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Review of Time-Independent Quantum Mechanics

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While some spectroscopic observations can be understood using purely classical concepts, most molecular spectroscopy experiments probe explicitly quantum mechanical properties. It is assumed that students using this text have already taken a course in basic quantum mechanics, but it is also recognized that there are likely to be some holes in the preparation of most students and that all can benefit from a brief review. As this is not a quantum mechanics textbook, many results in this chapter are given without proof and with minimal explanation. Students seeking a deeper treatment are encouraged to consult the references given at the end of this chapter (Das and Melissinos 1986; Fayer 2001; Levine 2009; McQuarrie 2008; Sakurai 1993).

This chapter, like most introductory quantum chemistry courses, focuses on solutions of the time-independent Schrödinger equation. Because of the importance of time-dependent quantum mechanics in spectroscopy, that topic is discussed in Chapter 5.

1.1 States, Operators, and Representations

A quantum mechanical system consisting of N particles (usually electrons and/or nuclei) is represented most generally by a state function or state vector Ψ. The state vector contains, in principle, all information about the quantum mechanical system.

In order to be useful, state vectors must be expressed in some basis. In the most commonly used position basis, the state vector is called the wavefunction, written as $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ where $\mathbf{r}_i$ is the position in space of particle i. The position $\mathbf{r}$ may be expressed in Cartesian coordinates (x, y, z), spherical polar coordinates (r, θ, φ), or some other coordinate system. Wavefunctions may alternatively be expressed in

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the momentum basis, $\Psi(\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N)$ where $\mathbf{p}_i$ is the momentum of particle *i*. Some state vectors cannot be expressed as a function of position, such as those representing the spin of an electron. But there's always a state function that describes the system, even if it's not a "function" of ordinary spatial coordinates.

The wavefunction itself, also known as the probability amplitude, is not directly measurable and has no simple physical interpretation. However, the quantity $|\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2\, d\mathbf{r}_1 d\mathbf{r}_{2...} d\mathbf{r}_N$ gives the probability that particles 1, 2, etc. are each in some infinitesimal volume element around $\mathbf{r}_1$, $\mathbf{r}_2$, etc. Integration over a finite volume then gives the probability that the system is found within that volume. A "legal" wavefunction must be single valued, continuous, differentiable, and normalizable.

The scalar product or inner product of two wavefunctions Ψ and Φ is given by $\int \Psi * \Phi$, where the asterisk means complex conjugation and the integration is performed over all of the coordinates of all the particles. The inner product is not a function but simply a number, generally a complex number if the wavefunctions are complex. In Dirac notation, this inner product is denoted $\langle \Psi \mid \Phi \rangle$. The absolute square of the inner product, $|\langle \Psi \mid \Phi \rangle|^2$, gives the probability (a real number) that a system in state Ψ is also in state Φ. If $\langle \Psi \mid \Phi \rangle = 0$, then Ψ and Φ are said to be orthogonal. Reversing the order in Dirac notation corresponds to taking the complex conjugate of the inner product: $\langle \Phi \mid \Psi \rangle = \int \Phi^* \Psi$ while $\langle \Psi \mid \Phi \rangle = \int \Psi^* \Phi = (\int \Phi^* \Psi)^*$.

The inner product of a wavefunction with itself, $\langle \Psi \mid \Psi \rangle = \int \Psi^* \Psi = \int |\Psi|^2$, is always real and positive. Usually single-particle wavefunctions are chosen to be normalized to $\int \Psi * \Psi = 1$. This means that the probability of finding the system somewhere in space is unity.

The quantities we are used to dealing with in classical mechanics are represented in quantum mechanics by operators. Operators act on wavefunctions or state vectors to give other wavefunctions or state vectors. Operator $\hat{A}$ acting on wavefunction Ψ to give wavefunction Φ is written as $\hat{A}\Psi = \Phi$. The action of an operator can be as simple as multiplication, although many (not all) operators involve differentiation.

Quantum mechanical operators are linear, which means that if λ_1 and λ_2 are numbers (not states or operators), then $\hat{A}(\lambda_1 \Phi_1 + \lambda_2 \Phi_2) = \lambda_1 \hat{A} \Phi_1 + \lambda_2 \hat{A} \Phi_2$, and $(\hat{A}\hat{B})\Phi = \hat{A}(\hat{B}\Phi) = \hat{A}\hat{B}\Phi$. However, it is *not* true in general that $\hat{A}\hat{B}\Phi = \hat{B}\hat{A}\Phi$; the order in which the operators are applied often matters. The quantity $\hat{A}\hat{B} - \hat{B}\hat{A}$ is called the commutator of $\hat{A}$ and $\hat{B}$ and is symbolized $[\hat{A}, \hat{B}]$, and it is zero for some pairs of operators but not for all. Most of what is "interesting" (i.e. nonclassical) about quantum mechanical systems arises from the noncommutation of certain operators.

A representation is a set of basis vectors, which may be discrete (finite or infinite) or continuous. An example of a finite discrete basis is the eigenstates of the z-component of spin for a spin-1/2 particle (two states, usually called α and β). An example of a discrete infinite basis is the set of eigenstates of a one-dimensional harmonic oscillator $\{\psi_v\}$ where v must be an integer but can go from 0 to ∞. An example of a continuous basis is the one-dimensional position basis $\{x\}$ where x can take on any real value. To be a representation, a set of basis vectors must obey certain extra conditions. One is orthonormality: $\langle u_i|u_j\rangle = \delta_{ij}$ (the Kronecker delta) for a discrete basis, or $\langle w_\alpha|w_{\alpha'}\rangle = \delta(\alpha-\alpha')$ (the Dirac delta function) for a continuous basis. The Kronecker delta is defined by $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$. The Dirac delta function $\delta(\alpha-\alpha')$ is a hypothetical function of the variable α that is infinitely sharply peaked around $\alpha = \alpha'$ and has an integrated area of unity. Three useful properties of the Dirac delta function are:

$$\int_{-\infty}^{\infty} \mathrm{d}k\, e^{ikx} = 2\pi\delta(x) \tag{1.1}$$

$$\int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta(x-a) = f(a) \tag{1.2}$$

$$\delta(ax) = \frac{\delta(x)}{|a|} \tag{1.3}$$

where a is a constant.

A set of vectors in a particular state space is a basis if every state in that space has a unique expansion, such that $\Psi = \sum_i c_i u_i$ (discrete basis) or $\Psi = \int \mathrm{d}\alpha\, c(\alpha) w_\alpha$ (continuous basis), where the c's are (generally complex) numbers. "In a particular state space" means, e.g. that if we want to describe only the spin state of a system, the basis does not have to include the spatial degrees of freedom. Or, the states of position in one dimension $\{x\}$ can be a basis for a particle in a one-dimensional box, but not a two-dimensional box, which requires a two-dimensional position basis $\{(x, y)\}$. An important property of a representation is closure:

$$\sum_i \langle\Phi \mid u_i\rangle\langle u_i \mid \Psi\rangle = \langle\Phi \mid \Psi\rangle \text{ or } \int \mathrm{d}\alpha \langle\Phi \mid w_\alpha\rangle\langle w_\alpha \mid \Psi\rangle = \langle\Phi \mid \Psi\rangle \tag{1.4}$$

Representations of states and operators in discrete bases are often conveniently written in matrix form (see Appendix C). A state vector is represented in a basis by a column vector of numbers: $\begin{pmatrix} \langle u_1|\Psi\rangle \\ \langle u_2|\Psi\rangle \\ \vdots \end{pmatrix}$ and its complex conjugate by a row vector: $(\langle\Phi \mid u_1\rangle\langle\Phi \mid u_2\rangle\cdots)$. The inner product is then obtained by the usual rules for matrix multiplication as

$$\langle \Phi \mid \Psi \rangle = (\langle \Phi \mid u_1 \rangle \langle \Phi \mid u_2 \rangle \cdots) \begin{pmatrix} \langle u_1 | \Psi \rangle \\ \langle u_2 | \Psi \rangle \\ \vdots \end{pmatrix} = \text{a number.}$$

An operator is represented by a square matrix:

$$\begin{pmatrix} \langle u_1 | \hat{A} | u_1 \rangle & \langle u_1 | \hat{A} | u_2 \rangle & \cdots \\ \langle u_2 | \hat{A} | u_1 \rangle & \langle u_2 | \hat{A} | u_2 \rangle & \\ \vdots & & \ddots \end{pmatrix}$$

For Hermitian operators, $A_{ji}{}^{*} = A_{ij}$. It follows that the diagonal elements (A_{ii}) must be real for Hermitian operators.

The operator expression $\hat{A}\Psi = \Phi$ is represented in the $\{u_i\}$ basis as the matrix equation

$$\begin{pmatrix} \langle u_1 | \hat{A} | u_1 \rangle & \langle u_1 | \hat{A} | u_2 \rangle & \cdots \\ \langle u_2 | \hat{A} | u_1 \rangle & \langle u_2 | \hat{A} | u_2 \rangle & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} \langle u_1 | \Psi \rangle \\ \langle u_2 | \Psi \rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} \langle u_1 | \Phi \rangle \\ \langle u_2 | \Phi \rangle \\ \vdots \end{pmatrix}.$$

1.2 Eigenvalue Problems and the Schrödinger Equation

The state Ψ is an eigenvector or eigenstate of operator $\hat{A}$ with eigenvalue λ if $\hat{A}\Psi = \lambda\Psi$ where λ is a number. That is, operating on Ψ with $\hat{A}$ just multiplies Ψ by a constant. The eigenvalue λ is nondegenerate if there is only one eigenstate having that eigenvalue. If more than one distinct state (wavefunctions that differ from each other by more than just an overall multiplicative constant) has the same eigenvalue, then that eigenvalue is degenerate.

To every observable (measurable quantity) in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics. Since observables correspond to measurable things, this means all observables have only real eigenvalues. It can be shown from this that eigenfunctions of the same observable having different eigenvalues are necessarily orthogonal (orthonormal if we require that they be normalized).

