1. Introduction
Want to describe “mechanics” of atomic-scale things, like electrons in atoms and molecules.

Why? These ultimately determine the shape, the energy, and all the properties of matter.

When do we need quantum mechanics?

de Broglie wavelength (1924)

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

\[ h = 6.626 \times 10^{-34} \text{ J s} \] (Planck's constant)

<table>
<thead>
<tr>
<th>Car</th>
<th>Electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m = 1000 \text{ kg} )</td>
<td>( 9.1 \times 10^{-31} \text{ kg} )</td>
</tr>
<tr>
<td>( v = 100 \text{ km/hr} )</td>
<td>( v = 0.01 c )</td>
</tr>
<tr>
<td>Typical value on the highway</td>
<td>Typical value in atom</td>
</tr>
<tr>
<td>( p = 2.8 \times 10^{-4} \text{ kg m/s} )</td>
<td>( p = 2.7 \times 10^{-24} \text{ kg m/s} )</td>
</tr>
<tr>
<td>( \lambda = 2.4 \times 10^{-38} \text{ m} )</td>
<td>( \lambda = 2.4 \times 10^{-10} \text{ m} )</td>
</tr>
<tr>
<td>Too small to detect. Classical object!</td>
<td>Comparable to size of atom. Must account for wave properties of an electron!</td>
</tr>
</tbody>
</table>

How to describe wave properties of an electron? Schrödinger equation (1926?)

Kinetic energy + Potential energy = Total Energy

Expressed as differential equation (Single particle, non-relativistic):

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi(r,t) + V(r,t)\Psi(r,t) = -i\hbar \frac{\partial}{\partial t} \Psi(r,t) \]

\( \Psi(r,t) \): wavefunction

Steady-state, or time-independent:

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r) \]

\[ \Psi(r,t) = \psi(r)e^{-iEt/\hbar} \]

\( E \): energy
2. Postulates of Non-relativistic Quantum Mechanics

**Postulate I:** The physical state of a system is completely described by its wavefunction $\Psi$. In general, $\Psi$ is a complex function of the spatial coordinates and time. $\Psi$ is required to be:
1. single-valued
2. continuous and twice-differentiable
3. square-integrable ($\int \Psi^* \Psi d\tau$ is defined over all finite domains)

For bound systems $\Psi$ can always be normalized such that $\int \Psi^* \Psi d\tau = 1$.

**Postulate II:** To every physically observable quantity $M$ there corresponds a Hermitian quantum mechanical operator $\hat{M}$. The only observable values of $M$ are the eigenvalues of $\hat{M}$.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Operator</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position $x, y, z$</td>
<td>$\hat{x}, \hat{y}, \hat{z}$</td>
<td>$x, y, z$</td>
</tr>
<tr>
<td>Linear momentum $p_x, \ldots$</td>
<td>$\hat{p}_x, \ldots$</td>
<td>$-i\hbar \frac{\partial}{\partial x}, \ldots$</td>
</tr>
<tr>
<td>Angular momentum $l_x, \ldots$</td>
<td>$\hat{l}_x, \ldots$</td>
<td>$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right), \ldots$</td>
</tr>
<tr>
<td>Kinetic energy $T$</td>
<td>$\hat{T}$</td>
<td>$\frac{\hbar^2}{2m} \nabla^2$</td>
</tr>
<tr>
<td>Potential energy $V$</td>
<td>$\hat{V}$</td>
<td>$V(r)$</td>
</tr>
<tr>
<td>Total energy $E$</td>
<td>$\hat{H}$</td>
<td>$-\frac{\hbar^2}{2m} \nabla^2 + V(r)$</td>
</tr>
</tbody>
</table>

**Postulate III:** If a particular observable $M$ is measured many times on many identical systems in a state $\Psi$, the average value of the result will be the expectation value of the operator $\hat{M}$:

$$\langle M \rangle = \int \Psi^* (\hat{M} \Psi) d\tau$$

**Postulate IV:** The energy-invariant states of a system are solutions of the equation

$$\hat{H} \Psi(r, t) = i\hbar \frac{\partial}{\partial t} \Psi(r, t), \quad \hat{H} = \hat{T} + \hat{V}$$

If the system is in a time-independent stationary state, this reduces to the Schrödinger equation:

$$\hat{H} \Psi(r) = E \Psi(r)$$

**Postulate V:** (The uncertainty principle.) Operators that do not commute $(\hat{A} \neq \hat{B})$ are called **conjugate**. Conjugate observables cannot be specified together to arbitrary accuracy. For example, the error (standard deviation) in the measured position and momentum of a particle must satisfy $\Delta x \Delta p_x \geq \hbar/2$. 

