

Basic Quantum Mechanics

Part I. Where Schrodinger's equation comes from.

A. Planck's quantum hypothesis, formulated in 1900, was that exchange of energy between an electromagnetic radiation field and atoms or molecules occurred in discrete amounts. Thus, not only were atomic oscillators quantized, but light waves could also be pictured as streams of massless particles or light quanta called photons. In Planck's model, the energy carried by a photon is proportional to the **frequency** of the classical wave field:

$$E_{\text{ph}} = h \nu \quad \text{or} \quad E_{\text{ph}} = \hbar \omega, \quad \text{eq. 1}$$

where h is Planck's constant, 6.62×10^{-34} Joule-sec, and $\hbar = h/2\pi$.

B. De Broglie's hypothesis, advanced in 1925, extended Planck's idea to material particles; All particles have wavelike properties. Specifically a particle's **wavelength** is inversely proportional to its **momentum**:

$$p = h / \lambda \quad \text{or, in vector form,} \quad \mathbf{p} = \hbar \mathbf{k} \quad \text{eq. 2}$$

where \mathbf{k} is the **wave vector** that points in the direction of wave propagation. The norm of \mathbf{k} is simply $k = 2\pi/\lambda$. De Broglie's definition of momentum for massive particles is identical to the definition of linear momentum for photons, which are massless.

In De Broglie's model, a **free particle**, which by definition has a perfectly defined momentum and perfectly defined frequency, is represented by a **plane-wave field**:

$$U(x, t) = U_0 \cos[k x - \omega t + \phi] \quad \text{eq. 3}$$

$$\begin{aligned} \text{momentum} &= p = \hbar k & \text{frequency} &= \omega = 2\pi\nu \\ \text{peak amplitude} &= U_0 & \text{phase shift} &= \phi \end{aligned}$$

$U(x,t)$ is a real-valued **wavefunction** representing the plane wave field at any location in space, and at any instant of time. In complex notation (see Note 3):

$$U(x, t) = U_0 e^{i[kx - \omega t]} \quad \text{eq. 4}$$

In optics, the **real part of U** represents the physical amplitude of the wave field, usually the electric or magnetic field strength. In quantum mechanics, the wavefunction represents a

complex-valued **probability amplitude** that is not directly detectable. In the example given, the plane wave propagates in the x-direction. The term $(kx - \omega t)$ can also be written $k(x - vt)$, from which the **wave speed** is seen to be $v = \omega/k$.

Note I.1: In accord with **Heisenberg's uncertainty principle**, the perfectly defined momentum requires the particle location to be completely undefined - i.e., the wavefunction extends throughout all space with no attenuation in amplitude. This is certainly true for plane waves represented by sine or cosine functions (such as in eq. 3 or eq. 4). If a single free particle is represented by a infinite plane wave field, then the field amplitude must be vanishingly small - otherwise, there could be no normalization. Therefore, plane wave components will generally represent *differential* contributions to a **superposition** that 'localizes' a particle by interference. The resulting wavefunction would be square-integrable and normalizable.

Note I.2: This example applies equally well to photons, where $U(x,t)$ is the amplitude of a plane-wave field that (in this example) propagates in the +x direction. However, in this case, an infinite plane-wave field such as eq. 4 represents a 'stream' of coherent, monochromatic photons, not a single photon. For photons, the frequency and wavelength are related by c , the speed of light:

$$\omega = k c = (2 \pi / \lambda) c \quad \text{or} \quad v \lambda = c$$

Note I.3: $e^{i\theta}$ represents both cosine and sine waves as $\cos \theta + i \sin \theta$. In this way, any phase shift (ϕ) can be represented by a phase factor, $e^{i\phi}$, applied to eq. 4.

C. Suppose now that a material particle, such as an electron in an atom, is to be represented by a wavefunction $U_{el}(x, t)$. In this case, the electron is quite localized due to the attractive potential of the nucleus, therefore we know that U_{el} will not be as simple as a plane-wave field. However, in the simplest case, U_{el} may be a **linear superposition** of plane waves having a range of wavelengths (equivalent to a range of momenta). In one dimension:

$$dU_{el}(x, t) = \mathcal{A}(k) e^{i[kx - \omega t]} dk$$

or

$$U_{el}(x, t) = \int \mathcal{A}(k) e^{i[kx - \omega t]} dk, \quad \text{eq. 5}$$

where $\mathcal{A}(k)$ is a weighting function for different plane-wave components. Using De Broglie's relation [eq. 2] to express k as p/\hbar , Planck's relation [eq. 1] to express ω as E/\hbar , and making a change of variable in the integral from k to p :

$$U_{el}(x, t) = \int A(p) e^{(i/\hbar)[px - Et]} dp, \quad \text{eq. 6}$$

where $A(p)$ is now the weighting function for the different momentum components. This representation of the wavefunction is interesting because it depends not only on the De Broglie relation, but also on extending Planck's relation (for monochromatic photons) to a wavefunction

that represents a material particle, and which is not 'monochromatic' in the usual sense.

