OVERVIEW OF TIME-INDEPENDENT QUANTUM MECHANICS

1. Describing a System Quantum Mechanically[1]

As a starting point it is useful to review the postulates of quantum mechanics, and use this as an opportunity to elaborate on some definitions and properties of quantum systems.

1. **The wavefunction.** Quantum mechanical matter exhibits wave-particle duality in which the particle properties emphasize classical aspects of the object's position, mass, and momentum, and the wave properties reflect its spatial delocalization and ability to interfere constructively or destructively with other particles or waves. As a result, in quantum mechanics the physical properties of the system are described by the wavefunction Ψ. The wavefunction is a time-dependent complex probability amplitude function that is itself not observable; however, it encodes all properties of the system's particles and fields. Depending on the context, *particle* is a term that will refer to a variety of objects—such as electron, nucleons, and atoms—that fill space and have mass, but also retain wavelike properties. *Fields* refer to a variety of physical quantities that are continuous in time and space, which have energy and influence the behavior of particles.

   In the general sense, the wavefunction, or *state*, does not refer to a three-dimensional physical space in which quantum particles exist, but rather an infinite-dimensional linear vector space, or *Hilbert space*, that accounts for all possible observable properties of the system. We can represent the wavefunction in physical space, $\Psi(\mathbf{r})$, by carrying out a projection onto the desired spatial coordinates. As a probability amplitude function, the wavefunction describes the statistical probability of locating particles or fields in space and time. Specifically, we claim that the square of the wavefunction is proportional to a probability density (probability per unit volume). In one dimension, the probability of finding a particle in a space between x and $x+dx$ at a particular time t is

$$P(\mathbf{x},\mathrm{t})\,dx = \Psi^{*}(\mathbf{x},\mathrm{t})\,\Psi(\mathbf{x},\mathrm{t})\;\mathrm{dx} \tag{1}$$

   We will always assume that the wavefunctions for a particle are properly normalized, so that $\int \mathrm{P}(\mathbf{x},\mathrm{t})\;\mathrm{dx} = 1$.

2. **Operators.** Quantum mechanics parallels Hamilton's formulation of classical mechanics, in which the properties of particles and fields are described in terms of their position and momenta. Each particle described by the wavefunction will have associated with it one or more *degrees of freedom* that are defined by the dimensionality of the problem. For each degree of freedom, particles which are described classically by a position x and

momentum p_x, will have associated with it a quantum mechanical operator $\hat{x}$ or $\hat{p}_x$, which will be used to describe physical properties and experimental observables. Operators correspond to dynamical variables, whereas static variables, such as mass, do not have operators associated with them. In practice there is a quantum/classical correspondence which implies that the quantum mechanical behavior can often be deduced from the classical dynamical equations by substituting the quantum mechanical operator for the corresponding classical variables. In the case of position and momenta, these operators are $x \to \hat{x}$ and $\hat{p}_x = -i\hbar(\partial/\partial x)$. Table 1 lists some important operators that we will use. Note that time does not have an operator associated with it, and for our purposes is considered an immutable variable that applies uniformly to the entire system.

Table 1. Operators in the position representation corresponding to observable classical dynamical variables in one and three dimensions

Classical variable			**Operator**
Position	(1D)	x	$\hat{x}$
	(3D)	2. r	$\hat{r}$
Linear momentum	(1D)	p_x	$\hat{p}_x = -i\hbar(\partial/\partial x)$
	(3D)	3. p	$\hat{p} = -i\hbar\nabla$
Function of position and momentum	(1D)	$f(x,p_x)$	$f(\hat{x},\hat{p}_x)$
Angular momentum	(3D)	$\overline{L} = \overline{r} \times \overline{p}$	$\hat{L} = -i\hbar\hat{r} \times \overline{\nabla}$
z-component of orbital angular momentum			$\hat{L}_z = -i\hbar(\partial/\partial\phi)$

What do operators do? Operators map one state of the system to another—also known as *acting* on the wavefunction:

$$\hat{A}\Psi_0 = \Psi_A \tag{2}$$

Here Ψ_0 is the initial wavefunction and Ψ_A refers to the wavefunction after the action of the operator $\hat{A}$. Whereas the variable x represents a position in physical space, the operator $\hat{x}$ maps the wavefunction from Hilbert space onto physical space. Operators also represent a mathematical operation on the wavefunction that influences or changes it, for instance moving in time and space. Operators may be simply multiplicative, as with the operator $\hat{x}$, or they may take differential or integral forms. The gradient $\overline{\nabla}$,

divergence $\nabla\cdot$, and curl $\nabla\times$ are examples of differential operators, whereas Fourier and Laplace transforms are integral operators.

When writing an operator, it is always understood to be acting on a wavefunction to the right. For instance, the operator $\hat{p}_x$ says that one should differentiate the wavefunction to its right with respect to x, and then multiply the result by $-i\hbar$. The operator $\hat{x}$ simply means multiply the wavefunction by x. Since operators generally do not commute, a series of operators must be applied in the prescribed right-to-left order.

$$\hat{\mathrm{B}}\hat{\mathrm{A}}\ \Psi_0 = \hat{\mathrm{B}}\ \Psi_A = \Psi_{\mathrm{B,A}} \tag{3}$$

One special characteristic of operators that we will look for is whether operators are Hermitian. A Hermitian operator obeys the equality $\hat{A} = \hat{A}^*$.

Of particular interest is the Hamiltonian, $\hat{H}$, an operator corresponding to the total energy of the system. The Hamiltonian operator describes all interactions between particles and fields, and thereby determines the state of the system. The Hamiltonian is a sum of the total kinetic and potential energy for the system of interest, $\hat{H} = \hat{T} + \hat{V}$, and is obtained by substituting the position and momentum operators into the classical Hamiltonian. For one particle under the influence of a potential,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{r},t) \tag{4}$$

Notation: In the following chapters, we will denote operators with a circumflex only when we are trying to explicitly note its role as an operator, but otherwise we take the distinction between variables and operators to be understood.

3. **Eigenvalues and Eigenfunctions.** The properties of a system described by mapping with the operator $\hat{A}$ can only take on the values a that satisfy an eigenvalue equation

$$\hat{A}\Psi = a\Psi \tag{5}$$

For instance, if the state of the system is $\Psi(x) = e^{ipx/\hbar}$, the momentum operator $\hat{p}_x = -i\hbar(\partial/\partial x)$ returns the eigenvalue p (a scalar) times the original wavefunction. Then $\Psi(x)$ is said to be an eigenfunction of $\hat{p}_x$. For the Hamiltonian, the solutions to the eigenvalue equation

$$\hat{H}\Psi = E\Psi \tag{6}$$

yield possible energies of the system. The set of all possible eigenvectors are also known as the eigenstates ψ_i. Equation (6) is the time-independent Schrödinger equation (TISE).

4. **Linear Superposition.** The eigenstates of $\hat{A}$ form a complete orthonormal basis. In Hilbert space the wavefunction is expressed as a linear combination of orthonormal functions,

$$\Psi = \sum_{i=0}^{\infty} c_i \psi_i \tag{7}$$

where c_i are complex numbers. The eigenvectors ψ_i are orthogonal and complete:

$$\int_{-\infty}^{+\infty} d\tau \, \psi_i^* \psi_j = \delta_{ij} \tag{8}$$

$$\sum_{i=0}^{\infty} |c_i|^2 = 1 \tag{9}$$

The choice of orthonormal functions in which to represent the system is not unique and is referred to as selecting a *basis set*. The change of basis set is effectively a transformation that rotates the wavefunction in Hilbert space.

5. **Expectation Values.** The outcome of a quantum measurement cannot be known with arbitrary accuracy; however, we can statistically describe the probability of measuring a certain value. The measurement of a value associated with the operator is obtained by calculating the expectation value of the operator

$$\langle A \rangle = \int d\tau \, \Psi^* \hat{A} \Psi \tag{10}$$

Here the integration is over Hilbert space. The brackets $\langle \ldots \rangle$ refer to an average value that will emerge from a large series of measurements on identically prepared systems. Whereas $\langle A \rangle$ is an average value, the variance in a distribution of values measured can be calculated from $\Delta A = \langle A^2 \rangle - \langle A \rangle^2$. Since an observable must be real valued, operators corresponding to observables are Hermitian:

$$\int d\tau \, \Psi^* \hat{A} \Psi = \int d\tau \, \hat{A}^* \Psi^* \Psi \tag{11}$$

As a consequence, a Hermitian operator must have real eigenvalues and orthogonal eigenfunctions.

