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)

$$\lambda = h/p = h/mv$$

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

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

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):

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

$\Psi(\mathbf{r},t)$: wavefunction

Steady-state, or time-independent:

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

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

E: energy

2. Postulates of Non-relativistic Quantum Mechanics

Postulate I: **The physical state of a system is completely described by its wavefunction Ψ.** In general, Ψ is a complex function of the spatial coordinates and time. Ψ 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 Ψ 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 $\hat{M}$.**

Physical quantity	Operator	Expression
Position x, y, z	$\hat{x}, \hat{y}, \hat{z}$	$x\cdot, y\cdot, z\cdot$
Linear momentum p_x, …	$\hat{p}_x$, …	$-i\mathrm{h}\frac{\partial}{\partial x}$, …
Angular momentum l_x, …	$\hat{l}_x$, …	$-i\mathrm{h}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$, …
Kinetic energy T	$\hat{T}$	$-\frac{\mathrm{h}^2}{2m}\nabla^2$
Potential energy V	$\hat{V}$	$V(\mathbf{r})$
Total energy E	$\hat{H}$	$-\frac{\mathrm{h}^2}{2m}\nabla^2 + V(\mathbf{r})$

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

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

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

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

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

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

Postulate V: (The **uncertainty principle**.) Operators that do not commute $\left(\hat{A}\left(\hat{B}\Psi\right) \neq \hat{B}\left(\hat{A}\Psi\right)\right)$ 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 $\Delta x \Delta p_x \geq \mathrm{h}/2$.

3. Note on constants and units

Resource on physical constants: http://physics.nist.gov/cuu/Constants/
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	$e = 1$	1.6021×10^{-19} C	
Length	$a_0 = 1$ (bohr)	5.29177×10^{-11} m	0.529177 Å
Mass	$m_e = 1$	9.10938×10^{-31} kg	
Angular momentum	$\hbar = 1$	$1.054\ 572\times10^{-34}$ J s	
Energy	E_h (hartree)	4.359744×10^{-18} J	27.2114 eV
Electrostatic force	$1/(4\pi\varepsilon_0) = 1$	8.987552×10^{9} C^{-2} N m^2	
Boltzmann constant		1.38065×10^{-23} J K^{-1}	8.31447 J/mol K

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

Energy units

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

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

3D box → 3 degrees of freedom

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

Schrødinger eq

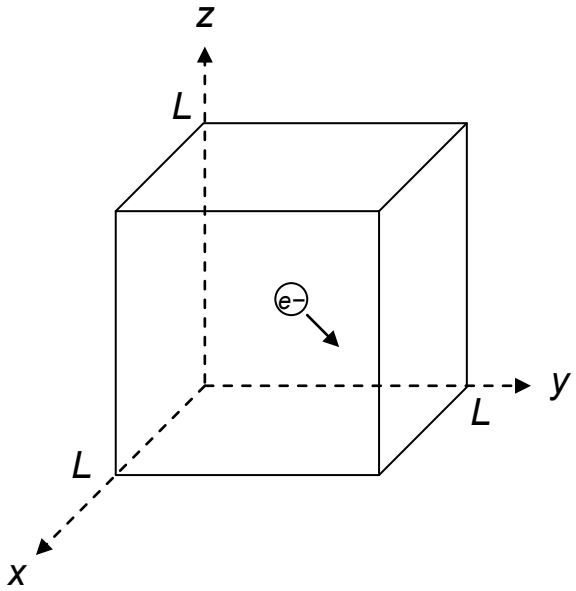
$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y,z) = E\psi(x,y,z)$$

$$\psi(x,y,z) = 0, \quad x,y,z \le 0,\ x,y,z \ge L$$

Second-order linear partial differential equation
Boundary value (eigenvalue) problem