Picturing the electron as a classical particle, both its momentum and kinetic energy will change as it moves along any path over which the potential energy varies. However, we assume that the total energy, E , is conserved. Additionally, we assume that the potential energy is a static scalar field, $V(x)$:

$$\begin{aligned}
 E &= \text{Kinetic energy} + \text{Potential energy} = \text{Total energy (a constant)} \\
 &= T + V \\
 &= p^2/2m + V(x) \qquad \qquad \qquad \text{eq. 7}
 \end{aligned}$$

D. Look for a relation between U_{el} and the energy of the electron. The **time-derivative** of U_{el} consists of two terms that are related to kinetic and potential energy:

$$\begin{aligned}
 \partial U_{el}(x, t)/\partial t &= -(i/\hbar) \int E A(p) e^{(i/\hbar)[px - Et]} dp \\
 &= -(i/\hbar) \int \{ p^2/2m + V(x) \} A(p) e^{(i/\hbar)[px - Et]} dp \\
 &= -(i/\hbar) \int (p^2/2m) A(p) e^{(i/\hbar)[px - Et]} dp \\
 &\qquad \qquad \qquad + V(x) \int A(p) e^{(i/\hbar)[px - Et]} dp
 \end{aligned}$$

where $V(x)$ can be factored from the integral because it does not depend upon p .

The kinetic energy term is related to the second spatial derivative of U_{el} :

$$\begin{aligned}
 \partial U_{el}(x, t)/\partial x &= (\partial/\partial x) \int A(p) e^{(i/\hbar)[px - Et]} dp \\
 &= (i/\hbar) \int p A(p) e^{(i/\hbar)[px - Et]} dp \\
 \partial^2 U_{el}(x, t)/\partial x^2 &= -(1/\hbar^2) \int p^2 A(p) e^{(i/\hbar)[px - Et]} dp \\
 &= -(1/\hbar^2) \int p^2 A(p) e^{(i/\hbar)[px - Et]} dp \\
 &= -(2m/\hbar^2) \int (p^2/2m) A(p) e^{(i/\hbar)[px - Et]} dp
 \end{aligned}$$

Comparing terms between $\partial U_{el}(x, t)/\partial t$ and $\partial^2 U_{el}(x, t)/\partial x^2$:

$$i \hbar \partial U_{el}/\partial t = -(\hbar^2/2m) \partial^2 U_{el}/\partial x^2 + V(x) \int A(p) e^{(i/\hbar)[px - Et]} dp$$

and, recognizing that the right-hand term is simply $V(x) U_{el}(x,t)$:

$i \hbar \partial U_{el}/\partial t = -(\hbar^2/2m) \partial^2 U_{el}/\partial x^2 + V(x) U_{el}$	This result is the Time-Dependent Schrodinger Equation (TDSE) in one dimension, for a single particle.
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eq. 8

The TDSE is the central dynamical equation of non-relativistic quantum mechanics. It is a differential equation that defines the wavefunction of a particle in terms of its mass and its interaction potential. We arrived at this point by use of only three concepts; (1) Planck's idea of energy quanta, (2) De Broglie's idea of momentum and wavelength, and (3) the principle of wave superposition to represent the mixing of fixed-momentum (plane wave) states.

Note I.4: The two terms on the right-hand side of Schrodinger's equation represent, respectively, the local kinetic and potential energy of the electron. Strictly, however, they are not energy densities (see section I. E.).

E. The wavefunction U_{el} can be thought of as representing a **probability amplitude** for the electron, analogous to the electric field amplitude for a light wave. The **squared norm** of U_{el} is therefore analogous to the **intensity** of light, which is proportional to the square of field strength. $\|U_{el}\|^2$ thus represents the **probability density** for the localization of the electron (just as the intensity of light represents the density of photons):

$$\text{electron density} = \|U_{el}\|^2 = U_{el} U_{el}^* \quad \text{eq. 9}$$

Part II. Stationary states.

