Wavelike properties of particles

De broglie Hypothesis

$$f = \frac{E}{h} \quad , \lambda = \frac{h}{p}$$

[1

Where E is the total energy, p is the momentum, and λ is the wavelength of the particle. $h = 6.63e\text{-}34 J \cdot s$ is the Planck constant.

- For a particle of zero rest energy,

$$E = pc = hf = \frac{hc}{\lambda},$$

[2

where p is the momentum of the particle.

- For a moving particle,

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

[3

Wavefunction for particles

$$\Psi(x,t) = A\sin(kx - \omega t)$$
$$\text{or } Ae^{i(kx-\omega t)}$$

[4

- probability density of the particle is

$$p(x,t) = |\Psi|^2 \equiv \Psi^*\Psi$$

[5

Uncertainty Principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \quad \Delta E \Delta t \geq \frac{\hbar}{2}$$

[6

Where x is position, p is momentum, E is energy, t is time, and $\hbar = \frac{h}{2\pi} = 1.05e\text{-}34 J \cdot s$ is the reduced Planck constant.

Min. Energy of Particle in a box

$$E = \frac{p^2}{2m} \geq \frac{\hbar^2}{2mL^2}$$

[7

Schrodinger's equation

Time-dependent Schrodinger's equation in 1D

1D Schrodinger's equation in position basis:

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

[8

Time-independent Schrodinger's equation in 1D

Via separation of variable, set $\Psi(x,t) = \psi(x)\varphi(t)$, and noticing $f = \frac{E}{h}$, we have

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

[9

time variation of wavefunction: $\varphi(t) = e^{-iEt/\hbar}$

- Probability density is thus simplified to

$$p(x) = |\Psi(x,t)|^2 = |\psi(x)|^2$$

[10

- Normalization condition:

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

[11

Potential Barrier

Potential Well

Infinite potential well- particle in a box $E < V_0$

- For a particle in a box of length L, where $V(x) = 0$ for $0 < x < L$, and $V(x) = \infty$ otherwise, the wavefunction inside box is found by

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

$$\Rightarrow \psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right).$$

[12

Noticing boundary values, the following is obtained:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = n^2\frac{\hbar^2\pi^2}{2mL^2} = n^2 E_1$$

[13

where $k = 2\frac{\pi}{\lambda}; k^2 = \left(\frac{p}{\hbar}\right)^2 = \frac{2mE}{\hbar^2}$

- Notably, $\lambda_n = 2\frac{L}{n}$; and the energy levels can be also expressed in terms of hc and mc^2:

$$E_1 = \frac{(hc)^2}{8mc^2 L^2}; \quad E_n = \frac{n^2(hc)^2}{8mc^2 L^2}$$

[14

These results are true for any potential well with $V(x) = 0$ inside the well.

- Normalization condition in box of length L:

$$\int_0^L |\psi(x)|^2\,\mathrm{d}x = 1$$

[15

Finite Square Well ($E < V_0$)

Consider Finite Square well with constant potential $V_0 > E$.

- Inside the well, The Schrodinger's eqn becomes

$$\psi'' = \frac{(E - V_0)2m}{-\hbar^2}\psi \equiv \alpha\psi$$

[16

and is solved with boundary conditions as

$$\psi_2(x) = A_1 \sin(kx) + A_2 \cos(kx) \tag{17}$$

- Outside well:

$$\psi_1(x) = B_1 e^{kx}; \quad \psi_3(x) = C_2 e^{-kx} \tag{18}$$

with

$$k = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{19}$$

Step potential: Transmission & Reflection

When $E > V_0$,

Now consider finite step potential $V(x) = V_0 H(x)$, $E > V_0$. The wave equation is solved as

$$\psi_1(x) = A e^{ik_1 x} + B e^{-ik_1 x};$$
$$\psi_2(x) = C e^{ik_2 x} \tag{20}$$

with $k_1 = \frac{\sqrt{2mE}}{\hbar}$, $k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$ Boundary condition further gives

$$B = \frac{k_1 - k_2}{k_1 + k_2} A;$$
$$C = \frac{2k_1}{k_1 + k_2} A. \tag{21}$$

We are thus motivated to define Reflection and Transmission coefficients as

$$R = \left| \frac{B}{A} \right|^2 = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2};$$
$$T = \frac{k_2 |C|^2}{k_1 |A|^2} = \frac{4k_1 k_2}{(k_1 + k_2)^2}; \tag{22}$$
$$R + T = 1.$$

They are the probability of reflection and transmission respectively.

When $E < V_0$,

we have $R = 1$ and thus no transmission. This is the case for a particle in a finite square well. Before potential step:

$$\psi_1(x) = A e^{ik_1 x} + B e^{-ik_1 x};$$
$$\psi_2(x) = C e^{-\alpha x} \tag{23}$$

where $\alpha = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$ and $k_1 = \frac{\sqrt{2mE}}{\hbar}$

Box potential: Tunneling

- consider $E < V_0$: Transmission: $T = Ge^{-2\alpha L}$; $G = 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)$ Particle can tunnel through the box potential before exponential decay to zero inside the box.

Expectations & Operators

- expectation

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} \psi^* \, f(x) \, \psi \, \mathrm{d}x \tag{24}$$

.