In Dirac notation using basis $\{u_i\}$, the eigenvalue equation is $\langle u_i \mid \hat{A} \mid \Psi \rangle = \lambda \langle u_i \mid \Psi \rangle$. Inserting closure gives $\sum_j \langle u_i \mid \hat{A} \mid u_j \rangle \langle u_j \mid \Psi \rangle = \lambda \langle u \mid \Psi \rangle$, or in a shorter form $\sum_j A_{ij} c_j = \lambda c_i$, or in an even more compact form $\sum_j \{A_{ij} - \lambda \delta_{ij}\} c_j = 0$. This is a system of N equations (one for each i) in N unknowns, which has a nontrivial

solution if and only if the determinant of the coefficients is zero: $|A - \lambda 1| = 0$ where $\mathbf{1}$ is an $N \times N$ unit matrix (1s along the diagonal). So to find the eigenvalues, we need to set up the determinantal equation $\begin{vmatrix} A_{11}-\lambda & A_{12} & \cdots \\ A_{21} & A_{22}-\lambda & \\ \vdots & & \ddots \end{vmatrix} = 0$ and solve for the N roots λ, then find the eigenvector corresponding to each eigenvalue $\lambda^{(i)}$ by solving the matrix equation $\begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} c_1^{(i)} \\ c_2^{(i)} \\ \vdots \end{pmatrix} = \lambda^{(i)} \begin{pmatrix} c_1^{(i)} \\ c_2^{(i)} \\ \vdots \end{pmatrix}$ (see Appendix C).

Any measurement of the observable associated with operator $\hat{A}$ can give only those values that are eigenvalues of $\hat{A}$. If the system is in an eigenstate of the operator, then every measurement will yield the same result, the eigenvalue. If the system is not in an eigenstate, different measurements will yield different values, but each will be one of the eigenvalues.

A particularly important observable is the one associated with the total energy of the system. This operator is called the Hamiltonian, symbolized $\hat{H}$, the sum of the kinetic and potential energy operators. The eigenstates of the Hamiltonian are therefore eigenstates of the energy, and the associated eigenvalues represent the only values that can result from any measurement of the energy of that system.

To find the energy eigenvalues and eigenstates, one must first write down the appropriate Hamiltonian for the problem at hand, which really amounts to identifying the potential function in which the particles move, since the kinetic energy is straightforward. One then solves the eigenvalue problem $\hat{H}\psi_n = E_n\psi_n$, which is the time-independent Schrödinger equation. For most Hamiltonians, there are many different pairs of wavefunctions ψ_n and energies E_n that can satisfy the equation.

Two observables of particular importance in quantum mechanics are the position $\hat{Q}$ and the linear momentum $\hat{P}$ along the same coordinate (e.g. x and p_x). The commutator is $\left[\hat{Q}, \hat{P}\right] = i\hbar$ and the action of $\hat{P}$ in the q representation is $-i\hbar(\partial/\partial q)$. That is, $\hat{P}\Psi(q) = -i\hbar(\partial/\partial q)\Psi(q)$ where $\Psi(q)$ is the wavefunction as a function of the coordinate q. The operator $\hat{P}^2 = \hat{P}\hat{P}$ in the q representation is $-\hbar^2(\partial^2/\partial q^2)$.

The Schrödinger equation in the position basis, $\hat{H}\Psi(q) = E\Psi(q)$, can therefore be written for a particle moving in one dimension as

$$\left[\left(\frac{p^2}{2m}\right) + V(q)\right]\Psi(q) = E\Psi(q) \tag{1.5}$$

or

$$-\left(\frac{\hbar^2}{2m}\right)\frac{\partial^2\Psi(q)}{\partial q^2} + V(q)\Psi(q) = E\Psi(q) \tag{1.6}$$

The position operator in three dimensions is a vector, $\boldsymbol{i}\hat{x} + \boldsymbol{j}\hat{y} + \boldsymbol{k}\hat{z}$ where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in the x, y, and z directions. The momentum operator in three dimensions is also a vector, which in the position basis is

$$\hat{\boldsymbol{p}} = -i\hbar(\boldsymbol{i}\partial/\partial x + \boldsymbol{j}\partial/\partial y + \boldsymbol{k}\partial/\partial z) = -i\hbar\nabla \tag{1.7}$$

where ∇ is called the del or grad operator. The square of the momentum is

$$\begin{aligned}\hat{\boldsymbol{p}}^2 = \hat{\boldsymbol{p}}\hat{\boldsymbol{p}} &= -\hbar^2(\boldsymbol{i}\,\partial/\partial x + \boldsymbol{j}\partial/\partial y + \boldsymbol{k}\partial/\partial z)\cdot(\,\boldsymbol{i}\partial/\partial x + \boldsymbol{j}\partial/\partial y + \boldsymbol{k}\partial/\partial z) \\ &= -\hbar^2\left(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\right) = -\hbar^2\nabla^2\end{aligned} \tag{1.8}$$

where ∇^2 is called the Laplacian. Notice that while the momentum is a vector, the momentum squared is not.

1.3 Expectation Values, Uncertainty Relations

When a system is in state Ψ, the mean value or expectation value of observable $\hat{A}$ is defined as the average of a large number of measurements. It is given by $\langle\hat{A}\rangle = \langle\Psi \mid \hat{A} \mid \Psi\rangle = \int \Psi^*\hat{A}\Psi$. If Ψ is an eigenfunction of $\hat{A}$ then every measurement gives the same result, the eigenvalue. If Ψ is not an eigenfunction of $\hat{A}$ then each measurement may yield a different value, but we can calculate its average with complete certainty from the above expression. Note that if $\hat{A}$ involves just multiplication, such as q to some power, we can just write this as $\langle\hat{q}^n\rangle = \int |\Psi(q)|^2 q^n \mathrm{d}q$. But if $\hat{A}$ does something like differentiation, then we have to make sure it operates on $\Psi(q)$ only, not also $\Psi(q)^*$. For example, for momentum, $\hat{P} = -i\hbar\,(\partial/\partial q)$, we have $\langle\hat{P}\rangle = -i\hbar\int\Psi(q)^*\{(\partial/\partial q)\Psi(q)\}\mathrm{d}q$.

The root-mean-square deviation of the value of operator $\hat{A}$ in state Ψ is

$$\Delta A = \sqrt{\left\langle\left(\hat{A} - \langle\hat{A}\rangle\right)^2\right\rangle} \tag{1.9a}$$

that is, $\Delta A = \sqrt{\left\langle\left(\hat{A} - A_{\mathrm{avg}}\right)^2\right\rangle}$. Note that if Ψ is an eigenstate of $\hat{A}$, then $\Delta A = 0$ since every measurement of $\hat{A}$ gives the same result. An alternative and sometimes preferable form for ΔA can be written by noting that since $\langle\hat{A}\rangle$ is a number,

$$\left\langle \left(\hat{A} - \langle \hat{A} \rangle\right)^2 \right\rangle = \left\langle \hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2 \right\rangle = \left\langle \hat{A}^2 \right\rangle - 2\langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2 = \left\langle \hat{A}^2 \right\rangle - \langle \hat{A} \rangle^2.$$

So,

$$\Delta A = \sqrt{\left\langle \hat{A}^2 \right\rangle - \langle \hat{A} \rangle^2} \tag{1.9b}$$

is an alternative equivalent form.

The product of the root-mean-square deviations of two operators $\hat{A}$ and $\hat{B}$, in any state, obeys the relationship

$$\Delta A \Delta B \geq \tfrac{1}{2} \left| \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle \right| \tag{1.10}$$

A particularly important example is for the various components of position and momentum; since $\left[\hat{Q}, \hat{P}\right] = i\hbar$, then $\Delta Q \Delta P \geq \hbar/2$. This is often known as the Heisenberg uncertainty relation between position and momentum. The interpretation is that you cannot simultaneously know both the position and the momentum along the same direction (e.g. $\hat{x}$ and $\hat{p}_x$) to arbitrary accuracy; their uncertainty product, $\Delta Q \Delta P$, has a finite nonzero value. Only for operators that commute can the uncertainty product vanish (although it is not *necessarily* zero in any state). Note that since different components of position and momentum (e.g. $\hat{x}$ and $\hat{p}_y$) do commute, their uncertainty product can be zero.

Because commuting observables can have an uncertainty product of zero, they are said to be compatible observables. This means that if $\left[\hat{A}, \hat{B}\right] = 0$, and $\hat{A}\Psi = a\Psi$, (Ψ is an eigenstate of the operator $\hat{A}$), then the state given by $\left(\hat{B}\Psi\right)$ is also an eigenstate of $\hat{A}$ with the same eigenvalue a. The result one gets from a measurement of $\hat{A}$ is not affected by having previously measured $\hat{B}$. One can have simultaneous eigenstates of $\hat{A}$ and $\hat{B}$. In general, this is not the case if the operators do not commute.

1.4 The Particle in a Box

The "particle in a box," in one dimension, refers to a particle of mass m in a potential defined by $V(x) = 0$ for $0 \leq x \leq a$ where a is a constant, and $V(x) = \infty$ everywhere else. In one dimension, this may be used to crudely model an electron in a delocalized molecular orbital (MO), e.g. the pi-electron system of a linear polyene molecule, conjugated polymer, or porphyrin. In three dimensions, it may be used to model the electronic states of a semiconductor nanocrystal.

Since the potential energy becomes infinite at the walls, the boundary condition is that the wavefunction must go to zero at both walls. Thus the relevant Schrödinger equation becomes, in on dimension,

$$-\left(\frac{\hbar^2}{2m}\right)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) = E\psi(x) \quad \text{for } 0 \le x \le a \tag{1.11}$$

where m is the mass of the particle. The solutions to this equation are

$$\psi_n(x) = B\sin\left(\frac{n\pi x}{a}\right) \quad \text{and} \quad E_n = \frac{h^2n^2}{8ma^2} \quad \text{for } n = 1, 2, \ldots \tag{1.12}$$

The function is a solution for any value of the constant B. We find B by requiring that $\psi_n(x)$ be normalized: that is, the total probability of finding the particle somewhere in space must be unity. This means that $\int_0^a \mathrm{d}x\,|\psi_n(x)|^2 = 1$, and we find $B = \sqrt{2/a}$. The first few solutions are plotted in Figure 1.1.

