CHEM 3541 Physical Chemistry
Lecture Notes

Textbooks

Atkins' Physical Chemistry, 7th ed., pp. 304-316
Atkins' Physical Chemistry, 10th ed., pp. 290, 292-305

Table of Contents

Lecture 1 – Fundamental Concepts in Quantum Physics

1. Schrödinger Equation

Time-independent S.E.

$$\hat{H}\Psi = E\Psi$$

- $\hat{H}$: Hamiltonian operator
- Ψ: Wavefunction, $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$
- $\hat{H} = \hat{K} + \hat{V}$: Kinetic energy operator and potential energy operator. In many situations, $\hat{V}$ operator is simply a function.

Time-dependent S.E.

- If potential V and thus wavefunction depend on time explicitly, one need to solve time-dependent S.E.

$$i\hbar \frac{\partial \Psi(\boldsymbol{r}, t)}{\partial t} = \hat{H}(t)\Psi(\boldsymbol{r}, \mathrm{t})$$

I. One-dimensional system with one particle

$$\hat{H} = -\frac{\hbar^2}{2m} \cdot \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

h is Planck constant, whereas $\hbar = \frac{h}{2\pi}$ is called reduced Planck constant. $\hat{V}(x)$ operator is simply a function. The S.E. reads

$$\left[-\frac{\hbar^2}{2m} \cdot \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right]\Psi(x) = E\Psi(x)$$

Wavefunction contains all the information of this system. The simplest one is probability density $|\Psi(x)|^2$, which tells that the probability to find the particle between x and $x + \mathrm{d}x$ is $|\Psi(x)|^2\mathrm{d}x$.

Since total probability to find the particle between $-\infty$ and $+\infty$ should be 1, we require the wavefunction to be normalized:

$$\int_{-\infty}^{+\infty} |\Psi(x)|^2 \mathrm{d}x = 1$$

For an unnormalized wavefunction, it can be normalized as

$$\Psi(x) = \frac{\Psi'(x)}{\sqrt{\int_{-\infty}^{+\infty} |\Psi'(x)|^2 \mathrm{d}x}}$$

Example 1: constant potential

For $V(x) = \text{const.}$, the S.E. is

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}(E - V)\Psi$$

If $E > V$, the general solution is $\Psi(x) = Ae^{ikx} + Be^{-ikx}$, where $A, B \in \mathbb{C}$. The wave vector is defined as $k = \sqrt{2m(E-V)}/\hbar$.

- Kinetic energy $K = E - V = \frac{\hbar^2 k^2}{2m}$.
- Momentum $p = \hbar k = \frac{h}{\lambda}$. λ is de Broglie wavelength. To see the meaning of λ, let $\widetilde{\Psi} = e^{ikx} + e^{-ikx} = 2\cos kx$, then the period of $\widetilde{\Psi}$ is $\frac{2\pi}{k} = \frac{h}{p} = \lambda$.

Example 2: normalization of wavefunction

Q. Given a wave function $\psi(\boldsymbol{r}) \propto e^{-r/a_0}$ where a_0 is a given constant, try to normalize it. Noted that r in the exponent is radial distance but not position vector.

A. $\int \left(e^{-r/a_0}\right)^2 \mathrm{d}\boldsymbol{r} = 4\pi \int_0^\infty r^2 e^{-2r/a_0} \mathrm{d}r = 4\pi I(k)$, where $k = 2/a_0$.

$$I(k) = \int_0^\infty r^2 e^{-kr} \mathrm{d}r = \frac{\mathrm{d}^2}{\mathrm{d}k^2} \int_0^\infty e^{-kr} \mathrm{d}r = \frac{\mathrm{d}^2}{\mathrm{d}k^2}\left(\frac{1}{k}\right) = \frac{2}{k^3}$$

Thus $\psi(\boldsymbol{r}) = (\pi a_0^3)^{-1/2} e^{-r/a_0}$.

II. Three-dimensional system with one particle

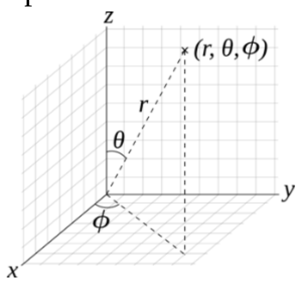
i. Cartesian coordinates

Wavefunction is $\Psi(x, y, z)$. The probability to find the particle in $[x, x+\mathrm{d}x] \cap [y, y+\mathrm{d}y] \cap [z, z+\mathrm{d}z]$ is $|\Psi(x,y,z)|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$.

$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$, where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian operator.

S.E. is $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]\Psi(x,y,z) = E\Psi(x,y,z)$. Wavefunction and energy are unknown variables.

ii. Spherical coordinates



Relationship to Cartesian coordinates

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$$

r: radial distance

θ: polar angle

ϕ: azimuth angle

Wavefunction is $\Psi(r, \theta, \phi)$. The probability to find the particle in $[r, r+\mathrm{d}r] \cap [\theta, \theta+\mathrm{d}\theta] \cap [\phi, \phi+\mathrm{d}\phi]$ is $|\Psi(r,\theta,\phi)|^2 r^2 \sin\theta\, \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$.

Laplacian operator is more complex in spherical coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\Lambda^2}{r^2}$$

where $\Lambda^2 = \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \csc^2\theta\frac{\partial^2}{\partial\phi^2}$.

S.E. is $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r,\theta,\phi)\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$

III. Eigenequation, eigenfunction and eigenvalue

The solution of S.E. $\hat{H}\Psi = E\Psi$ is a set of eigenenergy/value E_i and eigenfunction Ψ_i, $i = 1,2,\dots,\infty$.

For any operator $\hat{\Omega}$, if there exist some values satisfy $\hat{\Omega}\psi = \Omega\psi$, ψ is then called eigen function of operator $\hat{\Omega}$.

For example, since $\hat{\Omega}\psi = -\alpha\psi$, $\psi = e^{-\alpha x}$ is an eigenfunction of operator $\hat{\Omega} = \frac{\mathrm{d}}{\mathrm{d}x}$ with corresponding eigen value $-\alpha$. But $\psi = e^{-\alpha x^2}$ is not an eigenfunction of $\hat{\Omega}$.

For one-dimensional system with one particle, we can choose two wavefunctions with different eigenvalues E_1 and E_2,

- $\Psi_1 = e^{ik_1x}$, $k_1 = \frac{\sqrt{2m(E_1-V)}}{\hbar}$
- $\Psi_2 = e^{ik_2x}$, $k_2 = \frac{\sqrt{2m(E_2-V)}}{\hbar}$

Generally, $\Psi' = A\Psi_1 + B\Psi_2$, $(A, B \neq 0)$ is **NOT** a solution of S.E. $\hat{H}\Psi = E\Psi$. Only when $E_1 = E_2 = E$, $\hat{H}\Psi' = AE_1\Psi_1 + BE_2\Psi_2 = E(A\Psi_1 + B\Psi_2) = E\Psi'$.

2. Hermitian operator

For any two functions, if the following equation holds, then $\hat{\Omega}$ is called Hermitian operator.

$$\int \mathrm{d}\tau\psi_j^*\hat{\Omega}\psi_i = \left(\int \mathrm{d}\tau\psi_i^*\hat{\Omega}\psi_j\right)^*$$

For example, $\frac{\mathrm{d}}{\mathrm{d}x}$ is not a Hermitian operator since

$$\begin{aligned}\int_{-\infty}^{+\infty}\mathrm{d}x\psi_j^*\frac{\mathrm{d}\psi_i}{\mathrm{d}x} &= \psi_j^*\psi_i\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\mathrm{d}x\psi_i\frac{\mathrm{d}\psi_j^*}{\mathrm{d}x} \\ &= -\left(\int_{-\infty}^{+\infty}\mathrm{d}x\psi_i^*\frac{\mathrm{d}\psi_j}{\mathrm{d}x}\right)^* \\ &\neq \left(\int_{-\infty}^{+\infty}\mathrm{d}x\psi_i^*\frac{\mathrm{d}\psi_j}{\mathrm{d}x}\right)^*\end{aligned}$$

But $\frac{1}{i}\frac{\mathrm{d}}{\mathrm{d}x}$ is a Hermitian operator

$$\begin{aligned}\int_{-\infty}^{+\infty}\mathrm{d}x\psi_j^*\frac{1}{i}\frac{\mathrm{d}\psi_i}{\mathrm{d}x} &= -\frac{1}{i}\left(\int_{-\infty}^{+\infty}\mathrm{d}x\psi_i^*\frac{\mathrm{d}\psi_j}{\mathrm{d}x}\right)^* \\ &= \left(\int_{-\infty}^{+\infty}\mathrm{d}x\psi_i^*\frac{1}{i}\frac{\mathrm{d}\psi_j}{\mathrm{d}x}\right)^*\end{aligned}$$

I. Eigenvalues of Hermitian operator

- Theorem: Any eigenvalue of Hermitian operator is a real number.
- Proof:

  Given a Hermitian operator $\widehat{\Omega}$ with eigenvalue ω_i and normalized eigenfunction ψ_i, i.e., $\widehat{\Omega}\psi_i = \omega_i\psi_i$. Applying the definition of Hermitian operator, we have

$$\begin{aligned}\omega_i &= \int \mathrm{d}\tau\psi_i^*\widehat{\Omega}\psi_i \\ &= \left(\int \mathrm{d}\tau\psi_i^*\widehat{\Omega}\psi_i\right)^* \\ &= \omega_i^*\end{aligned}$$

  Thus ω_i must be real.