6. **Commutators.** Operators are associative but not necessarily commutative. Commutators determine whether two operators commute. The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$\left[\hat{A}, \hat{B} \right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{12}$$

If we first make an observation of an eigenvalue a for $\hat{A}$, one cannot be assured of determining a unique eigenvalue b for a second operator $\hat{B}$. This is only possible if the system is an eigenstate of both $\hat{A}$ and $\hat{B}$. This would allow one to state that $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$ or alternatively $[\hat{A}, \hat{B}]\psi = 0$. If the operators commute, the commutator is zero, and $\hat{A}$ and $\hat{B}$ have simultaneous eigenfunctions. If the operators do not commute, one cannot specify a and b exactly, however, the variance in their uncertainties can be expressed as $\Delta A^2 \Delta B^2 \geq \langle \frac{1}{2}[\hat{A}, \hat{B}] \rangle^2$. As an example, we see that $\hat{p}_x$ and $\hat{p}_y$ commute, but $\hat{x}$ and $\hat{p}_x$ do not. Thus we can specify the momentum of a particle in the x and y coordinates precisely, but cannot specify both the momentum and position of a particle in the x dimension to arbitrary resolution. We find that $[\hat{x}, \hat{p}_x] = i\hbar$ and $\Delta x \Delta p_x \geq \hbar / 2$.

Note that for the case that the Hamiltonian can be written as a sum of commuting terms, as is the case for a set of independent or separable coordinates or momenta, then the total energy is additive in eigenvalues for each term, and the total eigenfunctions can be written as product states in the eigenfunctions for each term.

7. **Time Dependence.** The wavefunction evolves in time as described by the time-dependent Schrödinger equation (TDSE):

$$-i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{13}$$

In the following chapter, we will see the reasoning that results in this equation. Note that it is not really a classical wave equation because it is linear in time. In fact, for a free particle Hamiltonian $\hat{H} = -\hbar^2 \overline{\nabla}^2 / 2m$, it looks like a diffusion equation with an imaginary diffusion constant.

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1. P. Atkins and R. Friedman, *Molecular Quantum Mechanics*, 4th ed. (Oxford University Press, Oxford; New York, 2005); G. Baym, *Lectures on Quantum Mechanics*. (Perseus Book Publishing, L.L.C., New York, 1969); C. Cohen-Tannoudji, B. Diu and F. Lalöe, *Quantum Mechanics*. (Wiley-Interscience, Paris, 1977); D. J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. (Pearson Prentice Hall, Upper Saddle River, NJ, 2005); E. Merzbacher, *Quantum Mechanics*, 3rd ed. (Wiley, New York, 1998); A. Messiah, *Quantum Mechanics*. (Dover Publications, 1999); J. J. Sakurai, *Modern Quantum Mechanics, Revised Edition*. (Addison-Wesley, Reading, MA, 1994).

2. Matrix Mechanics

Most of our work will make use of the matrix mechanics formulation of quantum mechanics. The wavefunction is written as $|\Psi\rangle$ and referred to as a *ket* vector. The complex conjugate $\Psi^* = \langle\Psi|$ is a *bra* vector, where $\langle a\Psi| = a^*\langle\Psi|$. The product of a *bra* and *ket* vector, $\langle\alpha|\beta\rangle$, is therefore an inner product (scalar), whereas the product of a ket and bra $|\beta\rangle\langle\alpha|$ is an outer product (matrix). The use of *bra–ket* vectors is the Dirac notation in quantum mechanics.

In the matrix representation, $|\Psi\rangle$ is represented as a column vector for the expansion coefficients c_i in a particular basis set.

$$|\Psi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} \tag{14}$$

The *bra* vector $\langle\Psi|$ refers to a row vector of the conjugate expansion coefficients c_i^*. Since wavefunctions are normalized, $\langle\Psi|\Psi\rangle = 1$. Dirac notation has the advantage of brevity, often shortening the wavefunction to a simple abbreviated notation for the relevant quantum numbers in the problem. For instance, we can write eq. (7) as

$$|\Psi\rangle = \sum_i c_i |i\rangle \tag{15}$$

where the sum is over all eigenstates and the i^{th} eigenstate $|i\rangle = \psi_i$. Implicit in this equation is that the expansion coefficient for the i^{th} eigenstate is $c_i = \langle i|\Psi\rangle$. With this brevity comes the tendency to hide some of the variables important to the description of the wavefunction. One has to be aware of this, and although we will use Dirac notation for most of our work, where detail is required, Schrödinger notation will be used.

The outer product $|i\rangle\langle i|$ is known as a projection operator because it can be used to project the wavefunction of the system onto the i^{th} eigenstate of the system as $|i\rangle\langle i|\Psi\rangle = c_i|i\rangle$. Furthermore, if we sum projection operators over the complete basis set, we obtain an identity operator

$$\sum_i |i\rangle\langle i| = 1 \tag{16}$$

which is a statement of the completeness of a basis set. The orthogonality of eigenfunctions (eq. (8)) is summarized as $\langle i|j\rangle = \delta_{ij}$.

The operator $\hat{A}$ is a square matrix that maps from one state to another

$$\hat{A}|\Psi_0\rangle = |\Psi_A\rangle \tag{17}$$

and from eq. (6) the TISE is

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \tag{18}$$

where E is a diagonal matrix of eigenvalues whose solution is obtained from the characteristic equation

$$\det\left(H - E\mathbf{I}\right) = 0 \tag{19}$$

The expectation value, a restatement of eq. (10), is written

$$\langle A\rangle = \langle \Psi\,|\,\hat{A}\,|\,\Psi\rangle \tag{20}$$

or from eq. (15)

$$\langle A\rangle = \sum_i \sum_j c_i^* c_j A_{ij} \tag{21}$$

where $A_{ij} = \langle i\,|\,A\,|\,j\rangle$ are the matrix elements of the operator $\hat{A}$. As we will see later, the matrix of expansion coefficients $\rho_{ij} = c_i^* c_j$ is known as the density matrix. From eq. (18), we see that the expectation value of the Hamiltonian is the energy of the system,

$$E = \langle \Psi\,|\,H\,|\,\Psi\rangle \tag{22}$$

Hermitian operators play a special role in quantum mechanics. The Hermitian adjoint of an operator $\hat{A}$ is written $\hat{A}^\dagger$, and is defined as the conjugate transpose of $\hat{A}$: $\hat{A}^\dagger = (\hat{A}^T)^*$. From this we see $\langle \hat{A}\psi\,|\,\phi\rangle = \langle \psi\,|\,\hat{A}^\dagger\phi\rangle$. A Hermitian operator is one that is self-adjoint, i.e., $\hat{A}^\dagger = \hat{A}$. For a Hermitian operator, a unique unitary transformation exists that will diagonalize it.

Each basis set provides a different route to representing the same physical system, and a similarity transformation S transforms a matrix from one orthonormal basis to another. A transformation from the state $|\Psi\rangle$ to the state $|\Phi\rangle$ can be expressed as

$$|\,\Theta\rangle = S\,|\,\Psi\rangle \tag{23}$$

where the elements of the matrix are $S_{ij} = \langle \theta_i\,|\,\psi_j\rangle$. Then the reverse transformation is

$$|\,\Psi\rangle = S^\dagger\,|\,\Theta\rangle \tag{24}$$

Therefore $S^\dagger S = 1$ and the transformation is said to be unitary. A unitary transformation refers to a similarity transformation in Hilbert space that preserves the scalar product, i.e., the length of the vector. The transformation of an operator from one basis to another is obtained from $S^\dagger AS$, and *diagonalizing* refers to finding the unitary transformation that puts the matrix A in diagonal form.

Properties of operators

1. The inverse of $\hat{A}$ (written $\hat{A}^{-1}$) is defined by

$$\hat{A}^{-1}\hat{A} = \hat{A}\hat{A}^{-1} = 1 \tag{25}$$

2. The transpose of $\hat{A}$ (written A^T) is

$$(A^T)_{nq} = A_{qn} \tag{26}$$

If $A^T = -A$, then the matrix is anti-symmetric.

3. The trace of $\hat{A}$ is defined as

$$Tr(\hat{A}) = \sum_q A_{qq} \tag{27}$$

The trace of a matrix is invariant to a similarity operation.

4. The Hermitian adjoint of $\hat{A}$ (written $\hat{A}^\dagger$) is

$$\begin{aligned} \hat{A}^\dagger &= (\hat{A}^T)^* \\ (\hat{A}^\dagger)_{nq} &= (\hat{A}_{qn})^* \end{aligned} \tag{28}$$

If $\hat{A}$ and $\hat{B}$ are unitary then $\hat{A}\hat{B}$ is unitary.

5. $\hat{A}$ is Hermitian if $\hat{A}^\dagger = \hat{A}$.

$$(\hat{A}^T)^* = \hat{A} \tag{29}$$

If $\hat{A}$ is Hermitian, then $\hat{A}^n$ is Hermitian and $e^{\hat{A}}$ is Hermitian. For a Hermitian operator, $\langle \psi | \hat{A}\varphi \rangle = \langle \psi \hat{A} | \varphi \rangle$. Expectation values of Hermitian operators are real, so all physical observables are associated with Hermitian operators.

