EE201/MSE207 Lecture 9

Quantum mechanics in three dimensions

(still only one particle)

Natural generalization

Schrödinger equation:

$$\boxed{i\hbar \frac{\partial \Psi(x,y,z,t)}{\partial t} = \widehat{H}\,\Psi}$$

usually no *t*-dependence

Hamiltonian

$$\boxed{\widehat{H} = \frac{\hat{p}^2}{2m} + V(x,y,z,t) = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(x,y,z,t)}$$

Momentum

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}\,, \qquad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}\,, \qquad \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

$$\boxed{\hat{\vec{p}} = -i\hbar\nabla}$$

(nabla or del) (sometimes $-i\hbar\vec{\nabla}$)

SE

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\,\Psi}$$

$$\nabla^2\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = \Delta\Psi$$

(Laplacian)

TISE and general solution of SE

If $V(x,y,z)$ (potential energy does not depend on time), then simplification

TISE
$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r}) + V\,\psi_n(\vec{r}) = E_n\psi_n(\vec{r})}$$

$$\hat{H}\psi_n = E_n\psi_n$$

$$\vec{r} = (x,y,z)$$

General solution of SE

$$\boxed{\Psi(\vec{r},t) = \sum_n c_n\,\psi_n(\vec{r})\ \exp\left(-i\,\frac{E_n}{\hbar}\,t\right)}$$

Normalization

$$\boxed{\iiint_{-\infty}^{\infty} |\Psi|^2\,dx\,dy\,dz\ = 1}$$

$$\boxed{\iiint_{-\infty}^{\infty} |\psi_n|^2\,dx\,dy\,dz\ = 1}$$

$$\boxed{\sum_n |c_n|^2 = 1}$$

Separation of variables in Cartesian coordinates

(not in the textbook)

Simplification if $V(\vec{r}) = V_1(x) + V_2(y) + V_3(z)$;

then 3D TISE can be replaced with three 1D equations

TISE $$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V(\vec{r})\,\psi = E\,\psi$$

Look for (assume) $$\psi(\vec{r}) = \psi_1(x)\,\psi_2(y)\,\psi_3(z)$$

Divide TISE by ψ, then

$$-\frac{\hbar^2}{2m}\left(\frac{\frac{\partial^2\psi_1(x)}{\partial x^2}}{\psi_1(x)} + \frac{\frac{\partial^2\psi_2(y)}{\partial y^2}}{\psi_2(y)} + \frac{\frac{\partial^2\psi_3(z)}{\partial z^2}}{\psi_3(z)}\right) + V_1(x) + V_2(y) + V_3(z) = E$$

Then three equations, with $E = E_1 + E_2 + E_3$

$$-\frac{\hbar^2}{2m}\,\frac{\frac{\partial^2\psi_1(x)}{\partial x^2}}{\psi_1(x)} + V_1(x) = E_1$$

and two similar equations for y and z

Simplification if $V(\vec{r}) = V_1(x) + V_2(y) + V_3(z)$ (cont.)

Rewrite as usual

$$\left\{\begin{aligned} &-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2} + V_1(x)\,\psi_1(x) = E_1\,\psi_1(x) \\ &-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2} + V_2(y)\,\psi_2(y) = E_2\,\psi_2(y) \\ &-\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2} + V_3(z)\,\psi_3(z) = E_3\,\psi_3(z) \\ &E = E_1 + E_2 + E_3 \qquad \psi(\vec{r}) = \psi_1(x)\psi_2(y)\psi_3(z) \end{aligned}\right.$$

Each equation has many solutions $\psi_{k,l,m}(\vec{r}) = \psi_{1,k}(x)\,\psi_{2,l}(y)\,\psi_{3,m}(z)$

Energy $E = E_{x,k} + E_{y,l} + E_{z,m}$ (replaced 1,2,3 with x, y, z)

