &= - \frac{y^2}{2} \\ \ln \frac{\psi(y)}{\psi(0)} &= - \frac{y^2}{2} \\ \psi(y) &= \psi(0) \exp \left(- \frac{y^2}{2} \right). \end{aligned}$$

Normalization gives

$$\psi_0(y) = \pi^{-1/4} \exp \left(- \frac{y^2}{2} \right).$$

The associated energy eigenvalue is determined by applying \hat{H} . Specifically,

$$\begin{aligned}
 \hat{H}\psi_0(y) &= \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\psi_0(y) \\
 &= \hat{a}^\dagger\hat{a}\psi_0(y) + \frac{1}{2}\psi_0(y) \\
 &= \hat{a}^\dagger \times 0 + \frac{1}{2}\psi_0(y) \\
 &= \frac{1}{2}\psi_0(y) \\
 &= \epsilon_0\psi_0(y).
 \end{aligned}$$

The ground state energy, ϵ_0 , is given by

$$\epsilon_0 = \frac{1}{2}.$$

This corresponds to

$$E_{\text{vib},0} = \frac{\hbar\omega}{2},$$

with the units of energy made explicit. This energy is called the zero point energy - it is the lowest energy attainable, and it is greater than the minimum in the potential energy.

1.3.3 The excited states

The remaining eigenfunctions are determined by repeated application of the raising operator.

$$\psi_v(y) = C_v \hat{a}^\dagger \psi_{v-1}(y), \quad (1.7)$$

with C_v determined by

$$\langle \psi_v | \psi_v \rangle = 1$$

which gives

$$C_v = v^{-1/2} \quad (1.8)$$

1.3.4 Expectation values

Raising and lowering operators can be used to determine position and momentum expectation values. For example, forming sums and differences of the raising and lowering operators gives

$$y = \frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger)$$

and

$$\hat{p} = -i\frac{\hbar}{\sqrt{2}} (\hat{a} - \hat{a}^\dagger).$$

The position expectation value is

$$\begin{aligned}\langle \psi_v | y \psi_v \rangle &= \frac{1}{\sqrt{2}} \langle \psi_v | (\hat{a} + \hat{a}^\dagger) \psi_v \rangle \\ &= \frac{1}{\sqrt{2}} (\langle \psi_v | \hat{a} \psi_v \rangle + \langle \psi_v | \hat{a}^\dagger \psi_v \rangle) \\ &= 0\end{aligned}$$

Note that

$$\hat{a}^\dagger \psi_v = (v+1)^{1/2} \psi_{v+1}$$

and

$$\hat{a} \psi_v = v^{1/2} \psi_{v-1}. \quad (1.9)$$

The expectation of y^2 gives the variance of the scaled displacement;

$$\langle \psi_v | y^2 \psi_v \rangle = v + \frac{1}{2}.$$

The standard deviation of the displacement, $x = \alpha y$, is just

$$\sigma_x = \langle \psi_v | x^2 \psi_v \rangle^{1/2} = \left(v + \frac{1}{2} \right)^{1/2} \alpha.$$

$\alpha = \hbar^{1/2} (mk)^{-1/4}$ is seen to be a characteristic distance scale - smaller for larger masses and stiffer bonds (i.e., large k).

The expectation of momentum is

$$\langle \psi_v | \hat{p} \psi_v \rangle = 0.$$

The expectation value of momentum is zero for any bound energy eigenstates. The expectation of \hat{p}^2 gives the variance of scaled-displacement momentum,

$$\langle \psi_v | \hat{p}^2 \psi_v \rangle = \hbar^2 \left(v + \frac{1}{2} \right).$$

Consequently, the standard deviation of the displacement momentum, $\hat{p}_x = -i\hbar d/dx = \hat{p}/\alpha$, is just

$$\sigma_{p_x} = \frac{\hbar}{\alpha} \left(v + \frac{1}{2} \right)^{1/2}.$$

The product of σ_x and σ_{p_x} is given by

$$\sigma_x \sigma_{p_x} = \hbar \left(v + \frac{1}{2} \right) \geq \frac{\hbar}{2},$$

in accord with the Heisenberg uncertainty principle. For the ground state, the equality holds - the ground state is a *minimum uncertainty* wavefunction.

1.4 The classical harmonic oscillator

To best understand the properties of the harmonic oscillator eigenstates, it is instructive to consider a classical treatment of the harmonic oscillator. In classical mechanics, the Hamiltonian is a function of variables, x and p_x . The shape of the path in the x, p_x plane is determined by energy conservation.

$$H = \frac{1}{2m}p_x^2 + \frac{k}{2}x^2 = E.$$

The oscillator follows a path along the ellipse determined by this equation. This ellipse extends from $-\sqrt{2E/k}$ to $\sqrt{2E/k}$ in the x direction, and $-\sqrt{2mE}$ to $\sqrt{2mE}$ in the p_x direction. The points,

$$x_{\min} = -\sqrt{2E/k}$$

and

$$x_{\max} = \sqrt{2E/k}$$

are called the *turning points* of the oscillator. They are found by setting $p = 0$ into the above energy conservation equation. When the oscillator reaches $x = x_{\min}$ or x_{\max} , the sign of p_x reverses and x begins to change in the reverse direction. Positions beyond $x = x_{\min}$ or x_{\max} (i.e., $x < x_{\min}$ or $x > x_{\max}$) are not accessible to oscillatory. These regions are said to be *classically forbidden*. Since the quantum mechanical energy eigenstates are non-zero for all x from $-\infty$ to ∞ , the quantum harmonic oscillator exhibits *barrier penetration*. The wavefunctions do, however, decay rapidly in the classically forbidden regions. Nevertheless, there is non-zero probability for finding the oscillator in classically forbidden configurations.

In classical mechanics, the probability density associated with position, is just the relative amount of time spent by the oscillator at each position - over one complete oscillation. This is proportional to the absolute value of the velocity, at each point,

$$\rho_{\text{CM}}(x) \propto \frac{1}{\sqrt{2(E - kx^2/2)/m}}.$$

The classical harmonic oscillator is more likely found near its turning points, since the velocity goes to zero there. It is least likely to be found at the equilibrium position where it is moving fastest.

For the ground state, the quantum position distribution (shown here in terms of unscaled displacement, x),

$$|\psi_0(x)|^2 = \frac{\alpha^2}{\pi} \exp\left(-\frac{x^2}{\alpha^2}\right),$$

is very different from the classical distribution - see Fig. 4.2 below. The quantum ground state distribution is peaked at the equilibrium position, and it

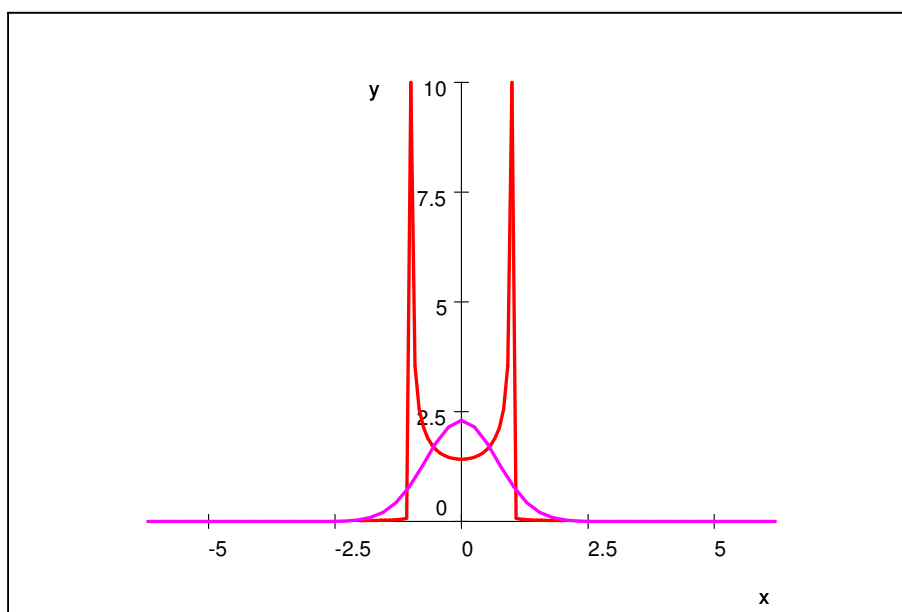


Figure 1.2: The quantum ground state position probability density (solid) of the harmonic oscillator, together with the classical probability density (dashed) - for the same energy.

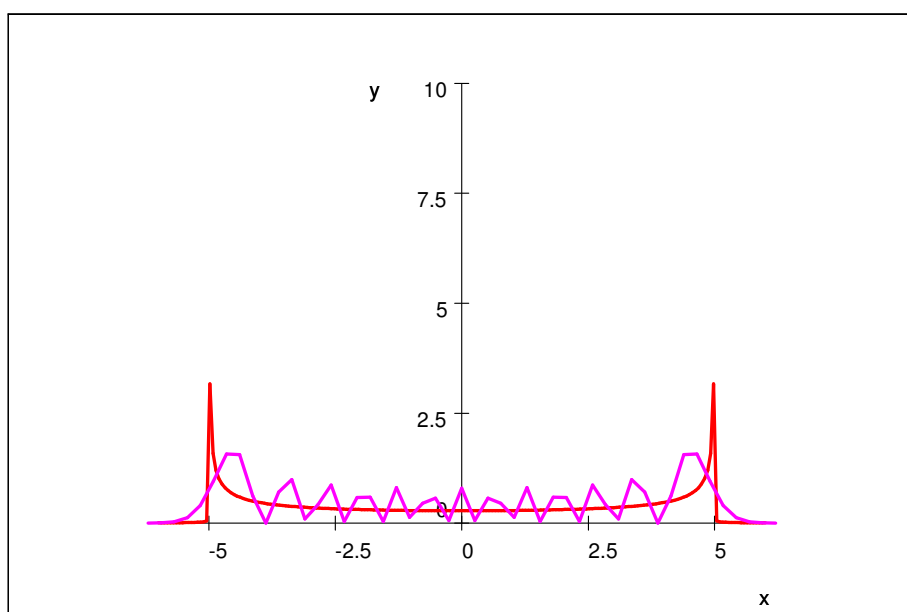


Figure 1.3: The position probability density (solid) for the twelfth excited state of the harmonic oscillator, together with the corresponding classical probability density (dashed).

exhibits significant penetration into classically forbidden regions. For the twelfth excited state of the harmonic oscillator, the quantum distribution oscillates about the classical distribution.

In the high quantum number limit, the quantum distribution oscillates rapidly between zero and twice the classical distribution. Averaging over small x intervals makes the quantum distribution indistinguishable from the quantum distribution, in the large v limit.

The time dependence of x and p_x , in a classical treatment is given by solving Hamilton's equations. The result is

$$x(t) = x(0) \cos(\omega t) + \frac{p_x(0)}{\omega} \sin(\omega t)$$

with corresponding momentum ($p_x = m dx/dt$),

$$p_x(t) = p_x(0) \cos(\omega t) - \omega x(0) \sin(\omega t).$$

The angular frequency, $\omega = (k/m)^{1/2}$, arises in the quantum treatment through the spacing of the vibrational energy levels, $\hbar\omega$. The vibrational frequency, in cycles per second, is just

$$\nu_{\text{vib}} = \frac{\omega}{2\pi} = \frac{1}{2\pi} \left(\frac{k}{m} \right)^{1/2}.$$

1.5 Infrared spectroscopy

A diatomic molecule can make vibrational transitions by absorbing or emitting a photon with energy,

$$h\nu = \Delta E,$$

where $\Delta E = E_{\text{final}} - E_{\text{initial}}$ is the transition energy difference. Transitions arise because of coupling of the molecular *electric dipole* to the oscillating electric field of light - see Sec. 6.3.1. The *transition probability* is proportional to the mod-square of the *transition matrix element*,

$$\langle \psi_{v'} | \hat{\mu}_e | \psi_v \rangle,$$

where $\hat{\mu}_e$ is the electric dipole of the diatomic molecule. Vibrational transitions depend upon $\hat{\mu}_e$ varying with deviation from the equilibrium geometry; i.e., $\hat{\mu}_e$ must vary with x . Note that for small x (the usual realm of the harmonic approximation),

$$\begin{aligned} \hat{\mu}_e(x) &= \mu(x) & \hat{\mu}_e \text{ is a multiplication operator} \\ &= \mu_{\text{eq}} + \frac{d\mu}{dx}x, & \text{small } x \end{aligned}$$

where $\mu_{\text{eq}} = \mu(0)$ is the equilibrium dipole moment of the molecule.