The particle in a box in two or three dimensions is a simple extension of the one-dimensional case. The Schrödinger equation for the three-dimensional case is

$$\begin{aligned} -\left(\hbar^2/2m\right)\left(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\right)\psi(x,y,z) &= -\left(\hbar^2/2m\right)\nabla^2\psi(x,y,z) \\ &= E\psi(x,y,z) \end{aligned} \tag{1.13}$$

for $0 \le x \le a$, $0 \le y \le b$, $0 \le z \le c$. Since the Hamiltonian for this system is a simple sum of operators in each of the three spatial dimensions, the total energy of the system is also a simple *sum* of contributions from x, y, and z motions, and the

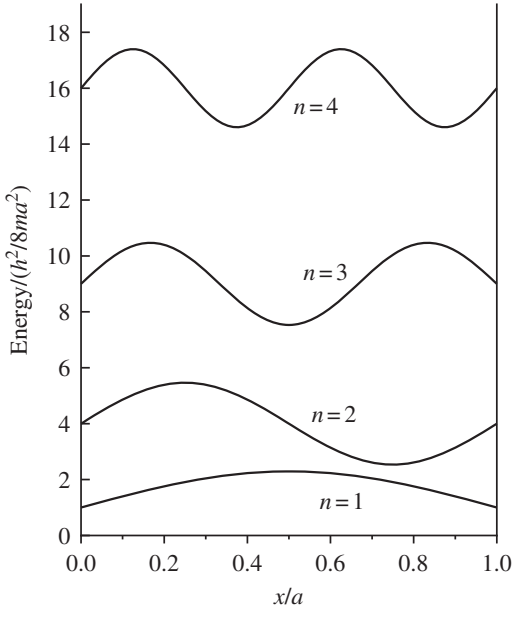


Figure 1.1 The one-dimensional particle in a box potential and its first four eigenfunctions.

wavefunctions that are eigenfunctions of the Hamiltonian are just *products* of wavefunctions for x, y, and z individually:

$$\Psi(x,y,z) = \left\{(2/a)^{1/2}\sin(n_x\pi x/a)\right\}\left\{(2/b)^{1/2}\sin(n_y\pi y/b)\right\}\left\{(2/c)^{1/2}\sin(n_z\pi z/c)\right\} \tag{1.14a}$$

$$E(n_x,n_y,n_z) = (h^2/8m)\left\{(n_x^2/a^2) + \left(n_y^2/b^2\right) + (n_z^2/c^2)\right\} \tag{1.14b}$$

$$n_x, n_y, n_z = 1, 2, 3, \ldots \tag{1.14c}$$

A separable Hamiltonian has eigenfunctions that are products of the solutions for the individual dimensions and energies that are sums. This result is general and important.

If all three dimensions a, b, and c are different and not multiples of each other, generally each set of quantum numbers (n_x, n_y, n_z) will have a different energy. But if any of the box lengths are the same or integer multiples of each other, then certain energies will correspond to more than one state, that is, more than one combination of quantum numbers. This degeneracy is a general feature of quantum mechanical systems that have some symmetry.

1.5 Harmonic Oscillator

Classically, the relative motion of two masses m_1 and m_2, connected by a Hooke's Law spring of force constant k, is described by Newton's Law as

$$\mu\frac{d^2x}{dt^2} + kx = 0 \tag{1.15}$$

where the reduced mass is $\mu = m_1m_2/(m_1 + m_2)$ (μ has units of mass). This is just $F = ma$ where the force is $-kx$ and the acceleration is d^2x/dt^2. Here x is the deviation of the separation from its equilibrium value, $x = (x_1 - x_2) - x_0$, and the motion of the center of mass (CM), $M = m_1 + m_2$, has been factored out. Remember the force is just $-dV/dx$, so $V(x) = (1/2)kx^2 + C$; the potential energy is a quadratic function of position. The classical solution to this problem is $x(t) = c_1 \sin \omega t + c_2 \cos \omega t$ where the constants depend on the initial conditions, and the frequency of oscillation in radians per second is $\omega = (k/\mu)^{1/2}$.

The form $V(x) = (1/2)kx^2$ is the lowest order nonconstant term in the Taylor series expansion of any potential function about its minimum:

$$\begin{aligned} V(\ell) = V(\ell_0) &+ (dV/d\ell)_0(\ell - \ell_0) + (1/2)\left(d^2V/d\ell^2\right)_0(\ell - \ell_0)^2 \\ &+ (1/6)\left(d^3V/d\ell^3\right)_0(\ell - \ell_0)^3 + \cdots \end{aligned} \tag{1.16}$$

But if ℓ_0 is the potential minimum, by definition $(dV/d\ell_0) = 0$, so the first nonzero term besides a constant is the quadratic one. Redefining $x = \ell - \ell_0$, we get

$$\begin{aligned} V(x) &= C + (1/2)\left(d^2V/dx^2\right)_0 x^2 + \text{higher "anharmonic" terms} \\ &= C + (1/2)kx^2 + \text{anharmonic terms} \end{aligned} \tag{1.17}$$

Since the anharmonic terms depend on higher powers of x, they will be progressively less important for very small displacements. Oscillations about a minimum can generally be described well by a harmonic oscillator as long as the amplitude of motion is small enough.

The quantum mechanical harmonic oscillator in one dimension has a Schrödinger equation given by

$$-\left(\hbar^2/2\mu\right)\left(d^2/dx^2\right)\Psi(x) + (1/2)kx^2\Psi(x) = E\Psi(x) \tag{1.18}$$

The solutions to this differential equation involve a set of functions called the Hermite polynomials, H_v. The eigenfunctions and eigenvalues are:

$$\Psi_v(x) = N_v\left[H_v\left(\alpha^{1/2}x\right)\right]\exp\left(-\alpha x^2/2\right), \quad E_v = \hbar\omega(v + 1/2), \quad v = 0, 1, 2, \ldots \tag{1.19}$$

with $\alpha = (k\mu/\hbar^2)^{1/2}$ and $\omega = (k/\mu)^{1/2}$ as in the classical case. Note the units: k is a force constant in N m^{-1} = (kg m s^{-2}) m^{-1} = kg s^{-2}; μ is a mass in kg; so ω has units of s^{-1} as it must. $\hbar$ has units of J s = (kg m^2 s^{-2}) s = kg m^2 s^{-1} so α has units of inverse length squared, making $(\alpha^{1/2}x)$ a unitless quantity. This quantity is often renamed as q, a dimensionless coordinate. N_v is a normalization constant that depends on the quantum number:

$$N_v = (\alpha/\pi)^{1/4}(2^v v!)^{-1/2} \tag{1.20}$$

(recall $v! = (v)(v-1)(v-2)\cdots(2)(1)$, and $0! = 1$ by definition). The Hermite polynomial H_v is a vth order polynomial; the number of nodes equals the quantum number v. The first four of them are

$$H_0(q) = 1 \quad H_1(q) = 2q \quad H_2(q) = 4q^2 - 2 \quad H_3(q) = 8q^3 - 12q$$

The quantity $\alpha^{1/2}$ scales the displacement coordinate to the force constant and masses involved.

The energy levels of the quantum mechanical harmonic oscillator are equally spaced by an energy corresponding to the classical vibrational frequency, $\hbar\omega$. There is a zero-point energy, $\hbar\omega/2$, arising from confinement to a finite region of coordinate space.

The lowest-energy wavefunction is

$$\Psi_0(x) = (\alpha/\pi)^{1/4}\exp\left(-\alpha x^2/2\right) \tag{1.21}$$

Its modulus squared, $|\Psi_0(x)|^2 = (\alpha/\pi)^{1/2} \exp(-\alpha x^2)$, gives the probability of finding the oscillator at a given position x. This probability has the form of a Gaussian function – it has a single peak at $x = 0$. This means that if this is a model for a vibrating diatomic molecule, the most probable bond length is the equilibrium length. Higher vibrational eigenstates do not all have this property. Note that the probability never goes to zero even for very large positive or negative displacements. In particular, this means that there is finite probability to find the oscillator at a position where the potential energy exceeds the total energy. This is an example of quantum mechanical tunneling.

For $v = 1$, the probability distribution is

$$\begin{aligned} |\Psi_1(x)|^2 &= \left|(\alpha/\pi)^{1/4} 2^{-1/2} 2\alpha^{1/2} x \, \exp\left(-\alpha x^2/2\right)\right|^2 \\ &= 2\alpha^{3/2}\pi^{-1/2} x^2 \exp\left(-\alpha x^2\right) \end{aligned} \tag{1.22}$$

which has a node at $x = 0$ and peaks on either side. The first few harmonic oscillator wavefunctions are plotted in Figure 1.2.

A classical oscillator is most likely to be found (i.e. spends most of its time) at the turning point, the outside edge where the total energy equals the potential energy. This is not true for the quantum oscillator, except at high quantum numbers.

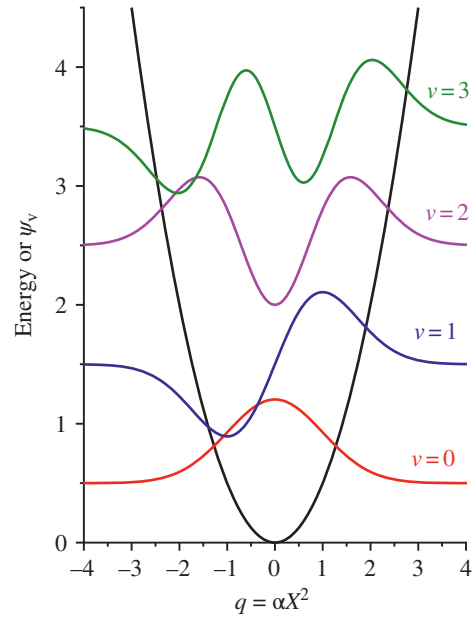


Figure 1.2 The harmonic oscillator potential energy function and its first four eigenfunctions.

In many ways, quantum systems act like classical ones only in the limit of large quantum numbers.