6. $\hat{A}$ is a unitary operator if its adjoint is also its inverse:

$$\begin{aligned} &\hat{A}^\dagger = \hat{A}^{-1} \\ &(\hat{A}^T)^* = \hat{A}^{-1} \\ &\hat{A}\hat{A}^\dagger = 1 \qquad \Rightarrow \qquad (\hat{A}\hat{A}^\dagger)_{nq} = \delta_{nq} \end{aligned} \tag{30}$$

7. If $\hat{A}^\dagger = -\hat{A}$ then $\hat{A}$ is said to be anti-Hermitian. Anti-Hermetian operators have imaginary expectation values. Any operator can be decomposed into its Hermitian and anti-Hermitian parts as

$$\begin{aligned} \hat{A} &= \hat{A}_H + \hat{A}_{AH} \\ \hat{A}_H &= \frac{1}{2}\left(\hat{A} + \hat{A}^\dagger\right) \\ \hat{A}_{AH} &= \frac{1}{2}\left(\hat{A} - \hat{A}^\dagger\right) \end{aligned} \tag{31}$$

Properties of commutators

From the definition of a commutator:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{32}$$

we find it is anti-symmetric to exchange:

$$\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right] \tag{33}$$

and distributive:

$$\left[\hat{A}, \hat{B} + \hat{C}\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{B}, \hat{C}\right] \tag{34}$$

These properties lead to a number of useful identities:

$$\left[\hat{A}, \hat{B}^n\right] = n\hat{B}^{n-1}\left[\hat{A}, \hat{B}\right] \tag{35}$$

$$\left[\hat{A}^n, \hat{B}\right] = n\hat{A}^{n-1}\left[\hat{A}, \hat{B}\right] \tag{36}$$

$$\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right] \tag{37}$$

$$\left[\left[\hat{C}, \hat{B}\right], \hat{A}\right] = \left[\left[\hat{A}, \hat{B}\right], \hat{C}\right] \tag{38}$$

$$\begin{aligned} &\left[\hat{A}, \left[\hat{B}, \hat{C}\right]\right] + \left[\hat{B}, \left[\hat{C}, \hat{A}\right]\right] \\ &+ \left[\hat{C}, \left[\hat{A}, \hat{B}\right]\right] = 0 \end{aligned} \tag{39}$$

The Hermetian conjugate of a commutator is

$$\left[\hat{A},\hat{B}\right]^{\dagger} = \left[\hat{B}^{\dagger},\hat{A}^{\dagger}\right] \tag{40}$$

Also, the commutator of two Hermitian operators is also Hermitian.

The anti-commutator is defined as

$$\left[\hat{A},\hat{B}\right]_{+} = \hat{A}\hat{B} + \hat{B}\hat{A} \tag{41}$$

and is symmetric to exchange. For two Hermitian operators, their product can be written in terms of the commutator and anti-commutator as

$$\hat{A}\hat{B} = \frac{1}{2}\left[\hat{A},\hat{B}\right] + \frac{1}{2}\left[\hat{A},\hat{B}\right]_{+} \tag{42}$$

The anti-commutator is the real part of the product of two operators, whereas the commutator is the imaginary part.

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3. Basic Quantum Mechanical Models

This section summarizes the results that emerge for common models for quantum mechanical objects. These form the starting point for describing the motion of electrons and the translational, rotational, and vibrational motions for molecules. Thus they are the basis for developing intuition about more complex problems.

a. Waves

Waves form the basis for our quantum mechanical description of matter. Waves describe the oscillatory amplitude of matter and fields in time and space, and can take a number of forms. The simplest form we will use is plane waves, which can be written as

$$\psi(\mathbf{r},t) = \mathbf{A}\exp[\mathrm{i}\,\mathbf{k}\cdot\mathbf{r} - \mathrm{i}\,\omega t] \tag{43}$$

The angular frequency ω describes the oscillations in time and is related to the number of cycles per second through $\nu = \omega/2\pi$. The wave amplitude also varies in space as determined by the wavevector **k**, where the number of cycles per unit distance (wavelength) is $\lambda = \omega/k$. Thus the wave propagates in time and space along a direction **k** with a vector amplitude **A** with a phase velocity $v_\phi = \nu\lambda$.

b. Free particles

For a free particle of mass *m* in one dimension, the Hamiltonian only reflects the kinetic energy of the particle

$$\hat{H} = \hat{T} = \frac{\hat{p}^2}{2m} \tag{44}$$

Judging from the functional form of the momentum operator, we assume that the wavefunctions will have the form of plane waves

$$\psi(x) = Ae^{ikx} \tag{45}$$

Inserting this expression into the TISE, eq. (6), we find that

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{46}$$

and set $A = 1/\sqrt{2\pi}$. Now, since we know that $E = p^2/2m$, we can write

$$k = \frac{p}{\hbar} \tag{47}$$

k is the wavevector, which we equate with the momentum of the particle.

Free particle plane waves $\psi_k(x)$ form a complete and continuous basis set with which to describe the wavefunction. Note that the eigenfunctions, eq. (45), are oscillatory over all space. Thus describing a plane wave allows one to exactly specify the wavevector or momentum of the particle, but one cannot localize it to any point in space. In this form, the free particle is not observable because its wavefunction extends infinitely and cannot be normalized. An observation, however, taking an expectation value of a Hermitian operator will collapse this wavefunction to yield an average momentum of the particle with a corresponding uncertainty relationship to its position.

c. Bound particles

Particle-in-a-Box

The minimal model for translational motion of a particle that is confined in space is given by the particle-in-a-box. For the case of a particle confined in one dimension in a box of length L with impenetrable walls, we define the Hamiltonian as

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{48}$$

$$V(x) = \begin{cases} 0 & 0 < x < L_x \\ \infty & \text{otherwise} \end{cases} \tag{49}$$

The boundary conditions require that the particle cannot have any probability of being within the wall, so the wavefunction should vanish at $x = 0$ and L_x, as with standing waves. We therefore assume a solution in the form of a sine function. The properly normalized eigenfunctions are

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad n = 1, 2, 3\ldots \tag{50}$$

Here n are the integer quantum numbers that describe the harmonics of the fundamental frequency π/L whose oscillations will fit into the box while obeying the boundary conditions. We

see that any state of the particle-in-a-box can be expressed in a Fourier series. On inserting eq. (50) into the time-independent Schrödinger equation, we find the energy eigenvalues

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{51}$$

Note that the spacing between adjacent energy levels grows as $n(n+1)$.

This model is readily extended to a three-dimensional box by separating the box into *x, y,* and *z* coordinates. Then

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z \tag{52}$$

in which each term is specified as eq. (48). Since $\hat{H}_x, \hat{H}_y,$ and $\hat{H}_z$ commute, each dimension is separable from the others. Then we find

$$\psi(x, y, z) = \psi_x \psi_y \psi_z \tag{53}$$

and

$$E_{x,y,z} = E_x + E_y + E_z \tag{54}$$

which follow the definitions given in (50) and (51) above. The state of the system is now specified by three quantum numbers with positive integer values: $n_x, n_y, n_z = 1, 2, 3\ldots$

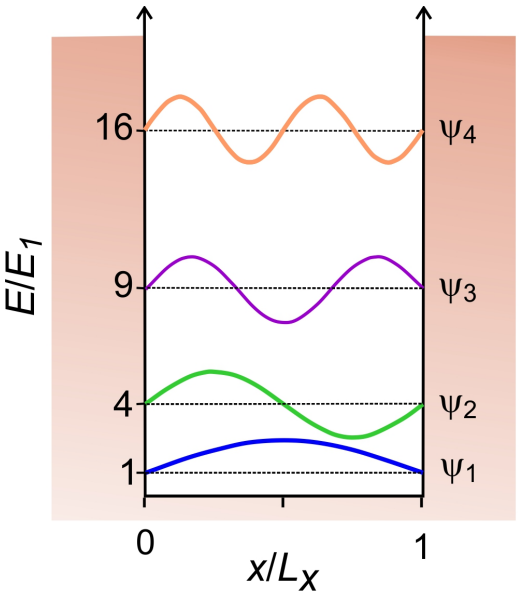

Figure 1. Particle-in-a-box potential wavefunctions that are plotted superimposed on their corresponding energy levels.