The transition matrix element takes the form,

$$\begin{aligned}
 \langle \psi_{v'} | \hat{\mu}_e | \psi_v \rangle &= \langle \psi_{v'} | \left(\mu_{\text{eq}} + \frac{d\mu}{dx} x \right) | \psi_v \rangle \\
 &= \mu_{\text{eq}} \langle \psi_{v'} | \psi_v \rangle + \frac{d\mu}{dx} \langle \psi_{v'} | x | \psi_v \rangle \quad \mu_{\text{eq}} \text{ and } \frac{d\mu}{dx} \text{ are constants} \\
 &= \frac{d\mu}{dx} \langle \psi_{v'} | x | \psi_v \rangle. \quad \langle \psi_{v'} | \psi_v \rangle = 0 \text{ for } v' \neq v
 \end{aligned}$$

Selection rule:

$$d\mu/dx \neq 0$$

For example, N_2 and O_2 have $\mu_{\text{eq}} = 0$ and $d\mu/dx = 0$. They are transparent to infrared light.

The transition matrix element is proportional to

$$\langle \psi_{v'} | x | \psi_v \rangle.$$

Since $x = \alpha y$ can be written as the difference of the raising and lowering operators, the right side of the inner product takes the form,

$$x \psi_v = \frac{\alpha}{\sqrt{2}} \left((v+1)^{1/2} \psi_{v+1} + v^{1/2} \psi_{v-1} \right)$$

and

$$\begin{aligned}
 \langle \psi_{v'} | x | \psi_v \rangle &= \left\langle \psi_{v'} \left| \frac{\alpha}{\sqrt{2}} \left((v+1)^{1/2} \psi_{v+1} + v^{1/2} \psi_{v-1} \right) \right. \right\rangle \\
 &= \begin{cases} \frac{\alpha}{\sqrt{2}} (v+1)^{1/2}, & v' = v+1 \\ \frac{\alpha}{\sqrt{2}} v^{1/2}, & v' = v-1 \\ 0, & \text{otherwise} \end{cases} \quad (1.10)
 \end{aligned}$$

This gives the *selection rule* for vibrational transitions:

$$\Delta v = \pm 1. \quad (1.11)$$

Vibrational transitions increase (case of absorption) or decrease (case of emission) the vibrational quantum number only by 1. The associated vibrational transition frequency is given by setting the photon energy to the change in energy of the oscillator. For absorption from state v , or emission from $v+1$, we have

$$\begin{aligned}
 h\nu &= E_{v+1} - E_v \\
 &= \hbar\omega \left(v + \frac{3}{2} \right) - \hbar\omega \left(v + \frac{1}{2} \right) \\
 &= \hbar\omega = h\nu_{\text{vib}}.
 \end{aligned}$$

The frequency of the light that induces a transition equals the oscillation frequency of the classical harmonic oscillator. It is also the frequency of light

emitted by the oscillator. Only for low frequency vibrations, is there significant population of first excited states (or higher).

Typically, the potential is less steep than quadratic for stretched bonds, and steeper than quadratic for compressed bonds. Deviation from a quadratic potential is called *anharmonicity*. It typically results in transition frequencies that are slightly smaller for excited states - the energy spacing actually decreases with increasing v . Since vibrational excited state populations are usually small at ordinary temperatures, transitions originating in vibrational excited states - appearing at lower frequency - have small intensity. The associated absorption or emission bands are called *hot bands*.

Polyatomic molecules have multiple vibrational modes. For example, CO_2 has two stretch modes - symmetric and antisymmetric combinations of the two bond stretch vibrations - and two degenerate (they have the same frequency) bends. Only the bending modes have $d\mu/dx \neq 0$ and produce infrared absorption spectra.

Chapter 2

Rotations of a diatomic molecule

2.1 Angular Momentum Eigenfunctions

The energy eigenfunctions for the relative motion of a diatomic molecule have the form,

$$\psi(r, \theta, \phi) = \frac{1}{r} \varphi(r) Y(\theta, \phi),$$

where $\varphi(r_{\text{eq}} + x)$ is a harmonic oscillator energy eigenfunction of x , and $Y(\theta, \phi)$ is an eigenfunction of $\hat{\mathbf{L}}^2$;

$$\hat{\mathbf{L}}^2 Y(\theta, \phi) = L^2 Y(\theta, \phi). \quad (2.1)$$

Since \hat{L}_z commutes with $\hat{\mathbf{L}}^2$, we find simultaneous eigenfunctions of \hat{L}_z and $\hat{\mathbf{L}}^2$.

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

and

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} + \left(\frac{1}{\sin^2 \theta} + 1 \right) \frac{\partial^2}{\partial \phi^2} \right)$$

Separation of angular variables:

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$$

such that

$$\hat{\mathbf{L}}^2 Y(\theta, \phi) = L^2 Y(\theta, \phi)$$

and

$$\hat{L}_z Y(\theta, \phi) = L_z Y(\theta, \phi).$$

Simultaneous eigenfunctions of $\hat{\mathbf{L}}^2$ and \hat{L}_z exist because these are commuting observables. The latter equation leads to

$$\hat{L}_z \Phi(\phi) = L_z \Phi(\phi)$$

which has the solution,

$$\Phi(\phi) = A \exp\left(\frac{iL_z \phi}{\hbar}\right).$$

Since

$$\begin{aligned} \Phi(\phi + 2\pi) &= \Phi(\phi), \\ \exp\left(\frac{2\pi i L_z}{\hbar}\right) &= 1. \end{aligned}$$

or

$$\frac{L_z}{\hbar} = m_\ell, \quad \text{where } m_\ell \text{ is any integer}$$

where m_ℓ is the L_z quantum number (the orbital magnetic quantum number when $\hat{\mathbf{L}}$ is the orbital angular momentum of an electron).

The eigenfunctions of \hat{L}_z :

$$\begin{aligned} \Phi_{m_\ell}(\phi) &= A \exp(im_\ell \phi) \\ &= \frac{1}{\sqrt{2\pi}} \exp(im_\ell \phi). \end{aligned} \tag{2.2}$$

The corresponding eigenvalues are

$$L_z = m_\ell \hbar. \tag{2.3}$$

Equation 2.1 leads to

$$-\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} - m_\ell^2 \left(\frac{1}{\sin^2 \theta} + 1 \right) \right) \Theta(\theta) = L^2 \Theta(\theta).$$

2.1.1 Angular momentum ladder operators:

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

and

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y.$$

Commutators:

$$[\hat{L}_z, \hat{L}_+] = \hbar \hat{L}_+$$

and

$$[\hat{L}_z, \hat{L}_-] = -\hbar \hat{L}_-.$$

From the first commutator, we get

$$\hat{L}_z \hat{L}_+ \Theta(\theta) \Phi_{m_\ell}(\phi) = (m_\ell + 1) \hbar \hat{L}_+ \Theta(\theta) \Phi_{m_\ell}(\phi);$$

i.e., $\hat{L}_+ \Theta(\theta) \Phi_{m_\ell}(\phi)$ is an eigenfunction of \hat{L}_z associated with quantum number, $m_\ell + 1$. \hat{L}_+ is a raising operator. Similarly,

$$\begin{aligned} \hat{L}_z \hat{L}_- \Theta(\theta) \Phi_{m_\ell}(\phi) &= \left[\hat{L}_z, \hat{L}_- \right] \Theta(\theta) \Phi_{m_\ell}(\phi) + \hat{L}_- \hat{L}_z \Theta(\theta) \Phi_{m_\ell}(\phi) \\ &= -\hbar \hat{L}_- \Theta(\theta) \Phi_{m_\ell}(\phi) + \hat{L}_- m_\ell \hbar \Theta(\theta) \Phi_{m_\ell}(\phi) \\ &= (m_\ell - 1) \hbar \hat{L}_- \Theta(\theta) \Phi_{m_\ell}(\phi). \end{aligned}$$

\hat{L}_- is a lowering operator which lowers the m_ℓ quantum number by 1. $\ell = \max |m_\ell|$ is the remaining quantum number; i.e.,

$$-\ell \leq m_\ell \leq \ell.$$

$$Y_{\ell, m_\ell}(\theta, \phi) = \Theta_{\ell, m_\ell}(\theta) \Phi_{m_\ell}(\phi),$$

$\ell = 0, 1, 2, \dots$ and $m_\ell = -\ell, \dots, \ell$. The ℓ quantum number is related to the total angular momentum.

In spherical coordinates, the raising and lowering operators take the form,

$$\hat{L}_+ = \hbar \exp(i\phi) \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right)$$

and

$$\hat{L}_- = \hbar \exp(-i\phi) \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right).$$

Since there is a top state - the state for which $m_\ell = \ell$ - it must be the solution to the equation,

$$\hat{L}_+ \Theta_{\ell, \ell}(\theta) \Phi_\ell(\phi) = 0, \quad (2.4)$$

or

$$\hbar \exp(i\phi) \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \Theta_{\ell, \ell}(\theta) \Phi_\ell(\phi) = 0$$

which gives

$$\Theta(\theta) = \Theta_{\ell, \ell}(\theta) = \left(\frac{(2\ell + 1)!!}{2^{\ell+1} \ell!} \right)^{1/2} \sin^\ell \theta.$$

Once we have the top state, we can obtain any other state (associated with the same value of ℓ) by applying the lowering operator, \hat{L}_- . However, we still need to express the eigenvalues of $\hat{\mathbf{L}}^2$ in terms of quantum number, ℓ . To that end, note that

$$\begin{aligned} \hat{L}_- \hat{L}_+ &= \left(\hat{L}_x - i \hat{L}_y \right) \left(\hat{L}_x + i \hat{L}_y \right) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + i \hat{L}_x \hat{L}_y - i \hat{L}_y \hat{L}_x \\ &= \hat{\mathbf{L}}^2 - \hat{L}_z^2 + i \left[\hat{L}_x, \hat{L}_y \right] \\ &= \hat{\mathbf{L}}^2 - \hat{L}_z^2 - \hbar \hat{L}_z. \end{aligned}$$

Therefore,

$$\hat{\mathbf{L}}^2 = \hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z$$

and

$$\begin{aligned} \hat{\mathbf{L}}^2 Y_{\ell, \ell}(\theta, \phi) &= \left(\hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z \right) Y_{\ell, \ell}(\theta, \phi) \\ &= \ell(\ell+1) \hbar^2 Y_{\ell, \ell}(\theta, \phi). \end{aligned}$$

The eigenvalues of $\hat{\mathbf{L}}^2$ are $\ell(\ell+1)\hbar^2$ where $\ell = 0, 1, 2, \dots$. There are $2\ell+1$ states with this eigenvalue. Since $[\hat{L}_-, \hat{\mathbf{L}}^2] = 0$, \hat{L}_- lowers the m_ℓ quantum number without affecting ℓ . Altogether,

$$\hat{\mathbf{L}}^2 Y_{\ell, m_\ell}(\theta, \phi) = \ell(\ell+1) \hbar^2 Y_{\ell, m_\ell}(\theta, \phi), \quad \ell = 0, 1, 2, \dots \quad (2.5)$$

and

$$\hat{L}_z Y_{\ell, m_\ell}(\theta, \phi) = m_\ell \hbar Y_{\ell, m_\ell}(\theta, \phi) \quad -\ell \leq m_\ell \leq \ell. \quad (2.6)$$

The eigenvalues, $L^2 = \ell(\ell+1)\hbar^2$, are *degenerate* when $\ell > 0$. The $Y_{\ell, m_\ell}(\theta, \phi)$ are called the *spherical harmonics*. They are products of complex exponential functions (in ϕ) and (associated) Legendre polynomials (in θ).

Explicit expressions for the actions of \hat{L}_+ and \hat{L}_- :

$$\hat{L}_- Y_{\ell, m_\ell} = (-1)^\ell [\ell(\ell+1) - (m_\ell - 1)m_\ell]^{1/2} \hbar Y_{\ell, m_\ell - 1}$$

and

$$\hat{L}_+ Y_{\ell, m_\ell} = (-1)^\ell [\ell(\ell+1) - m_\ell(m_\ell+1)]^{1/2} \hbar Y_{\ell, m_\ell + 1}.$$

The s state ($\ell = 0$) is the top state and bottom state of its ladder of states;

$$\begin{aligned} Y_{0,0}(\theta, \phi) &= \Theta_{0,0}(\theta) \Phi_0(\phi) \\ &= (4\pi)^{-1/2}. \end{aligned}$$

It is simply a constant. Since $|Y_{0,0}|^2 = (4\pi)^{-1}$ is constant, this is an isotropic state with no preferred direction.

