Quick review of Lecture 3

Photon: $E = h\nu$, $p = h/\lambda$.

Assuming $\Psi_t(\mathbf{r},t) = \Psi(\mathbf{r})Y(t)$, we use separation of variables to solve the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_t + U\Psi_t = i\hbar\frac{\partial\Psi_t}{\partial t}.$$

The solutions are

$$Y = C_1\exp\left[-i\frac{E}{\hbar}t\right] = C_1\exp[-i\omega t],$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + (U - E)\Psi = 0,$$

where the eigen value E represents the total energy of the system.

Heisenberg uncertainty principle states

$$<\Delta p><\Delta x>\geq\frac{\hbar}{2}; <\Delta t><\Delta E>\geq\frac{\hbar}{2}.$$

2.3 Example solutions:

Here we determine $u(\vec{r})$ by the boundary conditions and will not consider the $u(\vec{r},t)$ case.

2.3.1 Free particles in 1D

In this case, there are no constraints for the particles. The potential energy u=0 so that

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0.$$

This gives

$$\psi = Ae^{-ikx} + Be^{ikx},$$

where $k = \sqrt{2mE}/\hbar = p/\hbar$ (note $E = p^2/2m$). The final solution is

$$\Psi_t(x,t) = Ae^{-i(\omega t + kx)} + Be^{-i(\omega t - kx)},$$

in which the first term corresponds to negative-direction propagation, the second term is positive-direction wave. Please also recall problem 2.5 in assignment 2.

2.3.2 Quantum well

Consider the general case of a particle in a one-dimensional potential well, which can be, for example, an electron subject to an electric potential field as shown in the figure. This is actually the model for thin films. The steady-state Schrödinger equation for the particle in such a potential profile is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0 \text{ (0<x<D); } \Psi = 0 \text{ (x<0 or x>D).}$$

Note: for $u \to \infty$ (x<0 or x>D), only $\Psi = 0$ can satisfy the Schrödinger equation.
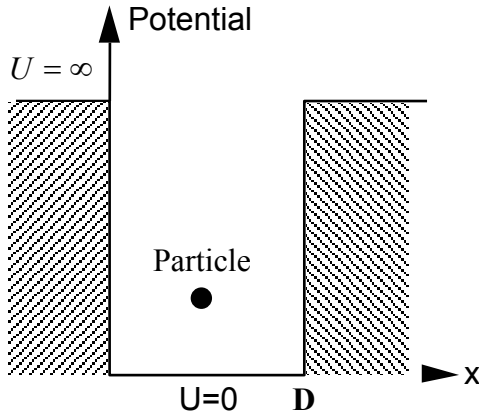
Same as the free particles, the solution for first equation is still

$\Psi = Ae^{-ikx} + Be^{ikx}$,

where $k = \sqrt{\dfrac{2mE}{\hbar^2}} = \dfrac{\sqrt{2mE}}{\hbar} = \dfrac{p}{\hbar}$.

The general boundary conditions are the continuity of the wave functions and their first derivatives at the boundaries. The latter derives from the continuity of particle flux at the boundary. For the current problem, the continuity of the first derivatives is not required because the wavefunction at the boundaries are already known to be zero. With the continuity of the wave function at x=0 and x=D, we have

$$\begin{cases} \text{x=0} \quad \text{A+B=0} \\ \\ \text{x=D} \quad A\exp[-ikD] + B\exp[ikD] = 0 \end{cases}$$

Above equations yield

$A(e^{-ikD} - e^{ikD}) = 0$.

Noticing $A \neq 0$, we obtain $\sin(kD) = 0$. Thus

$k_n D = n\pi$ (n=0, $\pm 1, \pm 2 \cdots$)

or

$D\sqrt{\dfrac{2mE_n}{\hbar^2}} = n\pi$, energy eigen value $E_n = \dfrac{1}{2m}\left(\dfrac{\pi \hbar n}{D}\right)^2$.

The material wave function inside the potential well is

$\Psi_n = -2iA \sin\left(\dfrac{n\pi x}{D}\right)$,

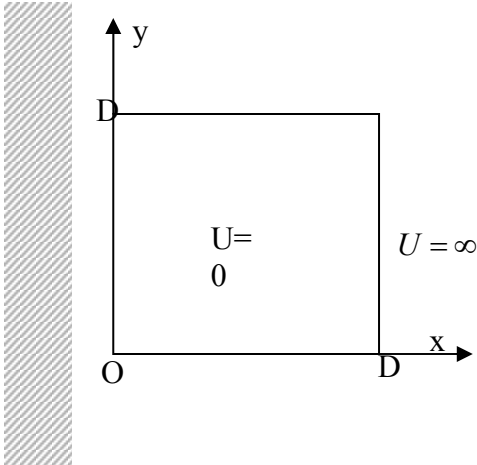which is identical with the previous results of standing wave.
Note: for n, obviously it is not zero. Since solutions of negative n values are equivalent to those of positive values, here we can just let n=1, 2$\cdots$

Normalization is still used to calculate A, i.e.