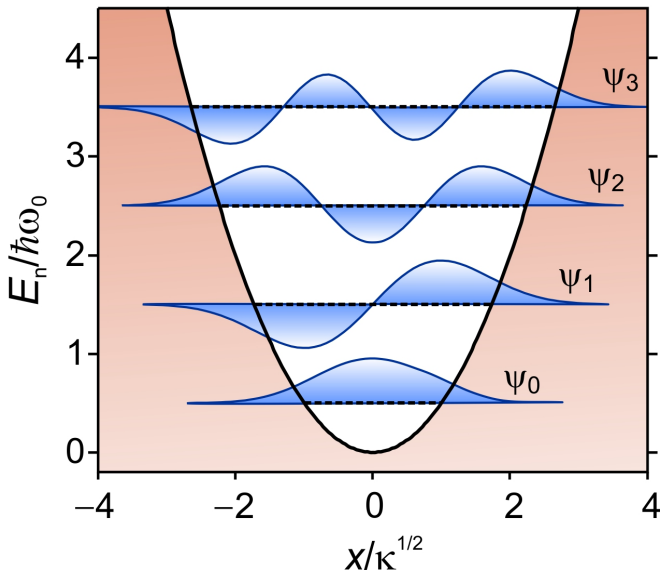

Figure 2. Harmonic oscillator potential showing wavefunctions that are superimposed on their corresponding energy levels.

Harmonic Oscillator

The harmonic oscillator Hamiltonian refers to a particle confined to a parabolic, or harmonic, potential. We will use it to represent vibrational motion in molecules, but it also becomes a general framework for understanding all bosons. For a classical particle bound in a one-dimensional potential, the potential near the minimum x_0 can be expanded as

$$V(x) = V(x_0) + \left(\frac{\partial V}{\partial x}\right)_{x=x_0}(x - x_0) + \frac{1}{2}\left(\frac{\partial V^2}{\partial x^2}\right)_{x=x_0}(x - x_0)^2 + \cdots \tag{55}$$

Setting x_0 to 0, the leading term with a dependence on x is the second-order (harmonic) term $V = -\kappa x^2/2$, where the force constant $\kappa = -(\partial^2 V / \partial x^2)_{x=0}$. The classical Hamiltonian for a particle of mass m confined to this potential is

$$H = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2 \tag{56}$$

Noting that the force constant and frequency of oscillation are related by $\kappa = m\omega_0^2$, we can substitute operators for p and x in eq. (56) to obtain the quantum Hamiltonian

$$\hat{H} = -\frac{1}{2}\frac{\hbar^2}{m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2\hat{x}^2 \tag{57}$$

We will also make use of reduced mass-weighted coordinates defined as

$$\begin{aligned} \underset{\sim}{p} &= \sqrt{\frac{2}{m\hbar\omega_0}}\hat{p} \\ \underset{\sim}{x} &= \sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} \end{aligned} \tag{58}$$

for which the Hamiltonian can be written as

$$\hat{H} = \hbar\omega_0\left(\underset{\sim}{p}^2 + \underset{\sim}{q}^2\right) \tag{59}$$

The eigenstates for the Harmonic oscillator are expressed in terms of Hermite polynomials

$$\psi_n(x) = \sqrt{\frac{\alpha}{2^n\sqrt{\pi}n!}}e^{-\alpha^2x^2/2}\mathcal{H}_n(\alpha x) \tag{60}$$

where $\alpha = \sqrt{m\omega_0/\hbar}$ and the Hermite polynomials are obtained from

$$\mathcal{H}_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}e^{-x^2} \tag{61}$$

The corresponding energy eigenvalues are equally spaced in units of the vibrational quantum $\hbar\omega_0$ above the zero-point energy $\hbar\omega_0/2$.

$$E_n = \hbar\omega_0\left(n+\frac{1}{2}\right) \qquad n = 0,1,2\ldots \tag{62}$$

Raising and Lowering Operators

From a practical point of view, it will be most useful for us to work problems involving harmonic oscillators in terms of raising and lower operators (also known as creation and annihilation operators, or ladder operators). We define these as

$$\hat{a} = \sqrt{\frac{2\hbar}{m\omega_0}}\left(\hat{x}+\frac{i}{m\omega_0}\hat{p}\right) \tag{63}$$

$$\hat{a}^\dagger = \sqrt{\frac{2\hbar}{m\omega_0}}\left(\hat{x}-\frac{i}{m\omega_0}\hat{p}\right) \tag{64}$$

Note a and $a^\dagger$ operators are Hermitian conjugates of one another. These operators get their name from their action on the harmonic oscillator wavefunctions, which is to lower or raise the state of the system:

$$\begin{aligned}\hat{a}\,|\,n\rangle &= \sqrt{n}\,|\,n-1\rangle \\ \hat{a}^\dagger|\,n\rangle &= \sqrt{n+1}\,|\,n+1\rangle\end{aligned} \tag{65}$$

Then we find that the position and momentum operators are

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega_0}}\left(\hat{a}^\dagger+\hat{a}\right) \tag{66}$$

$$\hat{p} = i\sqrt{\frac{m\hbar\omega_0}{2}}\left(\hat{a}^\dagger-\hat{a}\right) \tag{67}$$

When we substitute these ladder operators for the position and momentum operators—known as second quantization—the Hamiltonian becomes

$$\hat{H} = \hbar\omega_0\left(\hat{n}+\frac{1}{2}\right) \tag{68}$$

The number operator is defined as $\hat{n} = \hat{a}^\dagger\hat{a}$ and returns the state of the system: $\hat{n}\,|\,n\rangle = n\,|\,n\rangle$. The energy eigenvalues satisfying $\hat{H}\,|\,n\rangle = E_n\,|\,n\rangle$ are given by eq. (62). Since the quantum numbers cannot be negative, we assert a boundary condition $a|0\rangle = 0$, where 0 refers to the null vector. The harmonic oscillator Hamiltonian expressed in raising and lowering operators, together with its commutation relationship

$$\left[a, a^{\dagger}\right] = 1 \tag{69}$$

is used as a general representation of all bosons, which for our purposes includes vibrations and photons.

Properties of raising and lower operators

a and $a^{\dagger}$ operators are Hermitian conjugates of one another.

$$aa^{\dagger} + a^{\dagger}a = a^{\dagger}a + \tfrac{1}{2} \tag{70}$$

$$\left[a, a^{\dagger}\right] = 1 \tag{71}$$

$$\left[a, a\right] = 0 \quad \left[a^{\dagger}, a^{\dagger}\right] = 0 \tag{72}$$

$$\left[a, \left(a^{\dagger}\right)^{n}\right] = n\left(a^{\dagger}\right)^{n-1} \tag{73}$$

$$\left[a^{\dagger}, a^{n}\right] = -na^{n-1} \tag{74}$$

$$\left|n\right\rangle = \frac{1}{\sqrt{n!}}\left(a^{\dagger}\right)^{n}\left|0\right\rangle \tag{75}$$

Morse Oscillator

The Morse oscillator is a model for a particle in a one-dimensional anharmonic potential energy surface with a dissociative limit at infinite displacement.[2] It is commonly used for describing the spectroscopy of diatomic molecules and anharmonic vibrational dynamics, and most of its properties can be expressed through analytical expressions.[3] The Morse potential is

$$V(x) = D_e\left[1 - e^{-\alpha x}\right]^2 \tag{76}$$

where $x = (r - r_0)$. D_e sets the depth of the energy minimum at $r = r_0$ relative to the dissociation limit as $r \to \infty$, and α sets the curvature of the potential. If we expand V in powers of x as described in eq. (55)

$$V(x) \approx \tfrac{1}{2}\kappa x^2 + \tfrac{1}{6}g x^3 + \tfrac{1}{24}h x^4 + \cdots \tag{77}$$

we find that the harmonic, cubic, and quartic expansion coefficients are $\kappa = 2D_e\alpha^2$, $g = -6D_e\alpha^3$, and $h = 14D_e\alpha^4$.

The Morse oscillator Hamiltonian for a diatomic molecule of reduced mass m_R bound by this potential is

$$H = \frac{p^2}{2m_R} + V(x) \tag{78}$$

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2. P. M. Morse, Diatomic Molecules According to the Wave Mechanics. Ii. Vibrational Levels, Phys. Rev. **34**, 57-64 (1929).
3. H. l. n. Lefebvre-Brion and R. W. Field, *The Spectra and Dynamics of Diatomic Molecules*, 2nd ed. (Academic Press, Boston, 2004).

and has the eigenvalues

$$E_n = \hbar\omega_0\left[\left(n+\tfrac{1}{2}\right) - x_e\left(n+\tfrac{1}{2}\right)^2\right] \qquad n = 0,1,2,3... \tag{79}$$

Here $\omega_0 = \sqrt{2D_e\alpha^2/m_R}$ is the fundamental frequency and $x_e = \hbar\omega_0/4D_e$ is the anharmonic constant. Similar to the harmonic oscillator, the frequency $\omega_0 = \sqrt{\kappa/m_R}$. The anharmonic constant x_e is commonly seen in the spectroscopy expression for the anharmonic vibrational energy levels

$$G(v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3 + \cdots \tag{80}$$

From eq. (79), the ground state (or zero-point) energy is

$$E_0 = \tfrac{1}{2}\hbar\omega_0\left(1-\tfrac{1}{2}x_e\right) \tag{81}$$

So the dissociation energy for the Morse potential is given by $D_0 = D_e - E_0$. The transition energies are

$$E_n - E_m = \hbar\omega_0\left(n-m\right)\left[1-x_e\left(n+m+\tfrac{1}{2}\right)\right] \tag{82}$$

The proper harmonic expressions are obtained from the corresponding Morse oscillator expressions by setting $D_e \to \infty$ or $x_e \to 0$.