General solution

$$\Psi(\vec{r},t) = \sum_{k,\,l,\,m} c_{k,l,m}\,\psi_{1,k}(x)\,\psi_{2,l}(y)\,\psi_{3,m}(z)\,\exp\left(-i\,\frac{E_{x,k} + E_{y,l} + E_{z,m}}{\hbar}\,t\right)$$

Examples

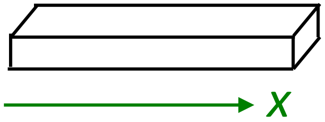
Unfortunately, not many examples when this trick is useful

Semiconductor quantum well, quantum wire, quantum dot

(terminology for semiconductor structures is slightly different than in QM)

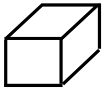
quantum well (QW), 2D electron gas (2DEG)

electrons do not move in z-direction, free motion in x and y



quantum wire (QWi), 1D electrons

electrons move only in x-direction, restricted along y and z



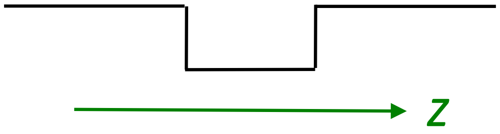
quantum dot (QD), 0D electrons

motion is restricted in all direction (x, y, and z)

Only the first case (QW) can be truly represented as $V_1(x) + V_2(y) + V_3(z)$; however, other cases can also be treated in this way approximately

Semiconductor Quantum Well

$$V(\vec{r}) = V(z) = 0 + 0 + V_3(z)$$



(finite depth QW along *z*)

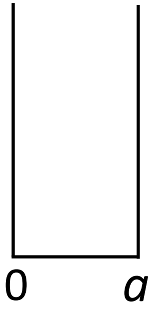
Wavefunctions

$$\psi(x,y,z) = \psi_n(z)\, e^{ik_x x} e^{ik_y y}\, \frac{1}{2\pi}$$

or $\frac{1}{2\pi\hbar}$

$$E = E_n + \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m}$$

If infinite depth, $V(\vec{r}) = \begin{cases} 0, & 0 \le z \le a \\ \infty, & \text{otherwise} \end{cases}$ then

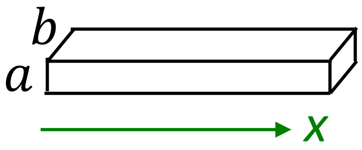


$$\psi(x,y,z) = \sqrt{2/a}\,\sin\left(\frac{n\pi}{a} z\right) e^{ik_x x}\, e^{ik_y y}\, \frac{1}{2\pi}$$

or $\frac{1}{2\pi\hbar}$

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} + \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m}$$

Rectangular Quantum Wire



If finite depth in y and z directions, then we cannot use this trick. However, it works for infinite depth.

Assume $$V(x,y,z) = \begin{cases} 0, & \text{if} \begin{cases} 0 \le z \le a \\ 0 \le y \le b \end{cases} \\ \infty, & \text{otherwise} \end{cases}$$

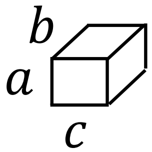
$$\psi(x,y,z) = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}} \sin\left(\frac{n_z \pi}{a} z\right) \sin\left(\frac{n_y \pi}{b} y\right) e^{i k_x x} \frac{1}{\sqrt{2\pi}}$$

or $\frac{1}{\sqrt{2\pi\hbar}}$

$$E = \frac{n_z^2 \pi^2 \hbar^2}{2ma^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mb^2} + \frac{\hbar^2 k_x^2}{2m}$$

If not rectangular and/or finite depth, then still 2+1 dimensions

Rectangular (cuboid) Quantum Dot



Again need to assume infinite depth

$$V(x,y,z) = \begin{cases} 0, & \text{if} \begin{cases} 0 \le z \le a \\ 0 \le y \le b \\ 0 \le x \le c \end{cases} \\ \infty, & \text{otherwise} \end{cases}$$

$$\psi(x,y,z) = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\sqrt{\frac{2}{c}}\,\sin\left(\frac{n_z\pi}{a}z\right)\sin\left(\frac{n_y\pi}{b}y\right)\sin\left(\frac{n_x\pi}{c}x\right)$$

$$E = \left(\frac{n_z^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_x^2}{c^2}\right)\frac{\pi^2\hbar^2}{2m}$$

Degeneracy if a, b, and c are equal or commensurate.