$\int_0^D \Psi_t^*(x)\Psi_t(x)dx = 1$.

Finally we get $A = i\sqrt{\dfrac{1}{2D}}$.

2.3.2 Particle in a 2D box

We establish a coordinate system as shown in the schematic above. Clearly, outside the potential well, we have $\Psi = 0$ because $U = \infty$. We thus focus on the solution inside the potential well. The Schrödinger equation inside the well (U=0) is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2}\right) - E\Psi = 0 .$$

We still use the separation-of-variables technique. Assuming $\Psi(x,y) = X(x)Y(y)$ and substituting into the above equation leads to

$$\frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{Y}\frac{d^2 Y}{dy^2} + \frac{2mE}{\hbar^2} = 0 .$$

In the above equation, the first term depends on x and the second term on y. The third term is a constant. This leads to the requirement that both the first and the second term must each be a constant. Since E is positive, we can prove neither of the first two terms can be positive. Errors will occur if we let one of them be positive. Thus, we write

$$\frac{1}{X}\frac{d^2 X}{dx^2} = -k_x^2, \quad \frac{1}{Y}\frac{d^2 Y}{dx^2} = -k_y^2 .$$

The solution for X is

$$X(x) = A\sin(k_x x) + B\cos(k_x x) .$$

To satisfy the boundary condition that $\Psi = 0$ at x=0 and x=D, we must have X=0 at x=0 and x=D. Applying these boundary conditions, we see that

$$k_x = \frac{n\pi}{D} \quad (n = 1,2,3\cdots) .$$

Similarly, $k_y = \dfrac{l\pi}{D} \quad (l = 1,2,3\cdots)$.

Thus

$$E_{\ell n} = \frac{\left(\ell^2 + n^2\right)\pi^2\hbar^2}{2mD^2} \quad (\ell, n = 1, 2, \ldots)$$

and

$$\Psi_{\ell n} = C_{\ell n} \sin\left(\frac{n\pi x}{D}\right) \sin\left(\frac{\ell\pi y}{D}\right).$$

We can further determine the constant $C_{\ell n} = 2/D$.

For quantum numbers: n, l, …

(1) n=1, l=2, E_{12}, Ψ_{12}

(2) n=2, l=1, E_{21}, Ψ_{21}

Note: $E_{12} = E_{21}$, but Ψ_{12} and Ψ_{21} are flipped in the x and y directions from $\Psi_{\ell n} = C_{\ell n} \sin\left(\frac{n\pi x}{D}\right) \sin\left(\frac{\ell\pi y}{D}\right)$. These states that have different wavefunctions but the same energy are said to be degenerate. The degeneracy of an energy state is the number of wavefunctions having the same energy.

2.3.3 Electron spin & Pauli exclusion principle

Each wavefunction obtained in the previous sections represents a possible quantum mechanical state at which a particle can exist under the given potential. The solution of the Schrödinger equation, however, does not tell the whole story on the quantum state of a particle. For example it cannot distinguish the spin of particles. For electrons, corresponding to each wavefunction obtained from the Schördinger equation, there are two quantum states (or two relativistic wavefunctions), which are usually denoted by an additional quantum number s that can have the following values:

$$s = \frac{1}{2} \quad or \quad -\frac{1}{2},$$

where s=1/2 is called spin up and s=-1/2 is called spin down.

The **Pauli exclusion principle** says that each quantum state can be occupied by at most one electron.
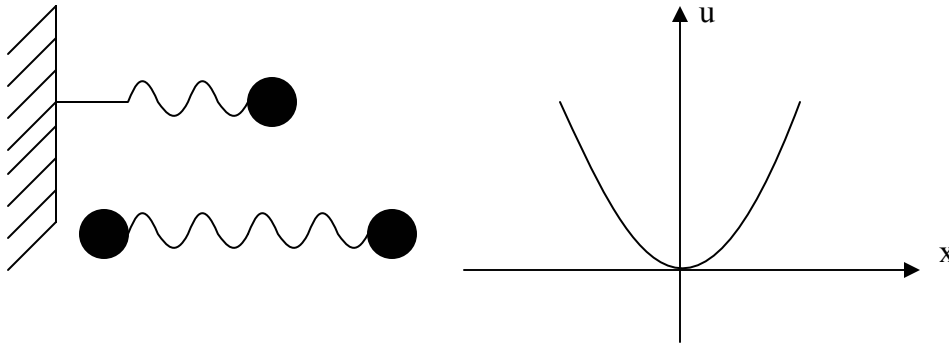
2.3.4 Other potentials