Separable

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$



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

ftn x + ftn y + ftn z = constant → each term must be constant

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2 X(x)}{\partial x^2}=E_x X(x) \qquad X(0)=X(L)=0$$

$$X(x)=\sin\frac{n_x\pi x}{L}, \qquad n_x=1,2,3,\ldots$$

function that twice differentiated returns itself

$$E_{n_x}=\frac{n_x^2\pi^2\hbar^2}{2m_eL^2}$$

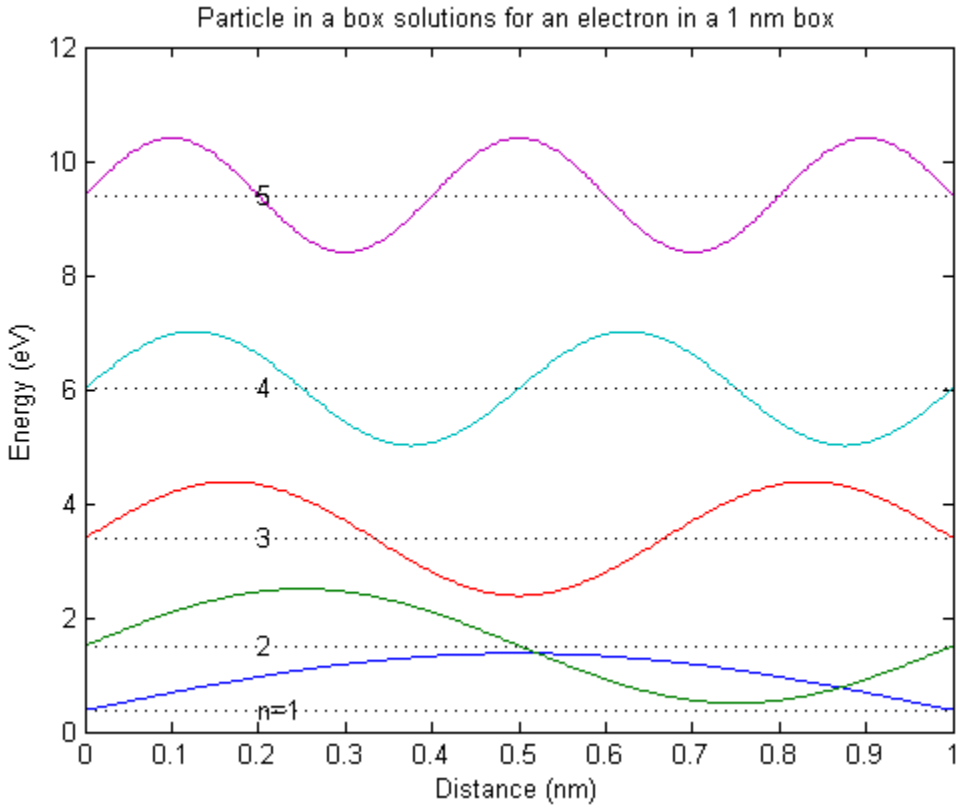
Solutions called *eignefunctions/wavefunctions* and *eigenvalues*
Characterized by *quantum number*, one for each degree of freedom

Normalization – require that wavefunction square integrates to 1

$$C^2\int_0^L\sin^2\frac{n_x\pi x}{L}dx\equiv C^2\left\langle X_{n_x}\middle|X_{n_x}\right\rangle=1 \Rightarrow C=\pm\sqrt{\frac{2}{L}}$$

Dirac notation

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



Note increasing *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.