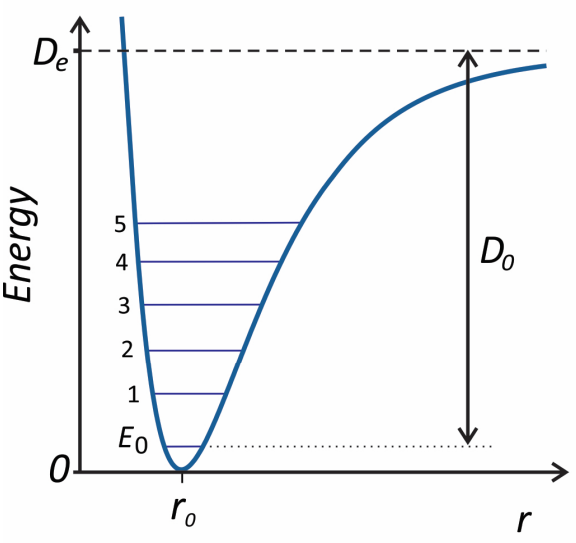

Figure 3. Shape of the Morse potential illustrating the first six energy eigenvalues.

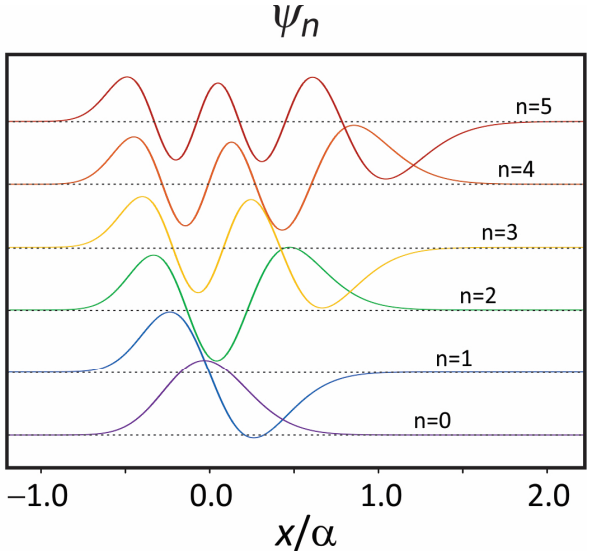

Figure 4. First six eigenfunctions of the Morse oscillator potential.

The wavefunctions for the Morse oscillator can also be expressed analytically in terms of associated Laguerre polynomials $\mathcal{L}_n^b(z)$:[4]

$$\psi_n = N_n e^{-z/2} z^{b/2} \mathcal{L}_n^b(z) \tag{83}$$

where $N_n = [\alpha \cdot b \cdot n!/\Gamma(k-n)]^{1/2}$, $z = k\exp[-\alpha q]$, $b = k - 2n - 1$, and $k = 4D_e/\hbar\omega_0$. These expressions and those for matrix elements in q, q^2, $e^{-\alpha q}$, and $qe^{-\alpha q}$ have been given by Vasan and Cross.[5]

d. Angular momentum

Angular Momentum Operators

To describe quantum mechanical rotation or orbital motion, one has to quantize angular momentum. The total orbital angular momentum operator is defined as

$$\hat{L} = \hat{r} \times \hat{p} = i\hbar(\hat{r} \times \nabla) \tag{84}$$

It has three components ($\hat{L}_x, \hat{L}_y, \hat{L}_z$) that generate rotation about the x, y, or z axis, and whose magnitude is given by $\hat{L}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$. The angular momentum operators follow the commutation relationships

$$\begin{aligned} [H, L_z] &= 0 \\ [H, L^2] &= 0 \end{aligned} \tag{85}$$

$$[L_x, L_y] = i\hbar L_z \tag{86}$$

(In eq. (86) the x,y,z indices can be cyclically permuted.) There is an eigenbasis common to H and L^2 and one of the L_i, which we take to be L_z. The eigenvalues for the orbital angular momentum operator L and z-projection of the angular momentum L_z are

$$L^2 \,|\, \ell m\rangle = \hbar^2\, \ell(\ell+1) \,|\, \ell m\rangle \qquad \ell = 0,1,2\ldots \tag{87}$$

$$L_z \,|\, \ell m\rangle = \hbar\, m \,|\, \ell m\rangle \qquad m = 0, \pm 1, \pm 2 \ldots \pm \ell \tag{88}$$

where the eigenstates $|\, \ell m\rangle$ are labeled by the orbital angular momentum quantum number ℓ, and the magnetic quantum number, m.

Similar to the strategy used for the harmonic oscillator, we can also define raising and lowering operators for the total angular momentum,

$$\hat{L}_\pm = \hat{L}_i \pm \mathrm{i}\,\hat{L}_y \tag{89}$$

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4. J. A. C. Gallas, Some Matrix Elements for Morse Oscillators, Phys. Rev. A **21**, 1829-1834 (1980).
5. V. S. Vasan and R. J. Cross, Matrix Elements for Morse Oscillators, J. Chem. Phys. **78**, 3869-3871 (1983).

which follow the commutation relations $[\hat{L}^2, \hat{L}_\pm] = 0$ and $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$, and satisfy the eigenvalue equation

$$\begin{aligned} \hat{L}_\pm \,|\, \ell m\rangle &= A_{\ell,m} \,|\, \ell m\rangle \\ A_{\ell,m} &= \hbar\left[\ell(\ell+1) - m(m\pm 1)\right]^{1/2} \end{aligned} \tag{90}$$

Spherically Symmetric Potential[6]

Let's examine the role of angular momentum for the case of a particle experiencing a spherically symmetric potential $V(r)$ such as the hydrogen atom, 3D isotropic harmonic oscillator, and free particles or molecules. For a particle with mass m_R, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{91}$$

Writing the kinetic energy operator in spherical coordinates,

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{1}{r^2}L^2\right) \tag{92}$$

where the square of the total angular momentum is

$$L^2 = -\frac{1}{\sin\theta}\left(\frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2} + \frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) \tag{93}$$

We note that this representation separates the radial dependence in the Hamiltonian from the angular part. We therefore expect that the overall wavefunction can be written as a product of a radial and an angular part in the form

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{94}$$

Substituting this into the TISE, we find that we solve for the orientational and radial wavefunctions separately. Considering solutions first to the angular part, we note that the potential is only a function of r, and only need to consider the angular momentum. This leads to the identities in eqs. (87) and (88), and reveals that the $|\,\ell m\rangle$ wavefunctions projected onto spherical coordinates are represented by the spherical harmonics

$$Y_\ell^m(\theta,\phi) = N_{\ell m}^Y P_\ell^{|m|}(\cos\theta)\,\mathrm{e}^{im\phi} \tag{95}$$

P_ℓ^m are the associated Legendre polynomials and the normalization factor is

$$N_{\ell m}^Y = (-1)^{(m+|m|)/2} i^\ell \left[\frac{2\ell+1}{4\pi}\frac{(\ell-|\,m\,|)!}{(\ell+|\,m\,|)!}\right]^{1/2}$$

6. N. Zettili, *Quantum Mechanics: Concepts and Applications*, 2nd ed. (Wiley, Chichester, New York, 2009).

The angular components of the wavefunction are common to all eigenstates of spherically symmetric potentials. In chemistry, it is common to use real angular wavefunctions instead of the complex form in eq. (95). These are constructed from the linear combinations $Y_{n,\ell} \pm Y_{n,-\ell}$.

Substituting eq. (92) and eq. (87) into eq. (91) leads to a new Hamiltonian that can be inserted into the Schrödinger equation. This can be solved as a purely radial problem for a given value of ℓ. It is convenient to define the radial distribution function $\chi(r) = r\,R(r)$, which allows the TISE to be rewritten as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + U(r,\ell)\right)\chi = E\chi \tag{96}$$

U plays the role of an effective potential

$$U(r,\ell) = V(r) + \frac{\hbar^2}{2mr^2}\ell\left(\ell+1\right) \tag{97}$$

Equation (96) is known as the radial wave equation. It looks like the TISE for a one-dimensional problem in r, where we could solve this equation for each value of ℓ. Note U has a barrier due to centrifugal kinetic energy that scales as r^{-2} for $\ell > 0$.

The wavefunctions defined in eq. (94) are normalized such that

$$\int |\psi|^2 d\Omega = 1 \tag{98}$$

where

$$\int d\Omega \equiv \int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \tag{99}$$

If we restrict the integration to be over all angles, we find that the probability of finding a particle between a distance r and $r+dr$ is $P(r) = 4\pi r^2 \,|\, R(r)\,|^2 = 4\pi \,|\, \chi(r)\,|^2$.