All of the Hermite polynomials are either even or odd functions. The ones with even v are even and those with odd v are odd. The Gaussian function is even. Thus, $\Psi_v(x)$ is even for even v and odd for odd v. Therefore $|\Psi_v(x)|^2$ is always an even function, and

$$\langle x \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \, \Psi_v^*(x) \, x \, \Psi_v(x) = \int_{-\infty}^{\infty} \mathrm{d}x \, x \, |\Psi_v(x)|^2 = 0$$

since the product of an even and an odd function is odd. The *average* position is always at the center (potential minimum) of the oscillator. Similarly,

$$\langle p \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \, \Psi_v^*(x) \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) \Psi_v(x) = 0$$

since the derivative of an even function is always odd and vice versa, so the integrand is always odd.

It is often more convenient to work in the reduced coordinates $q = \sqrt{\frac{\mu\omega}{\hbar}} x$ and $P = \frac{1}{\sqrt{\mu\omega\hbar}} p$. Notice that the operators $\hat{q}$ and $\hat{P}$ obey the same commutation relations as $\hat{x}$ and $\hat{p}$ without the factor of $\hbar$: $\left[\hat{q}, \hat{P}\right] = (1/\hbar)[\hat{x}, \hat{p}] = \mathrm{i}$. The harmonic oscillator Hamiltonian can be written in these reduced coordinates as

$$\hat{H} = \frac{1}{2} \hbar\omega \left(\hat{P}^2 + \hat{q}^2 \right) \tag{1.23}$$

We then introduce the raising and lowering operators, $\hat{a}^\dagger$ and $\hat{a}$, where

$$\hat{a} = \frac{1}{\sqrt{2}} \left(\hat{q} + i\hat{P} \right) \tag{1.24a}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(\hat{q} - i\hat{P} \right) \tag{1.24b}$$

so the reduced position and momentum operators can be written in terms of the raising and lowering operators as

$$\hat{q} = \frac{1}{\sqrt{2}} \left(\hat{a} + \hat{a}^\dagger \right) \tag{1.25a}$$

$$\hat{P} = -\frac{i}{\sqrt{2}} \left(\hat{a} - \hat{a}^\dagger \right) \tag{1.25b}$$

The raising and lowering operators act on the harmonic oscillator eigenstates $|v>$ as follows:

$$\hat{a} \mid v> = \sqrt{v} \mid v-1> \quad (v>0) \tag{1.26a}$$

$$\hat{a} \mid 0> = 0 \tag{1.26b}$$

$$\hat{a}^{\dagger} \mid v> = \sqrt{v+1} \mid v+1> \tag{1.26c}$$

Also note

$$\hat{a}^{\dagger}\hat{a} = \frac{1}{2}\left(\hat{P}^2 + \hat{q}^2 + i\,\hat{q}\hat{P} - i\hat{P}\hat{q}\right) = \frac{1}{2}\left(\hat{P}^2 + \hat{q}^2 + i\left[\hat{q},\hat{P}\right]\right) = \frac{1}{2}\left(\hat{P}^2 + \hat{q}^2 - 1\right)$$

so we can rewrite the Hamiltonian as

$$\hat{H} = \hbar\omega\left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) \tag{1.27}$$

$\hat{N} = \hat{a}^{\dagger}\hat{a}$ is called the number operator because the eigenstates of the Hamiltonian are also eigenstates of $\hat{N}$ with eigenvalues given by the quantum numbers.

1.6 The Rigid Rotor and Angular Momentum

The rigid rotor consists of two point masses, m_1 and m_2, separated by a fixed distance R. The rotational motion of this system is characterized by its moment of inertia I:

$$I = \mu R^2 \tag{1.28}$$

where $\mu = (m_1 m_2)/(m_1 + m_2)$ is the same reduced mass involved in the harmonic oscillator. The classical energy of this system is kinetic only; the potential energy does not depend on the positions of the masses within the constraint that they are separated by R, so the potential energy may be set to zero everywhere. The kinetic energy may be separated into a part that involves the overall translation of the CM of the body and a part that involves only the rotation of the two masses about their CM. We are interested only in the latter. The classical rotational kinetic energy is then given by

$$T = \frac{I\omega^2}{2} = \frac{L^2}{2I} \tag{1.29}$$

where ω is the angular velocity (do not confuse this with the harmonic oscillator frequency!) and $L = I\omega$ is the classical angular momentum. For the classical system, the angular velocity may take on any value and the kinetic energy is a

continuous variable; the faster the masses rotate about their CM, the greater the kinetic energy.

The solution to the corresponding quantum mechanical problem involves writing the angular momentum as a quantum mechanical operator in spherical polar coordinates. We do not derive that here, but simply give the result:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{1.30}$$

As in the usual spherical polar coordinate system, the two angles may take the values $0 \le \theta \le \pi$ and $0 \le \varphi \le 2\pi$. The Schrödinger equation to be solved for the rigid rotor wavefunctions and energies is then

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(\theta,\varphi) = E\psi(\theta,\varphi) \tag{1.31}$$

The solutions to this equation are

$$\psi(\theta,\varphi) = Y_J^m(\theta,\varphi), \quad J = 0, 1, 2, \ldots \text{and } m = -J, -J+1, \ldots +J \tag{1.32a}$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) = BJ(J+1) \quad \text{with } B = \frac{\hbar^2}{2I} \tag{1.32b}$$

The functions $Y_J^m(\theta,\varphi)$ are known as the spherical harmonics. They are normalized and orthogonal:

$$\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi\, Y_J^{m*}(\theta,\varphi)Y_{J'}^{m'}(\theta,\varphi) = \delta_{JJ'}\delta_{mm'} \tag{1.33}$$

They are the eigenstates of angular momentum:

$$\hat{L}^2 Y_J^m(\theta,\varphi) = \hbar^2 J(J+1)Y_J^m(\theta,\varphi) \tag{1.34}$$

The total angular momentum and therefore the energy depends only on J, but as we will see below, the quantum number m determines how the rotating body is oriented in space. Each energy level, defined by its quantum number J, has $2J+1$ degenerate values of m. The quantity B, which depends only on the moment of inertia, is called the rotational constant. Its value determines how closely spaced in energy the allowed energy levels are.

Unlike the classical rigid rotor, the quantum mechanical rotor can have only certain energies (and therefore certain values of the angular momentum) corresponding to integer values of J. In this respect, it is similar to the particle in a box and harmonic oscillator problems. However, the lowest available energy for the rigid rotor is $E_0 = 0$; there is no zero-point energy. This can be understood by recognizing that since the potential energy has no dependence on θ or φ, the rotor is not confined in angular space.

Angular momentum is a vector; it has both magnitude and direction. The quantity $\hat{L}^2$ in Eq. (1.30) is defined as $\hat{L}^2 = \hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{L}}$ where

$$\hat{\boldsymbol{L}} = \boldsymbol{i}\hat{L}_x + \boldsymbol{j}\hat{L}_y + \boldsymbol{k}\hat{L}_z \tag{1.35}$$

where $\boldsymbol{i}, \boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in the x, y, and z directions. The operator representing $\hat{L}_z$ has a particularly simple form:

$$\hat{L}_z = i\hbar\frac{\partial}{\partial\varphi} \tag{1.36}$$

The spherical harmonics are also eigenstates of $\hat{L}_z$:

$$\hat{L}_z Y_J^m(\theta,\varphi) = \hbar m \tag{1.37}$$

However, they are not eigenstates of $\hat{L}_x$ or $\hat{L}_y$. This is because $\hat{L}^2$ commutes with $\hat{L}_z$, but not with $\hat{L}_x$ or $\hat{L}_y$. As discussed in Section 1.3 above, this means that there may exist simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, but not $\hat{L}^2$ and $\hat{L}_x$ or $\hat{L}_y$. The J quantum number defines the total angular momentum of the rotor, while the m quantum number determines the projection of that angular momentum onto the z axis.

The explicit forms for the first three spherical harmonics are:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \tag{1.38a}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{1.38b}$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi} \tag{1.38c}$$

Angular momentum also plays a major role in the quantum mechanical motions of electrons in atoms, but different symbols are traditionally used for the quantum numbers. For rotational motion of a molecule, the total angular momentum quantum number is J and its z-component is called m or m_J. For the motions of electrons about a nucleus in an atom (orbital angular momentum), the symbols ℓ and m or m_ℓ are used to represent the corresponding quantities.

1.7 The Hydrogen Atom

The hydrogen atom consists of one electron and one proton, interacting through a Coulombic potential. If we assume that the nucleus is fixed in space, the

Hamiltonian consists of the kinetic energy of the electron (mass m_e) plus the Coulombic attraction between the electron and the nucleus:

$$\hat{H} = -\left(\frac{\hbar^2}{2m_e}\right)\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{1.39}$$

The problem is most readily solved in spherical polar coordinates. Transforming the Laplacian operator into spherical polar coordinates gives the Schrödinger equation,

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left\{\frac{1}{r^2}\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\Psi(r,\theta,\varphi) - \frac{e^2}{4\pi\varepsilon_0 r}\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi) \tag{1.40}$$

The solution to this equation is described in nearly all basic quantum mechanics textbooks. The wavefunctions are products of an r-dependent part and a (θ, φ)-dependent part, and they depend on three quantum numbers, n, ℓ, and m:

$$\Psi_{n\ell m}(r,\theta,\phi) = R_n(r)Y_\ell^m(\theta,\phi) \tag{1.41}$$

with allowed values for the quantum numbers of

$$n = 1, 2, 3, \ldots \tag{1.42a}$$

$$\ell = 0, 1, 2, \ldots (n-1) \tag{1.42b}$$

$$m = -\ell, (-\ell+1), \ldots (\ell-1), \ell \tag{1.42c}$$

The quantum number m is often designated m_ℓ to clarify that it corresponds to orbital angular momentum.

The associated energy eigenvalues depend only on n and are given by

$$E_n = \frac{-e^2}{8\pi\varepsilon_0 a_0 n^2} \tag{1.43}$$

The quantity $a_0 = 4\pi\varepsilon_0\hbar^2/(m_e e^2)$ is the Bohr radius. It has the numerical value 0.529 Å. It defines an intrinsic length scale for the H-atom problem, much as the constant α does for the harmonic oscillator.