F. The TDSE, like most differential equations, has a vast number of possible solutions. A particularly important group are wavefunctions that are analogous to **standing waves**. Wavefunctions of this type describe the stationary states, or stable orbits of an electron in an atom or molecule. A standing wave, such as may appear on a plucked guitar string, or in optics as a stationary **interference pattern**, consists of a fixed spatial pattern that oscillates in time. Mathematically, the wavefunction for a stationary state therefore can be separated into the **product** of a real-valued spatial factor and a time-harmonic factor:

$$\begin{aligned}
 U_{ss}(x, t) &= \Phi(x) e^{-i\omega t} \\
 &= (\text{fixed spatial pattern}) \times (\text{temporal sinewave})
 \end{aligned}
 \quad \text{eq. 10}$$

where, using Planck's relation, the oscillation frequency is proportional to the **energy** of the stationary state:

$$E = \hbar \omega \quad \text{or} \quad \omega = E / \hbar .$$

Putting $U_{ss}(x, t)$ into the TDSE as a trial wavefunction takes out the temporal factor, and produces a Schrodinger equation for $\Phi(x)$:

$E \Phi(x) = -(\hbar^2/2m) \partial^2\Phi(x)/\partial x^2 + V(x) \Phi(x)$	This result is the Time-Independent Schrodinger Equation (TISE) in one dimension, for a single particle.
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eq. 11

Note II.1: Solutions to the TISE are the **spatial orbital amplitudes**, $\Phi(x)$. However, the complete wavefunction **always** includes the temporal factor. The oscillation frequency is determined for the stationary state by the value of E for that state. Normally, the wavefunction is denoted ψ rather than U:

$$\psi_{ss}(x, t) = \Phi(x) e^{-i(E/\hbar)t} \quad \text{eq. 12}$$

Note II.2: Schrodinger's equation is often written in operator form; Defining

$$\mathbf{H} = -(\hbar^2/2m) \partial^2/\partial x^2 + V(x) \quad \text{eq. 13}$$

as the **Hamiltonian operator**, the time-independent Schrodinger equation can be written as:

$$\mathbf{H} \Phi(x) = E \Phi(x) \quad \text{eq. 14}$$

where it can now be seen that E must be an **eigenvalue** of the operator \mathbf{H} , and $\Phi(x)$ must be the corresponding **eigenfunction** (or eigenvector) of \mathbf{H} . In general, an infinite set of discrete solutions to Eq. 14 will be found, indexed by at least one **quantum number**:

$$\mathbf{H} \Phi_n(x) = E_n \Phi_n(x) \quad \text{eq. 14b}$$

It turns out that the Hamiltonian operator, \mathbf{H} , and other quantum-mechanical operators are **Hermitian** (self-adjoint), so that the set of eigenfunctions constitutes a complete, **orthogonal** basis in an infinite-dimensional Hilbert space. Orthogonality of the eigenfunctions is analogous to orthogonality of \mathbf{x} , \mathbf{y} , and \mathbf{z} unit vectors in conventional 3D space; the projection of one vector onto one of the others gives a zero result:

$$\mathbf{x} \cdot \mathbf{y} = 0 \quad \mathbf{x} \cdot \mathbf{x} = 1$$

$$\int (\Phi_m^*) \Phi_n dx = 0, \text{ for } m \neq n$$

Since each orbital function, $\Phi_n(x)$, represents the amplitude of the wave field for a single particle (electron), the function is usually normalized to 1 in the same way as a unit vector:

$$\int (\Phi_n^*) \Phi_n dx = 1$$

Note II.3: Extension of Schrodinger's equation to three dimensions is straightforward. With $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 = \nabla^2$:

$$i \hbar \partial\psi(\underline{r}, t)/\partial t = -(\hbar^2/2m) \nabla^2 \psi(\underline{r}, t) + V(\underline{r}) \psi(\underline{r}, t) \quad \text{TDSE}$$

and

$$E \Phi(\underline{r}) = -(\hbar^2/2m) \nabla^2 \Phi(\underline{r}) + V(\underline{r}) \Phi(\underline{r}) \quad \text{TISE}$$

Note II.4: For multi-electron atoms and molecules, multi-particle Schrodinger equations can be formulated in a straightforward procedure.

Part III. Solutions to Schrodinger's equation.

Almost all treatments of atomic and molecular quantum mechanics begin with discussion of three systems for which explicit stationary-state solutions to Schrodinger's equation can be obtained; the Particle-in-a-Box, the Harmonic Oscillator, and the Hydrogen Atom.