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3. Note on constants and units

Resource for unit conversions: http://www.digitaldutch.com/unitconverter/

Unit converter available in Calc for Gnu emacs

| Atomic units common for quantum mechanical calculations |
|-------------------------------|----------------|----------------|
| Atomic unit                  | SI unit        | Common unit    |
| Charge                       | $e = 1$        | $1.6021 \times 10^{-19}$ C |
| Length                       | $a_0 = 1$ (bohr) | $5.29177 \times 10^{-11}$ m      | $0.529177$ Å |
| Mass                         | $m_e = 1$      | $9.10938 \times 10^{-31}$ kg     |
| Angular momentum             | $\hbar = 1$   | $1.054 572 \times 10^{-34}$ J \ s |
| Energy                       | $E_h$ (hartree) | $4.359744 \times 10^{-18}$ J      | $27.2114$ eV |
| Electrostatic force          | $1/(4\pi\epsilon_0) = 1$ | $8.987552 \times 10^{9}$ C^{-2} N m^{-2} |
| Boltzmann constant           | $k_B = 1$      | $1.38065 \times 10^{-23}$ J K^{-1} | $8.31447$ J/mol K |

(see http://en.wikipedia.org/wiki/Atomic_units)

Energy units

$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J} = 96.485 \text{ kJ/mol} = 8065.5 \text{ cm}^{-1} = 11064 \text{ K} \ k_B$

4. Example: Energy states of an electron in a box

3D box $\rightarrow$ 3 degrees of freedom

$V(r) = \begin{cases} 0, & 0 < x, y, z < L \\ \infty, & x, y, z \leq 0, \ x, y, z \geq L \end{cases}$

Schrödinger eq

$$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E \psi(x, y, z)$$

$\psi(x, y, z) = 0, \quad x, y, z \leq 0, \ x, y, z \geq L$

Second-order linear partial differential equation

Boundary value (eigenvalue) problem

Separable

$\psi(x, y, z) = X(x)Y(y)Z(z)$
\[
- \frac{\hbar^2}{2m_e} \left( \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} \right) = E \quad 0 < x, y, z < L
\]

\(\text{fn} \ x + \text{fn} \ y + \text{fn} \ z = \text{constant} \rightarrow \text{each term must be constant}
\]

\[
- \frac{\hbar^2}{2m_e} \frac{\partial^2 X(x)}{\partial x^2} = E_n X(x) \quad X(0) = X(L) = 0
\]

\[X(x) = \sin \frac{n_x \pi x}{L}, \quad n_x = 1, 2, 3, \ldots\]

function that twice differentated returns itself

\[E_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2m_e L^2}\]

Solutions called \textit{eignefunctions/wavefunctions} and \textit{eigenvalues}
Characterized by \textit{quantum number}, one for each degree of freedom

\textit{Normalization} – require that wavefunction square integrates to 1

\[
C^2 \int_0^L \sin \frac{n_x \pi x}{L} dx = C^2 \langle X_{n_x} \mid X_{n_x} \rangle = 1 \Rightarrow C = \pm \sqrt{\frac{2}{L}}
\]

Dirac notation

\[X_{n_x} = \sqrt{\frac{2}{L}} \sin \frac{n_x \pi x}{L}, \quad 0 < X < L\]

Note increasing \textit{nodes} with increasing energy

\[E \propto n^2\]

\[\Delta E \propto n\]

\[\Delta E/E \propto 1/n\]

See Ho, JPC B 2005, 109, 20657.
Lecture 1

Refresher on Quantum Mechanics

3 dimensional solution

\[ \psi(x, y, z) = X(x)Y(y)Z(z) = \left(\frac{2}{L}\right)^{3/2} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L} \]

\[ E = E_x + E_y + E_z = \left(\frac{n_x^2 + n_y^2 + n_z^2}{2m_r L^2}\right) \pi^2 h^2 \]

\[ n_x, n_y, n_z = 1, 2, 3, K \]

One quantum number for each dof

Degeneracy
Symmetry
Energy levels – depend on volume \( \Rightarrow \) pressure!!