- for infinite square well: $\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$
- Momentum operator: $\hat{p}_q = \frac{\hbar}{i}\partial_q$, Hamiltonian operator: $\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$.
-

$$\langle \hat{p}\rangle = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i}\right)\partial_x\psi \, \mathrm{d}x \tag{25}$$

Schrodinger's equation in 3D

- time independent:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{26}$$

Infinite square well in 3D

Separation of variables:

$$\psi(\boldsymbol{x}) = \psi(x)\,\psi(y)\,\psi(z) \tag{27}$$

and Schrodinger's eqn is solved as

$$\psi(\boldsymbol{x}) = A\sin(k_1 x)\sin(k_2 y)\sin(k_3 z) \tag{28}$$

and we find descriptions on energy level by plugging this solution back:

$$E_{n_1 n_2 n_3} = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2) \tag{29}$$

or, when well is not cubic:

$$E_{n_1 n_2 n_3} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2} + \frac{n_3^2}{L_z^2}\right). \tag{30}$$

Where n is a quautum number $n \in \{1, 2, 3...\}$. Ground state: $n_1 = n_2 = n_3 = 1$

- when potential is cubic, notice degeneracy in energy levels. For example, the first energy state:

$$E_{112} = E_{121} = E_{211} \tag{31}$$

Scho's equation in spherical coord: atomic model, and quantum numbers

Due to ugliness of Spherical Laplacian, and out of our respect to Engeineering, we will skip the explicit Schrodinger's Eqn in spherical coord.

Sepration of variables:

$$\psi(r, \theta, \varphi) = R(r)\, f(\theta)\, g(\varphi) \tag{32}$$

- Solving partially using spherical harmonics:

$$Y_{lm}(\theta, \varphi) = f_{lm}(\theta)g_m(\varphi),$$
$$g_m(\varphi) = e^{im\varphi} \tag{33}$$

A list of Y_{lm} can be found in text p.274

- The radial part can be solved by Legendre polynomials:

$$R_{nl}(r) = A_{nl}e^{-r/a_0 n}r^l \mathcal{L}_{nl}^{r/a_0},$$
$$a_0 = \frac{\hbar^2}{ke^2\mu} \tag{34}$$

quantization of angular momentum

Angular momentum of a particle satisfying 3d Scho's eqn is

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \Rightarrow$$
$$|\boldsymbol{L}| = \hbar\sqrt{l(l+1)}, \quad L_z = m_l\hbar \tag{35}$$

Where $l = 0, 1, 2, ..., (n-1)$, and $m_l = 0, \pm 1, \pm 2, ..., \pm(l-1), \pm l$ are quantum numbers.

Atomic energy level

Using solution of $R_{nl}(r)$ and $f_{lm}(\theta)g_m(\varphi)$ on a Hydrogen atom, and using the potential due to nucleus being $V(r) = -Zke^2/r$, we can find the energy levels of an atom as

$$E_n = -\frac{\mu}{2n^2}\left(\frac{Zke^2}{\hbar}\right)^2 = -\frac{Z^2 E_1}{n^2} \tag{36}$$

- For a hydrogen atom with $Z = 1$, $E_1 = \frac{1}{2}\frac{ke^2}{\hbar}^2 \mu = 13.6$ eV.

Quantum numbers

- Principal quantum number $n = 1, 2, 3, ...$
- Azimuthal quantum number $l = 0(s), 1(p), 2(d), 3(f)..., (n-1)$
- Magnetic quantum number $m_l = 0, \pm 1, \pm 2, ..., \pm(l-1), \pm l$
- Spin quantum number $m_s = \pm\frac{1}{2}$

Puali exclusion principle & Hund's rule

- Puali: No two electrons in an atom can have the same set of quantum numbers.

- Hund: Maximize unpaired elctrons: fill each m_l in increasing order with $m_s = +\frac{1}{2}$, and then with $m_s = -\frac{1}{2}$.

Example: on 2p shell: $\{n, l, m_l, m_s\} = \{2,1,-1,1/2\}, \{2,1,0,1/2\}, \{2,1,1,1/2\}, \{2,1,-1,-1/2\}, \{2,1,0,-1/2\},$
$\{2,1,1,-1/2\}$.

Solids States

Energy bands

Many atoms couples together to form a solid, and the energy levels of a solid can be described by the energy bands.

What matters the most, under the scope of this exam, is the following:

- Valance band: The highest energy band occupied by electrons at 0K. Electrons here are considered to be bounded.

- Conduction band: The lowest energy band unoccupied by electrons at 0K. Electrons here are considered to be free moving and contributs to conductivity.

- Band gap: $E_g = E_c - E_v$, discribes the energy difference between the valance band and the conduction band. This is the difficulty for an electron to move from valance band to conduction band, and for an atom to be conductive.

  ‣ Insulator: $E_g > 4$eV,
  ‣ Semiconductor: $0 < E_g < 4$eV,
  ‣ Metal: $E_g = 0$ eV.

Fermi distribution

$$f(E) = \frac{1}{e^{(E-E_f)/(kT)} + 1} \tag{37}$$

where E_f is the Fermi energy, $k = 8.617e\text{-}5$ eV/K is the Boltzmann constant, and T is the temprature in Kelvin.

- This distribution describes the probability of an electron to be found at energy level E at temprature T, given the Fermi energy E_f.

Appendix

1. Useful integral for probability of wavefunction

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} \, \mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

[38

1. Useful constants:

- hc = 1240 eV nm.
- For an electron: $mc^2 = 0.511\text{MeV} = 5.11e5$ eV