The p states ($\ell = 1$) are obtained as follows: The top state is

$$\begin{aligned} Y_{1,1}(\theta, \phi) &= \Theta_{1,1}(\theta) \Phi_1(\phi) = (2\pi I_1)^{-1/2} \sin \theta \exp(i\phi) \\ &= \left(\frac{8\pi}{3} \right)^{-1/2} \sin \theta \exp(i\phi) \end{aligned}$$

Applying the lowering operator gives $Y_{1,0}$.

$$\begin{aligned} C_{1,0} Y_{1,0} &= \hat{L}_- Y_{1,1} \\ (-1)^1 [1(1+1) - 0(0+1)]^{1/2} \hbar Y_{1,0} &= \hbar \exp(-i\phi) \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) (2\pi I_1)^{-1/2} \sin \theta \exp(i\phi) \\ (2)^{1/2} Y_{1,0} &= -(2\pi I_1)^{-1/2} \exp(-i\phi) \left(-\frac{\partial}{\partial \theta} \sin \theta + (i \cos \theta) (i) \right) \exp(i\phi) \end{aligned}$$

or

$$\begin{aligned}
 Y_{1,0} &= (4\pi I_1)^{-1/2} \exp(-i\phi) (\cos\theta + \cos\theta) \exp(i\phi) \\
 &= (4\pi I_1)^{-1/2} 2 \cos\theta \\
 &= \left(\frac{4\pi}{3}\right)^{-1/2} \cos\theta
 \end{aligned}$$

The introduction of the $(-1)^\ell$ factor in the definition of $Y_{1,0}$ makes it a positive function. This state is concentrated at the poles - i.e., along the z axis - with a node in the $x y$ plane. The bottom state is given by another application of the lowering operator;

$$\begin{aligned}
 C_{1,-1} Y_{1,-1} &= \hat{L}_- Y_{1,0} \\
 (-1)^1 [1(1+1) - (-1)(-1+1)]^{1/2} \hbar Y_{1,-1} &= \hbar \exp(-i\phi) \left(-\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi}\right) (4\pi I_1)^{-1/2} 2 \cos\theta \\
 (2)^{1/2} Y_{1,-1} &= -(4\pi I_1)^{-1/2} 2 \exp(-i\phi) \left(-\frac{\partial}{\partial\theta} \cos\theta + 0\right)
 \end{aligned}$$

or

$$\begin{aligned}
 Y_{1,-1}(\theta, \phi) &= -(2\pi I_1)^{-1/2} \sin\theta \exp(-i\phi) \\
 &= -\left(\frac{8\pi}{3}\right)^{-1/2} \sin\theta \exp(-i\phi)
 \end{aligned}$$

In general,

$$Y_{\ell,-m_\ell}(\theta, \phi) = (-1)^{m_\ell} Y_{\ell,m_\ell}^*(\theta, \phi).$$

It is therefore sufficient to determine the spherical harmonics for $0 \leq m_\ell \leq \ell$.

Simplified the computation of the spherical harmonics:

$$(-1)^\ell [\ell(\ell+1) - (m_\ell-1)m_\ell]^{1/2} \hbar Y_{\ell,m_\ell-1} = \hbar \exp(-i\phi) \left(-\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi}\right) Y_{\ell,m_\ell}$$

leads to

$$\Theta_{\ell,m_\ell-1}(\theta) = (-1)^{\ell+1} [\ell(\ell+1) - (m_\ell-1)m_\ell]^{-1/2} \left(\frac{d}{d\theta} + m_\ell \cot\theta\right) \Theta_{\ell,m_\ell}(\theta)$$

Also,

$$\Theta_{\ell,m_\ell+1}(\theta) = (-1)^{\ell+1} [\ell(\ell+1) - m_\ell(m_\ell+1)]^{-1/2} \left(\frac{d}{d\theta} - m_\ell \cot\theta\right) \Theta_{\ell,m_\ell}(\theta)$$

Note that

$$\Theta_{\ell,-m_\ell}(\theta) = (-1)^{m_\ell} \Theta_{\ell,m_\ell}(\theta).$$

2.2 The rigid rotor

If a diatomic molecule is in its vibrational ground state (most diatomics at ordinary temperature), it is essentially a *rigid rotor* with Hamiltonian,

$$H_{\text{rr}} = \frac{1}{2mr_{\text{eq}}^2} \hat{\mathbf{L}}^2 = \frac{1}{2I_{\text{eq}}} \hat{\mathbf{L}}^2,$$

where $I_{\text{eq}} = mr_{\text{eq}}^2$ is the equilibrium moment of inertia of the molecule. If the vibrational quantum number is not too large, the relative Hamiltonian is the sum of vibrational and rotational Hamiltonians - the energy eigenvalues are sums of vibrational and rotational energies. Otherwise, the x dependence of the moment of inertia cannot be neglected. Under ordinary conditions, this separation of vibration and rotation is a good approximation, and the rotational energy eigenvalues are the energy eigenvalues of the rigid rotor,

$$E_{\text{rot}, J} = \frac{J(J+1)\hbar^2}{2I_{\text{eq}}}, \quad J = 0, 1, 2, \dots$$

The associated rotational eigenfunctions are

$$Y_{J,M_J}(\theta, \phi), \quad -J \leq M_J \leq J.$$

Expectation values of \hat{J}_x and \hat{J}_y , for rigid-rotor eigenstates:

$$\begin{aligned} \hat{J}_x Y_{J,M_J} &= \frac{\hat{J}_+ + \hat{J}_-}{2} Y_{J,M_J} \\ &= \frac{(-1)^J \hbar}{2} \left([J(J+1) - M_J(M_J+1)]^{1/2} Y_{J,M_J+1} + [J(J+1) - M_J(M_J-1)]^{1/2} Y_{J,M_J-1} \right) \end{aligned}$$

is a linear combination of Y_{J,M_J+1} and Y_{J,M_J-1} , functions orthogonal to Y_{J,M_J} ,

$$\langle Y_{J,M_J} | \hat{J}_x Y_{J,M_J} \rangle = 0.$$

Non-zero expectation values are obtained only for \hat{J}_x^2 or \hat{J}_y^2 which have $\hat{J}_- \hat{J}_+$ and $\hat{J}_+ \hat{J}_-$ terms which produce Y_{J,M_J} . For example, for the top state, $Y_{J,J}$, only the $\hat{J}_+ \hat{J}_-$ term gives a non-zero result;

$$\begin{aligned} \langle Y_{J,J} | \hat{J}_x^2 Y_{J,J} \rangle &= \frac{\hbar^2}{4} [J(J+1) - J(J-1)] \langle Y_{J,J} | Y_{J,J} \rangle \quad \text{arises from } \hat{J}_+ \hat{J}_- \\ &= \frac{\hbar^2}{2} J. \end{aligned}$$

This state has the maximum possible z component of angular momentum, yet still has x and y components. This is a manifestation of the angular momentum commutator relationships. If the z component of angular is known, the x and y components cannot be known - and hence cannot be zero. This means that the

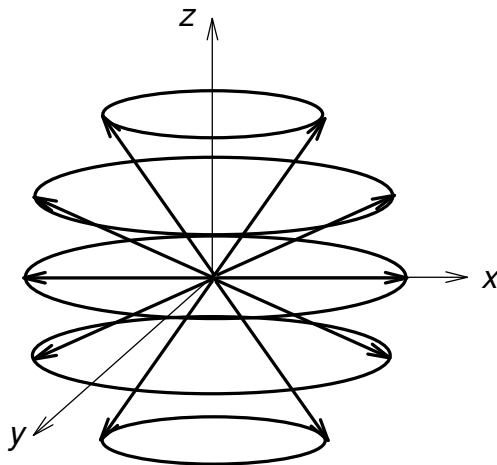


Figure 2.1: Space quantization. The possible angular momentum vector orientations associated with the Y_{2,M_J} states, $M_J = -2, -1, 0, 1, 2$ (from bottom to top).

angular momentum vector cannot point directly along the z axis. The $2J + 1$ states, Y_{J,M_J} correspond to angular momentum vectors of length, $\sqrt{J(J+1)}\hbar$, with component $M_J\hbar$ along z . The vector is otherwise uncertain. The possible orientations of the angular momentum vector, for each state, maps out a cone (or a disk, if $M_J = 0$). The discrete set of orientations are given by setting

$$\cos \theta_J = \frac{M_J}{\sqrt{J(J+1)}}.$$

This discretization of orientations is called *space quantization*. Figure 5.1 shows the angular momentum cones for $J = 2$.

2.3 Rotational Spectroscopy

Dipole transitions between rotational levels are associated with changes in quantum number J . Different M_J states with the same J value have the same energy. Transitions between these states requires a magnetic field to split these levels. Transitions between different J states occurs for states connected by a non-zero transition matrix element.

For z -polarized light, the z component of the dipole moment of the molecule couples to the incoming light; $\mu_z(r, \theta) = \mu(r) \cos \theta$. The $\mu(r)$ factor in this expression leads to *vibrational transitions*. The $\cos \theta$ factor leads to *rotational transitions*. For x and y -polarized light, we need $\mu_x(r, \theta, \phi) = \mu(r) \sin \theta \cos \phi$ and $\mu_y(r, \theta, \phi) = \mu(r) \sin \theta \sin \phi$.

For z -polarized rotational transitions, $\Delta M_J = 0$ because $\mu_z(r, \theta)$ is independent of ϕ . It is sufficient to consider the transition matrix element,

$$\mu_{\text{eq}} \langle Y_{J',0} | \cos \theta Y_{J,0} \rangle.$$

The $M_J = 0$ state, $Y_{J,0}$, is a J th order polynomial in $\cos \theta$. Multiplying by $\cos \theta$ gives a $J+1$ th order polynomial which can be written as a combination of $Y_{J+1,0}$ and $Y_{J-1,0}$. Consequently, the rotational transition selection rules are

$$\Delta J = \pm 1. \quad (2.7)$$

and

$$\Delta M_J = 0. \quad (2.8)$$

For x and y -polarized rotational transitions, the transition matrix elements are

$$\mu_{\text{eq}} \langle Y_{J',M_J'} | \sin \theta \cos \phi Y_{J,M_J} \rangle$$

and

$$\mu_{\text{eq}} \langle Y_{J',M_J'} | \sin \theta \sin \phi Y_{J,M_J} \rangle.$$

These give the selection rules,

$$\Delta J = \pm 1 \quad (2.9)$$

and

$$\Delta M_J = \pm 1. \quad (2.10)$$

For unpolarized light (i.e., all polarizations),

$$\Delta J = \pm 1 \quad (2.11)$$

and

$$\Delta M_J = 0, \pm 1. \quad (2.12)$$

2.3.1 Microwave absorption spectroscopy

The change in energy associated with a $\Delta J = +1$ transition - corresponding to absorption of light - is given by

$$\begin{aligned} \Delta E_{\text{rot}, J} &= E_{\text{rot}, J+1} - E_{\text{rot}, J} = \frac{(J+1)(J+2)\hbar^2}{2I_{\text{eq}}} - \frac{J(J+1)\hbar^2}{2I_{\text{eq}}} \\ &= 2(J+1) \frac{\hbar^2}{2I_{\text{eq}}} \\ &= 2(J+1) B_{\text{rot}}, \end{aligned} \quad (2.13)$$

where

$$B_{\text{rot}} = \frac{\hbar^2}{2I_{\text{eq}}}$$

is called the *rotational constant*. Rotational levels are not equally spaced. Consequently, each distinct J level gives its own frequency. The intensity of

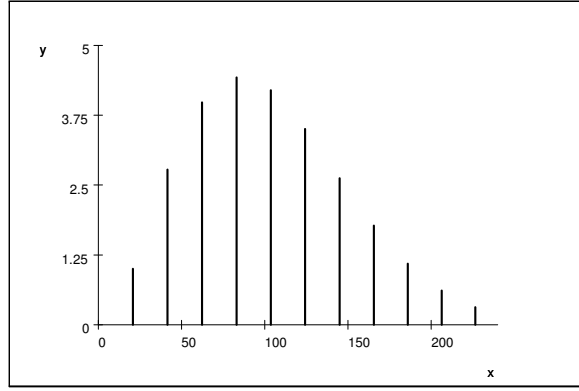


Figure 2.2: An ideal microwave absorption spectrum - i.e., the rotational spectrum - of HCl at 400 K. The horizontal axis is wavenumbers in cm^{-1} . The vertical axis is peak intensity relative to the $J = 0$ peak.

each peak is determined by the population of diatomic molecules initially in level J . Since there are $2J + 1$ states (the different M_J values) with energy, $E_{\text{rot}, J}$, the peak intensities are proportional to

$$\begin{aligned} \rho_{\text{rot}, J}(T) &= (2J + 1) \exp\left(-\frac{E_{\text{rot}, J}}{k_B T}\right) \\ &= (2J + 1) \exp\left(-\frac{J(J + 1) B_{\text{rot}}}{k_B T}\right). \end{aligned}$$

This is the *Boltzmann distribution* of rotational state populations.