To this point the treatment of orbital angular momentum is identical for any spherically symmetric potential. Now we must consider the specific form of the potential; for instance in the case of the isotropic harmonic oscillator, $U(r) = \frac{1}{2}\,\kappa\, r^2$. In the case of a free particle, we substitute $V(r) = 0$ in eq. (97) and find that the radial solutions can be written in terms of spherical Bessel functions, j_ℓ. Then the solutions to the full wavefunction for the free particle can be written as

$$\Psi(r,\theta,\phi) = j_\ell(\mathrm{k}\,r)Y_\ell^m(\theta,\phi) \tag{100}$$

where the wavevector k is defined as in eq. (46).

Hydrogen Atom

For a hydrogen-like atom, a single electron of charge e interacts with a nucleus of charge Ze under the influence of a Coulomb potential

$$V_H(r) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} \tag{101}$$

We can simplify the expression by defining atomic units for distance and energy. The Bohr radius is defined as

$$a_0 = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2} = 5.2918\times10^{-11} m \tag{102}$$

and the Hartree is

$$\mathcal{E}_H = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_0} = 4.3598\times10^{-18} J \;=\; 27.2\ eV \tag{103}$$

Written in terms of atomic units, we can see from eq. (103) that eq. (101) becomes $(V/\mathcal{E}_H) = -Z/(r/a_0)$. Thus the conversion effectively sets the SI variables $m_e = e = (4\pi\varepsilon_0)^{-1} = \hbar = 1$. Then the radial wave equation is

$$\frac{\partial^2\chi}{\partial r^2} + \left(\frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right)\chi = 2E\chi \tag{104}$$

The effective potential within the parentheses in eq. (104) is shown in Figure 5 for varying ℓ. Solutions to the radial wavefunction for the hydrogen atom take the form

$$R_{n\ell}(r) = N^R_{n\ell}\rho^\ell \mathcal{L}^{2\ell+1}_{n+\ell}(\rho)e^{-\rho/2} \tag{105}$$

where the reduced radius $\rho = 2r/na_0$ and $\mathcal{L}^\alpha_k(z)$ are the associated Laguerre polynomials. The primary quantum number takes on integer values n = 1,2,3…, and ℓ is constrained such that ℓ = 0,1,2…n–1. The radial normalization factor in eq. (105) is

$$N^R_{n\ell} = -\frac{2}{n^3 a_0^{3/2}}\left[\frac{(\mathrm{n}-\ell-1)!}{[(n+1)!]^3}\right]^{1/2} \tag{106}$$

The energy eigenvalues are

$$E_n = -\frac{Z^2}{2n^2}\mathcal{E}_H \tag{107}$$

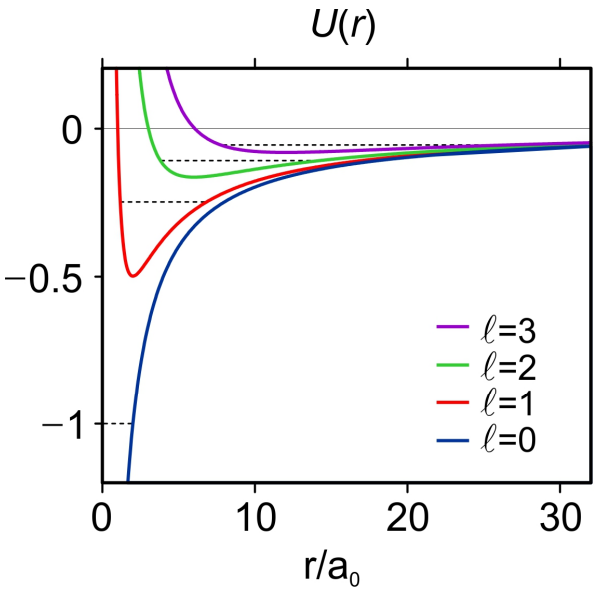

Figure 5. The radial effective potential, $U_{eff}(\rho)$.

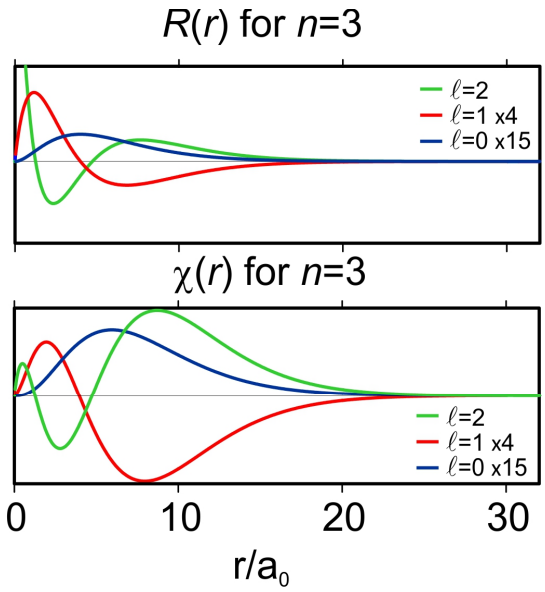

Figure 6. Radial probability density R and radial distribution function $\chi = rR$.

Electron Spin

In describing electronic wavefunctions, the electron spin also results in a contribution to the total angular momentum, and results in a spin contribution to the wavefunction. The electron spin angular momentum S and its z-projection are quantized as

$$S^2 \,|\, s\, m_s\rangle = \hbar^2\, s(s+1)\,|\, s\, m_s\rangle \qquad s = 0,\ {}^1/_2,\ 1,\ {}^3/_2,\ 2\ldots \tag{108}$$

$$S_z \,|\, s\, m_s\rangle = \hbar\ m_s \,|\, s\, m_s\rangle \qquad m_s = -s,\ -s{+}1,\ \ldots,\ s \tag{109}$$

where the electron spin eigenstates $|\, s\, m_s\rangle$ are labeled by the electron spin angular momentum quantum number s and the spin magnetic quantum number m_s. The number of values of S_z is $2s{+}1$ and is referred to as the spin multiplicity. As fermions, electrons have half-integer spin, and each unpaired electron contributes ½ to the electron spin quantum number s. A single unpaired electron has s = ½, for which $m_s = \pm$½ corresponding to *spin-up* and *spin-down* configurations. For multi-electron systems, the spin is calculated as the vector sum of spins, essentially ½ times the number of unpaired electrons.

The resulting total angular momentum for an electron is $J = L + S$. J has associated with it the total angular momentum quantum number j, which takes on values of $j = |\ell{-}s|, |\ell{-}s|{+}1, \ldots, \ell{+}s$. The additive nature of the orbital and spin contributions to the angular momentum leads to a total electronic wavefunction that is a product of spatial and spin wavefunctions.

$$\Psi_{tot} = \Psi(r,\theta,\phi)\,|\, s\, m_s\rangle \tag{110}$$

Thus the state of an electron can be specified by four quantum numbers $\Psi_{tot} = |\, n\, \ell\, m_\ell\, m_s\rangle$.

Rigid Rotor

In the case of a freely spinning anisotropic molecule, the total angular momentum J is obtained from the sum of the orbital angular momentum L and spin angular momentum S for the molecular constituents: $J = L + S$, where $L = \sum_i L_i$ and $S = \sum_i S_i$. The case of the rigid rotor refers to the minimal model for the rotational quantum states of a freely spinning object that has cylindrical symmetry and no magnetic spin. Then, the Hamiltonian is given by the rotational kinetic energy

$$H_{rot} = \frac{\hat{J}^2}{2I} \tag{111}$$

I is the moment of inertia about the principle axis of rotation. The eigenfunctions for this Hamiltonian are spherical harmonics $Y_{J,M}(\theta,\phi)$

$$\begin{aligned} \hat{J}^2 \left| Y_{J,M} \right\rangle &= \hbar^2 J\left(J+1\right) \left| Y_{J,M} \right\rangle \quad J = 0,1,2... \\ \hat{J}_z \left| Y_{J,M} \right\rangle &= M\hbar \left| Y_{J,M} \right\rangle \qquad\quad M = -J, -J+1, ..., J \end{aligned} \tag{112}$$

J is the rotational quantum number. M is its projection onto the z axis. The energy eigenvalues for H_{rot} are

$$E_{J,M} = \overline{B} J(J+1) \tag{113}$$

where the rotational constant is

$$\overline{B} = \frac{\hbar^2}{2I} \tag{114}$$

More commonly, $\overline{B}$ is given in units of cm^{-1} using $\overline{B} = h/8\pi^2 Ic$.

