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1 Refresher on Quantum Mechanics

1.1 Why quantum mechanics?

Want to describe "mechanics" (equations of motion) of atomic-scale things, like electrons in atoms and molecules

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

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

de Broglie wavelength (1924)

$$\lambda = h/p = h/mv \tag{1}$$

$$h = 6.626 \times 10^{-34} \text{ J s (Planck's constant)} \tag{2}$$

Table 1: Car vs electron as a quantum particle

	Car	Electron
mass m	1000 kg	$9.1\times$ 10^{-31} kg
velocity v	100 km/hr	$0.01c$
	typical value on the highway	typical value in an atom
momentum p	2.8×10^{-4} kg m/s	$2.7 \times$ 10^{-24} kg m/s
wavelength λ	$2.4 \times$ 10^{-38} m	$2.4 \times$ 10^{-10} m
	too small to detect. Classical!	Comparable to size of an atom. *Must* treat with QM!

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

$$\text{Kinetic energy} + \text{Potential energy} = \text{Total Energy}$$

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

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t) = -i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \tag{3}$$

If the potential V is time-invariant, can use separation of variables to show that the steady-state, time-independent solutions are characterized by an energy E and described by:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar} \tag{5}$$

Table 2: Postulates of Non-relativistic Quantum Mechanics

Postulate 1: 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:

I. Single-valued

II. continuous and twice differentiable

III. square-integrable ($\int \Psi^* \Psi d\tau$ is defined over all finite domains)

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

Postulate 2: To every physical observable quantity M there corresponds a Hermitian operator $\hat{M}$. **The only observable values of M are the eignevalues 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 $p_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar\dfrac{\partial}{\partial x}, \ldots$
Angular momentum $l_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right), \ldots$
Kinetic energy T	$\hat{T}$	$-\dfrac{\hbar^2}{2m}\nabla^2$
Potential energy V	$\hat{V}$	$V(\mathbf{r}, t)$
Total energy E	$\hat{H}$	$-\dfrac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)$

Postulate 3: If a particular observable M is measured many times on many identical systems is a state Ψ, the average resuts with be the expectation value of the operator $\hat{M}$:

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

Postulate 4: The energy-invariant states of a system are solutions of the equation

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

The time-independent, stationary states of the system are solutions to the equation

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

Postulate 5: (The **uncertainty principle**.) Operators that do not commute ($\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$) are called /conjugate/. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta of particles all described by the same Ψ must satisfy $\Delta x \Delta p_x \geq \hbar/2$.

1.2 Postulates of Non-relativistic quantum mechanics

See table

1.3 Notes 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 mode of Gnu emacs **highly recommended**

Table 3: Atomic units common for quantum mechanical calculations (see http://en.wikipedia.org/wiki/Atomic_units)

	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	$\hbar = 1$	1.054572×10^{-34} J s	
Energy	$E_h = 1$ (hartree)	4.359744×10^{-18} J	27.2114 eV
Electrostatic force	$1/(4\pi\epsilon_0) = 1$	8.987552×10^{9} C^{-2} N m^2	
Boltzmann constant		1.38065×10^{-23} J K^{-1}	8.31447 J/mol K

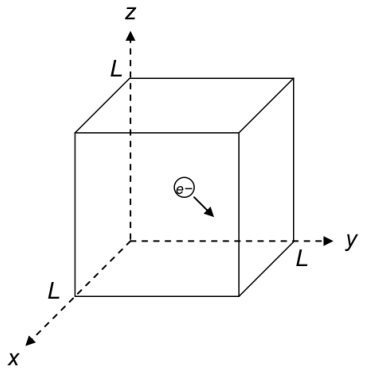
Energy units 1 eV = 1.60218× 10^{-19} J = 96.485 kJ/mol = 8065.5 cm^{-1} = 11064 K kB

1.4 Example: Energy states of an electron in a box

System defined by potential experienced by particle:

$V(\mathbf{r}) = 0, \qquad 0 < x, y, z < L$

$V(\mathbf{r}) = \infty, \qquad x, y, z \leq 0,\ x, y, z \geq L$



3D box → 3 degrees of freedom/coordinates

Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z) \tag{6}$$

$$\psi(x,y,z) = 0, \quad x, y, z \leq 0,\ x, y, z \geq L \tag{7}$$

A second-order, linear, partial differential equation. Boundary value problem. Solve by separation of variables. Postulate $\psi(x,y,z) = X(x)Y(y)Z(z)$. Substituting and rearrange to get

$$-\frac{\hbar^2}{2m_e}\left(\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2}\right) = E \qquad 0 < x,y,z < L \tag{8}$$

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

Equation for each dimension

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2 X(x)}{\partial x^2} = E_x X(x), \qquad X(0) = X(L) = 0 \tag{9}$$

Seek function that twice differentiated returns itself and satisfies boundary conditions.

$$X(x) = \sin\frac{n_x \pi x}{L}, \qquad n_x = 1,2,3,\ldots \tag{10}$$

$$E_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2m_e L^2} \tag{11}$$

Solutions called *eigenfunctions* (or *wavefunctions*) and *eigenvalues*. Characterized by *quantum numbers*, one for each degree of freedom. These (and all QM) solutions have certain special properties, including that they are orthonormal and form a complete set.