Rotational frequencies are usually reported as *wavenumbers* in cm^{-1} ;

$$\begin{aligned} \bar{\nu}_{\text{rot}, 0} &= \frac{\nu_{\text{rot}, 0}}{c} = \frac{2B_{\text{rot}}}{hc} \\ &= 2\bar{B}_{\text{rot}}, \end{aligned}$$

where \bar{B}_{rot} is the rotational constant in wavenumbers. The wavenumber spacings between successive peaks is

$$\begin{aligned} \Delta\bar{\nu}_{\text{rot}} &= \bar{\nu}_{\text{rot}, J+1} - \bar{\nu}_{\text{rot}, J} \\ &= 2\bar{B}_{\text{rot}}. \end{aligned}$$

Rotational transitions occur at $\bar{\nu}_{\text{rot}} = 2\bar{B}_{\text{rot}}, 4\bar{B}_{\text{rot}}, 6\bar{B}_{\text{rot}}, \dots$, with the Boltzmann distribution providing a peak intensity envelope. The maximum of this envelope occurs at

$$\begin{aligned}
J_{\max} &= \frac{1}{2} \left(\frac{2k_{\text{B}}T}{B_{\text{rot}}} \right)^{1/2} - \frac{1}{2} \\
&= \left(\frac{k_{\text{B}}T}{2B_{\text{rot}}} \right)^{1/2} - \frac{1}{2}.
\end{aligned}$$

2.3.2 The classical rigid rotor

It is instructive to consider the classical rigid rotor model of a diatomic molecule. If the diatomic molecule has angular momentum L , then the rotational frequency is given by (recall that $L = I_{\text{eq}}\omega$, where $\omega = 2\pi\nu_{\text{rot}}$ is the angular velocity - or angular frequency)

$$\nu_{\text{rot}} = \frac{1}{2\pi} \frac{L}{I_{\text{eq}}}.$$

In classical mechanics, the rotational frequency varies continuously with angular momentum. In quantum mechanics angular momentum is quantized. If we associate the J th level of the quantum system with a classical angular momentum, $L = (J+1)\hbar$, $J = 0, 1, \dots$, then the allowed rotational frequencies are

$$\begin{aligned}
\nu_{\text{rot}, J} &= \frac{1}{2\pi} \frac{(J+1)\hbar}{I_{\text{eq}}} \\
&= \frac{1}{h} \frac{(J+1)\hbar^2}{I_{\text{eq}}} \\
&= \frac{2(J+1)B_{\text{rot}}}{h} \quad \text{for } J \text{ to } J+1 \text{ transition.}
\end{aligned}$$

This is also the classical rotational frequency of the diatomic molecule with angular momentum, $L = (J+1)\hbar$, the root-mean-square of the angular momenta associated with the J th and $(J+1)$ th quantum states - $\sqrt{J(J+1)}\hbar$ and $\sqrt{(J+1)(J+2)}\hbar$, respectively.

2.4 Ro-vibrational spectroscopy

The infrared spectra of diatomic molecules do not correspond to a single peak at the vibrational frequency. The reason is that the vibrational quantum number selection rule, $\Delta v = \pm 1$, is accompanied by the rotational quantum number selection rules, $\Delta J = \pm 1$, $\Delta M_J = 0, \pm 1$. For example, in an infrared absorption spectrum ($\Delta v = +1$), the change in energy of the molecule is the change in vibrational energy plus the change in rotational energy (a much smaller value). The change in rotational energy cannot be zero because $\Delta J = 0$ is not allowed. Only $\Delta J = +1$ and $\Delta J = -1$ transitions are possible.

In the case of $\Delta J = +1$, the peaks of the rotational absorption spectrum (these lines correspond to $\Delta J = +1$) are seen again - this time shifted by

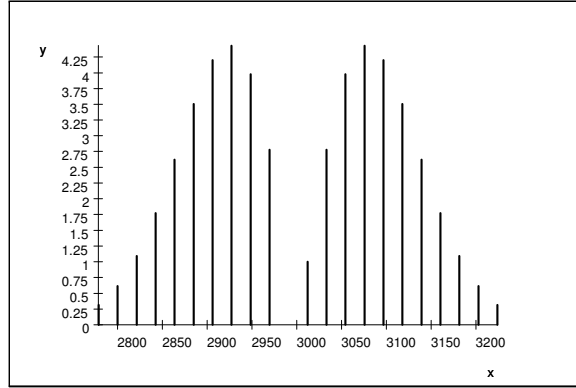


Figure 2.3: The idealized infrared absorption spectrum of $^1\text{H}^{35}\text{Cl}$. Relative peak intensity (relative to the R $J = 0$ peak) is plotted versus wavenumbers in cm^{-1} .

the vibrational frequency into the infrared range. These peaks constitute the *R branch* of the *ro-vibrational spectrum* - the *gas phase infrared absorption spectrum*. The associated wavenumbers are

$$\begin{aligned}\bar{\nu}_{R,J} &= \bar{\nu}_{\text{vib}} + \frac{E_{\text{rot}, J+1} - E_{\text{rot}, J}}{hc} \\ &= \bar{\nu}_{\text{vib}} + [(J+1)(J+2) - J(J+1)] \bar{B}_{\text{rot}} \\ &= \bar{\nu}_{\text{vib}} + 2(J+1) \bar{B}_{\text{rot}}, \quad J = 0, 1, 2, \dots\end{aligned}$$

In the case of $\Delta J = -1$, the transition wavenumbers are

$$\begin{aligned}\bar{\nu}_{P,J} &= \bar{\nu}_{\text{vib}} + \frac{E_{\text{rot}, J-1} - E_{\text{rot}, J}}{hc} \\ &= \bar{\nu}_{\text{vib}} + [(J-1)J - J(J+1)] \bar{B}_{\text{rot}} \\ &= \bar{\nu}_{\text{vib}} - 2J \bar{B}_{\text{rot}}, \quad J = 1, 2, \dots\end{aligned}$$

Note that there is no $J = 0$ transition because that is the lowest J state - it cannot be lowered to $J - 1$. This series of peaks, below $\bar{\nu}_{\text{vib}}$ is called the *P branch* of the *ro-vibrational spectrum*.

The *Q branch* - with $\Delta J = 0$ - is forbidden for diatomic molecules, and not seen. However, the Q branch is seen for triatomic and larger molecules. The selection rules are $\Delta J = 0$, or ± 1 , beyond diatomics.

The idealized infrared absorption spectrum of $^1\text{H}^{35}\text{Cl}$ is depicted below. The horizontal axis gives the wavenumbers in units of cm^{-1} . Note the asymmetry, about $\bar{\nu}_{\text{vib}} = 2991 \text{ cm}^{-1}$, resulting from the different initial states in the two series - the P branch starts with $J = 1$, while the R branch starts with $J = 0$.

In real ro-vibrational spectra, there are deviations from the above idealized spectrum. One deviation is due to centrifugal distortion. For large J states,

the angular momentum is large enough to shift the molecular equilibrium bond distance - the molecule is stretched. This shifts the moment of inertia to larger values. The spacing between peaks becomes J dependent, decreasing with increasing J . The P and R branches would appear to be compressed near the outside edges, compared to the idealized spectrum shown above.

2.4.1 Raman Spectroscopy

Raman spectroscopy has different selection rules. The transition matrix element for a Raman transition - inelastic scattering of a UV frequency photon - is a matrix element of the derivative of the molecule polarizability with respect to vibrational displacement. The latter has components proportional to $\cos^2 \theta$, $\sin^2 \theta \cos^2 \phi$ and $\sin^2 \theta \sin^2 \phi$ which give the *selection rules*, $\Delta J = 0$ or ± 2 . The O, Q and S branches ($\Delta J = -2, 0$ and 2 , respectively) are observed. Moreover, there are many vibrational modes that are not *infrared active* - electric dipole does not change - that are *Raman active*. The other Raman selection rule is that polarizability must change upon vibration. The polarizability often changes when the electric dipole does not. In fact, for *centrosymmetric* molecules - molecules with a center of symmetry - Raman active modes are always infrared inactive, and vice versa - they are mutually exclusive.

2.4.2 The normalization condition for a wavefunction expressed in terms of spherical coordinates

$$\int_0^{2\pi} \int_0^\pi \int_0^\infty |\psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi = 1.$$

The ranges of integration covers all of space. The radial coordinate extends from 0 to ∞ . The angle θ varies from 0 to π - from the positive z axis to the negative z axis. The angle in the $x y$ plane varies from 0 to 2π .

If the wavefunction is a product of functions of just r , just θ and just ϕ , then the factors can be separately normalized. Specifically, if

$$\psi(r, \theta, \phi) = \psi_r(r) Y(\theta, \phi),$$

then

$$\langle \psi_r | \psi_r \rangle = \int_0^\infty |\psi_r(r)|^2 r^2 dr = 1$$

and

$$\langle Y | Y \rangle = \int_0^{2\pi} \int_0^\pi |Y(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1.$$

If

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi),$$

then

$$\langle \Theta | \Theta \rangle = \int_0^\pi |\Theta(\theta)|^2 \sin \theta d\theta = 1.$$

and

$$\langle \Phi | \Phi \rangle = \int_0^{2\pi} |\Phi(\phi)|^2 d\phi = 1.$$

The inner product $\langle \cdot | \cdot \rangle$ is an integral defined by the context. It is an integral, with appropriate weight function (i.e., such as r^2 or $\sin \theta$), over all admissible values of the coordinates of the wavefunctions in the inner product.

Chapter 3

Perturbations

3.1 Time independent perturbation theory

Let

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)},$$

where λ is a convenient perturbation scaling parameter. In the end, we set it to 1. However, in the meantime, keeping λ free lets us keep track of the order of correction terms. Suppose $\{\psi_n^{(0)}\}$ are the known zero order eigenfunctions;

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}. \quad (3.1)$$

The eigenvalues and eigenfunctions of \hat{H} can be written as power series in the scaling parameter, λ :

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (3.2)$$

and

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \dots \quad (3.3)$$

Substituting the power series expressions into the perturbed system Schrödinger equation,

$$\hat{H}\psi_n = E_n\psi_n,$$

gives

$$\begin{aligned} & \hat{H}^{(0)}\psi_n^{(0)} + \lambda \left[\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} \right] + \lambda^2 \left[\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}^{(1)}\psi_n^{(1)} \right] + \dots \\ &= E_n^{(0)}\psi_n^{(0)} + \lambda \left[E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)} \right] + \lambda^2 \left[E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)} \right] + \dots \end{aligned}$$

Equating coefficients of like powers of λ on either side of the equation gives the following relations:

Coefficients of λ^0 :

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}.$$

This is just the unperturbed Schrödinger equation.