Q.E.D.

All operators corresponding to physical observables (properties that can be measured) are Hermitian operators.

II. Eigenfunctions of Hermitian operator

- Theorem: Eigenfunctions of Hermitian operator with different eigenvalues are orthogonal.
- Proof:

  Using the definition of Hermitian operator, we have

$$\begin{aligned}\int \mathrm{d}\tau\psi_i^*\widehat{\Omega}\psi_j &= \left(\int \mathrm{d}\tau\psi_j^*\widehat{\Omega}\psi_i\right)^* \\ &= \left(\omega_i \int \mathrm{d}\tau\psi_j^*\psi_i\right)^* \\ &= \omega_i \int \mathrm{d}\tau\psi_j\psi_i^*\end{aligned}$$

  Also,

$$\int \mathrm{d}\tau\psi_i^*\widehat{\Omega}\psi_j = \omega_j \int \mathrm{d}\tau\psi_i^*\psi_j$$

  Subtracting the first equation from the second one gives

$$0 = (\omega_j - \omega_i)\int \mathrm{d}\tau\psi_i^*\psi_j$$

  For $\omega_j \neq \omega_i$, we have

$$\int \mathrm{d}\tau\psi_i^*\psi_j = 0$$

Q.E.D.

Example1: one-dimensional momentum operator

For particle in constant potential, take the wavefunction as $\psi_k = e^{ikx}$. Define the momentum operator as

$$\hat{p}_x = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}$$

which has been proved to be Hermitian. Apply it to above wavefunction,

$$\hat{p}_x\psi_k = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\psi_k = \hbar k\psi_k$$

By definition, $p = \hbar k$, thus $\hat{p}_x\psi_k = p\psi_k$, and $\hat{p}_x$ is indeed the momentum operator.

Example2: three-dimensional momentum operator

Momentum operator $\hat{p} = \frac{\hbar}{i}\nabla = \frac{\hbar}{i}\left(\vec{e}_x\frac{\partial}{\partial x} + \vec{e}_y\frac{\partial}{\partial y} + \vec{e}_z\frac{\partial}{\partial z}\right)$ is Hermitian since all components of it are Hermitian.

3. Expectation value

For a Hamiltonian with normalized wavefunctions $\hat{H}\psi_i = E_i\psi_i$, $i = 1,2,\ldots$, we construct a wavefunction $\psi = c_1\psi_1 + c_2\psi_2$ where $|c_1|^2 + |c_2|^2 = 1$. The expectation value, or the average value of energy is then

$$\begin{aligned}
\langle E\rangle &= \int \mathrm{d}\tau\psi^*\hat{H}\psi \\
&= \int \mathrm{d}\tau(c_1^*\psi_1^* + c_2^*\psi_2^*)(c_1E_1\psi_1 + c_2E_2\psi_2) \\
&= |c_1|^2E_1\int \mathrm{d}\tau\,\psi_1^*\psi_1 + c_1^*c_2E_2\int \mathrm{d}\tau\,\psi_1^*\psi_2 + \\
&\quad c_2^*c_1E_1\int \mathrm{d}\tau\,\psi_2^*\psi_1 + |c_2|^2E_2\int \mathrm{d}\tau\,\psi_2^*\psi_2 \\
&= |c_1|^2E_1 + |c_2|^2E_2
\end{aligned}$$

Generally, for any operator $\hat{\Omega}$ in a quantum state ψ, its expectation value is

$$\langle\hat{\Omega}\rangle = \int \mathrm{d}\tau\,\psi^*\hat{\Omega}\psi$$

4. Heisenberg's uncertainty principle

Suppose we have measured an observable ω N times ($N \gg 1$), then the uncertainty of ω is defined as

$$\Delta\omega = \sqrt{\frac{\sum_{i=1}^{N}(\omega_i - \overline{\omega})^2}{N}}$$

For position and momentum, their uncertainties satisfy the following Heisenberg's uncertainty principle

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

Apply $\hat{p}_x\hat{x}$ to an arbitrary wavefunction $\phi(x)$ gives

$$\hat{p}_x\hat{x}\phi = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}(x\phi) = \frac{\hbar}{i}\phi + x\frac{\hbar}{i}\frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{\hbar}{i}\phi + \hat{x}\hat{p}_x\phi$$

Thus, $(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\phi = i\hbar\phi$. Since $\phi(x)$ is arbitrary, we have

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

Define commutator of two operators $\hat{A}$ and $\hat{B}$ as $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$, the above equation can be rewritten as

$$[\hat{x}, \hat{p}_x] = i\hbar$$

If $\hbar \to 0$, quantum mechanics will degenerate to classical mechanics.

- Heisenberg's uncertainty principle: If the commutator of two operators $\hat{A}$ and $\hat{B}$ is $[\hat{A}, \hat{B}] = i\hat{C}$, then their uncertainties satisfy the following inequality

$$\Delta A \cdot \Delta B \geq \frac{1}{2}\left|\langle \hat{C} \rangle\right|$$

- Proof:

Given an arbitrary wave function ϕ, constructing a non-negative integral with real variable ξ

$$I(\xi) = \int \mathrm{d}\tau \left|\xi \hat{A}\phi + i\hat{B}\phi\right|^2$$

Noted that for a complex number c, $|c|^2 = c^* c$. Expanding above integral, we have

$$\begin{aligned} I(\xi) &= \xi^2 \int \mathrm{d}\tau \left|\hat{A}\phi\right|^2 + \int \mathrm{d}\tau \left|\hat{B}\phi\right|^2 + i\xi \int \mathrm{d}\tau \left(\hat{A}\phi\right)^* \left(\hat{B}\phi\right) - i\xi \int \mathrm{d}\tau \left(\hat{B}\phi\right)^* \left(\hat{A}\phi\right) \\ &= \xi^2 \int d\tau \phi^* \hat{A}^2 \phi + \int d\tau \phi^* \hat{B}^2 \phi + i\xi \int d\tau \phi^* [\hat{A}, \hat{B}] \phi \\ &= \xi^2 \int d\tau \phi^* \hat{A}^2 \phi - \xi \int d\tau \phi^* \hat{C} \phi + \int d\tau \phi^* \hat{B}^2 \phi \\ &\geq 0 \end{aligned}$$

To ensure above quadratic function of ξ is non-negative, there must be

$$4\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle - \langle \hat{C} \rangle^2 \geq 0$$

i.e.

$$\sqrt{\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle} \geq \frac{1}{2}\left|\langle \hat{C} \rangle\right|$$

Define $\Delta\hat{A} = \hat{A} - \langle \hat{A} \rangle$, $\Delta\hat{B} = \hat{B} - \langle \hat{B} \rangle$, apparently,

$$\begin{aligned} [\Delta\hat{A}, \Delta\hat{B}] &= \left(\hat{A} - \langle \hat{A} \rangle\right)\hat{B} - \left(\hat{A} - \langle \hat{A} \rangle\right)\langle \hat{B} \rangle - \hat{B}\left(\hat{A} - \langle \hat{A} \rangle\right) + \langle \hat{B} \rangle\left(\hat{A} - \langle \hat{A} \rangle\right) \\ &= \hat{A}\hat{B} - \langle \hat{A} \rangle \hat{B} - \hat{B}\hat{A} + \hat{B}\langle \hat{A} \rangle \\ &= \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= [\hat{A}, \hat{B}] \end{aligned}$$

Thus

$$[\Delta\hat{A}, \Delta\hat{B}] = i\hat{C}$$

Substitute $\hat{A}$, $\hat{B}$ with $\Delta\hat{A}$ and $\Delta\hat{B}$ respectively in $\sqrt{\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle} \geq \frac{1}{2}\left|\langle \hat{C} \rangle\right|$,

$$\sqrt{\langle \left(\Delta\hat{A}\right)^2 \rangle \langle \left(\Delta\hat{B}\right)^2 \rangle} \geq \frac{1}{2}\left|\langle \hat{C} \rangle\right|$$

Noted that $\Delta A = \sqrt{\langle \left(\Delta\hat{A}\right)^2 \rangle}$ and $\Delta B = \sqrt{\langle \left(\Delta\hat{B}\right)^2 \rangle}$, finally we have

$$\Delta A \cdot \Delta B \geq \frac{1}{2}\left|\langle \hat{C} \rangle\right|$$

Q.E.D.