The angle-dependent functions $Y_\ell^m(\theta,\phi)$ are known as the spherical harmonics discussed earlier in Section 1.6. The radial part of the wavefunction is given by

$$R_{n\ell}(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\left(\frac{2r}{na_0}\right)^\ell \exp\left(-\frac{r}{na_0}\right)L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) \tag{1.44}$$

where the $L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ are called the associated Laguerre polynomials. The functions $R_{n\ell}(r)$ are normalized with respect to integration over the radial coordinate, such that $\int_0^\infty r^2 \mathrm{d}r\, |R_{n\ell}(r)|^2 = 1$. Note that the radial part of the volume element in spherical polar coordinates is $r^2\, \mathrm{d}r$.

The H-atom wavefunctions depend on three quantum numbers. The principal quantum number n, the only one on which the energy depends, mainly determines the overall size of the wavefunction (larger n gives a larger average distance from the nucleus). The angular momentum quantum number ℓ determines the overall shape of the wavefunction; $\ell = 0, 1, 2, 3, \ldots$ correspond to s, p, d, f, ... orbitals. The magnetic quantum number m determines the orientation of the orbital and causes each degenerate energy level to split into $2\ell + 1$ different energies in the presence of a magnetic field.

Recall that in general, the more nodes in a wavefunction, the higher its energy. The number of radial nodes (nodes in $R_{n\ell}(r)$) is given by $(n - \ell - 1)$ and the number of nodal planes in angular space is given by ℓ, so the total number of nodes is $(n-1)$ and the energy goes up with increasing n. For $\ell = 0$, there is no (θ, ϕ) dependence. The orbital is spherically symmetric and is called an s orbital. For $\ell = 1$, there is one nodal plane and the orbital is called a p orbital. Since in spherical polar coordinates $z = r\cos\theta, Y_1^0$ points along the z direction and we refer to the $\ell = 1$, $m = 0$ orbitals as p_z orbitals. Y_1^1 and Y_1^{-1} are harder to interpret because they are complex. However, since they are degenerate, any linear combination of them will also be an eigenstate of the Hamiltonian. It is traditional to work with the linear combinations

$$p_x = 2^{-1/2}\left(Y_1^1 + Y_1^{-1}\right) = (3/4\pi)^{1/2} \sin\theta \cos\varphi \tag{1.45a}$$

$$p_y = -i2^{-1/2}\left(Y_1^1 - Y_1^{-1}\right) = (3/4\pi)^{1/2} \sin\theta \sin\varphi \tag{1.45b}$$

which are real and point along the x and y directions, respectively. For $\ell = 2$, we can similarly make linear combinations of $m = \pm 1$ and $m = \pm 2$ to create five real d orbitals.

The H-atom wavefunctions are orthonormal. Remember that in spherical polar coordinates, the ranges of the coordinates are

$$r = 0 \text{ to } \infty, \quad \theta = 0 \text{ to } \pi, \quad \varphi = 0 \text{ to } 2\pi$$

and the volume element is $r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\varphi$. So the orthonormality condition can be written as

$$\int_0^\infty r^2 \mathrm{d}r \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi\, \Psi^*_{n'\ell'm'}(r,\theta,\phi)\, \Psi_{n\ell m}(r,\theta,\phi) = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$$

Note that if we are using the above real linear combinations of the $Y_\ell^{\pm m}$, p_x, and p_y instead of Y_1^1 and Y_1^{-1}, the orthonormality relations still hold because we defined p_x and p_y to be orthogonal linear combinations of Y_1^1 and Y_1^{-1}. The same holds for the d orbitals.

For future reference, here we give the complete normalized wavefunctions for $n = 1$ and $n = 2$:

$$\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \tag{1.46a}$$

$$\Psi_{200} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{2a_0}\right)^{3/2}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} \tag{1.46b}$$

$$\Psi_{21-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta e^{-i\varphi} \tag{1.46c}$$

$$\Psi_{210} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{2a_0}\right)^{5/2} re^{-r/2a_0}\cos\theta \tag{1.46d}$$

$$\Psi_{211} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta e^{i\varphi} \tag{1.46e}$$

For one-electron ions that have a nuclear charge greater than one, the wavefunctions are the same except that a_0 is replaced by a_0/Z where Z is the nuclear charge.

1.8 Approximation Methods

There are two basic ways to handle quantum mechanical problems that do not have an exact analytical solution (i.e. all of the interesting ones). The variational method is the most general and flexible and lies at the heart of most techniques for calculating the electronic structure of multielectron atoms and molecules. Perturbation theory is most useful when the real problem of interest is very similar to one of the simple problems that can be solved exactly.

The variational method expresses the unknown wavefunction as a function of one or more parameters, and then tries to find the best value(s) of those parameter(s) that make the resulting function and its energy as close as possible to the real one. But how do we find "best" if, by definition, we do not know the exact answer?

We take advantage of a theorem called the variational principle. Let $\Phi(\alpha, \beta, \gamma, ...)$ be this arbitrary function of one or more parameters, and let Ψ_0 be the true ground-state wavefunction of the Hamiltonian of interest, $\hat{H}$. We assume that we know $\hat{H}$ exactly but we cannot solve the resulting Schrödinger equation exactly to find Ψ_0

and its energy eigenvalue, E_0. Here we will not assume that Φ is normalized. If the system is in state Φ, then the expectation value of its energy is given by

$$E_\Phi = \frac{\int \Phi^* \hat{H} \Phi \, d\tau}{\int \Phi^* \Phi \, d\tau} \tag{1.47}$$

where the integrations are over all space. The variational principle says that for any function Φ, it is always true that $E_\Phi \geq E_0$; that is, the energy we get by using any approximate function can approach the true energy as a lower bound, but can never be lower. Thus the lower the energy we get by varying the parameters in the function $\Phi(\alpha, \beta, \gamma, ...)$, the closer this energy is to the true ground-state energy, and by assumption, the closer Φ is to the real wavefunction.

The way we implement this idea is to *minimize* E_Φ with respect to each of the parameters $\alpha, \beta, \gamma, ...$ i.e. set $\partial E_\Phi / \partial \alpha = 0$ and solve for α, and so on. Of course, how good the resulting energy and wavefunction are depends on how good a choice we made for the general functional form of $\Phi(\alpha, \beta, \gamma, ...)$. If we choose a different functional form, or one that depends on more parameters, and get a lower value for E_Φ, then that is a better approximation to the real wavefunction. Notice that if we "accidentally" choose a trial function that has the same functional form as the real ground-state wavefunction, then this procedure will result in the exact wavefunction and energy.

While using a trial function that depends in a nonlinear way on one or more variational parameters can be quite useful for analytical calculations, for numerical (computer) calculations it turns out to be much more efficient to choose a trial function that depends linearly on the variational parameters. That is, one assumes

$$\Phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots = \sum\nolimits_n c_n f_n \tag{1.48a}$$

where the f_n are known functions that one tries to select intelligently, and the c_n are parameters whose best values are to be determined using the variational principle. For just two functions,

$$\Phi = c_1 f_1 + c_2 f_2 \tag{1.48b}$$

Minimizing the energy with respect to both parameters gives two equations in two unknowns:

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{1.49a}$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{1.49b}$$

where the matrix elements of the Hamiltonian are defined as $H_{ij} = \left\langle f_i \mid \hat{H} \mid f_j \right\rangle$ and the overlap integrals are defined as $S_{ij} = \langle f_i | f_j \rangle$ (this is just the normalization

integral for $i = j$). By definition, it is clear that $S_{ij} = S_{ji}^*$, and using the Hermitian property of quantum mechanical operators, one can also show that $H_{ij} = H_{ji}^*$. In order for this system of two equations in two unknowns to have a nontrivial solution, the determinant of their coefficients must vanish:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{1.50}$$

Expanding this 2×2 determinant gives a quadratic equation in E, which has two roots. The lower value of the two corresponds to the lower bound on the energy. We then plug this value of E back into the original pair of equations,

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{1.51a}$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{1.51b}$$

and solve for the parameters c_1 and c_2. Actually, we can only solve for one of them in terms of the other (both equations will give the same relationship between c_1 and c_2) and the value of the remaining parameter is determined by normalization (see also Appendix C).

Generally, the more functions one combines (the larger is the basis set), the more accurate the result will be. This is because we are trying to approximate the (unknown) actual wavefunction by a sum of other functions, and the more free parameters this fitting function has, the more closely it can approximate the actual one. It is similar to trying to fit an arbitrary curve by a polynomial; the higher order the polynomial we use, in general the better we can fit the arbitrary function. Using a linear combination of N functions yields an $N \times N$ determinant. For large N, this gets pretty ugly to solve by hand, but computers can manipulate large determinants and matrices very efficiently.

The alternative approach to solving a quantum mechanical problem approximately, perturbation theory, is most useful for situations where the problem of interest is only slightly different from a problem that we do know how to solve exactly. What constitutes "slightly different" is a matter of experience and judgment.