Coefficients of λ^1 :

$$\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}. \quad (3.4)$$

Restrict $\psi_n^{(1)}$ to be orthogonal to $\psi_n^{(0)}$. This removes redundancy. Take the inner product of both sides of the above equation, with $\psi_n^{(0)}$, to get

$$\begin{aligned} \left\langle \psi_n^{(0)} \left| \hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle &= \left\langle \psi_n^{(0)} \left| E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)} \right. \right\rangle \\ \left\langle \psi_n^{(0)} \left| \hat{H}^{(0)}\psi_n^{(1)} \right. \right\rangle + \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle &= E_n^{(1)} \underbrace{\left\langle \psi_n^{(0)} \left| \psi_n^{(0)} \right. \right\rangle}_{=1} + E_n^{(0)} \underbrace{\left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right. \right\rangle}_{=0} \\ \left\langle \hat{H}^{(0)}\psi_n^{(0)} \left| \psi_n^{(1)} \right. \right\rangle + \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle &= E_n^{(1)} \quad \hat{H}^{(0)} \text{ is Hermitian} \\ \left\langle E_n^{(0)}\psi_n^{(0)} \left| \psi_n^{(1)} \right. \right\rangle + \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle &= E_n^{(1)} \\ E_n^{(0)} \underbrace{\left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right. \right\rangle}_{=0} + \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle &= E_n^{(1)} \quad E_n^{(0)} \text{ is real} \end{aligned}$$

The first order correction to the n th energy eigenvalue is

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle. \quad (3.5)$$

The n th energy eigenvalue, estimated to first order in the perturbation, is just the expectation value of the perturbed Hamiltonian,

$$\begin{aligned} E_n &\cong E_n^{(0)} + E_n^{(1)} \\ &= \left\langle \psi_n^{(0)} \left| \hat{H}^{(0)}\psi_n^{(0)} \right. \right\rangle + \left\langle \psi_n^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle \\ &= \left\langle \psi_n^{(0)} \left| \hat{H}\psi_n^{(0)} \right. \right\rangle. \end{aligned}$$

The first order correction (non-degenerate case) to the n th energy eigenvalue is

$$\psi_n^{(1)} = - \sum_{n' \neq n} \frac{\left\langle \psi_{n'}^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle}{E_{n'}^{(0)} - E_n^{(0)}} \psi_{n'}^{(0)} \quad (3.6)$$

Higher powers of λ : The second order corrections to the energy eigenvalues:

$$E_n^{(2)} = - \sum_{n' \neq n} \frac{\left| \left\langle \psi_{n'}^{(0)} \left| \hat{H}^{(1)}\psi_n^{(0)} \right. \right\rangle \right|^2}{E_{n'}^{(0)} - E_n^{(0)}} \quad (3.7)$$

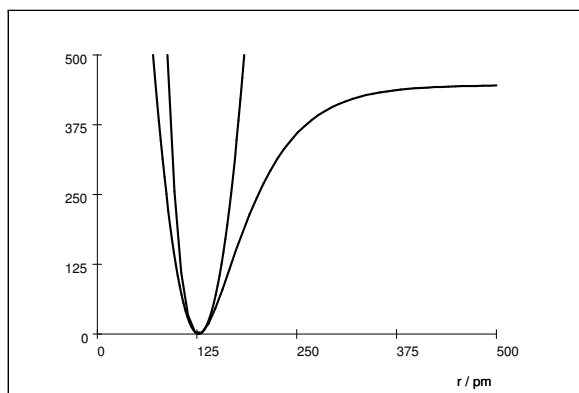
3.2 Anharmonicity

Taylor series vibrational potential in x up to the x^4 term:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k}{2}x^2 - \gamma x^3 + \delta x^4,$$

where the coefficient of x^3 is made explicitly negative ($\gamma > 0$) as the potential well typically becomes wider than the harmonic well for large positive x values.

Figure 6.1 shows a typical vibrational potential energy, together with the harmonic (quadratic) approximation. The *equilibrium dissociation energy*, $D_{\text{eq}} = D_0 + \hbar\omega/2$, is the large r asymptotic value of the potential. It is written here in terms of the bond dissociation energy, D_0 ; $D_0 = D_{\text{eq}} - \hbar\omega/2$ is the difference in the dissociated diatomic and the molecule in its vibrational ground state. The vibrational ground state energy, $\hbar\omega/2$, is called the zero point energy.



The Morse potential (solid line) for $^1\text{H}^{35}\text{Cl}$. This is a more realistic model of a diatomic vibration potential than the harmonic potential (dashed line). The well depth here is $D_e = 446 \text{ kJ mol}^{-1}$. The displacement is given in units of $(\frac{2D_e}{m\omega^2})^{1/2} = 54 \text{ pm}$ for $^1\text{H}^{35}\text{Cl}$.

To first order, the energy shift of the v th state is given by

$$\begin{aligned} E_v^{(1)} &= \langle \psi_v^{(0)} | \hat{H}^{(1)} \psi_v^{(0)} \rangle \\ &= \langle \psi_v^{(0)} | (-\gamma x^3 + \delta x^4) \psi_v^{(0)} \rangle \\ &= -\gamma \langle \psi_v^{(0)} | x^3 \psi_v^{(0)} \rangle + \delta \langle \psi_v^{(0)} | x^4 \psi_v^{(0)} \rangle. \end{aligned}$$

We know that x can be written as a lowering operator plus a raising operator. x^3 consists of the eight possible combinations of raising or lowering three times, in succession. Since it is impossible to return to quantum number v with an odd number of raising or lowerings, the matrix element $\langle \psi_v^{(0)} | x^3 \psi_v^{(0)} \rangle = 0$

and no first order shift results from the third order anharmonicity. Third order anharmonicity does produce a second order shift in energy. This result is rationalized by noting that, while the third order anharmonicity widens the well on the right, it narrows the well on the left. The two effects partly balance, making the effect on energy more subtle. In contrast, the fourth order anharmonicity produces a first order correction to energy. This is because x^4 includes terms with two raising and two lowering operators, taking $\psi_v^{(0)}$ back to $\psi_v^{(0)}$ in order to give non-zero contributions to the $\psi_v^{(0)}$ expectation value of x^4 . There are six such terms. The expectation value is positive for all v . So the sign of the shift in energy is controlled by δ .

$$\begin{aligned}
E_v^{(1)} &= \delta \left\langle \psi_v^{(0)} \left| x^4 \psi_v^{(0)} \right. \right\rangle \\
&= \alpha^4 \delta \left\langle \psi_v^{(0)} \left| y^4 \psi_v^{(0)} \right. \right\rangle \\
&= \frac{\alpha^4 \delta}{4} \left\langle \psi_v^{(0)} \left| (\hat{a} + \hat{a}^\dagger)^4 \psi_v^{(0)} \right. \right\rangle \\
&= \frac{\alpha^4 \delta}{4} \left((v+1)(v+2) + (v+1)^2 + (v+1)v + v(v+1) + v^2 + v(v-1) \right) \\
&= \frac{\alpha^4 \delta}{4} (6v^2 + 6v + 3).
\end{aligned}$$

For the Morse potential, the energy levels are given - in wavenumbers - by

$$\bar{E}_{\text{vib}, v} = \frac{E_{\text{vib}, v}}{hc} = \left(v + \frac{1}{2} \right) \bar{\nu}_{\text{vib}} - \left(v + \frac{1}{2} \right)^2 x_{\text{eq}} \bar{\nu}_{\text{vib}},$$

for

$$v = 1, 2, \dots, v_{\text{max}} = \left\lfloor \frac{1}{2x_{\text{eq}}} \right\rfloor,$$

where

$$x_{\text{eq}} = \frac{\bar{\nu}_{\text{vib}}}{4\bar{D}_{\text{eq}}}$$

is called the *anharmonicity constant*.

Anharmonicity also generally results in a shift in the mean bond distance - i.e., expectation of r - it increases with increasing v . This increases the moment of inertia, decreasing the spacing between levels. Hot bands thus have narrower spacings between lines within bands.

3.3 Time Dependent Perturbation Theory

Expand the time dependent wavefunction as a sum over unperturbed system eigenstates,

$$\Psi(x, t) = \sum_{n'} b_{n'}(t) \exp\left(\frac{-iE_{n'}t}{\hbar}\right) \psi_{n'}(x),$$

with time dependent expansion coefficients. This leads to

$$b_n(t) = b_n(0) - \frac{i}{\hbar} \sum_{n'} \int_0^t \langle \psi_n | \hat{H}^{(1)}(t') | \psi_{n'} \rangle \exp(i\omega_{n,n'}t') b_{n'}(t') dt'.$$

The zero order approximation of $b_n(t')$ is just $b_n(0)$.

The first order approximation is

$$b_n^{(1)}(t) = b_n(0) - \frac{i}{\hbar} \sum_{n'} \int_0^t \langle \psi_n | \hat{H}^{(1)}(t') | \psi_{n'} \rangle \exp(i\omega_{n,n'}t') dt' b_{n'}(0). \quad (3.8)$$

3.3.1 Electric dipole transitions

We consider the first order approximation to the expansion coefficients in case of incident light - i.e., an electromagnetic field - interacting with the electric dipole, $\hat{\mu}$, of the system. The time dependent perturbation is the interaction energy,

$$\hat{H}^{(1)}(t) = -\hat{\mu}_e \cdot \mathcal{E}(t) = -\hat{\mu}_{e,z} \mathcal{E}_z(t),$$

where we choose the z axis to be the direction of the time dependent electric field, $\mathcal{E}(t)$, associated with the incident electromagnetic radiation. The electric field oscillates with angular frequency, $\omega = 2\pi\nu$;

$$\begin{aligned} \mathcal{E}_z(t) &= \mathcal{E}_z(0) \cos(\omega t) \\ &= \frac{1}{2} \mathcal{E}_z(0) (\exp(i\omega t) + \exp(-i\omega t)). \end{aligned}$$

Consider just the second of the two complex exponential terms. Substituting the associated time dependent perturbation into Eq. 3.8 gives

$$\begin{aligned} b_n^{(1)}(t) &= b_n(0) + \frac{i}{\hbar} \sum_{n'} \int_0^t \langle \psi_n | \frac{1}{2} \mathcal{E}_z(0) \exp(-i\omega t') \hat{\mu}_{e,z} | \psi_{n'} \rangle \exp(i\omega_{n,n'}t') dt' b_{n'}(0) \\ &= b_n(0) + \frac{1}{\hbar} \frac{1}{2} \mathcal{E}_z(0) \sum_{n'} \langle \psi_n | \hat{\mu}_{e,z} | \psi_{n'} \rangle \left[\frac{\exp(i(\omega_{n,n'} - \omega)t) - 1}{\omega_{n,n'} - \omega} \right] b_{n'}(0) \\ &= \frac{1}{\hbar} \frac{1}{2} \mathcal{E}_z(0) \langle \psi_n | \hat{\mu}_{e,z} | \psi_{n'} \rangle \left[\frac{\exp(i(\omega_{n,n'} - \omega)t) - 1}{\omega_{n,n'} - \omega} \right], \end{aligned}$$

if the system is initially in one state - the n' th state; $b_{n'}(0) = 1$ and $b_n(0) = 0$.

On-resonance - limit of $\Delta\omega = (\omega_{n,n'} - \omega) \rightarrow 0$:

$$\frac{\exp(i\Delta\omega t) - 1}{\Delta\omega} \cong \frac{i\Delta\omega t}{\Delta\omega} = it.$$

$b_n^{(1)}(t)$ increases with time, with rate,

$$r = -\frac{i}{2\hbar} \mathcal{E}_z(0) \langle \psi_n | \hat{\mu}_{e,z} | \psi_{n'} \rangle.$$

This is the rate at which the coefficient of the resonant state increases - at the expense of the coefficient of the initial state (subsequent to normalization) - per unit time. However, the probability that a transition occurs is given by

$$|b_n(t)|^2 = \frac{t^2}{4\hbar^2} \mathcal{E}_z^2(0) |\langle \psi_n | \hat{\mu}_{e,z} | \psi_{n'} \rangle|^2.$$

$\mathcal{E}_z^2(0)$ is proportional to the energy density of the incident light - i.e., the light intensity. The quantum transition probability increases as t^2 with coefficient,

$$|r|^2 = \frac{\mathcal{E}_z^2(0)}{4\hbar^2} |\langle \psi_n | \hat{\mu}_{e,z} | \psi_{n'} \rangle|^2.$$

If the light has a broadband spectrum - it is spread over a range of frequencies including the resonance frequency - there is little energy density exactly on resonance. In this case, after a short time of $|b_n(t)|^2$ increasing as t , it increases linearly with time - with $|r|^2$ giving (with a few extra constants and the energy density of the electromagnetic field averaged across the resonance) the *rate of transition*.

Chapter 4

Electronic structure of atoms

4.1 The hydrogen atom

The hydrogen atom, or hydrogen-like ion (He^+ , Li^{2+} , ...), is the simplest atom (ion) with only one electron. The radial TISE takes the form,

$$\left(-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + V(r) + \frac{1}{2mr^2} \hat{\mathbf{L}}^2 \right) R(r) = ER(r),$$

where

$$\hat{\mathbf{L}}^2 Y_{\ell, m_\ell}(\theta, \phi) = \ell(\ell+1) \hbar^2 Y_{\ell, m_\ell}(\theta, \phi),$$

and

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

is the Coulombic attraction between the electron and nucleus - the latter with charge $+Ze$ to include hydrogen-like ions. The complete relative motion wavefunction is the product,

$$R_{n,\ell}(r) Y_{\ell, m_\ell}(\theta, \phi).$$

With

$$R_{n,\ell}(r) = \frac{1}{r} \varphi_{n,\ell}(r),$$

we get

$$\left(-\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} \right) \varphi_{n,\ell}(r) = E_n \varphi_{n,\ell}(r).$$

Here, we approximate the reduced mass as the mass of an electron. The solutions we get are more useful as starting points in the treatment of many electron atoms and molecules.

Atomic units

Unit of distance, the *Bohr*:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52.918 \text{ pm}$$

It is radius of the ground state orbit in the Bohr model of the hydrogen atom.