Examples

- $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}_x$. $[\hat{x}, \hat{p}_x] = i\hbar$, $\hat{C} = \hbar$. $\Delta x \cdot \Delta p_x \geq \hbar/2$.
    - $\psi_k = e^{ikx}$ has definite momentum $p_x = \hbar k$, so that $\Delta p_x = 0$. Δx must be $+\infty$, which means the particle is diffused in the whole x space.
    - If $\Delta x = 0$, we have $\Delta p_x \to +\infty$, thus $\langle \hat{H} \rangle = \langle \frac{\hat{p}_x^2}{2m} + V \rangle = \frac{\langle \hat{p}_x^2 \rangle}{2m} + \langle V \rangle \to +\infty$. This means we need infinite energy to constrain one quantal particle to a certain position.
- If two operators commute, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$, $\hat{C} = 0$, we have $\Delta A \cdot \Delta B \geq 0$. So $\hat{A}$ and $\hat{B}$ **can** be measured precisely at the same time.
    - $[\hat{x}, \hat{p}_y] = 0$
- A particle with mass m moves along x direction subjected to a potential $V(x)$. $\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$, $\hat{p}_x = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}$. $[\hat{H}, \hat{p}_x]\psi(x) = i\hbar\psi(x)\frac{\mathrm{d}V(x)}{\mathrm{d}x}$, i.e. $[\hat{H}, \hat{p}_x] = i\hbar\frac{\mathrm{d}V(x)}{\mathrm{d}x}$
    - If and only if $V(x)$ is equal to some constant will $\hat{H}$ and $\hat{p}_x$ commute, thus energy and x momentum can be measured precisely at the same time.
- From time-dependent S.E. $i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi$, we define $\hat{H} = i\hbar\frac{\partial}{\partial t}$. Since $[\hat{H}, t]\phi = \hat{H}(t\phi) - t(\hat{H}\phi) = i\hbar\phi$, $\Delta E \cdot \Delta t \geq \hbar/2$.
    - If a quantum state has definite energy, i.e. $\Delta E = 0$, then the lifetime of this state will be $\Delta t \to \infty$.
    - In reality, energy level is broadened, and $\Delta t \sim \hbar/\Delta E$ is regarded as lifetime of the energy level.

Lecture 2 – Translational Motion

1. One-dimensional particle-in-a-box model

Suppose we have one particle with mass m confined in a box $[0, L]$, then its Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

where the potential is

$$V(x) = \begin{cases} 0, & 0 < x < L \\ +\infty, & x \leq 0 \text{ or } x \geq L \end{cases}$$

I. Wavefunctions and energy levels

Within $(0, L)$, this S.E. has solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx},\ k = \sqrt{2mE}/\hbar$$

Outside $(0, L)$

$$\psi = 0$$

Since wavefunction should be continuous, we impose following boundary conditions

$$\psi(0) = \psi(L) = 0$$

Plug $x = 0$ and $x = L$ into $\psi(x) = Ae^{ikx} + Be^{-ikx}$, we have

$$\psi(0) = A + B = 0 \Longrightarrow A = -B$$

$$\psi(L) = -Be^{ikL} + Be^{-ikL} = -2iB\sin kL = 0 \Longrightarrow kL = n\pi,\ n = 1,2,\dots$$

So that after normalization, within $(0, L)$,

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right),\ n = 1,2,\dots$$

Energy levels corresponding to each $\psi_n(x)$ is

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2},\ n = 1,2,\dots$$

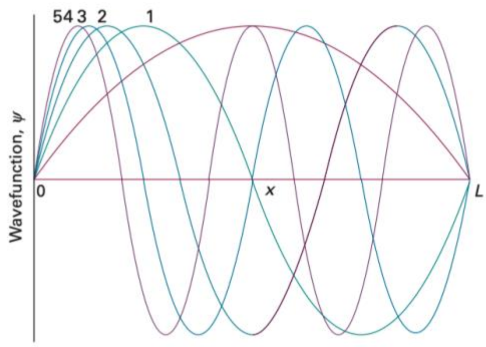


Figure 1 First five normalized wavefunctions

II. Orthogonality of wavefunctions

For $n \neq m$,

$$\int_0^L \mathrm{d}x\psi_n^*\psi_m = \frac{2}{L}\int_0^L \mathrm{d}x \sin\frac{n\pi x}{L}\sin\frac{m\pi x}{L}$$
$$= -\frac{1}{L}\int_0^L \mathrm{d}x\left[\cos\frac{(n+m)\pi x}{L} - \cos\frac{(n-m)\pi x}{L}\right]$$
$$= -\frac{1}{L}\left[\frac{L}{(n+m)\pi}\cdot\sin\frac{(n+m)\pi x}{L}\Big|_0^L - \frac{L}{(n-m)\pi}\cdot\sin\frac{(n-m)\pi x}{L}\Big|_0^L\right]$$
$$= 0$$

III. Uncertainty principle for ground state

Noted that $\Delta A = \sqrt{\langle(\Delta\hat{A})^2\rangle}$ and $\Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle$, we can rewrite uncertainty as

$$\Delta A = \sqrt{\left\langle \hat{A}^2 - 2\hat{A}\langle\hat{A}\rangle + \langle\hat{A}\rangle^2\right\rangle} = \sqrt{\langle\hat{A}^2\rangle - 2\langle\hat{A}\rangle\langle\hat{A}\rangle + \langle\hat{A}\rangle^2} = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$$

$\langle\hat{A}^2\rangle$ and $\langle\hat{A}\rangle$ are needed to calculate ΔA.

$$\langle\hat{x}\rangle = \frac{2}{L}\int_0^L x\sin^2\frac{\pi x}{L}\mathrm{d}x = \frac{1}{L}\int_0^L x\left(1-\cos\frac{2\pi x}{L}\right)\mathrm{d}x = \frac{L}{2} - \frac{1}{L}\int_0^L x\cos\frac{2\pi x}{L}\mathrm{d}x$$
$$= \frac{L}{2}$$
$$\langle\hat{p}\rangle = \frac{2\hbar}{iL}\cdot\frac{\pi}{L}\int_0^L \sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\mathrm{d}x = \frac{\hbar\pi}{iL^2}\int_0^L \sin\frac{2\pi x}{L}\mathrm{d}x = \frac{L}{2}$$

$$\langle\hat{x}^2\rangle = \frac{2}{L}\int_0^L x^2\sin^2\frac{\pi x}{L}\mathrm{d}x = \frac{1}{L}\int_0^L x^2\left(1-\cos\frac{2\pi x}{L}\right)\mathrm{d}x = \frac{L^2}{3} - \frac{1}{L}\int_0^L x^2\cos\frac{2\pi x}{L}\mathrm{d}x$$
$$= \frac{L^2}{3} - \frac{L^2}{2\pi^2}$$
$$\langle\hat{p}^2\rangle = \frac{2\hbar^2}{L}\cdot\frac{\pi^2}{L^2}\int_0^L \sin^2\frac{\pi x}{L}\mathrm{d}x = \frac{\pi^2\hbar^2}{L^3}\int_0^L\left(1-\cos\frac{2\pi x}{L}\right)\mathrm{d}x = \frac{\pi^2\hbar^2}{L^2}$$

$$\Delta x = \sqrt{\left(\frac{L^2}{3} - \frac{L^2}{2\pi^2}\right) - \left(\frac{L}{2}\right)^2} = \frac{L}{2\pi}\sqrt{\frac{\pi^2}{3} - 2}$$
$$\Delta p = \frac{\pi\hbar}{L}$$

Thus

$$\Delta x\cdot\Delta p = \frac{\hbar}{2}\cdot\sqrt{\frac{\pi^2}{3} - 2} \approx 1.136\cdot\frac{\hbar}{2} > \frac{\hbar}{2}$$

- Calculation details

  Let $\alpha(k) = \int_0^L \sin kx\,\mathrm{d}x = \frac{1-\cos kL}{k}$

$$\frac{\mathrm{d}\alpha(k)}{\mathrm{d}k} = \int_0^L x \cos kx \, \mathrm{d}x = \frac{L \sin kL}{k} + \frac{\cos kL - 1}{k^2}$$

So

$$\int_0^L x \cos \frac{2\pi x}{L} \mathrm{d}x = \frac{\mathrm{d}\alpha(k)}{\mathrm{d}k}\bigg|_{k=2\pi/L} = 0$$

Let $\beta(k) = \int_0^L \cos kx \, \mathrm{d}x = \frac{\sin kL}{k}$

$$\frac{\mathrm{d}^2\beta(k)}{\mathrm{d}k^2} = -\int_0^L x^2 \cos kx \, \mathrm{d}x = -\frac{L^2 \sin kL}{k} - \frac{2L \cos kL}{k^2} + \frac{2 \sin kL}{k^3}$$

So

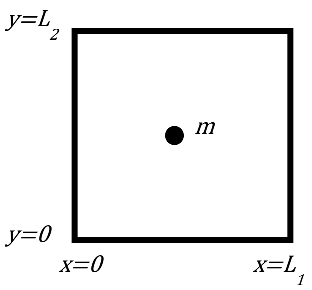
$$\int_0^L x^2 \cos \frac{2\pi x}{L} \mathrm{d}x = -\frac{\mathrm{d}^2\beta(k)}{\mathrm{d}k^2}\bigg|_{k=2\pi/L} = \frac{L^3}{2\pi^2}$$

- Example 8A.2 (pp. 321)
  - Problem: β-Carotene is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If we take each C-C bond length to be about 140 pm, then the length L of the molecular box in β-carotene is L = 2.94 nm. Estimate the wavelength of the light absorbed by this molecule from its ground state to the next higher excited state.
  - Answer:

$$\Delta E = E_{12} - E_{11} = 1.60 \times 10^{-19}\,\mathrm{J}$$

$$\lambda = \frac{h}{\Delta E} = 1.24\ \mu\mathrm{m}$$

2. Two-dimensional model



Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)$$

$$V(x,y) = \begin{cases} 0, & 0 < x < L_1 \text{ and } 0 < y < L_2 \\ +\infty, & \text{otherwise} \end{cases}$$

S.E. is $\hat{H}\psi(x,y) = E\psi(x,y)$.