4. Exponential Operators

Throughout our work, we will make use of exponential operators of the form

$$\hat{T} = e^{-i\hat{A}} \tag{115}$$

We will see that these exponential operators act on a wavefunction to move it in time and space, and are therefore also referred to as propagators. Of particular interest to us is the time-evolution operator, $\hat{U} = e^{-i\hat{H}t/\hbar}$, which propagates the wavefunction in time. Note the operator $\hat{T}$ is a *function of an operator,* $f(\hat{A})$. A function of an operator is defined through its expansion in a Taylor series, for instance

$$\hat{T} = e^{-i\hat{A}} \;=\; \sum_{n=0}^{\infty} \frac{(-i\hat{A})^n}{n!} = 1 - i\hat{A} - \frac{\hat{A}\hat{A}}{2} - \cdots \tag{116}$$

Since we use them so frequently, let's review the properties of exponential operators that can be established with eq. (116). If the operator $\hat{A}$ is Hermitian, then $\hat{T} = e^{-i\hat{A}}$ is unitary, i.e., $\hat{T}^{\dagger} = \hat{T}^{-1}$. Thus the Hermitian conjugate of $\hat{T}$ reverses the action of $\hat{T}$. For the time-propagator $\hat{U}$, $\hat{U}^{\dagger}$ is often referred to as the time-reversal operator.

The eigenstates of the operator $\hat{A}$ also are also eigenstates of $f(\hat{A})$, and eigenvalues are functions of the eigenvalues of $\hat{A}$. Namely, if you know the eigenvalues and eigenvectors of $\hat{A}$, i.e., $\hat{A}\varphi_n = a_n\varphi_n$, you can show by expanding the function

$$f\left(\hat{A}\right)\varphi_n = f\left(a_n\right)\varphi_n \tag{117}$$

Our most common application of this property will be to exponential operators involving the Hamiltonian. Given the eigenstates φ_n, then $\hat{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$ implies

$$e^{-i\hat{H}t/\hbar}\left|\varphi_n\right\rangle = e^{-iE_nt/\hbar}\left|\varphi_n\right\rangle \tag{118}$$

Just as $\hat{U} = e^{-i\hat{H}t/\hbar}$ is the time-evolution operator that displaces the wavefunction in time, $\hat{D}_x = e^{-i\hat{p}_x x/\hbar}$ is the spatial displacement operator that moves ψ along the x coordinate. If we define $\hat{D}_x(\lambda) = e^{-i\hat{p}_x\lambda/\hbar}$, then the action of is to displace the wavefunction by an amount λ.

$$\left|\psi\left(x-\lambda\right)\right\rangle = \hat{D}_x(\lambda)\left|\psi\left(x\right)\right\rangle \tag{119}$$

Also, applying $\hat{D}_x(\lambda)$ to a position operator shifts the operator by λ

$$\hat{D}_x^{\dagger}\hat{x}\hat{D}_x = x + \lambda \tag{120}$$

Thus $e^{-i\hat{p}_x\lambda/\hbar}|x\rangle$ is an eigenvector of $\hat{x}$ with eigenvalue $x + \lambda$ instead of x. The operator $\hat{D}_x = e^{-i\hat{p}_x\lambda/\hbar}$ is a displacement operator for x position coordinates. Similarly, $\hat{D}_y = e^{-i\hat{p}_y\lambda/\hbar}$ generates displacements in y and $\hat{D}_z$ in z. Similar to the time-propagator $\hat{U}$, the displacement operator $\hat{D}$ must be unitary, since the action of $\hat{D}^{\dagger}\hat{D}$ must leave the system unchanged. That is if $\hat{D}_x$ shifts the system to x from x_0, then $\hat{D}_x^{\dagger}$ shifts the system from x back to x_0.

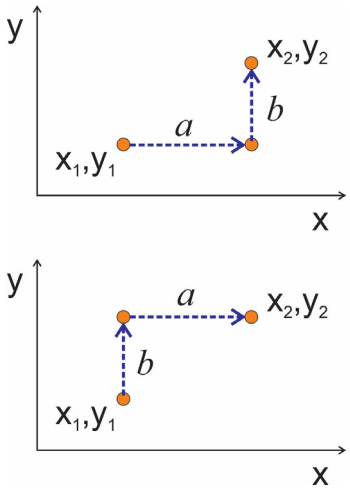

Figure 7. (Top) Displacement first along x by an amount a, then along y by b. (Bottom) Displacement in the reverse order yields the same state.

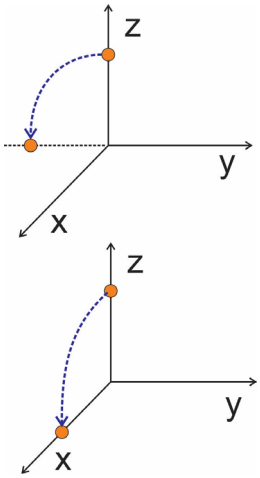

Figure 8. (Top) Rotation first about x by π/2, then about y by π/2, leaves the particle on the –y axis. (Bottom) Changing order by first rotating about y, then about x, leads to particle along +x axis.

We know intuitively that linear displacements commute. For example, if we wish to shift a particle in two dimensions, x and y, the order of displacement does not matter. We end up at the same position, whether we move along x first or along y, as illustrated in Figure 7. In terms of displacement operators, we can write

$$\begin{aligned} \left|x_2, y_2\right\rangle &= e^{-ibp_y/\hbar} e^{-iap_x/\hbar} \left|x_1, y_1\right\rangle \\ &= e^{-iap_x/\hbar} e^{-ibp_y/\hbar} \left|x_1, y_1\right\rangle \end{aligned} \tag{121}$$

These displacement operators commute, as expected from $[p_x, p_y] = 0$.

Similar to the displacement operator, we can define rotation operators that depend on the angular momentum operators, L_x, L_y, and L_z. For instance, $\hat{R}_x(\phi) = e^{-i\phi L_x/\hbar}$ gives a rotation by angle ϕ about the x axis. Unlike linear displacement, rotations about different axes do not commute. For example, consider a state representing a particle displaced along the z axis, $|z_0\rangle$. Now the action of two rotations $\hat{R}_x$ and $\hat{R}_y$ by an angle of $\phi = \pi/2$ on this particle differs depending on the order of operation, as illustrated in Figure 8. If we rotate first about x, the operation

$$e^{-i\frac{\pi}{2}L_y/\hbar} e^{-i\frac{\pi}{2}L_x/\hbar} \left|z_0\right\rangle \rightarrow \left|-y\right\rangle \tag{122}$$

leads to the particle on the $-y$ axis, whereas the reverse order

$$e^{-i\frac{\pi}{2}L_x/\hbar} e^{-i\frac{\pi}{2}L_y/\hbar} \left|z_0\right\rangle \rightarrow \left|+x\right\rangle \tag{123}$$

leads to the particle on the $+x$ axis. The final state of these two rotations taken in opposite order differ by a rotation about the z axis. Since rotations about different axes do not commute, we expect the angular momentum operators not to commute. Indeed, we know that $[L_x,L_y] = i\hbar L_z$, where the commutator of rotations about the x and y axes is related by a z-axis rotation. As with rotation operators, we will need to be careful with time-propagators to determine whether the order of time-propagation matters. This, in turn, will depend on whether the Hamiltonians at two points in time commute.

Properties of exponential operators

1. If $\hat{A}$ and $\hat{B}$ do not commute, but $[\hat{A},\hat{B}]$ commutes with $\hat{A}$ and $\hat{B}$, then

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}\left[\hat{A},\hat{B}\right]} \tag{124}$$

$$e^{\hat{A}}\, e^{\hat{B}} = e^{\hat{B}}\, e^{\hat{A}}\, e^{-\left[\hat{B},\hat{A}\right]} \tag{125}$$

2. More generally, if $\hat{A}$ and $\hat{B}$ do not commute,

$$e^{\hat{A}} e^{\hat{B}} = \exp\left[\hat{A}+\hat{B}+\frac{1}{2}\left[\hat{A},\hat{B}\right]+\frac{1}{12}\left(\left[\hat{A},\left[\hat{A},\hat{B}\right]\right]+\left[\hat{A},\left[\hat{B},\hat{B}\right]\right]\right)+\cdots\right] \tag{126}$$

3. The Baker–Hausdorff relationship:

$$\begin{aligned} \mathrm{e}^{i\hat{G}\lambda}\,\hat{A}\,\mathrm{e}^{-i\hat{G}\lambda} = \hat{A} + i\lambda\left[\hat{G},\hat{A}\right] + \left(\frac{i^2\lambda^2}{2!}\right)\left[\hat{G},\left[\hat{G},\hat{A}\right]\right]+\ldots \\ + \left(\frac{i^n\lambda^n}{n!}\right)\left[\hat{G},\left[\hat{G},\left[\hat{G}\ldots\left[\hat{G},\hat{A}\right]\right]\right]\ldots\right]+\ldots \end{aligned} \tag{127}$$

where λ is a number.