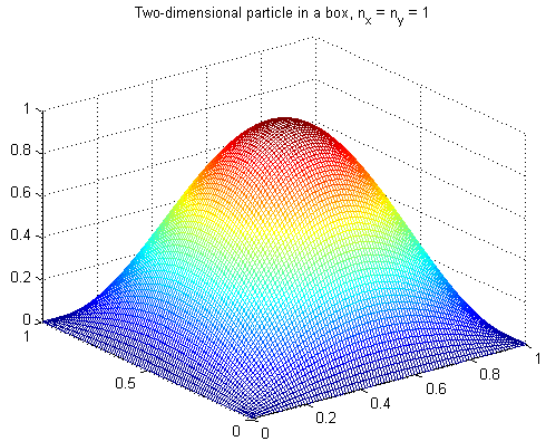
3 dimensional solution

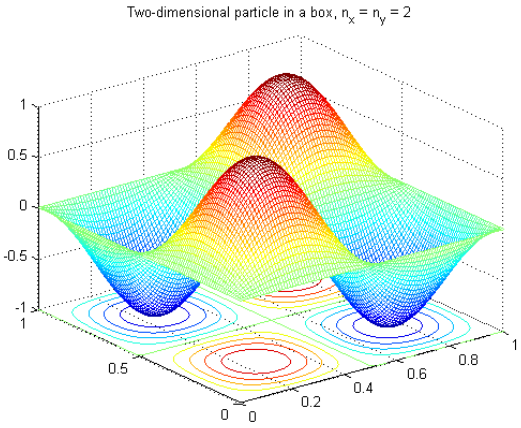
$$\psi(x,y,z) = X(x)Y(y)Z(z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L}$$

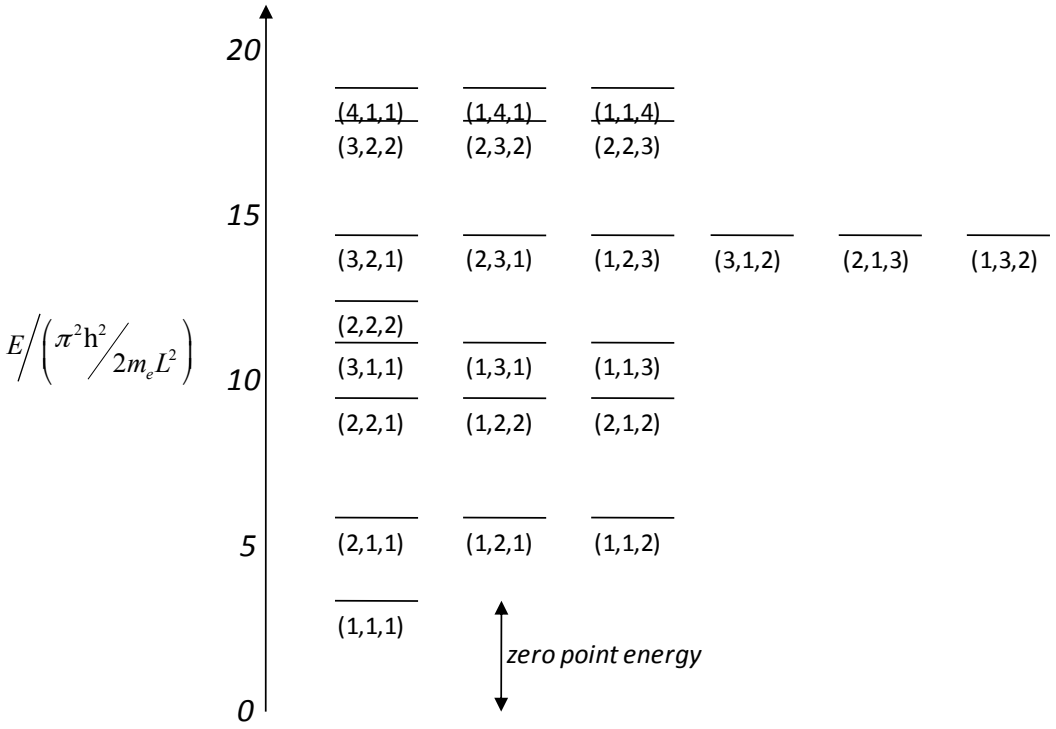
$$E = E_x + E_y + E_z = \frac{\left(n_x^2 + n_y^2 + n_z^2\right)\pi^2 \mathrm{h}^2}{2m_e L^2}$$

$$n_x, n_y, n_z = 1, 2, 3, \mathrm{K}$$

One quantum number for each dof







Degeneracy
Symmetry
Energy levels – depend on volume → pressure!!