Within $0 < x < L_1$ and $0 < y < L_2$, S.E. is

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

Boundary conditions are

$$\psi(0,y) = \psi(L_1,y) = \psi(x,0) = \psi(x,L_2) = 0$$

To solve this multivariable equation, we perform **separation of variables**. Let $\psi(x,y) = X(x)Y(y)$ and plug this equation into S.E., we get

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2X}{\mathrm{d}x^2}Y + X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right) = EXY$$

Divide both sides by XY

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right) = E$$

To ensure $-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right) = E$, each term in the LHS should be some constant, viz.

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_1,\ -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_2$$

with $E_1 + E_2 = E$.

Now the 2D S.E. of $\psi(x,y)$ has been decomposed into two 1D S.E., thus its solution is just the product of two separated equations,

$$\psi_{n_1,n_2} = \begin{cases} \dfrac{2}{\sqrt{L_1L_2}}\sin\dfrac{n_1\pi x}{L_1}\sin\dfrac{n_2\pi y}{L_2}, & \text{within 2D box} \\ 0, & \text{outside box} \end{cases}$$

Its energy levels are

$$E_{n_1,n_2} = \frac{n_1^2\pi^2\hbar^2}{2mL_1^2} + \frac{n_2^2\pi^2\hbar^2}{2mL_2^2}$$

where $n_1,\ n_2 = 1,2,3,\ldots$.

3. Three-dimensional model

Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)$$

$$V(x,y,z) = \begin{cases} 0, & 0 < x < L_1 \text{ and } 0 < y < L_2 \text{ and } 0 < z < L_3 \\ +\infty, & \text{otherwise} \end{cases}$$

S.E.: $\hat{H}\psi(x,y,z) = E\psi(x,y,z)$, within $0 < x < L_1$, $0 < y < L_2$, and $0 < z < L_3$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] = E\psi$$

Boundary conditions

$$\psi(0,y,z) = \psi(L_1,y,z) = 0$$
$$\psi(x,0,z) = \psi(x,L_2,z) = 0$$
$$\psi(x,y,0) = \psi(x,y,L_3) = 0$$

Now we perform similar procedures as 2D model. Let $\psi(x,y,z) = X(x)Y(y)Z(z)$ and plug this equation into S.E., we get

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2X}{\mathrm{d}x^2}YZ + \frac{\mathrm{d}^2Y}{\mathrm{d}y^2}XZ + \frac{\mathrm{d}^2Z}{\mathrm{d}Z^2}XY\right) = EXYZ$$

Divide above equation by XYZ

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}\right)=E$$

Each term in the LHS should be some constant, viz.

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=E_1,\ -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=E_2,\ -\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}=E_3$$

where $E_1+E_2+E_3=E$. So, the solution is

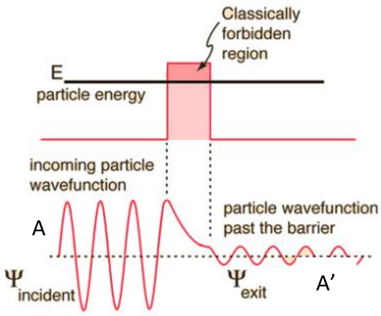
$$\psi_{n_1,n_2,n_3}=\begin{cases}\sqrt{\frac{8}{L_1L_2L_3}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}\sin\frac{n_3\pi z}{L_3},\ \text{within 3D box}\\ 0,\ \text{outside box}\end{cases}$$

with energy levels

$$E_{n_1,n_2,n_3}=\frac{n_1^2\pi^2\hbar^2}{2mL_1^2}+\frac{n_2^2\pi^2\hbar^2}{2mL_2^2}+\frac{n_3^2\pi^2\hbar^2}{2mL_3^2}$$

where $n_1,\ n_2, n_3=1,2,3,\ldots$.

4. Tunnelling



In this quantum tunnelling model, potential is set to be zero in $x<0$ or $x>L$ and be constant V in $0\le x\le L$. The energy of incident wavefunction is E and $E<V$. Denote the amplitude of incident and exit wave functions as A and A' respectively and define transmission coefficient as $T=\left|\frac{A'}{A}\right|$.

In zero-potential region, S.E. and wavefunction are

$$-\frac{\hbar^2}{2m}\cdot\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=E\psi,\ \psi=e^{\pm ikx},\ k=\sqrt{2mE}/\hbar$$

For incident region $x<0$, we choose $\psi_1(x)=Ae^{ikx}+Be^{-ikx}$, where two terms stand for incident and reflection wavefunctions respectively. For $x>L$, $\psi_3(x)=A'e^{ikx}$ stands for tunnelling wavefunction.

In potential barrier region, $-\frac{\hbar^2}{2m}\cdot\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V\psi=E\psi$. The general solution is

$$\psi_2(x)=Ce^{\kappa x}+De^{-\kappa x}$$

where $\kappa=\sqrt{2m(V-E)}/\hbar$.

At the two interfaces, wavefunction shall be smooth, i.e.

$$\psi_1(0)=\psi_2(0),\ \psi_2(L)=\psi_3(L),\psi_1'(0)=\psi_2'(0),\ \psi_2'(L)=\psi_3'(L)$$

thus we can obtain four equations

$$A+B=C+D(1)$$
$$ikA-ikB=\kappa C-\kappa D(2)$$
$$Ce^{\kappa L}+De^{-\kappa L}=A'e^{ikL}(3)$$
$$\kappa Ce^{\kappa L}-\kappa De^{-\kappa L}=ikA'e^{ikL}(4)$$

C, D and A can all be expressed in A' as

$\kappa(3)+(4)$: $C=\frac{\kappa+ik}{2\kappa}e^{(ik-\kappa)L}A'$, $\kappa(3)-(4)$: $D=\frac{\kappa-ik}{2\kappa}e^{(ik+\kappa)L}A'$

$ik(1)+(2)$: $A=\frac{(ik+\kappa)C+(ik-\kappa)D}{2ik}=\frac{A'}{4i\kappa k}\left[(\kappa+ik)^2e^{(ik-\kappa)L}-(\kappa-ik)^2e^{(ik+\kappa)L}\right]$

Then we try to solve transmission coefficient.

$$\begin{aligned}\frac{A}{A'e^{ikL}}&=\frac{1}{4i\kappa k}[(\kappa+ik)^2e^{-\kappa L}-(\kappa-ik)^2e^{\kappa L}]\\&=\frac{1}{4i\kappa k}[(\kappa^2-k^2)(e^{-\kappa L}-e^{\kappa L})+2i\kappa k(e^{-\kappa L}+e^{\kappa L})]\\&=\frac{1}{2}(e^{-\kappa L}+e^{\kappa L})-i\frac{V-2E}{4\sqrt{E(V-E)}}\cdot(e^{-\kappa L}-e^{\kappa L})\end{aligned}$$

denote $\epsilon=\frac{E}{V}$,

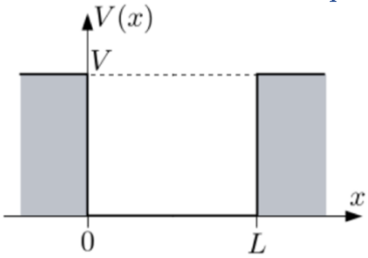
$$\begin{aligned}\left|\frac{A}{A'}\right|^2&=\frac{1}{4}(e^{-\kappa L}+e^{\kappa L})^2+\frac{1}{16}\frac{1-4\epsilon(1-\epsilon)}{\epsilon(1-\epsilon)}(e^{-\kappa L}-e^{\kappa L})^2\\&=\frac{1}{4}(e^{-\kappa L}+e^{\kappa L})^2-\frac{1}{4}(e^{-\kappa L}-e^{\kappa L})^2+\frac{(e^{-\kappa L}-e^{\kappa L})^2}{16\epsilon(1-\epsilon)}\\&=1+\frac{(e^{-\kappa L}-e^{\kappa L})^2}{16\epsilon(1-\epsilon)}\end{aligned}$$

Finally,

$$T=\left|\frac{A'}{A}\right|=\left[1+\frac{(e^{-\kappa L}-e^{\kappa L})^2}{16\epsilon(1-\epsilon)}\right]^{-1/2}$$

- If $\epsilon\ll 1$, i.e. $E\ll V$: $T\approx\frac{4\sqrt{\epsilon(1-\epsilon)}}{e^{\kappa L}-e^{-\kappa L}}\approx 0$.
- If $\kappa L\gg 1$, i.e. high, wide barrier: $T\approx 4\sqrt{\epsilon(1-\epsilon)}e^{-\kappa L}$.
- The heavier the mass, the smaller the T.