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5. Numerically Solving the Schrödinger Equation

Often the bound potentials that we encounter are complex, and the time-independent Schrödinger equation will need to be evaluated numerically. There are two common numerical methods for solving for the eigenvalues and eigenfunctions of a potential. Both methods require truncating and discretizing a region of space that is normally spanned by an infinite dimensional Hilbert space. The Numerov method is a finite difference method that calculates the shape of the wavefunction by integrating step-by-step across along a grid. The DVR method makes use of a transformation between a finite discrete basis and the finite grid that spans the region of interest.

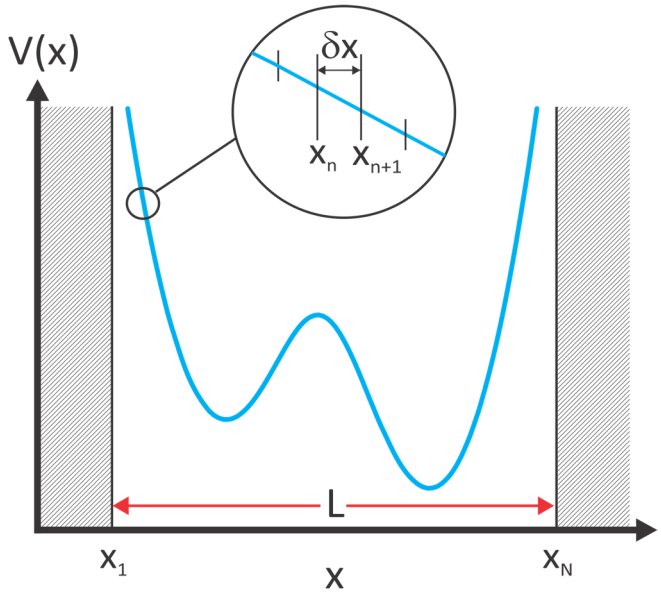

Figure 9. Selection and discretization of a space bounding the region for which the TISE will be solved numerically. A space of length L is discretized into N points separated by a spacing δx over which the potential varies slowly.

a. The Numerov Method[7]

A one-dimensional Schrodinger equation for a particle in a potential can be numerically solved on a grid that discretizes the position variable using a finite difference method. The TISE is

$$\left[T+V(x)\right]\psi(x)=E\psi(x) \tag{128}$$

with $T=-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$, which we can write as

$$\psi''(x)=-k^2(x)\psi(x) \tag{129}$$

where $k^2(x)=\dfrac{2m}{\hbar^2}\left[E-V(x)\right]$.

If we discretize the variable x, choosing a grid spacing δx over which V varies slowly, we can use a three point finite difference to approximate the second derivative:

$$f_i''\approx\frac{1}{\delta x^2}\left(f(x_{i+1})-2f(x_i)+f(x_{i-1})\right) \tag{130}$$

The discretized Schrodinger equation can then be written in the form

$$\psi(x_{i+1})-2\psi(x_i)+\psi(x_{i-1})=-k^2(x_i)\psi(x_i) \tag{131}$$

7. I. N. Levine, *Quantum Chemistry*, 5th ed. (Prentice Hall, Englewood Cliffs, NJ, 2000).

Using the equation for $\psi(x_{i+1})$, one can iteratively solve for the eigenfunction. In practice, you discretize over a range of space such that the highest and lowest values lie in a region where the potential is very high or forbidden. Splitting the space into *N* points, chose the first two values $\psi(x_1)=0$ and $\psi(x_2)$ to be a small positive or negative number, guess *E*, and propagate iteratively to $\psi(x_N)$. A comparison of the wavefunctions obtained by propagating from x_1 to x_N with that obtained propagating from x_N to x_1 tells you how good your guess of *E* was.

The Numerov Method improves on eq. (131) by taking account for the fourth derivative of the wavefunction $\Psi^{(4)}$, leading to errors on the order $O(\delta x^6)$. Equation (130) becomes

$$f_i'' \approx \frac{1}{\delta x^2}\left(f(x_{i+1})-2f(x_i)+f(x_{i-1})\right)-\frac{\delta x^2}{12}f_i^{(4)} \tag{132}$$

By differentiating eq. (129) we know $\psi^{(4)}(x)=-\left(k^2(x)\psi(x)\right)''$, and the discretized Schrödinger equation becomes

$$\begin{aligned}\psi''(x_i)=&\frac{1}{\delta x^2}\left(\psi(x_{i+1})-2\psi(x_i)+\psi(x_{i-1})\right)+\\&\frac{1}{12}\left(k^2(x_{i+1})\psi(x_{i+1})-2k^2(x_{i+1})\psi(x_i)+k^2(x_{i+1})\psi(x_{i-1})\right)\end{aligned} \tag{133}$$

This equation leads to the iterative solution for the wavefunction

$$\psi(x_{i+1})=\left(1-\frac{\delta x^2}{12}k^2(x_{i+1})\right)^{-1}\left(\psi(x_i)\left(2+\frac{10\delta x^2}{12}k^2(x_i)\right)-\psi(x_{i-1})\left(1-\frac{\delta x^2}{12}k^2(x_{i-1})\right)\right) \tag{134}$$

b. Discrete variable representation[8]

Numerical solutions to the wavefunctions of a bound potential in the position representation require truncating and discretizing a region of space that is normally spanned by an infinite dimensional Hilbert space. The DVR approach uses a real space basis set whose eigenstates $\varphi_i(x)$ we know and that span the space of interest—for instance harmonic oscillator wavefunctions—to express the eigenstates of a Hamiltonian in a grid basis (θ_j) that is meant to approximate the real space continuous basis $\delta(x)$. The two basis sets, which we term the eigenbasis (φ) and grid basis (θ), will be connected through a unitary transformation

$$\Phi^{\dagger}\varphi(x) = \theta(x) \qquad \Phi\theta(x) = \varphi(x) \tag{135}$$

For *N* discrete points in the grid basis, there will be *N* eigenvectors in the eigenbasis, allowing the properties of projection and completeness will hold in both bases. Wavefunctions can be

8. J. C. Light and T. Carrington, "Discrete-Variable Representations and Their Utilization" in *Advances in Chemical Physics* (John Wiley & Sons, Inc., 2007), pp. 263-310; D. J. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective*. (University Science Books, Sausilito, CA, 2007).

obtained by constructing the Hamiltonian in the eigenbasis, $H = T(\hat{p}) + V(\hat{x})$, transforming to the DVR basis, $H^{DVR} = \Phi H \Phi^{\dagger}$, and diagonalizing.

Here we will discuss a version of DVR in which the grid basis is set up to mirror the continuous $|x\rangle$ eigenbasis. We begin by choosing the range of x that contain the bound states of interest and discretizing these into N points (x_i) equally spaced by δx. We assume that the DVR basis functions $\theta_j(x_i)$ resemble the infinite dimensional position basis

$$\theta_j(x_i) = \sqrt{\Delta x}\,\delta_{ij} \tag{136}$$

Our truncation is enabled using a projection operator in the reduced space

$$P_N = \sum_{i=1}^{N} |\theta_i\rangle\langle\theta_i| \approx 1 \tag{137}$$

which is valid for appropriately high N. The complete Hamiltonian can be expressed in the DVR basis $H^{DVR} = T^{DVR} + V^{DVR}$. For the potential energy, since $\{\theta_i\}$ is localized with $\langle\theta_i|\theta_j\rangle = \delta_{ij}$, we make the DVR approximation, which casts V^{DVR} into a diagonal form that is equal to the potential energy evaluated at the grid point:

$$V_{ij}^{DVR} = \langle\theta_i|V(\hat{x})|\theta_j\rangle \approx V(x_i)\delta_{ij} \tag{138}$$

This comes from approximating the transformation as $\Phi V(\hat{x})\Phi^{\dagger} \approx V\left(\Phi\hat{x}\Phi^{\dagger}\right)$.

For the kinetic energy matrix elements $\langle\theta_i|T(\hat{p})|\theta_j\rangle$, we need to evaluate second derivatives between different grid points. Fortunately, Colbert and Miller have simplified this process by finding an analytical form for the T^{DVR} matrix for a uniformly gridded box with a grid spacing of Δx.[9]

$$T_{ij}^{\mathrm{DVR}} = \frac{\hbar^2(-1)^{i-j}}{2m\Delta x^2}\begin{cases} \pi^2/3 & i = j \\ 2/(i-j)^2 & i \neq j \end{cases} \tag{139}$$

This comes from a Fourier expansion in a uniformly gridded box. Naturally this looks oscillatory in x at period of δx. Expression becomes exact in the limit of $N\to\infty$ or $\Delta x\to 0$.

The numerical routine becomes simple and efficient. We construct a Hamiltonian filling with matrix elements whose potential and kinetic energy contributions are given by eqs. (138) and (139). Then we diagonalize H^{DVR}, from which we obtain N eigenvalues and the N corresponding eigenfunctions.

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9. D. T. Colbert and W. H. Miller, A Novel Discrete Variable Representation for Quantum Mechanical Reactive Scattering Via the S-Matrix Kohn Method, J. Chem. Phys. **96**, 1982-1991 (1992).