G. The particle-in-a-box.

The particle-in-a-box (PB) model can be solved in 1-, 2-, or 3- dimensions, and for finitely-deep potential wells as well as for perfectly-reflecting barriers. In optics, this model describes the wavefunctions of a photon between two parallel mirrors. In chemical physics, the PB model has been applied to many organic, metallic, and semiconductor systems. Notably, it provides an approximate, but useful molecular-orbital description for conjugated bond systems.

The simplest PB model is one-dimensional, with infinite-potential (perfectly reflecting) barriers. The box length, 'a', spans $[-a/2, +a/2]$ on the x-axis. Inside the box, $V(x) = 0$, whereas $V(x)$ is infinite at the boundaries. The time-independent Schrodinger equation (TISE) for this system

then takes the simple form:

$$-(\hbar^2/2m) \partial^2\Phi(x)/\partial x^2 = E \Phi(x). \quad \text{eq. 15}$$

With the boundary condition that $\Phi(x) = 0$ at the box walls (i.e., $\Phi(\pm a/2) = 0$), the solution of Eq. 15 is found to be a **quantized** set of sinusoidal functions each with a corresponding stationary-state energy:

$$\Phi_n(x) = N \cos[n \pi x/a] \quad \text{for } -a/2 < x < a/2 \quad n = 1, 3, 5, 7, \dots \quad \text{eq. 16a}$$

$$\Phi_n(x) = N \sin[n \pi x/a] \quad \text{for } -a/2 < x < a/2 \quad n = 2, 4, 6, 8, \dots \quad \text{eq. 16b}$$

and $\Phi_n(x) = 0$ outside the box (all n).

For each spatial wavefunction $\Phi_n(x)$, there is a corresponding quantized energy:

$$E_n = \hbar^2 n^2 / 8 m a^2 \quad \text{eq. 17}$$

Several fundamental points can be made regarding this set of wavefunctions:

1. Each wavefunction and energy level is defined by its **quantum number, n**, which can take on the integer values 1, 2, 3, 4, Therefore,

$$\Phi_1(x) = N_1 \cos[\pi x/a]$$

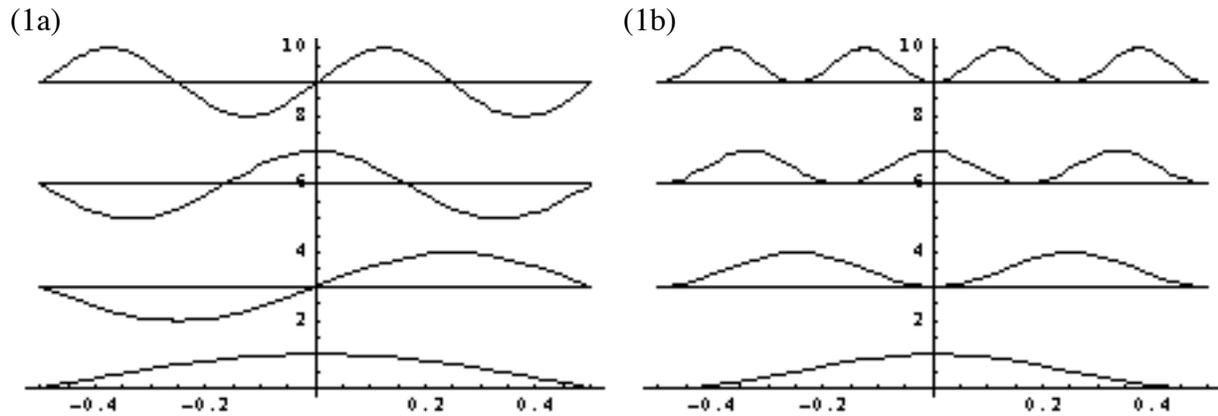
$$\Phi_2(x) = N_2 \sin[2 \pi x/a]$$

$$\Phi_3(x) = N_3 \cos[3 \pi x/a]$$

$$\Phi_4(x) = N_4 \sin[4 \pi x/a] \quad \dots \text{ etc.}$$

These are shown graphically in **Figure 1a**, for the first four stationary states of the particle. **Figure 1b** shows $\|\Phi_n\|^2$, the probability density function for each state. It can be seen that, in the ground state, the particle is localized around the center of the box. With increasing quantum number, the density becomes more evenly distributed between the box walls. However, for every case except Φ_1 , the wavefunction always includes nodes of zero amplitude within the box

(in addition to the nodes at the walls).



2. There is **no state** for which the energy of the particle is zero; The energy of the **ground state**, E_1 (the lowest-energy state of the particle), is greater than zero. The quantized energy levels increase as the square of the quantum number; $E_2 = 4E_1$, $E_3 = 9E_1$, ...etc. If the box is reduced in size, the energy levels rise.