Assume we can write the complete Hamiltonian whose solutions we are interested in as the sum of a part we know how to solve exactly, $\hat{H}^{(0)}$, and another part, $\hat{H}^{(1)}$, so that $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$. Let the normalized eigenfunctions and eigenvalues of $\hat{H}^{(0)}$ be $\Psi_v^{(0)}$ and $E_v^{(0)}$, where v represents a generalized quantum number. We now assume that the eigenfunctions and eigenvalues of $\hat{H}$ can be written in the form of an expansion,

$$\Psi_v = \Psi_v^{(0)} + \Psi_v^{(1)} + \Psi_v^{(2)} + \cdots \tag{1.52a}$$

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} + \cdots \tag{1.52b}$$

where each term is assumed to be successively smaller than the previous one. Expressions can be derived for each of these corrections, but here we will address only the first-order corrections. The first-order correction to the energy, $E_v^{(1)}$, is simply the expectation value of the perturbation part of the Hamiltonian, $\hat{H}^{(1)}$, when the system is in the zeroth-order wavefunction, $\Psi_v^{(0)}$:

$$E_v^{(1)} = \left\langle \Psi_v^{(0)} \mid \hat{H}^{(1)} \mid \Psi_v^{(0)} \right\rangle \tag{1.53}$$

The first-order correction to the wavefunction, $\Psi_v^{(1)}$, is

$$\Psi_v^{(1)} = \sum\nolimits_{n \neq v} \frac{\left\langle \Psi_n^{(0)} \mid \hat{H}^{(1)} \mid \Psi_v^{(0)} \right\rangle}{E_v^{(0)} - E_n^{(0)}} \Psi_n^{(0)} \tag{1.54}$$

That is, the first-order correction to the wavefunction for the vth state involves a sum of contributions from all the other zeroth-order wavefunctions, each weighted by a matrix element of the perturbation Hamiltonian divided by an energy denominator. The energy denominator has the effect of weighting most heavily the states that are closest in energy to the state of interest.

1.9 Electron Spin

You should remember from first-year chemistry the aufbau or "building-up" process for determining the electron configurations of atoms beyond He: order the hydrogenlike atomic orbitals (AOs) by energy, 1s, 2s, 2p, 3s, etc., and then start putting electrons into these orbitals, two electrons per orbital, until all the electrons are used up. The reason only two electrons can go into each orbital is that each electron can be in either of two spin states, which are usually labeled α and β (or + and −, or "up" and "down"), and the Pauli Exclusion Principle says that it is not possible for two electrons to be in exactly the same quantum state. Thus if two electrons are in the same orbital (same *spatial* part of the wavefunction), they must be in different spin states.

All subatomic particles (electrons and nuclei) have associated with them a quality called spin, which acts in some ways like a spinning top having a certain angular momentum, but really does not have a classical analog. Spin is quantized and can have either integer (including zero) or half-integer values. Particles having integer spins are called bosons and they do not have any exclusion principle; any number of bosons can occupy the same quantum state. Particles having

half-integer spin are called fermions and no two fermions can occupy the same quantum state. Electrons have spin 1/2 and are fermions.

We define operators for the square of the total spin angular momentum, $\hat{S}^2$, and the z-component of the spin angular momentum, $\hat{S}_z$, which are entirely analogous to those for ordinary ("orbital") angular momentum, $\hat{L}^2$ and $\hat{L}_z$, except that they have different eigenvalues:

$$\hat{S}^2\alpha = (½)(½ + 1)\hbar^2\alpha \tag{1.55a}$$

$$\hat{S}^2\beta = (½)(½ + 1)\hbar^2\beta \tag{1.55b}$$

$$\hat{S}_z\alpha = \left(\frac{\hbar}{2}\right)\alpha \tag{1.55c}$$

$$\hat{S}_z\beta = \left(-\frac{\hbar}{2}\right)\beta \tag{1.55d}$$

That is, the two spin states, α and β, are both eigenstates of the total spin angular momentum, $\hat{S}^2$, with eigenvalue $\hbar^2 s(s+1)$ where $s = ½$; s is analogous to the quantum number ℓ for orbital angular momentum, but it has half-integer rather than integer values. α and β are also both eigenstates of the z-component of the total angular momentum with eigenvalue $\hbar m_s$, where $m_s = +½$ for α and $-½$ for β ("spin-up" and "spin-down"). The eigenvalue $\hbar m_s$ refers to the projection of the spin angular momentum onto the z axis. The operators $\hat{S}^2$ and $\hat{S}_z$ are Hermitian, so their eigenstates corresponding to different eigenvalues must be orthogonal and are chosen to be normalized:

$$\langle\alpha \mid \alpha\rangle = \langle\beta \mid \beta\rangle = 1 \tag{1.56a}$$

$$\langle\alpha \mid \beta\rangle = \langle\beta \mid \alpha\rangle = 0 \tag{1.56b}$$

where the brackets imply integration over a spin variable often called σ which has no classical analog.

We assume that the spatial and spin degrees of freedom are independent, so the whole wavefunction for an electron is just a product of the spatial and spin parts:

$$\Psi(r,\theta,\varphi,\sigma) = \psi(r,\theta,\varphi)\alpha(\sigma) \text{ or } \psi(r,\theta,\varphi)\beta(\sigma) \tag{1.57}$$

The complete one-electron function $\Psi(r, \theta, \varphi, \sigma)$ is called a spin orbital or spinorbital. For the H atom, the spinorbitals depend on four quantum numbers, m_s as well as n, ℓ, and m. The two lowest-energy spinorbitals combine the 1s spatial orbital with the α or β spin function:

$$\Psi_{100\alpha}(r,\theta,\varphi,\sigma) = \psi_{1s}(r,\theta,\varphi)\alpha(\sigma) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\alpha \tag{1.58a}$$

$$\Psi_{100\beta}(r,\theta,\varphi,\sigma) = \psi_{1s}(r,\theta,\varphi)\beta(\sigma) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\,\beta \tag{1.58b}$$

Spinorbitals for other values of n, ℓ, and m are constructed in the same way. Since the spatial and spin parts are individually orthonormal and they represent independent sets of coordinates, the spinorbitals are also orthonormal, e.g.

$$\begin{aligned}&\langle\Psi_{100\alpha}|\Psi_{100\alpha}\rangle \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\vartheta \int_0^{2\pi} d\phi\ \psi_{1s}^*(r,\theta,\varphi)\psi_{1s}(r,\theta,\varphi)\\ &\int d\sigma\alpha^*(\sigma)\alpha(\sigma) = (1)(1) = 1\end{aligned} \tag{1.59a}$$

$$\begin{aligned}&\langle\Psi_{100\alpha}|\Psi_{100\beta}\rangle = \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\vartheta \int_0^{2\pi} d\phi\psi_{1s}^*(r,\theta,\varphi)\psi_{1s}(r,\theta,\varphi)\\ &\int d\sigma\alpha^*(\sigma)\beta(\sigma) = (1)(0) = 0\end{aligned} \tag{1.59b}$$

It might seem reasonable to guess that an atom or molecule with two electrons could be described by a wavefunction like $\Psi(1, 2) = \psi(1)\alpha(1)\psi(2)\beta(2)$, i.e. both electrons in the same spatial orbital ψ, but having different spin states. There is one problem with this wavefunction: it implies that electron 1 and electron 2 are *distinguishable* by having different spins. But in fact they are not; they are the same kind of particle and occupy the same region of space, and they hold no "labels" to tell them apart. None of the physically observable properties associated with the wavefunction can be changed by simply changing the labels of the electrons. This requirement can be satisfied by constructing wavefunctions that are either symmetric or antisymmetric combinations of the above function with the labels reversed, i.e. $\Psi \pm (1, 2) = \psi(1)\alpha(1)\psi(2)\beta(2) \pm \psi(2)\alpha(2)\psi(1)\beta(1)$. For electrons, which are fermions, only the *antisymmetric* (minus) combination is legal. This actually turns out to be a more general statement of the Pauli Exclusion Principle: wavefunctions must be antisymmetric under the exchange of any two fermions. A legal wavefunction for a two-electron atom or molecule (unnormalized) is thus given by

$$\begin{aligned}\Psi(1,2) &= \psi(1)\alpha(1)\psi(2)\beta(2) - \psi(2)\alpha(2)\psi(1)\beta(1)\\ &= \psi(1)\psi(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}\end{aligned} \tag{1.60}$$

In the example with only two electrons, it is easy to just write down a wavefunction that has the proper behavior of changing its sign when the two electrons are interchanged. It is not so obvious how to do this for a system with more than two electrons. Fortunately, there is a well-defined way to do this which makes use of one of the properties of determinants: exchanging any two rows or columns

changes the sign of the determinant. For N electrons occupying N spinorbitals, the wavefunction is

$$\Psi(1,2,...,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & \cdots & u_N(1) \\ \vdots & \ddots & \vdots \\ u_1(N) & \cdots & u_N(N) \end{vmatrix} \tag{1.61}$$

where $u_i(j)$ represents the jth electron in the ith spinorbital. Each column represents a different spinorbital and each row represents a different electron. This formula automatically makes the wavefunction normalized (by the $1/\sqrt{N!}$) and antisymmetric with respect to interchange of any two electrons.

Another nice property of determinants is that if any two rows or columns are identical, the determinant is zero. This means that if we try to put two electrons into the same spinorbital, the determinant will vanish. Thus this determinantal form for the wavefunction (also called a Slater determinant) automatically obeys the Pauli Exclusion Principle that every electron must occupy a different spinorbital.

Equation (1.60) describes a wavefunction that is symmetric with respect to the spatial part of the wavefunction and antisymmetric with respect to the spin part. This is the only acceptable overall wavefunction that places both electrons in the lowest-energy spatial wavefunction. If we instead consider states in which the two electrons are in two different spatial functions, ψ and φ, it turns out there are four different total wavefunctions we can write that satisfy the requirement to be antisymmetric with respect to interchange of electrons:

$$\Psi(1,2) = \frac{1}{2}\{\psi(1)\phi(2) + \phi(1)\psi(2)\}\,\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{1.62}$$

$$\Psi(1,2) = \frac{1}{2}\{\psi(1)\phi(2) - \phi(1)\psi(2)\}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \tag{1.63a}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\{\psi(1)\phi(2) - \phi(1)\psi(2)\}\alpha(1)\alpha(2) \tag{1.63b}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\{\psi(1)\phi(2) - \phi(1)\psi(2)\}\beta(1)\beta(2) \tag{1.63c}$$

Equation (1.62) has a symmetric spatial part and an antisymmetric spin part, and there is only one such function. This is referred to as a singlet state, as is the function in Eq. (1.60). Equations (1.63a)–(1.63c) have antisymmetric spatial parts and symmetric spin parts, and there are three such functions. These are referred to a triplet states. The three triplet states are degenerate in the absence of external magnetic fields, and they are nearly always lower in energy than the corresponding singlet. Note that only two of these four wavefunctions can be

represented by a single Slater determinant; the other two are linear combinations of more than one Slater determinant.