Normalization

Seek a constant such that the inner eigenfunction product is unity.

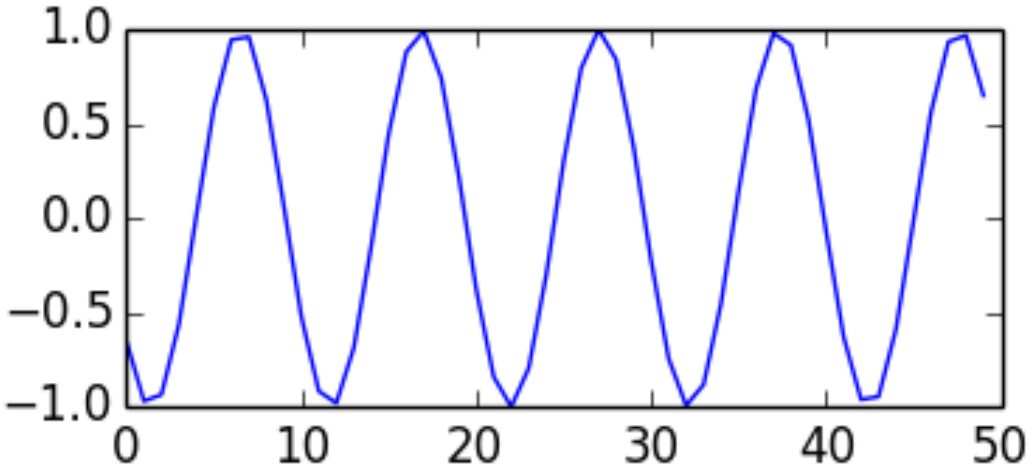
$$C^2 \int_0^L \sin^2\frac{n_x \pi x}{L} dx = C^2 L/2 = 1 \rightarrow C = \pm\sqrt{\frac{2}{L}} \tag{12}$$

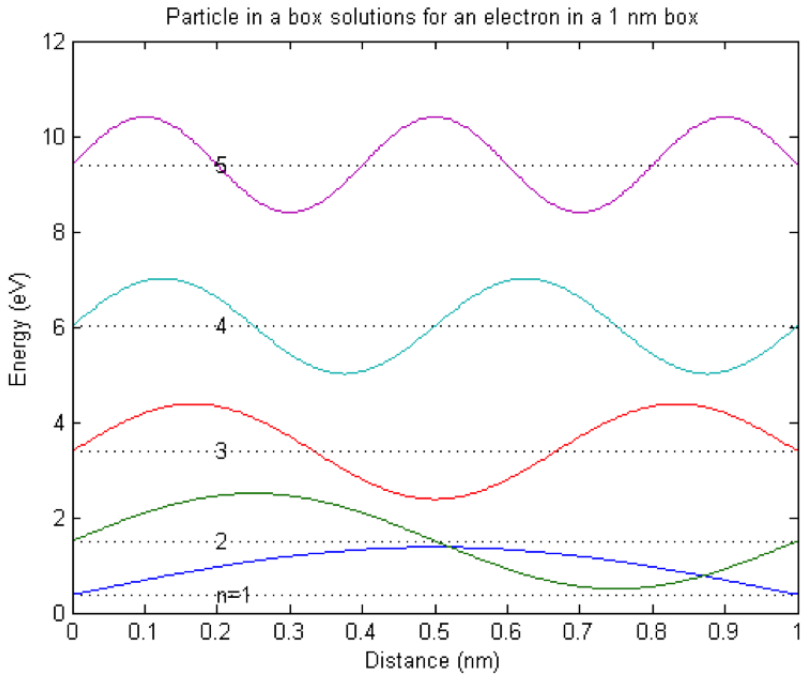
$$X(x) = \pm\sqrt{\frac{2}{L}}\sin\frac{n_x \pi x}{L}, \qquad n_x = 1,2,3,\ldots \tag{13}$$

Orthonormal

$$\langle X_{n_x} | X_{n'_x} \rangle = \delta_{n_x, n'_x} \qquad \text{Dirac notation} \tag{14}$$

```
1  import matplotlib, numpy
2  matplotlib.use('Agg')
3  import matplotlib.pyplot as plt
4  fig=plt.figure(figsize=(4,2))
5  x=numpy.linspace(-15,15)
6  plt.plot(numpy.sin(x))
7  fig.tight_layout()
8  plt.savefig('images/python-matplot-fig.png')
9  return 'images/python-matplot-fig.png' # return filename to org-mode
```