3. As defined by Eq. 12, the complete wavefunction for each stationary state is equal to $\Phi_n(x)$ multiplied by the oscillating factor $\exp[-i(E_n/\hbar)t]$. Since $\exp[-i(E_n/\hbar)t]$ equals $\cos[(E_n/\hbar)t] - i \sin[(E_n/\hbar)t]$, (E_n/\hbar) is therefore the **oscillation frequency** in radians/sec:

$$\begin{aligned} \Psi_n(x, t) &= N \cos[n \pi x/a] \exp[-i (E_n/\hbar) t] & n = 1, 3, 5, 7, \dots \\ \Psi_n(x, t) &= N \sin[n \pi x/a] \exp[-i (E_n/\hbar) t] & n = 2, 4, 6, 8, \dots \end{aligned} \quad \text{eqs. 18}$$

where

$$\begin{aligned} \omega_n &= E_n/\hbar &= 2\pi h n^2/8ma^2 & \text{radians/sec} \\ \text{or} \\ \nu_n &= E_n/h &= h n^2/8ma^2 & \text{cycles/sec.} \end{aligned} \quad \text{eqs. 19}$$

For a box that is 10 Angstroms in length, and a particle having the mass of an electron (9.11×10^{-31} kg), the ground-state wavefunction oscillates at $\nu_1 = 9.08 \times 10^{13}$ cycles/sec (90.8 THz). If the box is reduced to 1 Angstrom, about the size of an atom, the frequency would be 100-fold higher, 9.08×10^{15} Hz.

4. Each wavefunction has an amplitude N that is set by the requirement that $|\Psi_n|^2$ is the probability density function for the particle (see Section E, Eq. 9), and, therefore, the integral of

$\|\Psi_n\|^2$ over the length of the box ($x = -a/2$ to $x = a/2$) must equal 1:

$$\begin{aligned} \int \|\Psi_n\|^2 dx &= \int (\Psi_n^*) \Psi_n dx \\ &= N^2 \int \cos^2[n \pi x/a] dx \quad \text{or} \quad N^2 \int \sin^2[n \pi x/a] dx \\ &= N^2 (a/2) = 1. \end{aligned}$$

In this case the non-normalized integral is independent of 'n', and is equal to $a/2$. Thus, for normalization, $N = (2/a)^{1/2}$. Therefore, within the box, the **complete single-particle wavefunctions** are:

$$\begin{aligned} \Psi_n(x, t) &= (2/a)^{1/2} \cos[n \pi x/a] \exp[-i (E_n/\hbar) t] & n = 1, 3, 5, 7, \dots \\ \Psi_n(x, t) &= (2/a)^{1/2} \sin[n \pi x/a] \exp[-i (E_n/\hbar) t] & n = 2, 4, 6, 8, \dots \end{aligned} \quad \text{eqs. 20}$$

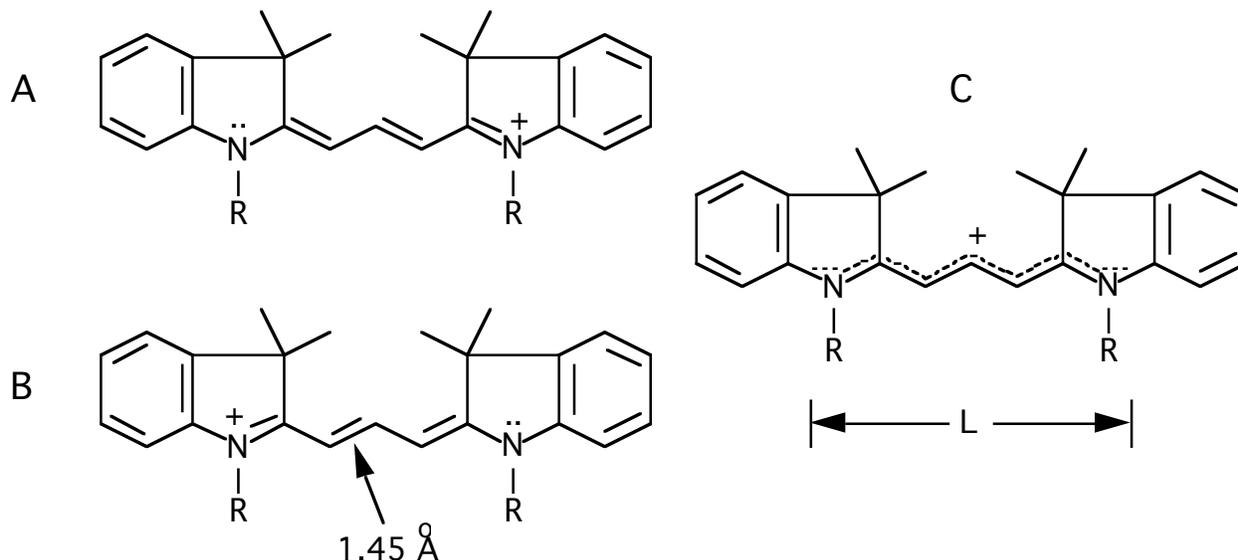
5. For finite-potential boxes, $\Phi_n(x)$ is generally not zero on or outside of the box walls, but may drop to zero exponentially in the 'out-of-box' region. This phenomenon is known as tunneling, and is analogous to evanescent waves in classical optics.