1.10 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is a very useful and usually quite good approximation made in finding the electronic energy levels and wavefunctions of molecules. It may be most easily introduced by reference to the simplest possible diatomic molecule, H_2^+: two nuclei and only one electron. Its full Hamiltonian is

$$\begin{aligned}\hat{H}_{H_2^+} = &-\left(\hbar^2/2M\right)\left(\nabla_A{}^2 + \nabla_B{}^2\right) - \left(\hbar^2/2m_e\right)_1 \nabla_1{}^2 \\ &-\left(e^2/4\pi\varepsilon_0\right)\left(1/r_{1A} + 1/r_{1B}\right) + e^2/4\pi\varepsilon_0 R\end{aligned} \tag{1.64}$$

Here A and B label the two nuclei, R is the distance between them, and 1 labels the electron. M is the nuclear mass and m_e is the electron mass. The four terms represent, respectively, the nuclear kinetic energy, electronic kinetic energy, electron–nuclear attraction, and nuclear–nuclear repulsion.

We simplify this equation by recognizing that since nuclei are much heavier than electrons (three orders of magnitude or more), they move much more slowly than the electrons. As far as the electrons are concerned, the nuclei appear nearly stationary, and the electrons are always able to "solve" their own wavefunction for each value of the nuclear position. Therefore, to find out what the electrons are doing, it is a good approximation to neglect the nuclear kinetic energy operator in the H_2^+ Hamiltonian and leave the internuclear separation R as a *parameter* in the Schrödinger equation for the electronic motion. The energy will depend on this parameter R. If we then want to deal with the motions of the nuclei explicitly, we will have to find the dependence of this energy on the internuclear separation. For example, to calculate the vibrational spectrum of a molecule, we need its force constant, which means we need to find both the value of R that minimizes the energy and the second derivative of the energy with respect to R.

Wavefunctions and Hamiltonians for atoms and molecules are often written using atomic units, in which $\hbar$, m_e, $4\pi\varepsilon_0$, and e are all set equal to 1. Within the Born-Oppenheimer approximation and in atomic units, the electronic Hamiltonian for the H_2^+ molecule is

$$\hat{H}_{H_2^+}(1) = -\tfrac{1}{2}\nabla_1^2 - 1/r_{1A} - 1/r_{1B} + 1/R \tag{1.65}$$

where the (1) just emphasizes that the Hamiltonian is a *function* of only the coordinates of electron 1, with R being a parameter. Because there is only one electron, it is possible to solve this problem exactly by transforming to elliptic coordinates.

The exact solution will not be discussed further because it is not possible to treat any molecule with more than one electron exactly.

1.11 Molecular Orbitals

The simplest way to think about H_2^+ is to consider it as two H nuclei with the electron on one or the other nucleus. We know that the lowest-energy solution for a single H atom is for the electron to occupy the 1s orbital. So one might guess that a reasonable variational trial function for H_2^+ is

$$\psi = c_A 1s_A + c_B 1s_B$$

where $1s_A$ and $1s_B$ are 1s orbitals centered at nuclei A and B, respectively, and c_A and c_B are variational parameters. To solve this problem, we first need to solve the determinantal equation,

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0 \tag{1.66}$$

where

$$H_{AA} = H_{BB} = \langle 1s_A \mid \hat{H} \mid 1s_A \rangle = \langle 1s_B \mid \hat{H} \mid 1s_B \rangle \tag{1.67a}$$

$$H_{AB} = H_{BA} = \langle 1s_A \mid \hat{H} \mid 1s_B \rangle = \langle 1s_B \mid \hat{H} \mid 1s_A \rangle \tag{1.67b}$$

$$S_{AA} = S_{BB} = \langle 1s_A \mid 1s_A \rangle = \langle 1s_B \mid 1s_B \rangle = 1 \text{ for normalized 1s orbitals} \tag{1.68a}$$

$$S_{AB} = S_{BA} = \langle 1s_A \mid 1s_B \rangle = \langle 1s_B \mid 1s_A \rangle = S \left(\text{the "overlap integral"}\right) \tag{1.68b}$$

Plugging in the H_2^+ Hamiltonian and doing the integrals give, in atomic units,

$$H_{AA} = H_{BB} = E_{1s} + J \tag{1.69a}$$

$$H_{AB} = H_{BA} = E_{1s} S + K \tag{1.69b}$$

where

$$E_{1s} = \int d\mathbf{r} 1s_A(\mathbf{r}) \{ -\nabla^2/2 - 1/r_A \} 1s_A(\mathbf{r}) \quad \text{the ground-state H atom energy}$$

$$J = \int d\mathbf{r} 1s_A(\mathbf{r}) \{ -1/r_B + 1/R \} 1s_A(\mathbf{r}) \quad \text{the "Coulomb integral"} \tag{1.70a}$$

$$K = \int \mathrm{d}\mathbf{r} 1s_B(\mathbf{r})\{-1/r_B + 1/R\}1s_A(\mathbf{r}) \quad \text{the "exchange integral"} \tag{1.70b}$$

Therefore the determinant to be solved becomes

$$\begin{vmatrix} E_{1s} + J - E & E_{1s}S + K - ES \\ E_{1s}S + K - ES & E_{1s} + J - E \end{vmatrix} = 0 \tag{1.71}$$

which we can solve to find two values of E,

$$E_{\pm} = E_{1s} + \frac{J \pm K}{1 \pm S} \tag{1.72}$$

with E_+ being lower than E_-. Going back and solving for the coefficients, we find $|c_A| = |c_B|$ as required by the symmetry of the problem, and the wavefunctions are $\psi_{\pm} = c_{\pm}(1s_A \pm 1s_B)$ where $c_{\pm}$ are overall normalization constants that are different for the two solutions. These are referred to as MOs which have the explicit form of linear combinations of atomic orbitals (LCAOs). The wavefunction corresponding to the lower energy, ψ_+, has no nodes and is called a bonding orbital; ψ_- has a node halfway between the two nuclei and is called an antibonding orbital. The normalized solutions are

$$\psi_{\pm} = [2(1 \pm S)]^{-1/2}(1s_A \pm 1s_B) \tag{1.73}$$

ψ_+ is the first approximation for the ground state spatial wavefunction of H_2^+.

The simplest model for H_2 puts two electrons, spin paired, into the same kind of bonding MO that we found as the lowest-energy solution for the one-electron H_2^+ molecular ion. The wavefunction must be antisymmetric with respect to interchange of electrons, and is most easily written as a Slater determinant. Expanding this determinant gives a wavefunction that factors into a product of spin and space parts,

$$\Psi(1,2) = \psi_+(1)\psi_+(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2} \tag{1.74}$$

The ground-state energy of H_2 at this level of approximation is given by $E = \int \mathrm{d}r_1\, \mathrm{d}r_2\, \Psi(1,2)\hat{H}_{H_2}\Psi(1,2)$, with $\hat{H}_{H_2}$ being the Hamiltonian for H_2, given within the Born-Oppenheimer approximation in atomic units by

$$\hat{H}_{H_2} = -\nabla_1^2/2 - \nabla_2^2/2 - 1/r_{1A} - 1/r_{1B} - 1/r_{2A} - 1/r_{2B} + 1/r_{12} + 1/R \tag{1.75}$$

The result for the energy, after doing the integrals, is that the binding energy (the difference in energy between the H_2 molecule and two isolated H atoms) is 260 kJ mol^{-1} and the equilibrium nuclear separation is $R_e = 1.61a_0 = 0.85$ Å, compared

with experimental values of 457 kJ mol^{-1} and $R_e = 0.74$ Å. This is a pretty bad estimate for the energy, for two reasons. First, the best functional form for the one-electron MO is not a simple sum of two 1s AOs. This was also a reason given for the bad result for H_2^+. But H_2 has a second problem, and that is that the real wavefunction is not just a Slater determinant where the spatial wavefunction is a product of two one-electron orbitals. In the real wavefunction, there is correlation between the motions of the two electrons due to their repulsive interaction. A number of different methods are used to handle this electron correlation in quantum chemistry calculations.

A useful first approximation to the ground-state wavefunctions of other homonuclear diatomic molecules is obtained by constructing MOs as plus and minus combinations of the hydrogenlike AOs. The MOs found for H_2^+, ψ_+, and ψ_-, are the two lowest-energy such orbitals, being constructed from the 1s hydrogenlike AOs. A similar pair of MOs can be made by taking the plus and minus combinations of the 2s hydrogenlike orbitals. Six more MOs can be formed from each of the three pairs of 2p orbitals. For symmetry reasons, p_x orbitals combine only with p_x, p_y with p_y, and p_z with p_z. This is because one type of p orbital on one atom has zero overlap integral with different type of p orbital on the other atom. Thus we build up a set of MOs, ordered according to their energies. First approximations to the ground-state wavefunctions of higher diatomic molecules are then constructed by putting two electrons with opposite spin into each MO, starting from the lowest-energy MOs and working up.

In principle one could form MOs from linear combinations of different AOs – e.g. a 1s orbital on one atom and a 2s on another atom. However, because the isolated 1s and 2s orbitals have quite different energies, they do not "couple" strongly to make MOs – the MOs formed from them turn out to be nearly the same as the original AOs, and the plus (bonding) combination is higher in energy than the plus combination formed from two 1s orbitals.

To get the best possible wavefunction, one uses a trial function that is a linear combination of a very large number of basis functions – hydrogenlike orbitals, Slater-type orbitals, Gaussian-type orbitals, etc. – and uses the variational method to find the best values of the coefficients. For example, for a homonuclear diatomic, one might use a trial function of the type

$$\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B + c_5 2pz_A + c_6 2pz_B + c_7 3s_A + c_8 3s_B$$

Employing the variational method then gives eight different energies, corresponding to the orbital energies, and eight different sets of coefficients $\{c_n\}$ describing the orbitals. What is found is that the lowest-energy orbital is mostly $1s_A + 1s_B$ with some other stuff mixed in, the next lowest is mostly $1s_A - 1s_B$, etc.