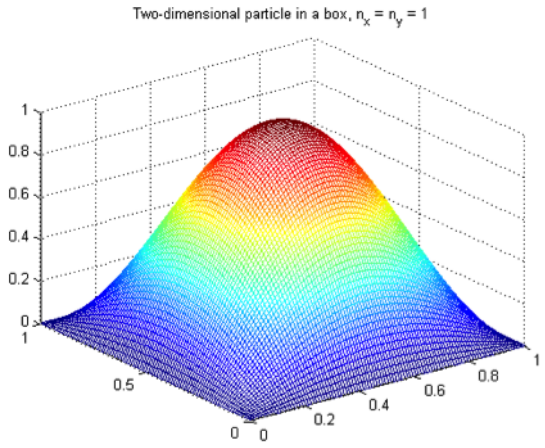


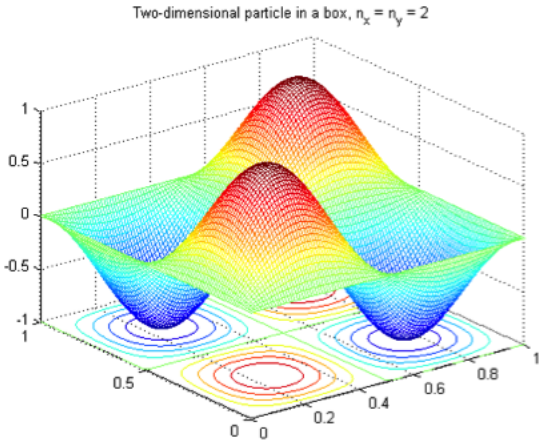
- Energy increase with number of *nodes*.
- $E \propto n^2, \Delta E \propto n, \Delta E/E \propto 1/n$. *Relative* spacing decreases with n.
- Is this real? See Ho, *J. Phys. Chem. B* **2005**, *109*, 20657.

Three-dimensional solutions

$$\psi(x,y,z) = X(x)Y(y)Z(z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{n_x\pi x}{L} \sin\frac{n_y\pi y}{L} \sin\frac{n_z\pi z}{L}, \qquad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{15}$$

$$E = E_x + E_y + E_z = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2} \tag{16}$$





Properties of solutions:

- Symmetry of system introduces degeneracy in solutions
- Energy depends on volume → pressure!

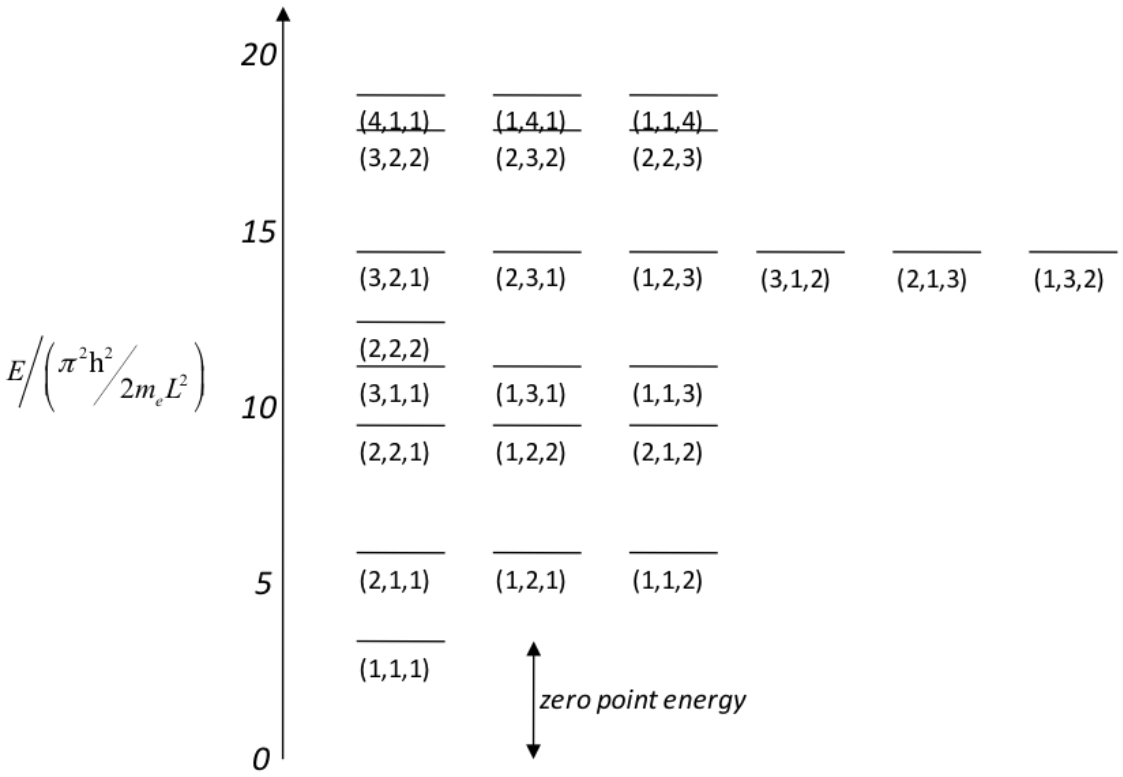


Figure 1: Energy sates of 3D Particle in a box