In semiconductors m is effective mass.

Another example: 3D oscillator (e.g., atom in a lattice)

$$V(\vec{r}) = \frac{1}{2}m\omega_x^2 x^2 + \frac{1}{2}m\omega_y^2 y^2 + \frac{1}{2}m\omega_z^2 z^2$$

$$E_{n_x,n_y,n_z} = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y + \left(n_z + \frac{1}{2}\right)\hbar\omega_z$$

Again, degeneracy if ω_x, ω_y, or ω_z are equal or commensurate.

Spherically symmetric potential (similar trick)

$$V(\vec{r}) = V(|\vec{r}|)$$

Most important for atoms

Then it is natural to look for $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

where r,θ,φ are spherical coordinates

TISE

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

Rewriting Laplacian in spherical coordinates

$$-\frac{\hbar^2}{2m}\left[\underline{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)} + \frac{1}{r^2\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\,\frac{\partial^2\psi}{\partial\varphi^2}\right] + \underline{V(r)\,\psi} = \underline{E\,\psi}$$

combine

Divide by $\psi = RY$ and multiply by $-2mr^2/\hbar^2$

$$\underbrace{\left[\frac{1}{R}\,\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]\right]}_{\substack{\text{const}\\ l\,(l+1)}} + \underbrace{\frac{1}{Y}\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2 Y}{\partial\varphi^2}\right]}_{\substack{\text{const}\\ -l\,(l+1)}} = 0$$

(so far just a notation)

Spherical harmonics Y

Assume $Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$, again separation of variables

$$\underbrace{\frac{1}{\Theta(\theta)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta\right]}_{\text{const}\qquad m^2}+\underbrace{\frac{1}{\Phi(\varphi)}\,\frac{\partial^2\Phi}{\partial\varphi^2}}_{\text{const}\quad -m^2}=0$$

$\Phi(\varphi)=e^{im\varphi}$, $\quad m=0,\pm1,\pm2,\ldots$ (since should be periodic with 2π)

This is why m is integer.

$\Theta(\theta)=A\,P_l^m(\cos\theta)$

Associated Legendre function

This is why l is integer.

$$\boxed{\begin{array}{l} l=0,1,2,\ldots\quad \text{(integer)} \\ m=-l,-l+1,\ldots 0,\ldots l-1,l \end{array}}$$

l: anguar momentum quantum number (azimuthal q. n., orbital q. n.)

m: magnetic quantum number

$Y_l^m(\theta,\varphi)=\Theta_l^m(\theta)\,\Phi_m(\varphi)$ are called spherical harmonics

These function are the same for any spherically symmetric potential $V(r)$.

Radial function R

$$\psi = \underline{R(r)}\, Y(\theta, \varphi)$$

Let us introduce $u(r) = r\, R(r)$, for this function the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \underbrace{\frac{\hbar^2}{2m}\frac{l\,(l+1)}{r^2}}_{\text{centrifugal term}}\right] u = E\, u$$

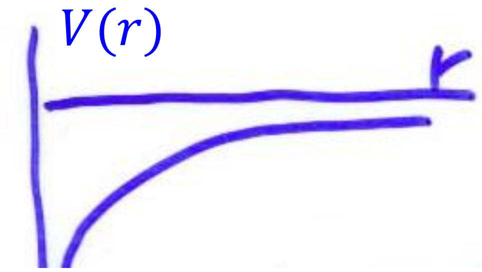
So, the equation for $u(r)$ is similar to 1D TISE, but with the centrifugal term.