5. Particle in a finite square-well potential



Potential is constant V in $x<0$ or $x>L$ and zero in $0\le x\le L$. The energy of particle is E and $E<V$. Denote $k=\sqrt{2mE}/\hbar$ and $\kappa=\sqrt{2m(V-E)}/\hbar$.

Similar to above tunnelling model, we use following wavefunctions

$$\begin{aligned}x<0&: \psi_1(x)=Ce^{\kappa x}+C'e^{-\kappa x}\\0<x<L&: \psi_2(x)=Ae^{ikx}+Be^{-ikx}\\x>L&: \psi_3(x)=De^{-\kappa(x-L)}+D'e^{\kappa(x-L)}\end{aligned}$$

At infinity, wavefunction should vanish, thus $C'=D'=0$. At $x=0$, applying boundary conditions $\psi_1(0)=\psi_2(0)$ and $\psi_1'(0)=\psi_2'(0)$, we get $C=A+B$ and $\kappa C=ik(A-B)$, i.e.

$$A=\frac{ik+\kappa}{2ik}C,\ B=\frac{ik-\kappa}{2ik}C$$

Similarly, at $x=L$ we have $Ae^{ikL}+Be^{-ikL}=D$ and $ik\left(Ae^{ikL}-Be^{-ikL}\right)=-\kappa D$, i.e.

$$A=\frac{ik-\kappa}{2ik}e^{-ikL}D,\ B=\frac{ik+\kappa}{2ik}e^{ikL}D$$

Then C can be expressed in terms of D as $C = \frac{ik-\kappa}{ik+\kappa} e^{-ikL} D$ or $C = \frac{ik+\kappa}{ik-\kappa} e^{ikL} D$. Use the first expression, we have

$$\psi(x) = D \cdot \begin{cases} \dfrac{ik-\kappa}{ik+\kappa} e^{-ikL} e^{\kappa x} & , x \le 0 \\ \dfrac{ik-\kappa}{2ik} e^{-ikL} e^{ikx} + \dfrac{ik+\kappa}{2ik} e^{ikL} e^{-ikx} & , 0 < x < L \\ e^{-\kappa(x-L)} & , x \ge L \end{cases}$$

At $x = 0$, $\psi(x)$ should be continuous

$$\frac{ik-\kappa}{ik+\kappa} e^{-ikL} = \frac{ik-\kappa}{2ik} e^{-ikL} + \frac{ik+\kappa}{2ik} e^{ikL}$$

i.e.

$$(\kappa^2 - k^2 - 2i\kappa k)(\cos kL - i \sin kL) = (\kappa^2 - k^2 + 2i\kappa k)(\cos kL + i \sin kL)$$

Real parts of LHS and RHS are identical, and the imaginary parts should be equal

$$-[2\kappa k \cos kL + (\kappa^2 - k^2) \sin kL] = 2\kappa k \cos kL + (\kappa^2 - k^2) \sin kL$$

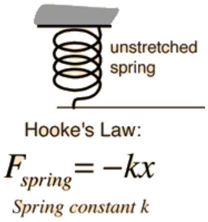
i.e.

$$4\kappa k \cos kL = 2(k^2 - \kappa^2) \sin kL$$

- When $\cos kL \neq 0$, we have $\tan kL = \frac{2\kappa k}{k^2-\kappa^2}$, i.e. $\tan \frac{\sqrt{2mE}L}{\hbar} = \frac{2\sqrt{E(V-E)}}{2E-V}$.
- When $\cos kL = 0$ and $k^2 = \kappa^2$, we have $E = \frac{V}{2}$ and $E = \frac{\left(n+\frac{1}{2}\right)^2 \pi^2 \hbar^2}{2mL^2}$ where $n = 0,1,2, \ldots$. For a given V, if there is no such E satisfy these two equations, then this state is quantum forbidden.

Lecture 3 – Vibrational Motion

1. One-dimensional harmonic oscillator



The force of spring is $F = -k_f x$, thus its potential can be calculated as $V(x) = -\int_0^x F\mathrm{d}x' = \frac{1}{2}k_f x$. The Hamiltonian is then $\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2$, and its corresponding S.E. is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2\psi(x) = E\psi(x)$$

We first change variable from x to $y = x/\alpha$ where $\alpha = \left(\frac{\hbar^2}{mk_f}\right)^{\frac{1}{4}}$. Under this operation, $\psi(x)$ changes to $\phi(y)$. After some algebra, we have

$$\frac{\mathrm{d}^2\phi(y)}{\mathrm{d}y^2} + (\lambda - y^2)\phi(y) = 0$$

where $\lambda = \frac{2E}{\hbar\omega}$ and $\omega = \sqrt{k_f/m}$.

Now we take a look at asymptotic behaviour of above equation. When $y \to \pm\infty$,

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}y^2} - y^2\phi = 0$$

thus $\phi \to e^{-\frac{y^2}{2}}$. Rewrite $\phi(y) = N \cdot H(y)e^{-\frac{y^2}{2}}$, we have following Hermite equation

$$\frac{\mathrm{d}^2H}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}H}{\mathrm{d}y} + (\lambda - 1)H = 0$$

Expand $H(y)$ as $H(y) = \sum_{n=0}^{\infty} c_n y^n$ and plug this expansion into Hermite equation,

$$\sum_{n=0}^{\infty} y^n[c_{n+2}(n+2)(n+1) - (2n - \lambda + 1)c_n] = 0$$

$$c_{n+2} = \frac{2n + 1 - \lambda}{(n+2)(n+1)}c_n$$

But when $y \to \pm\infty$, $\sum_{n=0}^{\infty} c_n y^n \to \infty$ as fast as e^{y^2}, causing $\phi \sim e^{-\frac{y^2}{2}}\sum_{n=0}^{\infty} c_n y^n \to \infty$ as fast as $e^{\frac{y^2}{2}}$. To ensure $\phi(\pm\infty) = 0$ the expansion of $H(y)$ must be truncated, i.e.

$$c_v \neq 0,\ c_{v+2} = 0$$

Thus we get quantized energy as

$$2v + 1 = \lambda = \frac{2E}{\hbar\omega}$$

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right),\ v = 0,1,2,\dots$$

It is worthwhile noting that the ground state energy, also called zero-point energy, $E_0 = \frac{1}{2}\hbar\omega$ is non-zero.

I. Wavefunction

Solutions of Hermite equation are called Hermite polynomials. They satisfy following recursive and orthonormal relations

$$H_{\nu+1} - 2yH_\nu + 2\nu H_{\nu-1} = 0$$
$$\int_{-\infty}^{+\infty} \mathrm{d}y H_{\nu'} H_\nu e^{-y^2} = \begin{cases} 0 & ,\text{if } \nu' \neq \nu \\ \sqrt{\pi}2^\nu \nu! & , \text{ if } \nu' = \nu \end{cases}$$
First three Hermite polynomials are listed below.