(1) Harmonic oscillator

From $F = -Kx = -\frac{du}{dx}$, we have $u = \frac{1}{2}Kx^2$ (shown in the figure). The Schrödinger equation becomes

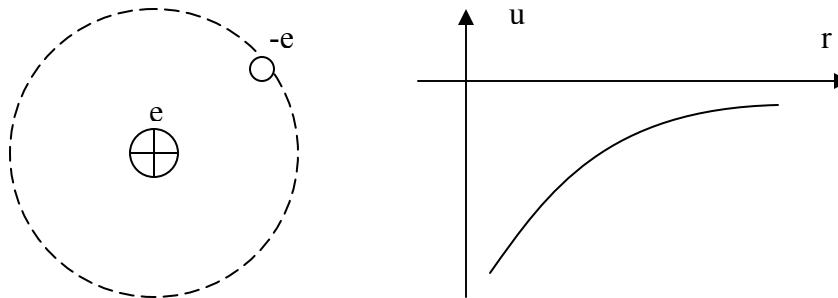$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + (\frac{Kx^2}{2} - E)\Psi = 0,$$

which gives $E_n = h\nu(n + 1/2); \nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$.

Note: the zero point (intrinsic) energy $\frac{h\nu}{2}$ is required by the Heisenberg uncertainty principle ($<\Delta t><\Delta E> \geq \frac{\hbar}{2}$). It shows that the oscillator has some energy even at the rest.

Note: to calculate the intrinsic frequency for diatomic molecules with two atoms of mass m_1 and m_2, the reduced mass should be used,

$$m = \frac{m_1 m_2}{m_1 + m_2}.$$

Now consider the case that an electron moves around the nucleus, which is assumed to be stationary. The interaction between the nucleus and the orbiting electron is governed by the Coulomb force

$$F = -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r^2} = -\frac{du}{dr},$$

where $\varepsilon_o = 1.124 \times 10^{-10}/4\pi$ [C^2/(m^{2}N)] is the electrical permittivity of the vacuum. It yields

$$u(r) = -\frac{e^2}{4\pi\varepsilon_0 r}.$$

Using separation of variables, we assume $\Psi_{n\ell m} = R_{n\ell}(r)Y_\ell^m(\theta, \varphi)$. The allowable energy levels of the electron-nucleus system are

$$E_n{}^{el} = -\frac{Mc_1^2}{2\hbar^2 n^2} = -\frac{13.6\,eV}{n^2} \quad (n \geq 1,\ n \geq \ell+1 \text{ and } |m| \leq \ell,\ \ell = 0, 1, 2, \ldots)$$

in which M is the electron mass. For quantum number n=1, we have
n=1, l=0, m=0, Ψ_{100}, s (two quantum states determined by spin), 1s orbital.

$$n=2 \text{---}> \begin{cases} l=0 & m=0 & 2s \quad orbital \\ l=1 & m=-1,0,1 & 2p \quad orbital \end{cases}$$

Basically there are four wave functions for n=2 and totally eight quantum states. The energy levels of different orbitals are drawn in the following figure. The spherical s orbital and dumb-bell p orbitals are also presented here. The degeneracy is determined by $g=2n^2$.
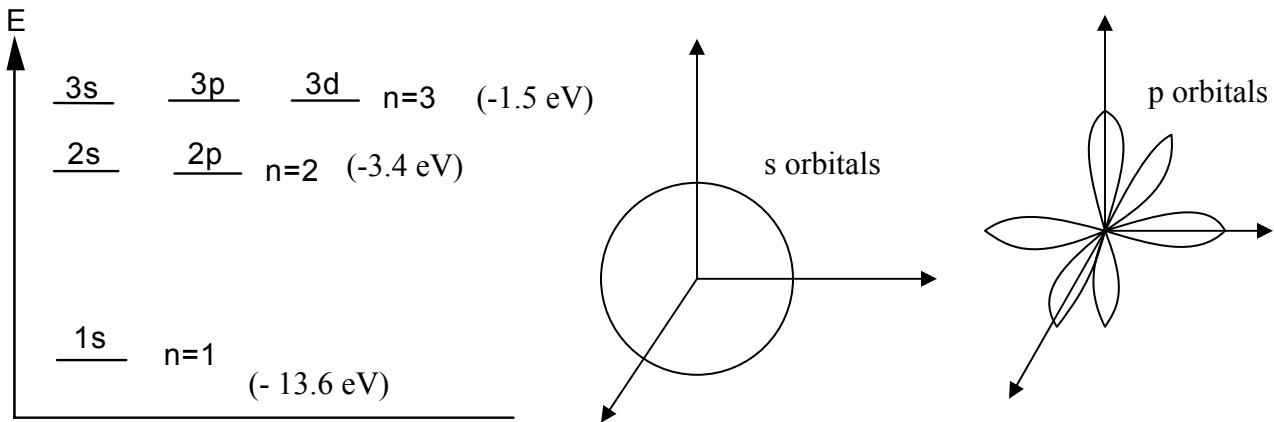