6. The stationary-state spatial wavefunctions for the particle-in-a-box are mutually **orthogonal**, and, in fact, constitute an **orthonormal basis set** for the 1D box. They show alternating even/odd **parity** with respect to the center of the box; The ground-state wavefunction and other odd-numbered wavefunctions have even parity. The even-numbered wavefunctions have odd parity.

7. The particle-in-a-box wavefunctions are identical in *spatial* form to the standing waves set up on a plucked guitar string of length 'a'. The ground-state spatial wavefunction, Φ_1 , corresponds to the fundamental vibration mode of the string; Φ_2 to the second harmonic, Φ_3 to the 3rd, etc. However, the analogy is not perfect; The oscillation frequencies of the string modes are harmonically related ($\omega_n = (n\pi/a)(T/\mu)^{1/2}$, where T is the string tension and μ is the string mass per unit length), whereas the quantum wavefunction oscillation frequencies grow with n^2 (eq. 19) in the case of a simple box.

8. Particle-in-a-box (PB) model for linear cyanine dyes: H. Kuhn showed in the 1940s that the peak absorption wavelengths for cyanine dyes were accurately given by a PB model. Electrons in conjugated π -bonds along the nitrogen-terminated polymethine chain act as free particles in a 1-dimensional box of length "L" (as shown) with reflecting ends:

di-indocarbocyanine-3



In the ground state, electrons fill the lowest PB orbitals in accord with the Exclusion Principle; two electrons with opposite spin in each. Thus, for example, the cyanine dye shown, having 8 electrons in the box (6 electrons in the 3 Pi bonds, plus 2 electrons on the 'other' nitrogen atom), would have filled PB orbitals 1 through 4. The lowest-energy transition of this molecule would then be 1-electron excitation from $\Phi_4 \rightarrow \Phi_5$, i.e., from the **highest occupied molecular orbital** (HOMO) to the **lowest unoccupied molecular orbital** (LUMO). If excitation from $\Phi_n \rightarrow \Phi_{n+1}$ occurs via electric dipole interaction (absorption of a photon), the photon energy must equal the energy difference between the LUMO and the HOMO; $\Delta E_{\text{photon}} = E_{n+1} - E_n$.

$$\Delta E_{n \rightarrow n+1} = hc/\lambda = (h^2/8mL^2) ((n+1)^2 - n^2) = (2n + 1) h^2/8mL^2$$

For the dye molecule shown, the transition energy would be $E_5 - E_4 = 9h^2/8mL^2$.

9. Of the many possible transitions between energy levels, only certain ones are seen spectroscopically, and not all with equal extinction or intensity. For simple quantum systems such as "electron in a box", an elementary analysis gives the **selection rules** and **transition moments** which determine, respectively, which transitions may occur, and, of these, their relative strengths. For electrons in a 1-D box, it can be shown that excitation by absorption of a photon, or de-excitation by emission of light depends upon the degree to which the final-state wavefunction, $\Psi_{\text{final}}(x,t)$, resembles the result of the 1-electron dipole moment operator, $\mu_x(x) = ex$, acting on the initial-state wavefunction, $\Psi_{\text{initial}}(x,t)$. The degree of similarity is given by the projection of one state on the other in a **transition moment integral**:

$$M_{i \rightarrow f} = \langle \Psi_{\text{final}} | \mu_x | \Psi_{\text{initial}} \rangle \quad (-L/2 \leq x \leq L/2)$$

which can be simplified to :

$$M_{m \rightarrow n} = \int \Phi_n^*(x) e x \Phi_m(x) dx \quad (-L/2 \leq x \leq L/2) \quad \text{eq. 21}$$