It has some solutions, depending on l (orbital q.n.) and n (solution index).

Corresponding energy: $E_{n,l}$.

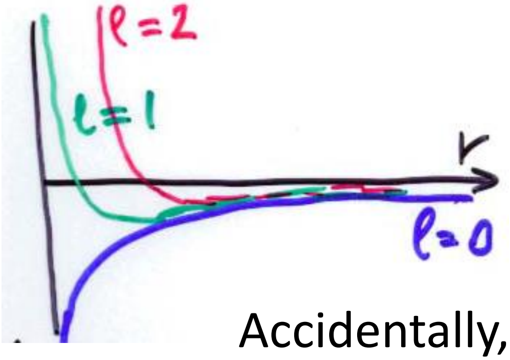
Overall, 3 quantum numbers: n, l, m. However, energy depends only on n and l.

Hydrogen atom



$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Consider only bound states (since atom) $\Rightarrow$ $E < 0$



Effective potential

$$-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l\,(l+1)}{r^2}$$

Accidentally, for this potential $E_{n,l}$ is highly degenerate

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}}$$

$n = 1, 2, 3, \ldots$

$E_1 = -13.6$ eV (ground state)

$$\boxed{\begin{aligned} &n = 1, 2, 3, \ldots \\ &l = 0, 1, \ldots n-1 \\ &m = 0, \pm 1, \pm 2, \ldots \pm l \end{aligned}}$$

principal
azimuthal (ang.mom.)
magnetic

Ground state: $\psi_{100}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.53\ \text{Å}$$

Bohr radius

Total degeneracy: $\sum_{l=0}^{n-1}(2l+1) = n^2$

(almost same theory for dopant levels and excitons)

Hydrogen atom (cont.)

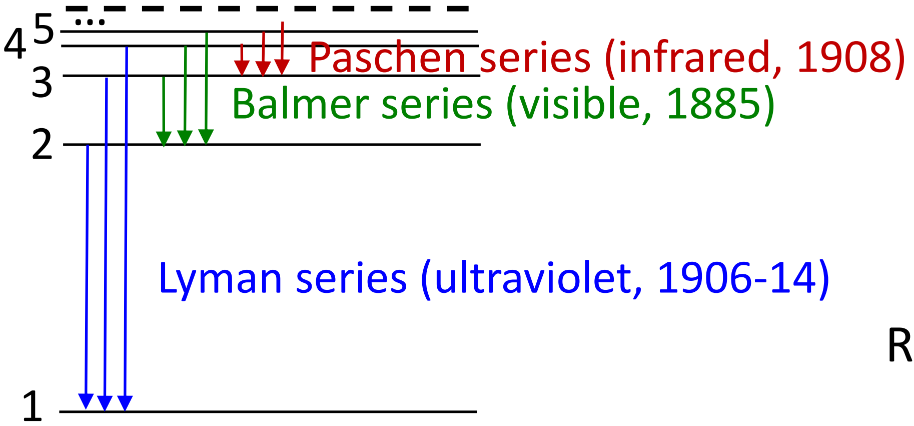
$$\psi_{nlm}(r,\theta,\varphi) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho) \times Y_l^m(\theta,\varphi)$$

$$\rho = \frac{r}{an} \qquad a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$ (Bohr radius, $0.53 \cdot 10^{-10}$ m)

$v(\rho)$ is some polynomial of degree $n - l - 1$ (related to generalized Laguerre polynomial)

Spectrum

$$\hbar\omega_{\mathrm{ph}} = E_i - E_f = -13.6\ \mathrm{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$$



Paschen series (infrared, 1908)

Balmer series (visible, 1885)

Lyman series (ultraviolet, 1906-14)

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Rydberg formula, 1888

Rydberg constant $1.1 \cdot 10^7\,\mathrm{m}^{-1}$

$$R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$