Unit of energy, the *Hartree*:

$$E_h = \frac{\hbar^2}{m_e a_0^2} = \frac{m_e e^4}{16\pi\epsilon_0 \hbar^2} = 27.211386 \text{ eV} = 4.359744 \times 10^{-18} \text{ J}$$

It is twice the ionization energy of a hydrogen atom.

In atomic units, the TISE takes the form,

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} \right) \varphi(r) = E\varphi(r). \quad (4.1)$$

It is instructive to examine the behavior of the solutions to this equation near the boundary radius values - specifically, $r \rightarrow 0$ and $r \rightarrow \infty$. Both cases begin by re-writing the above equation in the form,

$$\frac{d^2}{dr^2} \varphi(r) = \left(-2E - \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2} \right) \varphi(r). \quad (4.2)$$

Small radius: For small r there are two possibilities: $\ell > 0$ and $\ell = 0$.

- (a) If $\ell > 0$, the centrifugal potential term is much larger than the other two terms inside the parentheses. Consequently, the solution to the above equation must be close to the solution of

$$\frac{d^2}{dr^2} \varphi(r) = \frac{\ell(\ell+1)}{r^2} \varphi(r).$$

This equation is clearly solved by $Cr^{\ell+1}$. There is another solution, $C'r^{-\ell}$, but it blows up as $r \rightarrow 0$. Since $R = \varphi/r$ also blows up in this case, this solution is inadmissible. Consequently,

$$\varphi(r) \cong Cr^{\ell+1} \quad r \text{ close to } 0$$

and

$$R(r) \cong Cr^\ell. \quad r \text{ close to } 0.$$

For $\ell > 0$, the electron is excluded from the nucleus - the radial wavefunction goes to zero as $r \rightarrow 0$. The decay to zero is in accord with a power law, r^ℓ . The exclusion of the electron from the nucleus is stronger with increasing ℓ , consistent with the increasing centrifugal repulsion.

- (b) If $\ell = 0$, there is no centrifugal repulsion - angular momentum is zero. In this case, $R(r)$ extends right to $r = 0$. It is a constant, $C > 0$, in the vicinity of the nucleus. This is consistent with the above radial wavefunction, with $\ell = 0$, even though the analysis only applies to $\ell > 0$.

Large radius: For large r , the Coulomb and centrifugal potentials approach zero. All that is left is the equation of a free particle in one dimension; i.e., the TISE reduces to

$$\frac{d^2}{dr^2}\varphi(r) = -2E\varphi(r).$$

Since the energy of bound states must be negative ($E = 0$ corresponds to the ionization threshold), the solutions to this equation are

$$A \exp\left(\sqrt{-2E}r\right) \quad \text{inadmissible}$$

and

$$B \exp\left(-\sqrt{-2E}r\right).$$

The first of these solutions blows up as $r \rightarrow \infty$, and is inadmissible. The remaining solution, exponential decay as $r \rightarrow \infty$, applies equally to $R(r)$, at large r . The actual solutions consist of polynomials (of successively higher order) multiplying the above exponential function.

For each value ℓ , there is a ladder of the radial states. The ground state of each ladder has the form,

$$\varphi(r) = Cr^{\ell+1} \exp\left(-\frac{r}{a}\right).$$

The associated energy eigenvalue is

$$E = -\frac{1}{2a^2}.$$

The parameter a is determined by satisfying the Schrodinger equation.

Left side of Eq. 4.2 equals

$$\begin{aligned} \frac{d^2}{dr^2}\varphi(r) &= C \frac{d}{dr} \left(-\frac{r^{\ell+1}}{a} + (\ell+1)r^\ell \right) \exp\left(-\frac{r}{a}\right) \\ &= C \left(\frac{r^{\ell+1}}{a^2} - 2(\ell+1)\frac{r^\ell}{a} + (\ell+1)\ell r^{\ell-1} \right) \exp\left(-\frac{r}{a}\right) \end{aligned}$$

Right side equals

$$\left(-2E - \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2} \right) \varphi(r) \quad (4.3)$$

$$= C \left(-2Er^{\ell+1} - 2Zr^\ell - \ell(\ell+1)r^{\ell-1} \right) \exp\left(-\frac{r}{a}\right) \quad (4.4)$$

1. Equating coefficients of $r^{\ell+1}$ (within parentheses on both sides) gives

$$-2E = \frac{1}{a^2},$$

which is already known.

2. Equating coefficients of r^ℓ gives

$$\frac{2(\ell+1)}{a} = 2Z$$

or

$$a = \frac{\ell+1}{Z}$$

which gives

$$E = -\frac{1}{2a^2} = -\frac{Z^2}{2(\ell+1)^2},$$

the ground state energy of the ℓ ladder of states. It is written as

$$E_n = -\frac{Z^2}{2n^2},$$

where $n = 1, 2, \dots$ is the principle quantum number, and the first state in the ℓ ladder of states begins at $n = \ell + 1$; e.g., $n = 2, 3, \dots$, for $\ell = 1$, and $n = 3, 4, \dots$, for $\ell = 2$.

Normalization of the the lowest energy state of the ℓ ladder,

$$R_{n=\ell+1,\ell}(r) = Cr^\ell \exp\left(-\frac{Z}{n}r\right).$$

Normalization condition:

$$\int_0^\infty |R_{\ell+1,\ell}(r)|^2 r^2 dr = 1$$

gives

$$\begin{aligned} |C|^2 &= \frac{1}{\int_0^\infty r^{2+2\ell} \exp\left(-\frac{2Z}{n}r\right) dr} \\ &= \left(\frac{2Z}{n}\right)^{3+2\ell} \frac{1}{\int_0^\infty u^{2+2\ell} \exp(-u) du} \\ &= \left(\frac{2Z}{n}\right)^{3+2\ell} \frac{1}{(2+2\ell)!} \end{aligned}$$

and

$$R_{\ell+1,\ell}(r) = \left(\frac{2Z}{n}\right)^{\frac{3}{2}+\ell} \frac{1}{((2+2\ell)!)^{1/2}} r^\ell \exp\left(-\frac{Z}{n}r\right).$$

The k th state in the ℓ ladder, $k = 1, 2, \dots$, has the form,

$$\begin{aligned}\varphi_k(r) &= (C_1 r^{\ell+1} + \dots + C_{k-1} r^{\ell+k-1} + C_k r^{\ell+k}) \exp\left(-\frac{r}{a}\right) \\ &= (P_{k-3}(r) r^{\ell+1} + C_{k-1} r^{\ell+k-1} + C_k r^{\ell+k}) \exp\left(-\frac{r}{a}\right),\end{aligned}$$

where $P_{k-3}(r)$ is a polynomial of order $k-3$. Substituting the above form into Eq. 4.2 gives

$$\begin{aligned}& \frac{d^2}{dr^2} (P_{k-3}(r) r^{\ell+1} + C_{k-1} r^{\ell+k-1} + C_k r^{\ell+k}) \exp\left(-\frac{r}{a}\right) \\ &= 2 \left(-\frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} - E \right) (P_{k-3}(r) r^{\ell+1} + C_{k-1} r^{\ell+k-1} + C_k r^{\ell+k}) \exp\left(-\frac{r}{a}\right).\end{aligned}$$

After the derivatives are evaluated, equating the coefficients of $r^{\ell+k}$ gives

$$\frac{C_k}{a^2} = -2EC_k$$

which gives the usual relationship,

$$E = -\frac{1}{2a^2}.$$

Equating the coefficients of $r^{\ell+k-1}$ gives

$$\begin{aligned}\frac{C_{k-1}}{a^2} - 2(\ell+k) \frac{C_k}{a} &= -2ZC_k - 2EC_{k-1} \\ \frac{C_{k-1}}{a^2} - 2(\ell+k) \frac{C_k}{a} &= -2ZC_k + \frac{C_{k-1}}{a^2}\end{aligned}$$

which leads to

$$\begin{aligned}a &= \frac{\ell+k}{Z}, & k = 1, 2, \dots \\ &= \frac{n}{Z} & n = \ell+1, \ell+2, \dots\end{aligned}$$

We label the states by $n = \ell+k$, instead of k , the $\ell > 0$ energy levels are the same as those of $\ell = 0$, except that they start at $n = \ell+1$. This means the largest ℓ consistent with *principle quantum number*, n , is $n-1$. The centrifugal potential term does not contribute to the determination of E and a above because it lowers the power of r by 2. It contributes only to the coefficients of the polynomial - determined by equating the lower order coefficients.

The energy levels of hydrogen:

Energy is labeled by a single quantum number, n , which varies from 1 to ∞ . For each n - i.e., for each energy level - the angular momentum quantum number varies from $\ell = 0$ to $\ell = n-1$. For each n and ℓ values, m_ℓ varies from

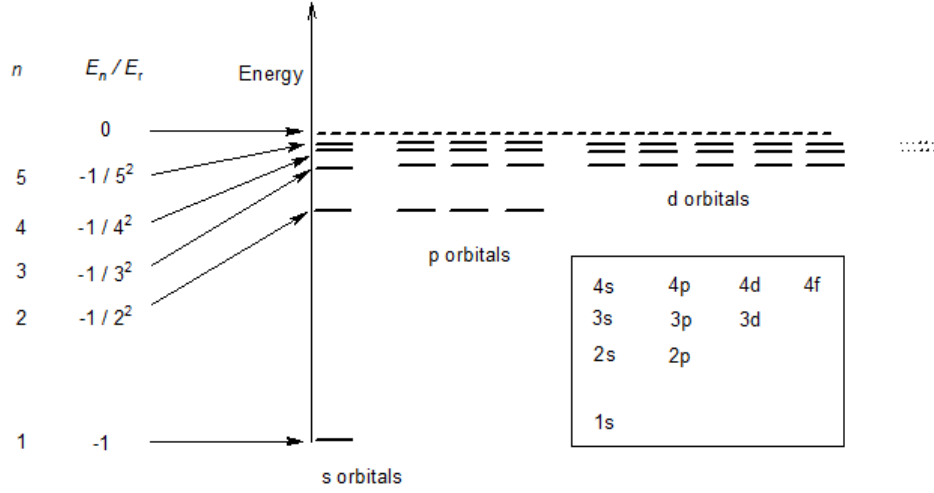


Figure 4.1: The energy levels of hydrogen, with associated orbitals indicated. The inset shows the subshell structure of each shell, up to $n = 4$.

$m_\ell = -\ell$ to $m_\ell = \ell$. The wavefunctions that represent these states have the form,

$$\begin{aligned}
 R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta, \phi) &= P_{n,\ell} \left(\frac{2Zr}{n} \right) \left(\frac{2Zr}{n} \right)^\ell \exp \left(-\frac{Zr}{n} \right) Y_{\ell,m_\ell}(\theta, \phi) \\
 m_\ell &= -\ell, \dots, \ell \\
 \ell &= 0, \dots, n-1.
 \end{aligned}$$

Here, $P_{n,\ell}(\rho_n)$ is a $n-\ell$ th order polynomial. $\{P_{n,\ell}(\rho_n) \rho_n^\ell \exp(-\frac{\rho_n}{2})\}_{n=\ell+1, \ell+2, \dots}$ is the ladder of radial eigenfunctions for the angular momentum, ℓ , radial TISE. $\rho_n = 2Zr/n$.

The angular functions are the spherical harmonics - the same functions that represent the rotations of diatomic molecules. The radial functions are indexed by $n-\ell$ since the first radial state of the hydrogen atom for angular momentum quantum number, ℓ , has the same energy as the $n = \ell + 1$ th radial state for zero angular momentum arising from the radial TISE. It is instructive to derive the familiar shapes of p and d orbitals from the spherical harmonics with $\ell = 1$ and 2.

The p orbitals, $Y_{1,m_\ell}(\theta, \phi)$, are given as follows:

$$\begin{array}{lll}
 m_\ell & Y_{1,m_\ell}(\theta, \phi) & r Y_{1,m_\ell}(\theta, \phi) \\
 1 & p_1 = (2\pi I_1)^{-1/2} \sin \theta \exp(i\phi) & (2\pi I_1)^{-1/2} (x + iy) \\
 0 & p_0 = p_z = (4\pi I_1)^{-1/2} 2 \cos \theta & (4\pi I_1)^{-1/2} 2z \\
 -1 & p_{-1} = -(2\pi I_1)^{-1/2} \sin \theta \exp(-i\phi) & -(2\pi I_1)^{-1/2} (x - iy)
 \end{array}$$

Real p orbitals are obtained from plus and minus combinations of the p_1 and

p_{-1} orbitals:

$$rp_x = \frac{r}{\sqrt{2}} (p_1 - p_{-1}) = (4\pi I_1)^{-1/2} 2x$$

and

$$rp_y = \frac{r}{i\sqrt{2}} (p_1 + p_{-1}) = (4\pi I_1)^{-1/2} 2y.$$

The $1/\sqrt{2}$ factors are to ensure normalized orbitals. Dividing the sum of any two orthogonal, normalized orbitals by $\sqrt{2}$ gives a normalized orbital.