1.12 Energies and Time Scales; Separation of Motions

A molecule consists of a collection of nuclei and electrons. The first step in describing its spectroscopy is generally to factor out the CM motion, defining a new coordinate system that has its origin at the molecule's CM. The total Hamiltonian can then be written as a sum of the kinetic energy of motion of the CM and the kinetic and potential energies of motion relative to that CM. The CM motion is not very interesting and for most purposes not very important and we will not consider it further. From now on, we will treat the molecule's CM as fixed – in other words, let the coordinate system move with the CM.

One then typically makes the Born-Oppenheimer approximation as mentioned earlier. This consists of assuming that the total position–space wavefunction for the electrons and the nuclei can be factored into a function of the electronic positions $\mathbf{r}$ and the nuclear positions $\mathbf{R}$:

$$\Psi(\mathbf{r},\mathbf{R}) \approx \psi_{\text{nuc}}(\mathbf{R})\psi_{\text{elec}}(\mathbf{r};\mathbf{R}) \tag{1.76}$$

The notation $(\mathbf{r};\mathbf{R})$ means that ψ_{elec} is explicitly a function of $\mathbf{r}$ only but depends parametrically on the nuclear coordinates $\mathbf{R}$. The Born-Oppenheimer approximation is based on an approximate separation of time scales between nuclear and electronic motions. The electronic wavefunction does depend on the nuclear positions, but as the nuclei move, the electrons are able to keep up with that motion such that the electronic wavefunction is always at "equilibrium" with the nuclear motion. The idea that the electronic wavefunction adjusts itself instantaneously to keep up with the nuclei is also known as the adiabatic approximation. The nuclear wavefunction, on the other hand, depends on what the electrons are doing but not *explicitly* on their positions since the electrons move so fast that all the nuclei see is their blurred-out average charge distribution. The combination of the nuclear–nuclear repulsions and the attraction of the nuclei to this averaged electron distribution produces a potential energy surface, $V(\mathbf{R})$, on which the nuclei move. It is different for each electronic state.

This separation of time scales implies a hierarchy of states and also of energy separations. Different electronic states tend to be widely spaced in energy (thousands to tens of thousands of cm^{-1}), and each state has an energy that depends on the internal coordinates $\mathbf{Q}$; this energy dependence, together with the internuclear repulsions, defines a potential surface $V(\mathbf{Q})$ for vibrational motion. Each electronic state has its own set of vibrational states, which are usually more closely spaced in energy (10–3000 cm^{-1}). Therefore, one can sensibly talk about making transitions between different vibrational levels of the same electronic state. However, when considering a transition that changes the electronic state, we also have to consider what happens to the vibrations, since the effective Hamiltonians for nuclear motion are often quite different in different electronic states.

Problems

1 Consider a quantum-mechanical system in the state

$$\Psi = \frac{1}{\sqrt{5}}(\phi_1 + 2\phi_2)$$

where ϕ_1 and ϕ_2 are normalized eigenstates of the Hamiltonian with energy eigenvalues E and $2E$, respectively. Calculate the expectation value of the energy.

2 Find the expectation value of the energy of the state defined by $\Psi = \hat{q}\phi_v$, where ϕ_v is an eigenstate of the one-dimensional harmonic oscillator (arbitrary v) and $\hat{q}$ is the reduced position operator, $\hat{q} = (\mu\omega/\hbar)^{1/2}\hat{x}$. Hint: write $\hat{q}$ in terms of the harmonic oscillator raising and lowering operators.

3 Consider a simple model for an electron in a symmetric linear triatomic molecule,

$$\mathrm{A-B-C}$$

and assume that the electron can be described by a basis $\{\varphi_A, \varphi_B, \varphi_C\}$, denoting three orthonormal states localized on atoms A, B, and C. When we neglect "tunneling" of the electron from one center to another, its energy is described by the zero-order Hamiltonian $\hat{H}_0$ whose eigenstates and eigenvalues are

$$\hat{H}_0\,\varphi_A = E_0\,\varphi_A \quad \hat{H}_0\,\varphi_B = E_0\,\varphi_B \quad \hat{H}_0\,\varphi_C = E_0\,\varphi_C$$

The coupling is described by an additional Hamiltonian $\hat{W}$ defined by

$$\hat{W}\varphi_A = -\varepsilon\varphi_B \quad \hat{W}\varphi_B = -\varepsilon(\varphi_A + \varphi_C) \quad \hat{W}\varphi_C = -\varepsilon\varphi_B$$

where ε is a real positive constant having units of energy. Find the eigenvalues and eigenvectors of the total Hamiltonian, $\hat{H}_{\text{total}} = \hat{H}_0 + \hat{W}$.

4 Find the expectation values $\langle\hat{p}_i\rangle$ and $\langle\hat{p}_i^{\,2}\rangle$ for each of the three components of the linear momentum ($i = x$, y, or z) for an arbitrary energy eigenstate of a three-dimensional particle in a box having sides of length a, b, and c.

5 What are the degeneracies of the first four energy levels of a three-dimensional particle in a box with sides of length $a = b = 1.5c$?

6 Use raising and lowering operators to find general expressions for the expectation values $\langle\hat{x}^2\rangle$ and $\langle\hat{x}^4\rangle$ for a one-dimensional harmonic oscillator.

Express your results in terms of the inverse length parameter $\alpha = (k\mu/\hbar^2)^{1/2}$ and the quantum number v.

7 The force constant of $^{79}Br^{79}Br$ is 240 N m^{-1} and the equilibrium bond length is 2.28 Å. Calculate the fundamental vibrational frequency ω in radians per second, the period of one full vibration in picoseconds, and the zero-point energy in joules per mole, electron volts, and wavenumbers. Also, find the root-mean-square displacement, $\langle \hat{x}^2 \rangle^{1/2}$, of this oscillator in its $v = 0$ state and express it as a percentage of the equilibrium bond length.

8 Show that the sum of the probability densities of the three 2p hydrogen atom orbitals is spherically symmetric by using the explicit forms for the complex wavefunctions. This is a special case of the general theorem

$$\sum_{m=-\ell}^{\ell} \left| Y_\ell^m(\theta, \varphi) \right|^2 = \text{constant}$$

known as Unsöld's theorem. Use this result to show that the sum of the probability densities for all the $n = 2$ hydrogen atom wavefunctions is spherically symmetric. Do you expect this to hold for other values of n? Explain.

9 Calculate the expectation value of the electron–nuclear separation, $\langle \hat{r} \rangle$, for the hydrogen atom in states $(n, \ell, m) = (2, 1, 1)$, $(2, 1, 0)$, and $(2, 0, 0)$.

10 The Hamiltonian for a hydrogen atom in an external magnetic field along the z axis is given by

$$\hat{H} = \hat{H}_0 + (\beta_B B_z/\hbar)\hat{L}_z$$

where $\hat{H}_0$ is the Hamiltonian for the hydrogen atom in the absence of the external field. β_B is the Bohr magneton, a constant having units of joules per tesla (J T^{-1}), and B_z is the strength of the external magnetic field in units of T. Find the eigenfunctions and eigenvalues of $\hat{H}$.

11 Consider the anharmonic oscillator defined by the potential

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}\delta x^4$$

where γ and δ are small constants.

(a) Use perturbation theory to estimate the ground-state energy to first order in the perturbation.

(b) Use the variational method to estimate the ground-state energy, taking a trial function of the form $\phi(x) = c_0\psi_0(x) + c_2\psi_2(x)$ where ψ_0 and ψ_2 are the

$v = 0$ and $v = 2$ eigenfunctions of the corresponding harmonic oscillator and c_0 and c_2 are variational parameters.

12 In terms of the two spatial molecular orbitals

$$\psi_+ = [2(1+S)]^{-1/2}(1s_A + 1s_B) \quad \text{and} \quad \psi_- = [2(1-S)]^{-1/2}(1s_A - 1s_B)$$

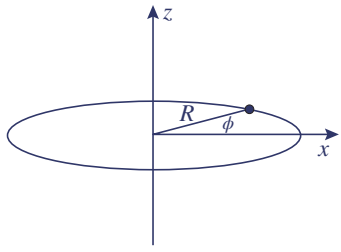
and the spin functions α and β,

(a) Write the wavefunction $\Psi(1, 2)$ that corresponds to the ground state of the H_2 molecule as a normalized Slater determinant.

(b) Write the three components of the wavefunction that correspond to the lowest energy triplet state of the H_2 molecule as normalized Slater determinants. In some cases, a linear combination of Slater determinants may be required.

(c) Write the two equivalent Slater determinants that correspond to the lowest energy singlet excited configurations of H_2. These differ only in the association of spin states with spatial functions.

13 Using your result for Problem 12(a), calculate the probability that when an H_2 molecule is in its ground electronic state, both electrons are found on the same atom (i.e. in either $1s_A$ or $1s_B$). Does this probability depend on the internuclear separation R? Discuss what this means physically.



14 A variation on the particle in a box problem is the particle on a ring, where a particle of mass m is constrained to move in the xy plane on a ring of radius R. The position of the particle is defined by a single angular variable φ. The Hamiltonian is given by $\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}$ where $I = mR^2$ is the moment of inertia.

(a) Find the eigenvalues and eigenfunctions of this Hamiltonian.

(b) Consider the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2} + k\sin^2\varphi$ where k is a constant. Use first-order perturbation theory to estimate the three lowest energy levels of this Hamiltonian.

15 The vibrational motion of a diatomic molecule having reduced mass μ and equilibrium bond length R_e can be well represented as a harmonic oscillator. The Hamiltonian is $\hat{H}_a(R) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}k(R-R_e)^2$. The system starts out in the ground state of this harmonic oscillator potential, $\psi_0(R)$.

(a) The potential function is changed suddenly by adding a new term, $\hat{V}'(R) = -\gamma R$ where γ is a constant. Show that this new Hamiltonian, $\hat{H}_b(R) = \hat{H}_a(R) + \hat{V}'(R)$, still represents a harmonic oscillator with an added constant potential and a different equilibrium bond length.

(b) What is the probability that the molecule initially in $\psi_0(R)$ will be found in the ground state of this new harmonic oscillator potential?

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