for the 1-D electron-in-a-box. The dipole moment operator ex has strictly odd parity with respect to the center of the box. Since the PB orbitals have even parity for states 1, 3, 5, 7, ..., and odd parity for states 2, 4, 6, 8, ..., the selection rule can be immediately seen; all pairs of orbitals which give an odd-parity *integrand* in eq. 21 have a **zero** transition moment. Therefore, no transitions between even-parity states are allowed, and no transitions between odd-parity states. The selection rule is: Only transitions between two states of opposite parity are allowed, $m\text{-even} \rightarrow n\text{-odd}$, or $m\text{-odd} \rightarrow n\text{-even}$. When the integral is computed for two wavefunctions satisfying this condition,

$$M_{m \rightarrow n} = (8eL/\pi^2) m n / (n^2 - m^2)^2$$

and the strength of the transition is proportional to the square of M :

$$|M_{m \rightarrow n}|^2 = (8eL/\pi^2)^2 m^2 n^2 / (n^2 - m^2)^4$$

For the dye molecule shown (diI(3)), M^2 is much larger for $4 \rightarrow 5$ than for $4 \rightarrow 7$ or $3 \rightarrow 6$.

H. The harmonic oscillator.

I. The hydrogen atom.

Part IV. Pauli's exclusion principle.

indistinguishability of electrons
 antisymmetry of the total wavefunction
 two-electron wavefunctions
 Helium
 Singlets and triplets

J. In classical mechanics, individual objects are distinguishable; For example, in a dynamical model of the solar system, the sun and planets are tracked by name. However, at the level of atoms, there is a fundamental indistinguishability between like particles, whether they be electrons, protons, neutrons, atoms, or molecules (ignoring for now isotopic differences). Pauli (1925) realized that identity of like particles had far-reaching consequences, which resulted in his formulation of the Exclusion Principle. For electrons (and any other half-integer-spin particles - i.e., fermions), the Exclusion Principle requires that the total wavefunction $\Psi_{el}(\mathbf{x}_1, \mathbf{x}_2, \dots)$ be **antisymmetric** with respect to the identity of any pair of particles. In the simplest case of a 2-electron wavefunction;

$$\Psi_{el}(\mathbf{x}_1, s_1, \mathbf{x}_2, s_2) = -\Psi_{el}(\mathbf{x}_2, s_2, \mathbf{x}_1, s_1)$$

In these complete wavefunctions, the coordinates of each electron include the three spatial

coordinates, x, y, and z, and the spin coordinate which may take on one of two values, usually designated α and β , or 'up' and 'down'. In terms of atomic structure, the Exclusion Principle is often put in the form of a statement about quantum numbers: no two electrons in an atom may have the same set of quantum numbers. If two electrons have the same orbital quantum numbers (n , l , and m_l), they must differ in spin orientation (m_s). Since electrons are 'spin-1/2' particles, there are only two possible values for m_s , $+1/2$ and $-1/2$. The result is that each spatial orbital $\Phi(\mathbf{x} | n, l, m_l)$ can 'hold' no more than two electrons, one with spin 'up', and one with spin 'down'.

K. When the potential, $V(\mathbf{x})$, is independent of spin (no coupling between orbit angular momentum and spin angular momentum - generally a good approximation for light atoms), solutions to Schrodinger's equation are factorable into spatial and spin functions:

$$\Psi(\mathbf{x}, s) = \Psi(\mathbf{x}) \xi(s)$$

A trial 2-electron orbital can then be constructed as follows:

$$\Phi_{el}(\mathbf{x}_1, s_1, \mathbf{x}_2, s_2) = \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) \alpha(s_1) \beta(s_2) = \phi_a(1) \phi_b(2) \alpha(1) \beta(2)$$

which has the obvious defect that electron '1' and electron '2' are distinguishable by both spatial orbital and by spin. The required antisymmetry can be incorporated in two ways - by making the spatial 2-electron orbital antisymmetric, with a symmetric 2-electron spin function, or vice-versa:

$$\Phi_A = \phi_A(1,2) \xi_S(1,2)$$

or
$$\Phi_A = \phi_S(1,2) \xi_A(1,2)$$

Three symmetric 2-electron spin functions can be constructed very simply using the two 1-electron functions $\alpha(-)$ and $\beta(-)$:

$$\xi_S(1,2) = \alpha(1) \alpha(2)$$

$$\text{or } 2^{-1/2} \{ \alpha(1) \beta(2) + \beta(1) \alpha(2) \}$$

$$\text{or } \beta(1) \beta(2)$$

along with one antisymmetric spin function:

$$\xi_A(1,2) = 2^{-1/2} \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \}$$