The d orbitals, $Y_{2,m_\ell}(\theta, \phi)$, are given as follows:

m_ℓ	$Y_{2,m_\ell}(\theta, \phi)$	$r^2 Y_{2,m_\ell}(\theta, \phi)$
2	$d_2 = (2\pi I_2)^{-1/2} \sin^2 \theta \exp(2i\phi)$	$(2\pi I_2)^{-1/2} (x + iy)^2$ $= (2\pi I_2)^{-1/2} (x^2 - y^2 + 2ixy)$
1	$d_1 = -(2\pi I_2)^{-1/2} 2 \sin \theta \cos \theta \exp(i\phi)$	$-(2\pi I_2)^{-1/2} 2(x + iy)z$
0	$d_0 = d_{z^2} = (3\pi I_2)^{-1/2} (3 \cos^2 \theta - 1)$	$(3\pi I_2)^{-1/2} (3z^2 - r^2)$
-1	$d_{-1} = (2\pi I_2)^{-1/2} 2 \sin \theta \cos \theta \exp(-i\phi)$	$(2\pi I_2)^{-1/2} 2(x - iy)z$
-2	$d_{-2} = (2\pi I_2)^{-1/2} \sin^2 \theta \exp(-2i\phi)$	$(2\pi I_2)^{-1/2} (x - iy)^2$ $= (2\pi I_2)^{-1/2} (x^2 - y^2 - 2ixy)$

Real d orbitals are obtained from plus and minus combinations of the d_2 and d_{-2} and, separately, the d_1 and d_{-1} orbitals:

$$r^2 d_{x^2-y^2} = \frac{1}{\sqrt{2}} (d_2 + d_{-2}) = (4\pi I_1)^{-1/2} 2(x^2 - y^2),$$

$$r^2 d_{xy} = \frac{1}{i\sqrt{2}} (d_2 - d_{-2}) = (4\pi I_1)^{-1/2} 4xy,$$

$$r^2 d_{xz} = \frac{1}{\sqrt{2}} (-d_1 + d_{-1}) = (4\pi I_1)^{-1/2} 4xz$$

and

$$r^2 d_{yz} = \frac{1}{i\sqrt{2}} (-d_1 - d_{-1}) = (4\pi I_1)^{-1/2} 4yz.$$

The first few radial wavefunctions of hydrogen-like ions - in atomic units and expressed in terms of $\rho = 2Zr/n$ - are tabulated as follows:

n	$Z^{-3/2} R_{n,0}(r)$	$Z^{-3/2} R_{n,1}(r)$	$Z^{-3/2} R_{n,2}(r)$
3	$243^{-1/2} (6 - 6\rho + \rho^2) \exp(-\frac{\rho}{2})$	$486^{-1/2} (4 - \rho) \rho \exp(-\frac{\rho}{2})$	$2430^{-1/2} \rho^2 \exp(-\frac{\rho}{2})$
2	$8^{-1/2} (2 - \rho) \exp(-\frac{\rho}{2})$	$24^{-1/2} \rho \exp(-\frac{\rho}{2})$	
1	$2 \exp(-\frac{\rho}{2})$		

The polynomial prefactors of $\exp(-\frac{\rho}{2})$ for $\ell = 0$ are the Laguerre polynomials. For $\ell > 0$, they are associated Laguerre polynomials.

4.2 Transitions of the hydrogen atom.

Hydrogen atom transitions are subject to the same transition rule as rotations of a diatomic molecule - namely, $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0$ or ± 1 . This is because

the angular dependence of the dipole operator has the same form in both cases - it is $\cos \theta$ ($\sin \theta \cos \phi$ for $\Delta m_\ell = \pm 1$ transitions). The radial transitions of the hydrogen atom are not subject to the selection rule of the diatomic vibrational transitions. The latter transitions are harmonic oscillator transitions. The transition integrals of radial transitions of the hydrogen atom,

$$\int_0^\infty R_{n',\ell\pm 1}(r) r R_{n,\ell}(r) r^2 dr,$$

are non-zero for all n' and n .

Because the energy level spacings in hydrogen decrease dramatically with increasing n , the transitions of hydrogen are labeled according to the lower level involved. For example, transitions to or from $n = 1$ levels are called Lyman transitions - the observed lines constitute the Lyman series. Transitions to or from $n = 2$ (except involving $n = 1$) are Balmer transitions, and so on (Paschen, Brackett, ...). The Lyman series lines are all in the UV portion of the EM spectrum. The Balmer lines are visible transitions. The other series are in the infrared, and beyond. After the Balmer series, the other series begin to overlap - increasingly so with larger smallest n .

4.3 Electron spin

When a magnetic field is applied, states with different m_ℓ have different energy - the *Zeeman effect*. It arises because of the interaction of the magnetic field and the magnetic dipole of the electron "orbiting" the nucleus. An orbiting electron has a *magnetic dipole* associated with its orbital angular momentum,

$$\hat{\boldsymbol{\mu}}_{m,\text{orb}} = -\frac{e}{2m_e} \hat{\mathbf{L}}.$$

The interaction energy - the orbital *Zeeman energy* - is given by

$$\hat{H}_{\text{orb}, Z}^{(1)} = -\hat{\boldsymbol{\mu}}_{m,\text{orb}} \cdot \mathbf{B},$$

where \mathbf{B} is the *magnetic field* - in Tesla (SI units) Choose the magnetic field to be along the z axis. In this case,

$$\hat{H}_{\text{orb}, Z}^{(1)} = \frac{e}{2m_e} B \hat{L}_z.$$

The eigenstates of this operator are the eigenstates of \hat{L}_z - i.e., the distinct m_ℓ states of hydrogen. The Zeeman energy shifts are the eigenvalues of $\hat{H}_{\text{orb}, Z}^{(1)}$, given by

$$\begin{aligned} E_{\text{orb}, Z, m_\ell}^{(1)} &= \frac{e\hbar}{2m_e} B m_\ell \\ &= \mu_B B m_\ell, \end{aligned}$$

where

$$\mu_B = \frac{e\hbar}{2m_e} = 5.7883818066(38) \times 10^{-5} \text{ eV T}^{-1}$$

is called the *Bohr magneton* - it is the *atomic unit of magnetic dipole moment*. Subshells split into a set of distinct energy levels (with plus or minus energy shift in accord with the sign of m_ℓ) that are detected by the associated splitting of spectral lines when hydrogen is in a magnetic field. Spectral lines appear subject to the selection rules, $\Delta m_\ell = 0$ or ± 1 . The associated frequencies are proportional to the applied magnetic field. This is the origin of the term *magnetic quantum number*, and the m_ℓ notation. However, in addition to the orbital Zeeman splitting experiments show splitting due to *electron spin* and *nuclear spin*.

An electron beam in an inhomogeneous magnetic field (plus a transverse electric field to counter the Lorentz force that causes the electrons to spiral) splits into two beams. This shows that electrons have two spin states, which corresponds to a *spin angular momentum quantum number*, $s = 1/2$. s is analogous to the orbital quantum number, ℓ . One key difference (other than the half-integral nature of s) is that there is only this one s state. The Zeeman interaction energy, accounting for both orbital and spin contributions, is

$$\begin{aligned} \hat{H}_Z &= -(\hat{\mu}_{\text{orb}, z} + \hat{\mu}_{\text{spin}, z}) B \\ &= \left(\frac{\mu_B}{\hbar} \hat{L}_z + \frac{g_e \mu_B}{\hbar} \hat{S}_z \right) B, \end{aligned}$$

where $g_e = 2.002319304361(53)$ is called the electron g-factor. Its value is known to extraordinary precision with experiment and theory in lock step. Classical relativity theory predicts a value of 2. Quantum electrodynamics predicts the correction as shown - in agreement with experiment. The eigenvalues of the Zeeman Hamiltonian are

$$E_{Z, m_\ell, m_s} = \mu_B B (m_\ell + g_e m_s),$$

where m_s ($= 1/2$ or $-1/2$) labels the two eigenstates of \hat{S}_z (called α and β , respectively) in the same way m_ℓ labels the eigenstates of \hat{L}_z . Nuclear spin contributes an additional level of splitting sensitive to the M_I quantum number associated with the z component of nuclear spin angular momentum, \hat{I}_z . However, this splitting is orders of magnitude smaller. Nevertheless, the nuclear spin Zeeman splitting is the basis for *nuclear magnetic resonance* (NMR) spectroscopy and *magnetic resonance imaging* (MRI). The electron orbital and spin Zeeman splittings are the basis for *electron spin resonance* (ESR) spectroscopy (a.k.a. electron paramagnetic resonance - EPR - spectroscopy).

4.4 The helium atom and the Pauli principle

Spin orbit interaction is very small for light atoms. With no spin dependence in the Hamiltonian, the state of an atom factors into a spin state and a spatial

state. The full state of a system with more than one electron must be *antisymmetric* with respect to exchange of any two electrons. This is called the *Pauli principle*. It applies to systems of *fermions* - particles with half-integral spin. All elementary particles of matter are fermions.

$\hat{P}_{1,2}$ is the electron 1 and 2 *exchange operator*. Its effect on a two electron state, $\psi(1, 2)$,

$$\hat{P}_{1,2}\psi(1, 2) = \psi(2, 1)$$

Because the two electron state of a helium atom is also a product of spin and spatial states, the spin and spatial states must separately be either symmetric or antisymmetric with respect to exchange, such that their product is antisymmetric. Spin and space states have opposite symmetry with respect to exchange.

Antisymmetric wavefunctions can be constructed from product states - i.e., each electron is assigned to an orbital - by applying the *antisymmetrizer*. The antisymmetrizer operator, \hat{A} , for two electrons is

$$\hat{A} = \frac{1}{\sqrt{2}} (1 - \hat{P}_{1,2}).$$

Applying the antisymmetrizer to any state with two electrons occupying the same spin-orbital (same orbital and same spin) gives zero. This gives the filling rule for the product states: two electrons per orbital, with spins paired - i.e., $+1/2$ (α) and $-1/2$ (β) spin states.

$$\begin{aligned} \psi_{\text{He g.s.}}^{(0)} &= \frac{1}{\sqrt{2}} ((1s)(1)(1s)(2)\alpha(1)\beta(2) - (1s)(2)(1s)(1)\alpha(2)\beta(1)) \\ &= (1s)(1)(1s)(2) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\ &= (1s)(1)(1s)(2) \chi_{0,0}(1, 2), \end{aligned}$$

where $\chi_{0,0}(1, 2)$ is the two spin *singlet state* wherein the electrons have opposite spin and the total spin angular momentum is zero. The total spin quantum numbers are $(S, M_S) = (0, 0)$.