ν	0	1	2
H_ν	1	$2y$	$4y^2 - 2$

Now we need to normalize wavefunction $\phi(y) = N \cdot H(y)e^{-\frac{y^2}{2}}$.
$$\int_{-\infty}^{+\infty} \mathrm{d}x\psi_\nu^*(x)\psi_\nu(x) = N_\nu^2 \alpha \int_{-\infty}^{+\infty} \mathrm{d}y H_\nu^2 e^{-y^2} = N_\nu^2 \alpha\sqrt{\pi}2^\nu \nu!$$
Thus $N_\nu = \left(\alpha\sqrt{\pi}2^\nu \nu!\right)^{-\frac{1}{2}}$ and the normalized result is
$$\psi_\nu(x) = \left(\alpha\sqrt{\pi}2^\nu \nu!\right)^{-\frac{1}{2}} H_\nu\left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{2\alpha^2}}$$

II. Uncertainty of position

$$\begin{aligned}
\langle \hat{x} \rangle &= \int_{-\infty}^{+\infty} dx\psi_\nu^*(x)x\psi_\nu(x) \\
&= N_\nu^2\alpha^2 \int_{-\infty}^{+\infty} dyH_\nu(y)yH_\nu(y)e^{-y^2} \\
&= N_\nu^2\alpha^2 \int_{-\infty}^{+\infty} dyH_\nu \frac{H_{\nu+1} + 2\nu H_{\nu-1}}{2} e^{-y^2} \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\langle \hat{x}^2 \rangle &= \int_{-\infty}^{+\infty} dx\psi_\nu^*(x)x^2\psi_\nu(x) \\
&= N_\nu^2\alpha^3 \int_{-\infty}^{+\infty} dy[yH_\nu(y)][yH_\nu(y)]e^{-y^2} \\
&= N_\nu^2\alpha^3 \int_{-\infty}^{+\infty} dy\left(\frac{H_{\nu+1} + 2\nu H_{\nu-1}}{2}\right)^2 e^{-y^2} \\
&= \frac{1}{4}N_\nu^2\alpha^3 \int_{-\infty}^{+\infty} dy(H_{\nu+1}^2 + 4\nu H_{\nu+1}H_{\nu-1} + 4\nu^2 H_{\nu-1})e^{-y^2} \\
&= \frac{\alpha^2}{\sqrt{\pi}2^{\nu+2}\nu!}\left[\sqrt{\pi}2^{\nu+1}(\nu+1)! + \nu\sqrt{\pi}2^{\nu+1}\nu!\right] \\
&= \alpha^2\left(\nu + \frac{1}{2}\right)
\end{aligned}$$

Thus $\Delta x = \alpha\sqrt{\nu + \frac{1}{2}}$.

III. Potential energy

$$\langle \hat{V} \rangle = \left\langle \frac{1}{2}k_f\hat{x}^2 \right\rangle = \frac{1}{2}k_f\alpha^2\left(\nu + \frac{1}{2}\right) = \frac{1}{2}\hbar\omega\left(\nu + \frac{1}{2}\right) = \frac{1}{2}E_\nu$$

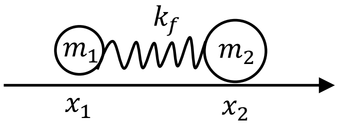
IV. Tunnelling – classically forbidden region

Classically forbidden region is where $V(x) > E_v$. Quantal oscillator can reach classically forbidden region with some tunnelling probability.

For ground state, $\psi_0 = N_0 e^{-\frac{x^2}{2\alpha^2}}$, $E_0 = \frac{1}{2}\hbar\omega$. Denote x_L and x_R as the negative and positive solutions of $V(x) = E_0$ respectively. The tunnelling probability is then

$$P(x < x_L) + P(x > x_R) = 2\int_{x_R}^{+\infty} \mathrm{d}x\psi_0^2(x) \approx 15.7\%$$

2. The vibration of a diatomic molecule



Consider a diatomic molecule moving along x axis. The coordinates of two atoms with mass m_1 and m_2 are x_1 and x_2 respectively. The force constant is k_f.

$$\hat{H} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + \frac{1}{2}k_f(x_1 - x_2)^2$$

Classically, the kinetic energy of this system is

$$K = \frac{1}{2}m_1\dot{x}_1^2 + \frac{1}{2}m_2\dot{x}_2^2$$

where $\dot{x}_i = \mathrm{d}x_i/\mathrm{d}t$. Define the coordinate of centre-of-mass as

$$x_\mathrm{c} = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}$$

and the distance between two atoms as

$$x = x_1 - x_2$$

It is easy to find the inverse transformations as

$$\begin{cases} x_1 = x_\mathrm{c} + \dfrac{m_2}{m_1 + m_2}x \\ x_2 = x_\mathrm{c} - \dfrac{m_1}{m_1 + m_2}x \end{cases}$$

Thus the kinetic energy can be expressed in $\{x, x_\mathrm{c}\}$ as

$$K = \frac{1}{2}m_1\left(\dot{x}_\mathrm{c} + \frac{m_2}{m_1 + m_2}\dot{x}\right)^2 + \frac{1}{2}m_2\left(\dot{x}_\mathrm{c} - \frac{m_1}{m_1 + m_2}\dot{x}\right)^2 = \frac{1}{2}M\dot{x}_\mathrm{c}^2 + \frac{1}{2}\mu\dot{x}^2$$

Here $M = m_1 + m_2$ is the total mass and $\mu = m_1m_2/M$ is the reduced mass.

Define the momentum of centre-of-mass and vibration as

$$P_\mathrm{c} = M\dot{x}_\mathrm{c}, p = \mu\dot{x}$$

The kinetic energy is then

$$K = \frac{P_\mathrm{c}^2}{2M} + \frac{p^2}{2\mu}$$

Its corresponding quantum Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_\mathrm{c}^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}k_f x^2$$

The Schrödinger equation $\hat{H}\psi(x_1,x_2) = E\psi(x_1,x_2)$ is now separable. Assuming that

$$\psi(x_1,x_2) = \Phi(x_\mathrm{c})\varphi(x)$$

we have

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2\Phi(x_\mathrm{c})}{\mathrm{d}x_\mathrm{c}^2}\cdot\varphi(x) + \left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\varphi(x)}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2\varphi(x)\right]\Phi(x_\mathrm{c}) = E\Phi(x_\mathrm{c})\varphi(x)$$

Divide both sides by $\Phi(x_\mathrm{c})\varphi(x)$,

$$-\frac{\hbar^2}{2M}\frac{1}{\Phi(x_\mathrm{c})}\frac{\mathrm{d}^2\Phi(x_\mathrm{c})}{\mathrm{d}x_\mathrm{c}^2} + \left[-\frac{\hbar^2}{2\mu}\frac{1}{\varphi(x)}\frac{\mathrm{d}^2\varphi(x)}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2\right] = E$$

Thus

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2\Phi(x_\mathrm{c})}{\mathrm{d}x_\mathrm{c}^2} = E_1\Phi(x_\mathrm{c})$$

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2\right)\varphi(x) = E_2\varphi(x)$$

$$E_1 + E_2 = E$$

The solution is

$$\Phi(x_\mathrm{c}) = Ae^{ikx_\mathrm{c}} + Be^{-ikx_\mathrm{c}}, k = \frac{\sqrt{2mE_1}}{\hbar}$$

$$\varphi(x) = \left(\alpha\sqrt{\pi}2^\nu\nu!\right)^{-\frac{1}{2}}H_\nu\left(\frac{x}{\alpha}\right)e^{-\frac{x^2}{2\alpha^2}}, \alpha = \left(\frac{\hbar^2}{\mu k_f}\right)^{\frac{1}{4}}$$

$$E_2 = \hbar\omega\left(\nu + \frac{1}{2}\right), \omega = \sqrt{\frac{k_f}{\mu}},\ \nu = 0,1,2,\ldots$$

Appendix: Direct coordinate transformations of Hamiltonian

It's straightforward to find that

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial x} + \frac{m_1}{M}\frac{\partial}{\partial x_\mathrm{c}}, \qquad \frac{\partial}{\partial x_2} = -\frac{\partial}{\partial x} + \frac{m_2}{M}\frac{\partial}{\partial x_\mathrm{c}}$$

Thus

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial^2}{\partial x^2} + \frac{2m_1}{M}\frac{\partial^2}{\partial x\partial x_\mathrm{c}} + \frac{m_1^2}{M^2}\frac{\partial^2}{\partial x_\mathrm{c}^2}$$

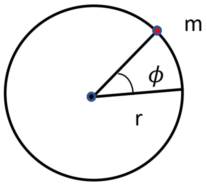
$$\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial x^2} - \frac{2m_2}{M}\frac{\partial^2}{\partial x\partial x_\mathrm{c}} + \frac{m_2^2}{M^2}\frac{\partial^2}{\partial x_\mathrm{c}^2}$$

Finally,

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + \frac{1}{2}k_f(x_1 - x_2)^2\\ &= -\frac{\hbar^2}{2}\left[\frac{1}{M}\frac{\partial^2}{\partial x_\mathrm{c}^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2}\right] + \frac{1}{2}k_f x^2\\ &= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_\mathrm{c}^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}k_f x^2\end{aligned}$$

Lecture 4 – Rotational Motion

1. Two-dimensional rotational motion



A particle of mass m moves in a ring of radius r in the xy-plane with zero potential. We use cylindrical coordinates for convenience. Laplace operator has following form

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$$

Since $r,\ z$ are fixed, it can be simplified to $\nabla^2 = \frac{1}{r^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$.

S.E. is $-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}\psi = E\psi$. Denote $I = mr^2$ as **moment of inertia**, we have

$$-\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}\psi(\phi) = E\psi(\phi)$$

The solution is $\psi(\phi) = Ne^{\pm i\sqrt{\epsilon}\phi}$ where $\epsilon = \frac{2IE}{\hbar^2}$. We then apply cyclic boundary condition $\psi(0) = \psi(2\pi)$, i.e. $N = Ne^{\pm i2\pi\sqrt{\epsilon}}$. $e^{\pm i2\pi\sqrt{\epsilon}} = 1$ leads to $\sqrt{\epsilon} = 0,1,2,\ldots$, thus

$$\psi(\phi) = Ne^{im\phi}, m = 0, \pm 1, \pm 2,\ \ldots$$

After normalization, we have $N = \frac{1}{\sqrt{2\pi}}$ and

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}, m = 0, \pm 1, \pm 2,\ \ldots$$

I. Energy

$$\hat{H}\psi_m = \frac{\hbar^2}{2I}m^2\psi_m, E_m = \frac{m^2\hbar^2}{2I}, m = 0, \pm 1, \pm 2,\ \ldots$$

- Ground state energy is zero.
- First excited states are **degenerated**. $E_{\pm 1} = \frac{\hbar^2}{2I}$ with degeneracy 2.