Using two distinct orbital functions, $\phi_a(-)$ and $\phi_b(-)$, symmetric and antisymmetric 2-electron orbitals can also be simply constructed:

$$\begin{aligned} \phi_S(1,2) &= 2^{-1/2} \{ \phi_a(1) \phi_b(2) + \phi_b(1) \phi_a(2) \} \\ \text{and} \\ \phi_A(1,2) &= 2^{-1/2} \{ \phi_a(1) \phi_b(2) - \phi_b(1) \phi_a(2) \} \end{aligned}$$

(Note: Clearly, two additional symmetric spatial functions would be $\phi_a(1)\phi_a(2)$ and $\phi_b(1)\phi_b(2)$, discussed below.)

From this set of functions, four combinations have the required antisymmetry:

$$\begin{aligned} \Phi_A(1,2) &= 2^{-1/2} \{ \phi_a(1) \phi_b(2) + \phi_b(1) \phi_a(2) \} 2^{-1/2} \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \} \\ \text{or} & 2^{-1/2} \{ \phi_a(1) \phi_b(2) - \phi_b(1) \phi_a(2) \} \alpha(1) \alpha(2) \\ \text{or} & 2^{-1/2} \{ \phi_a(1) \phi_b(2) - \phi_b(1) \phi_a(2) \} 2^{-1/2} \{ \alpha(1) \beta(2) + \beta(1) \alpha(2) \} \\ \text{or} & 2^{-1/2} \{ \phi_a(1) \phi_b(2) - \phi_b(1) \phi_a(2) \} \beta(1) \beta(2) \end{aligned}$$

The first, which is spatially symmetric and spin-antisymmetric, has **zero total spin** ($S = 0$), and constitutes a **singlet state**. The latter three, which are spatially antisymmetric and spin-symmetric, together constitute a **triplet state** having a **total spin of one** ($S = 1$) due to two spin-unpaired electrons. Triplet states can be detected spectroscopically by the effect of an applied magnetic field.

In the case where the two electrons are in the same spatial orbital ($\phi_S(1,2) = \phi_a(1)\phi_a(2)$), the only antisymmetric wavefunction is the singlet:

$$\Phi_A(1,2) = \phi_a(1)\phi_a(2) 2^{-1/2} \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \}$$

The usual statement of this restriction is that no more than two electrons may share an orbital, and must be spin-paired (have opposite spins) when they do.

Another interesting result of the exclusion principle is that interaction between electrons is reduced in triplet states. This can be seen by noting that the spatial part of the wavefunction is antisymmetric in the triplet state. Using $\phi_A(1,2)$ as defined above, but writing in \mathbf{r}_1 and \mathbf{r}_2 explicitly for the coordinates of the two electrons,

$$\phi_A(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2} \{ \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1) \phi_a(\mathbf{r}_2) \}$$

If we look at the amplitude of the wavefunction for the condition where both electrons have the **same coordinates** (i.e., $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$):

$$\phi_A(\mathbf{r}, \mathbf{r}) = 2^{-1/2} \{ \phi_a(\mathbf{r}) \phi_b(\mathbf{r}) - \phi_b(\mathbf{r}) \phi_a(\mathbf{r}) \} = 0$$

no matter what \mathbf{r} is chosen. Thus, there is reduced electrostatic repulsion between electrons in

the triplet state, and therefore lower energy. For atoms, this is usually stated as **Hund's Rule**: given electrons in a specific set of orbitals, the lowest-energy state is the one with the highest spin multiplicity. In the energy-level diagram for **helium** (the simplest 2-electron system) Hund's Rule is evident when comparing the energy levels for helium **1-electron excited states**. This energy-level diagram includes one manifold of singlet levels (Parahelium) in which the two electrons have opposite spin, and one manifold of triplet levels (Orthohelium) in which the two electrons have parallel spin. One electron is in the **1s orbital**. If, for example, the other electron is in the **2s orbital**, the energy is lower for the **1s¹2s¹** triplet (unpaired spins) than for the **1s¹2s¹** singlet (opposite spins). It can be seen that every Orthohelium state is shifted to a slightly lower energy than the corresponding Parahelium state.

Citation for helium energy-level diagram:

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/helium.html>

"One electron is presumed to be in the ground state, the **1s** state. An electron in an upper state can have spin antiparallel to the ground state electron (S=0, singlet state, Parahelium) or parallel to the ground state electron (S=1, triplet state, Orthohelium)."