Note: the energy gap between different n values is much larger than the thermal energy (k_BT~26 meV) and it is almost impossible to thermally excite electrons to a higher n level. A stable element is obtained only if all the orbitals for the highest n are completely filled, such as He.

Now one may wonder why the energy eigenvalue E has different relationships with n. Here we will give a simple argument, without solving the Schrodinger equation, to show that this is indeed the case. My argument is based on the requirement of forming standing waves in given potential. For harmonic oscillators, as shown in the following figure, the standing waves inside the potential, assuming at the boundaries, wavefunction is zero, give

$$x_n = \frac{\lambda n}{4}.$$

Kinetic energy is $KE = p^2 / 2m = \frac{1}{2m}(\frac{h}{\lambda})^2 = \frac{1}{2m}(\frac{hn}{4x_n})^2$.
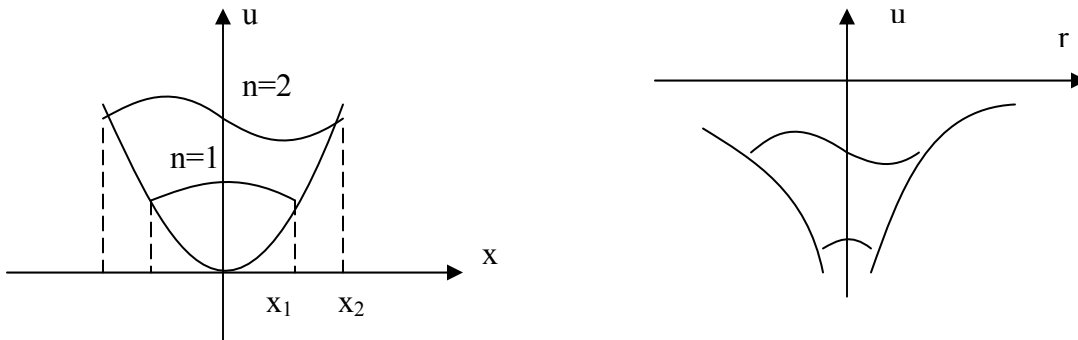
Equating the kinetic and potential energies (sort of equipartition of energy, but only a hand waving argument), we obtain

$$\frac{K}{2}x_n^{\,2} = \frac{1}{2m}(\frac{hn}{4x_n})^2$$

or

$$x_n^{\,2} = (\frac{1}{Km})^{1/2}\frac{nh}{4}.$$

Thus

$$E \propto Kx_n^{\,2} = \frac{nh}{4}\sqrt{\frac{K}{m}},$$

which is a linear functions of n, similar to what we obtain from solving Schrodinger equation. Similarly, we can deal with electrons moving around the nucleus but changing the potential energy to $u = \dfrac{e^2}{4\pi\varepsilon_0 x_n}$. Finally we get $E \propto \dfrac{1}{n^2}$.
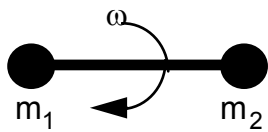
Rigid rotation
In classic mechanics, the angular momentum is expressed as $\vec{r}\times\vec{p}$. However, because of the uncertainty principle, it is difficult to give such an expression in quantum mechanics.

In classical mechanics, a quantity often used to describe the rotation is the moment of inertia. For a two-mass system rotating relative to its mass center, the moment of inertia is

$$I = \frac{m_1 m_2 r_0^2}{m_1 + m_2}$$

where r_0 is the effective separation between the two atoms.

The energy eigenvalues are

$$E_1 = \frac{\hbar^2}{2I}\ell(\ell+1) = hB\ell(\ell+1) \qquad\qquad (\text{for } |m|\le\ell,\ \ell=0,1,2,\ldots).$$

Note: the discussion on harmonic oscillators and rigid rotors gives other useful information. For example, we can calculate the spring constant of an oscillator by measured vibrational frequency, from $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{K}{m}}$.