II. Linear momentum

$$\hat{p} = \frac{\hbar}{i}\nabla = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}(r\phi)} = \frac{\hbar}{ir}\frac{\mathrm{d}}{\mathrm{d}\phi}$$

$$\hat{p}\psi_m = \frac{m\hbar}{r}\psi_m, p_m = \frac{m\hbar}{r}$$

Thus ψ_m are also eigenfunctions of $\hat{p}$.

III. Angular momentum

Classically, $\vec{l} = \vec{r} \times \vec{p}$. In quantum mechanics, for a particle in a circle

$$\hat{l} = \hat{r}\hat{p} = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}\phi}$$

$$\hat{l}\psi_m = m\hbar\psi_m, l_m = m\hbar$$

Thus ψ_m are also eigenfunctions of $\hat{l}$.

These co-eigenfunction phenomenon are described by compatibility theorem next section.

2. Compatibility theorem

- Theorem: Giving two Hermitian operators $\hat{A}$ and $\hat{B}$, if $\hat{A}$ and $\hat{B}$ are commuting, viz $[\hat{A},\hat{B}]=0$, we can conclude that $\hat{A}$ and $\hat{B}$ have a common eigen basis, i.e. we can find a set of ψ_i satisfying $\hat{A}\psi_i = a_i\psi_i$ and $\hat{B}\psi_i = b_i\psi_i$
  - Examples: $[\hat{H},\hat{p}] = [\hat{H},\hat{l}] = [\hat{l},\hat{p}] = 0$, so $\psi_m = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ are their common eigenfunctions.

3. Three-dimensional rotational motion

A particle of mass m moves on the surface of a sphere of radius r with zero potential. Now we use spherical coordinates where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\Lambda^2}{r^2}$$

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

Since r is fixed, Laplace operator is simplified to $\nabla^2 = \frac{\Lambda^2}{r^2}$. The S.E. is

$$\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$$

i.e. $\Lambda^2 Y = -\epsilon Y$ with the same definition for ϵ as in 2D motion.

Let $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$, we have

$$\frac{\Theta}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) = -\epsilon\Theta\Phi$$

Dividing two sides by $\Theta\Phi$ and rearranging the equation,

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\epsilon\sin^2\theta = 0$$

Thus,

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -\beta$$

and

$$\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\epsilon\sin^2\theta = \beta$$

should hold, where β is a constant.

For $\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -\beta$, the solution is

$$\Phi_{m_l} = \frac{1}{\sqrt{2\pi}}e^{im_l\phi},\ m_l = 0,\pm1,\pm2,\ldots$$

For $\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\epsilon\sin^2\theta = m_l^2$, let $u=\cos\theta$, this equation can be rewritten as associated Legendre equation

$$(1-u^2)\frac{\mathrm{d}^2\Theta}{\mathrm{d}u^2}-2u\frac{\mathrm{d}\Theta}{\mathrm{d}u}+\left(\epsilon-\frac{m_l^2}{1-u^2}\right)\Theta = 0$$

Its solutions $\Theta_{lm_l}(\theta)$ are called **associated Legendre functions** where $l = 0,1,2,\ldots$ and $m_l = 0,\pm1,\pm2,\ldots,\pm l$.

The overall solutions $Y_{lm_l}(\theta,\phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$ are called spherical harmonics which satisfy following equation

$$\Lambda^2 Y_{lm} = -l(l+1)Y_{lm}$$

Hereafter we will drop out subscript l from m_l for simplicity. First few of them are listed below.

- $l = 0$
  - $m = 0$: $\sqrt{1/4\pi}$
- $l = 1$
  - $m = 0$: $\sqrt{3/4\pi}\cos\theta$
  - $m = \pm 1$: $\mp\sqrt{3/8\pi}\sin\theta\, e^{\pm i\phi}$
- $l = 2$
  - $m = 0$: $\sqrt{5/16\pi}(3\cos^2\theta - 1)$
  - $m = \pm 1$: $\mp\sqrt{15/8\pi}\cos\theta\sin\theta\, e^{\pm i\phi}$
  - $m = \pm 2$: $\sqrt{15/32\pi}\sin^2\theta\, e^{\pm 2i\phi}$

I. Energy and square of angular momentum

The Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\cdot\frac{\Lambda^2}{r^2}$,

$$\hat{H}Y_{lm} = \frac{\hbar^2}{2I}\cdot l(l+1)Y_{lm}$$

gives out energy levels

$$E_l = \frac{l(l+1)\hbar^2}{2I}$$

For square of angular momentum, $\hat{L}^2$, classically we have $E = L^2/2I$ and quantum mechanically $\hat{L}^2 = -\hbar^2\Lambda^2$.

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

thus

$$\langle \hat{L}^2 \rangle_l = l(l+1)\hbar^2$$

II. Angular momentum

Classically, angular momentum is defined as $\vec{L} = \vec{r}\times\vec{p}$. In quantum mechanics, we change it into $\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{p}}$, where $\hat{\vec{r}} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$, $\hat{\vec{p}} = \hat{p}_x\vec{e}_x + \hat{p}_y\vec{e}_y + \hat{p}_z\vec{e}_z$ and $\hat{p}_\mu = \frac{\hbar}{i}\frac{\partial}{\partial\mu}$ for $\mu = x, y, z$. Here '×' means cross product. Some basic properties of cross product are shown below

$$\vec{a}\times(k\vec{b}) = k(\vec{a}\times\vec{b}),\ \vec{a}\times\vec{a} = \vec{0},\ \vec{a}\times\vec{b} = -\vec{b}\times\vec{a},\ \vec{a}\times(\vec{b}+\vec{c}) = \vec{a}\times\vec{b} + \vec{a}\times\vec{c}$$

And for bases, their cross products are

$$\vec{e}_x\times\vec{e}_y = \vec{e}_z,\ \vec{e}_y\times\vec{e}_z = \vec{e}_x,\ \vec{e}_z\times\vec{e}_x = \vec{e}_y$$

Using these relations, we have

$$\hat{\vec{L}} = \left(x\vec{e}_x + y\vec{e}_y + z\vec{e}_z\right) \times \frac{\hbar}{i}\left(\frac{\partial}{\partial x}\vec{e}_x + \frac{\partial}{\partial y}\vec{e}_y + \frac{\partial}{\partial z}\vec{e}_z\right)$$
$$= \frac{\hbar}{i}\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\vec{e}_z + \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\vec{e}_x + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\vec{e}_y\right]$$

The components of $\hat{\vec{L}}$ are then

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),\ \hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),\ \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

respectively.

We then calculate commutators between these operators since the commutation relation is a key feature of angular momentum. Take $\hat{L}_x$ and $\hat{L}_y$ as example,

$$\left[\hat{L}_x, \hat{L}_y\right] = -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$
$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right)$$
$$+ \hbar^2\left(zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right)$$
$$= \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$
$$= i\hbar\hat{L}_z$$

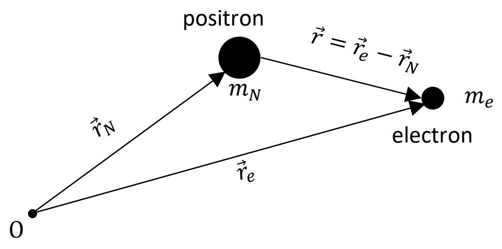
Similarly, we have $\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$, $\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$. For $\left[\hat{L}^2, \hat{L}_z\right]$, we first decompose it into $\left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right]$. Then it is straightforward to write

$$\left[\hat{L}_z^2, \hat{L}_z\right] = \hat{L}_z^3 - \hat{L}_z^3 = 0$$
$$\left[\hat{L}_x^2, \hat{L}_z\right] = \hat{L}_x^2\hat{L}_z - \hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x^2$$
$$= \hat{L}_x\left[\hat{L}_x, \hat{L}_z\right] + \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_x$$
$$= -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)$$
$$\left[\hat{L}_y^2, \hat{L}_z\right] = i\hbar\left(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y\right)$$

Thus $\left[\hat{L}^2, \hat{L}_z\right] = 0$, and $\left[\hat{H}, \hat{L}_z\right] = \left[\frac{\hat{L}^2}{2I}, \hat{L}_z\right] = 0$. $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ are mutual commuting, which confirms that Y_{lm} are the common eigenfunctions for them, i.e.

$$\hat{H}Y_{lm} = \frac{l(l+1)\hbar^2}{2I}Y_{lm}$$
$$\hat{L}^2Y_{lm} = l(l+1)\hbar^2Y_{lm}$$
$$\hat{L}_zY_{lm} = m\hbar Y_{lm}$$

Lecture 5 – Hydrogen Atom



In this last lecture, we will try to solve a real system – hydrogen atom. The system is composed of two particles – one electron and one positron, and thus its total degree of freedom (DoF) is 6. Three of DoFs belong to translational motion, two of them rotational motion, and the last one is the relative radial motion.