With the above approximate ground state for helium, we can approximate the ground state energy by forming the expectation value of the helium Hamiltonian, including the electron-electron repulsion. Since the above state is an eigenstate of the Hamiltonian of the two electron Hamiltonian without electron-electron repulsion, this estimate corresponds to a first-order-perturbation-theory corrected (with respect to electron-electron repulsion) of the helium ground state energy. The helium Hamiltonian can be written (in atomic units) as

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}.$$

This Hamiltonian does not affect spin states. The ground state, $\psi_{\text{He g.s.}}^{(0)}$, consequently factors into orbital and spin parts. The expectation value of the

Hamiltonian for a helium atom in this state correspondingly factors into space and spin inner products,

$$\begin{aligned}
& E_{\text{He g.s.}}^{(0 \text{ \& } 1)} \\
&= \left\langle \psi_{\text{He g.s.}}^{(0)} \left| \hat{H} \psi_{\text{He g.s.}}^{(0)} \right. \right\rangle \\
&\quad \text{total inner product for 2 e}^-\text{s, space and spin} \\
&= \left\langle (1s)(1)(1s)(2) \left| \hat{H}(1s)(1)(1s)(2) \right. \right\rangle \left\langle \chi_{0,0}(1,2) \left| \chi_{0,0}(1,2) \right. \right\rangle \\
&\quad \begin{array}{cc} \text{this is a spatial inner product for 2 e}^-\text{s} & \text{this is a spin inner product for 2 e}^-\text{s} \\ \text{a six dimensional integral} & =1, \chi_{0,0}(1,2) \text{ is normalized} \end{array} \\
&= \left\langle (1s)(1)(1s)(2) \left| \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) (1s)(1)(1s)(2) \right. \right\rangle \\
&= \left\langle (1s)(1) \left| \hat{H}_1(1s)(1) \right. \right\rangle \left\langle (1s)(2) \left| (1s)(2) \right. \right\rangle + \left\langle (1s)(1) \left| (1s)(1) \right. \right\rangle \left\langle (1s)(2) \left| \hat{H}_2(1s)(2) \right. \right\rangle \\
&\quad + \left\langle (1s)(1)(1s)(2) \left| \frac{1}{r_{12}}(1s)(1)(1s)(2) \right. \right\rangle \\
&= \underbrace{-\frac{2^2}{2 \times 1^2}}_{1s \text{ e}^- \text{ in He}^+} - \underbrace{\frac{2^2}{2 \times 1^2}}_{1s \text{ e}^- \text{ in He}^+} + J_{1s,1s} \\
&= -4 + J_{1s,1s},
\end{aligned}$$

where $J_{1s,1s} > 0$ is called the 1s-1s Coulomb integral - it gives the repulsion energy of the two 1s electrons. Here, we see that the ground state energy of He is somewhat higher than -4 Hartree (the energy without electron-electron repulsion). The Coulomb integral,

$$J_{1s,1s} = \int \frac{(1s)^2(\mathbf{x}_1)(1s)^2(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2,$$

is the six dimensional integral over the coordinates of electron 1 and electron 2. The integrand consists of the product of the 1s orbital probability density, $(1s)^2$, for both electron 1 and electron 2, divided by the distance, $r_{12} = \|\mathbf{x}_1 - \mathbf{x}_2\|$, separating the electrons. The integrals can be evaluated analytically. The result is

$$J_{1s,1s} = \frac{5}{4} \text{ Hartree (remember, we are in atomic units).}$$

The first order perturbation theory estimate of the ground state energy is

$$E_{\text{He g.s.}}^{(0 \text{ \& } 1)} = -4 + 1.25 = -2.75 \text{ Hartree} = -74.83 \text{ eV}$$

The true ground state energy of helium is

$$E_{\text{He g.s.}} = -2.9036 \text{ Hartree} = -79.01 \text{ eV}.$$

4.4.1 The variational principle

Our first order perturbation theory estimate of the ground state energy is higher than the true value. It is easy to prove that the expectation value of the Hamiltonian is a minimum when the state is the true ground state. Thus, any other state produces higher value - this is called the *variational principle*. We can estimate the ground state energy of a system by minimizing the expectation value of the Hamiltonian with respect to parameters that define the state. For example, the Coulomb integral defined above is quite large, making the ground state energy estimate too high. This is because the electrons partially shield each other from the nucleus - there is an effective nuclear charge, Z_{eff} , which is less than $Z = 2$ for helium. Consequently, if we replace the Z that appears in exponential portion of the radial wavefunction, $\exp(-Zr)$, and in the normalization constant, by variable Z_{eff} , then the above expectation value can be minimized with respect to Z_{eff} to give a better estimate of the ground state energy. We also get a better estimate of the ground state itself, and a "best" effective nuclear charge value for $1s^2$ electrons.

4.4.2 The ionization energy of helium

The ionization energy of helium is the change in energy change of the process,



where the free electron on the right has zero kinetic energy. The ionization of helium is thus

$$\begin{aligned} I_{\text{He}} &= E_{\text{He}^+ \text{ g.s.}} - E_{\text{He g.s.}} \\ &= -2 - (-2.9036) \\ &= 0.9036 \text{ Hartree} = 24.59 \text{ eV}. \end{aligned}$$

Using our first order perturbation theory estimate for the ground state of He, the ionization energy is approximated as

$$\begin{aligned} &E_{\text{g.s. He}^+} - E_{\text{g.s. He}}^{(0 \ \& \ 1)} \\ &= -2 - (-2.75) \\ &= 0.75 \text{ Hartree} = 20.41 \text{ eV}. \end{aligned}$$

4.5 Excited states of helium

The excited states of helium are similarly approximated as antisymmetrized product states. For example, consider the $1s^1 2s^1$ electron configuration. Here, there are two different orbitals, $1s$ and $2s$, as well as two different spin states. Now, the two-orbital state can be either symmetric or antisymmetric (with respect to exchange). In the symmetric case, the spin state will be antisymmetric

as in the ground state. However, if the two-orbital state is antisymmetric, the spin state must be symmetric. This corresponds to the three spin states,

$$\chi_{1,1}(1,2) = \alpha(1)\alpha(2),$$

$$\chi_{1,0}(1,2) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$$

and

$$\chi_{1,-1}(1,2) = \beta(1)\beta(2).$$

These two-spin states are eigenstates of the total spin operators, \hat{S}^2 and \hat{S}_z , where

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2,$$

associated with the quantum numbers, S and M_S , listed in the two-spin state subscripts. All of the two-orbital states mentioned so far,

$$\psi_{\text{He g.s.}}^{(0)} = (1s)(1)(1s)(2), \quad \text{goes with singlet spin state - } S = 0$$

$$\begin{aligned} \psi_{\text{He 1st sing}}^{(0)} &= \frac{1}{\sqrt{2}}((1s)(1)(2s)(2) + (1s)(2)(2s)(2)) && \text{goes with singlet spin state - } S = 0 \\ &= \hat{B}(1s)(1)(2s)(2) && \begin{aligned} \hat{B} \text{ is the symmetrizer operator} \\ = 2^{-1/2} \left(1 + \hat{P}_{1,2} \right) \end{aligned} \end{aligned}$$

and

$$\begin{aligned} \psi_{\text{He 1st trip}}^{(0)} &= \frac{1}{\sqrt{2}}((1s)(1)(2s)(2) - (1s)(2)(2s)(2)) && \text{goes with triplet spin state - } S = 1 \\ &= \hat{A}(1s)(1)(2s)(2) \end{aligned}$$

have zero orbital angular momentum, and total orbital angular momentum quantum numbers, $L = 0$ and $M_L = 0$. Of these, the antisymmetric two-orbital state has the lowest energy. This can be seen by evaluating the expectation value of the Hamiltonian for helium atoms in these two states. First consider the symmetric two-orbital state which pairs with the antisymmetric spin state

- the singlet state.

$$\begin{aligned}
& E_{\text{He 1st sing}}^{(0 \text{ \& } 1)} \\
&= \left\langle \psi_{\text{He 1st sing}}^{(0)} \left| \hat{H} \psi_{\text{He 1st sing}}^{(0)} \right. \right\rangle \\
&= \left\langle \hat{B}(1s)(1)(2s)(2) \left| \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) \hat{B}(1s)(1)(2s)(2) \right. \right\rangle \quad \text{two-spin state is normalized} \\
&= \langle (1s)(1)(2s)(2) \left| \hat{B} \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) \hat{B}(1s)(1)(2s)(2) \right. \rangle \quad \hat{B} \text{ is Hermitian} \\
&= \langle (1s)(1)(2s)(2) \left| \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) \hat{B}^2(1s)(1)(2s)(2) \right. \rangle \quad \hat{B} \text{ commutes with } \hat{H} \\
&= \langle (1s)(1)(2s)(2) \left| \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) \sqrt{2} \hat{B}(1s)(1)(2s)(2) \right. \rangle \quad \hat{B}^2 = \sqrt{2} \hat{B} \\
&= \langle (1s)(1)(2s)(2) \left| \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right) ((1s)(1)(2s)(2) + (1s)(2)(2s)(2)) \right. \rangle \\
&= \underbrace{-\frac{2^2}{2 \times 1^2}}_{1s \text{ e}^- \text{ in He}^+} - \underbrace{\frac{2^2}{2 \times 2^2}}_{2s \text{ e}^- \text{ in He}^+} + J_{1s,2s} + K_{1s,2s} \\
&= -\frac{5}{2} + J_{1s,2s} + K_{1s,2s},
\end{aligned}$$

where $J_{1s,2s}$ and $K_{1s,2s}$ are the 1s-2s *Coulomb* and *exchange* integrals:

$$J_{1s,2s} = \int \frac{(1s)^2(\mathbf{x}_1)(2s)^2(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

and

$$K_{1s,2s} = \int \frac{(1s)(\mathbf{x}_1)(2s)(\mathbf{x}_1)(1s)(\mathbf{x}_2)(2s)(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2.$$

Whereas the Coulomb integral can be viewed as the electrostatic repulsion of two classical spherical charge distributions, the exchange integral has no classical analogue. Both of these terms are positive. The singlet state is shifted up by both Coulomb and exchange integrals.

When we construct the expectation value of the Hamiltonian with the first triplet state, the result is

$$\left\langle \psi_{\text{He 1st trip}}^{(0)} \left| \hat{H} \psi_{\text{He 1st trip}}^{(0)} \right. \right\rangle = -\frac{5}{2} + J_{1s,2s} - K_{1s,2s}.$$

Here, the exchange energy enters with a minus sign. This means the triplet state has lower energy than the singlet state. This is an example of the first of *Hund's rules*: The states with highest spin multiplicity ($2S + 1$, largest for largest S) have the lowest energy.

Evaluating the Coulomb and exchange integrals for the $1s^1 2s^1$ configuration gives

$$J_{1s,2s} = 0.420$$

and

$$K_{1s,2s} = 0.044.$$

The triplet and singlet state energies are estimated to be

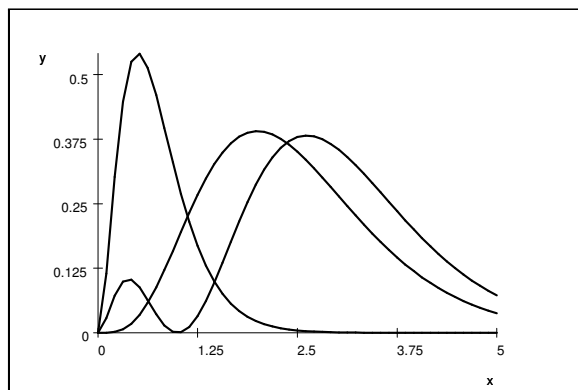
$$\begin{aligned} E_{\text{He 1st trip.}}^{(0 \ \& \ 1)} &= -2.5 + 0.420 - 0.044 \\ &= -2.124 \text{ Hartree} = -57.80 \text{ eV} \end{aligned}$$

$$\begin{aligned} E_{\text{He 1st sing.}}^{(0 \ \& \ 1)} &= -2.5 + 0.420 + 0.044 \\ &= -2.036 \text{ Hartree} = -55.40 \text{ eV}. \end{aligned}$$

The true values are -2.176 and -2.147 Hartree, respectively.

The next excited states of helium are the triplet and singlet states associated with the $1s^1 2p^1$ electron configuration. These states have total orbital angular momentum quantum number, $L = 1$. There are three distinct, degenerate triplet and singlet states, associated with the three $2p$ orbitals, $2p_1$, $2p_0$ and $2p_{-1}$. The total degeneracy of these states is $(2S + 1)(2L + 1) = 9$ for the $S = 1$ (triplet) states, and 3 for the $S = 0$ (singlet) states. These states are higher in energy than the $1s^1 2s^1$ states because the Coulomb integral is larger for these states. This energy difference is often attributed to the inner lobe of the $2s$ penetrating the $1s$ shell, and experiencing a larger effective nuclear charge. Here, the energy difference is attributed to $J_{1s,2s} < J_{1s,2p}$. This inequality, can be understood in terms of the two radial lobes of the $2s$ orbital as follows:

Figure 7.2 shows the radial electron density for the $1s$, $2s$ and $2p$ orbitals: $r^2 |R_{1,0}|^2$ (solid), $r^2 |R_{2,0}|^2$ (dashed) and $r^2 |R_{2,1}|^2$ (dotted), respectively. We see that because of the inner lobe of $2s$, the outer lobe is further from the nucleus and does not overlap the $1s$ electron density very much. The overlap of the $2p$ electron density with $1s$ is greater. It is in the overlapping regions where the electron-electron repulsion, $1/r_{12}$, is greatest. Note that the traditional first year explanation - that the inner lobe of $2s$ gives $2s$ a greater effective nuclear charge - becomes evident if we do a variational calculation. Specifically, if we minimized the expectation value of the Hamiltonian with respect to Z (use separate Z 's in the exponential portion of the orbital radial functions), we would find that both $2s$ and $2p$ are pushed further from the nucleus (they have smaller effective nuclear charges than $1s$), with $2p$ pushed further in order to avoid the overlap with $1s$. This larger shift, to larger r , of $2p$ gives it a higher energy than $2s$.



The radial probability density, $|\varphi(r)|^2 = r^2 |R(r)|^2$, for the 1s orbital (solid), the 2s orbital (dashed) and the 2p orbital (dotted). The units of r are Bohr = 52.918 pm.