To begin with, we define following notations.

- Mass: nucleus m_N, electron m_e, total $m_{\mathrm{CM}} = m_N + m_e$, reduced $\mu = \frac{m_e m_N}{m_e + m_N}$
- Position vector: nucleus $\vec{r}_N$, electron $\vec{r}_e$, centre of mass (CM) $\vec{R} = \frac{m_e \vec{r}_e + m_N \vec{r}_N}{m_e + m_N}$, electron relative to nucleus $\vec{r} = \vec{r}_e - \vec{r}_N$
- $\vec{R} = R_x \vec{e}_x + R_y \vec{e}_y + R_z \vec{e}_z$, $\nabla_{\vec{R}}^2 = \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2}$ (similar for $\nabla_{\vec{r}}^2$)
- Classical momentum: nucleus $\vec{p}_N = m_N \dot{\vec{r}}_N$, electron $\vec{p}_e = m_e \dot{\vec{r}}_e$, CM $\vec{p}_{\mathrm{CM}} = m_{\mathrm{CM}} \dot{\vec{R}}$, electron relative to nucleus $\vec{p}_\mu = \mu \dot{\vec{r}}$
- Vector without arrow means modulus $r = |\vec{r}|$, etc

Then we can separate out CM motion and relative motion in classical energy expression as

$$E = \frac{p_e^2}{2m_e} + \frac{p_N^2}{2m_N} - \frac{e^2}{r} = \frac{p_{\mathrm{CM}}^2}{2m_{\mathrm{CM}}} + \frac{p_\mu^2}{2\mu} - \frac{e^2}{r}$$

Thus quantum Hamiltonian can also be written as sum of two parts

$$\hat{H} = -\frac{\hbar^2}{2m_{\mathrm{CM}}} \nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 - \frac{e^2}{r}$$

S.E.

$$\left(-\frac{\hbar^2}{2m_{\mathrm{CM}}} \nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 - \frac{e^2}{r} \right) \Phi(\vec{r}, \vec{R}) = E \Phi(\vec{r}, \vec{R})$$

1. Separation of CM motion and relative motion

Let $\Phi(\vec{r}, \vec{R}) = \chi(\vec{R}) \psi(\vec{r})$,

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}} (\nabla_{\vec{R}}^2 \chi) \psi - \frac{\hbar^2}{2\mu} \chi \nabla_{\vec{r}}^2 \psi - \frac{e^2}{r} \chi \psi = E \chi \psi$$

Divide both sides by $\chi\psi$:

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}} \frac{\nabla_{\vec{R}}^2 \chi}{\chi} - \frac{\hbar^2}{2\mu} \frac{\nabla_{\vec{r}}^2 \psi}{\psi} - \frac{e^2}{r} = E$$

Thus

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}} \frac{\nabla_{\vec{R}}^2 \chi}{\chi} = E_{\mathrm{CM}} \text{ and } -\frac{\hbar^2}{2\mu} \frac{\nabla_{\vec{r}}^2 \psi}{\psi} - \frac{e^2}{r} = E_e$$

where $E_{\mathrm{CM}} + E_e = E$.

Since $m_N \gg m_e$, $m_{\text{CM}} \approx m_e$. Roughly, $\chi(\vec{R})$ and $\psi(\vec{r})$ are nuclear and electron wavefunctions respectively.

I. CM motion $\chi(\vec{R})$

$$-\frac{\hbar^2}{2m_{\text{CM}}}\nabla_{\vec{R}}^2\chi = E_{\text{CM}}\chi$$

This is just a free particle moving in 3D space. Its solution is plane wave

$$\chi(\vec{R}) = Ae^{i\vec{k}_{\text{CM}}\cdot\vec{R}}$$

Its wave vector $\vec{k}_{\text{CM}}$ has modulus $\frac{\sqrt{2m_{\text{CM}}E_{\text{CM}}}}{\hbar}$ and is parallel to $\vec{v}_p$.

II. Relative motion ψ

$$-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi - \frac{e^2}{r}\psi = E_e\psi$$

$\nabla_{\vec{r}}^2$ can be expressed in spherical coordinate system located at nucleus

$$\nabla_{\vec{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\Lambda^2}{r^2}$$

From now on, we will omit the subscript of E_e for simplicity.

2. Separation of radial motion and rotational motion

Let $\psi(\vec{r}) = R(r)Y(\theta,\phi)$,

$$-\frac{\hbar^2}{2\mu}r^2\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right)Y - e^2rRY - Er^2RY - \frac{\hbar^2}{2\mu}R\Lambda^2Y = 0$$

Divide both sides by RY,

$$-\frac{\hbar^2r^2}{2\mu R}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) - e^2r - Er^2 - \frac{\hbar^2}{2\mu Y}\Lambda^2Y = 0$$

Thus we have

$$-\frac{\hbar^2}{2\mu Y}\Lambda^2Y = A$$

$$-\frac{\hbar^2r^2}{2\mu R}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) - e^2r - Er^2 = -A$$

I. Rotational motion $Y(\theta,\phi)$

Rearrange $-\frac{\hbar^2}{2\mu Y}\Lambda^2Y = A$ as $\Lambda^2Y = -\frac{2\mu A}{\hbar^2}Y$. The solution is apparently spherical harmonic functions, $Y = Y_{lm}(\theta,\phi)$ with eigenvalues $-\frac{2\mu A}{\hbar^2} = -l(l+1)$. Thus,

$$A = \frac{l(l+1)\hbar^2}{2\mu}$$

II. Radial motion $R(r)$

$$-\frac{\hbar^2r^2}{2\mu R}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) - e^2r - Er^2 = -\frac{l(l+1)\hbar^2}{2\mu}$$

i.e.

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}-\frac{e^2}{r}\right]R=ER$$

Remember $\langle\hat{L}^2\rangle=l(l+1)\hbar^2$, here $l(l+1)\hbar^2/2\mu r^2$ can be regarded as effective potential due to angular momentum.

Solution for above equation is

$$R_{nl}(r)=N_{nl}\rho^l L_{n-l-1}^{2l+1}(\rho)e^{-\rho/2}$$

- $\rho=2r/na$, $a=\hbar^2/\mu e^2\approx 0.529$ Å.
  - $a_0=\hbar^2/m_e e^2$, called Bohr radius, is the unit length in atomic unit.
- L_b^a: associated Laguerre polynomial.
- Normalization factor $N_{nl}=\left\{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]}\right\}^{1/2}$.
- $n=1,2,3,\ldots;\ l=0,1,2,\ldots,n-1$.
- Energy $E_n=-\frac{1}{n^2}\frac{e^2}{2a}$ (or in SI $-\frac{1}{n^2}\frac{e^2}{8\pi\varepsilon_0 a}$).

Overall, electronic wavefunction is

$$\psi_{nlm}(\vec{r})=R_{nl}(r)Y_{lm}(\theta,\phi)$$

It depends on three quantum numbers,

- Principal quantum number: $n=1,2,3,\ldots$.
- Azimuthal quantum number: $l=0,1,2,\ldots,n-1$.
- Magnetic quantum number: $m=0,\pm1,\pm2,\ldots,\pm l$.

But its energy levels $E_n=-\frac{1}{n^2}\frac{e^2}{2a}$ only depend on principal quantum number n. For ground state, $n=1, l=0, m=0$, it is non-degenerate. For first excited state it is 4-fold degenerated.

$$n=2,\begin{cases}l=0,\ m=0\\ l=1,\begin{cases}m=0\\ m=\pm1\end{cases}\end{cases}$$

First few electronic wavefunctions are listed below

$$\psi_{1s}=\psi_{100}=\frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}}$$

$$\psi_{2s}=\psi_{200}=\frac{1}{\sqrt{8\pi a^3}}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}}$$

$$\psi_{2p_z}=\psi_{210}=\frac{1}{4\sqrt{2\pi a^5}}re^{-\frac{r}{2a}}\cos\theta$$

$$\psi_{2p_x}=\frac{\psi_{211}+\psi_{21-1}}{\sqrt{2}}=\frac{1}{4\sqrt{2\pi a^5}}re^{-\frac{r}{2a}}\sin\theta\cos\phi$$

$$\psi_{2p_y}=\frac{\psi_{211}-\psi_{21-1}}{i\sqrt{2}}=\frac{1}{4\sqrt{2\pi a^5}}re^{-\frac{r}{2a}}\sin\theta\sin\phi$$