Quantum Mechanics

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Schrödinger Equation

$$H\boldsymbol{\psi}(\boldsymbol{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\boldsymbol{r})\right]\boldsymbol{\psi}(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\boldsymbol{\psi}(\boldsymbol{r},t)$$

Where H is a hamiltonian operator. If H is time independent separation of variables gives:

$$\boldsymbol{\psi}(\boldsymbol{r},t) = \boldsymbol{\Phi}(\boldsymbol{r}) \cdot e^{-\frac{i}{\hbar}Et}$$

$$\left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\boldsymbol{r})\right]\boldsymbol{\Phi}(\boldsymbol{r}) = E\boldsymbol{\Phi}(\boldsymbol{r})$$

The general time dependent solution is:

$$\boldsymbol{\psi}(\boldsymbol{r},t) = \sum_n a_n \cdot \boldsymbol{\Phi}(\boldsymbol{r})e^{-\frac{i}{\hbar}Et}$$

Where a_n are found through the boundary conditions ($t = 0$):

$$a_n = \int \boldsymbol{\Phi}_n * (\boldsymbol{r}) \cdot \boldsymbol{\psi}(\boldsymbol{r}, t = 0)\, d^3r$$

Operators

Linear Operator

$$F(a\boldsymbol{\Phi}_1 + b\boldsymbol{\Phi}_2) = a \cdot F\boldsymbol{\Phi}_1 + b \cdot F\boldsymbol{\Phi}_2 \quad \forall \boldsymbol{\Phi}_1, \boldsymbol{\Phi}_2$$

Eigenvalue, Eigenfunction

$$Fu_n = f_n u_n$$

u_n is a eigen function to the operator F with corresponding eigenvalue f_n.

Hermitian Operator

$$\int (Hu) * v\, d^3r = \int u * Hv\, d^3r, \quad \forall u, v$$

A hermitian operator has real eigenvalues and corresponding eigenfunctions can be choosen to be orthonormal. Practically all operators in quantum mechanics are linear and hermitian.

Eigenfunction Expansion

$$\boldsymbol{\psi}(\boldsymbol{r}) = \sum_n a_n m \cdot u_n(\boldsymbol{r}), \quad a_n = \int u_n * \cdot \boldsymbol{\psi} \cdot d^3r$$

Expansion Postulate

At a meassurement of an observable F on a system described by a wavefunction $\boldsymbol{\psi}$ only eigenvalues of the operator F can be found. The probability of the result $F = f_n$ is given by

$$P(F = f_n) = \left|\int u_n * \boldsymbol{\psi}\, d^3r\right|^2, \quad Fu_n = f_n u_n$$

Momentum Operators

$$L^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

L^2 and L_z have normalized eigenfunctions $\Upsilon_l^m(\theta,\varphi)$ for which it holds that:

$$L^2\Upsilon_l^m = \hbar^2 l(l+1)\Upsilon_l^m$$

$$L_z\Upsilon_l^m = m\hbar\Upsilon_l^m$$

l	m	$\Upsilon_l^m(\theta,\varphi)$
0	0	$\Upsilon_0^0 = \frac{1}{\sqrt{4\pi}}$
1	0	$\Upsilon_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$
1	±1	$\Upsilon_1^{\pm1} = \pm\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}$
2	0	$\Upsilon_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$
2	±1	$\Upsilon_2^{\pm1} = \pm\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$
2	±2	$\Upsilon_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$

Commutators and Momentum Operators

$$\epsilon_{ijk} = \begin{cases} 1 & ijk \text{ even} \\ -1 & ijk \text{ odd} \\ 0 & \text{otherwise} \end{cases}$$

$$[x_i, p_j] = i\hbar \cdot \delta_{ij}$$

$$[x_i, L_j] = i\hbar \cdot \epsilon_{ijk} \cdot x_k$$

$$[L_i, L_j] = i\hbar \cdot \epsilon_{ijk} \cdot L_k$$

$$[x_i, x_j] = [p_i, p_j] = 0$$

$$[p_i, L_j] = i\hbar \cdot \epsilon_{ijk} \cdot p_k$$

$$J_+ = J_x + iJ_y$$
$$J_- = J_x - iJ_y$$

$$J_\pm J_\mp = J^2 - J_z^2 \pm \hbar \cdot J_z$$

$$[J_+, J_-] = 2\hbar \cdot J_z$$

$$[J_z, J_\pm] = \pm\hbar \cdot J_\pm$$

$$J_+\phi_{j,m} = \sqrt{(j-m)(j+m+1} \cdot \hbar \cdot \phi_{j,m+1}$$

$$J_-\phi_{j,m} = \sqrt{(j+m)(j-m+1} \cdot \hbar \cdot \phi_{j,m-1}$$

$$\Upsilon_l^l(\theta,\varphi) = (-1)^l \sqrt{\frac{2l+1)}{4\pi}\frac{(2l)!}{2^{2l}(l!)^2}} \cdot \sin^l\theta \cdot e^{il\varphi}$$

Applications

0.0.1 Low potential with infinitely rigid walls in one dimension

$$\mathcal{U}(x) = \begin{cases} \infty & x \leq 0,\ a \leq x \\ 0 & 0 < x < a \end{cases}$$

$$\Phi_n(x) = \begin{cases} 0 & \text{for } x \leq 0 \text{ and } a \leq x \\ \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} & \text{for } 0 < x < a \end{cases}$$

$$E_n = \frac{\pi^2\hbar^2 n^2}{2ma^2}$$

Harmonic Oscillator 1D

$$\mathcal{U}(x) = \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}kx^2$$

$$N_n = (2^n n!)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

Hermites polynom:

$$H_n(\xi) = (-1)^n \cdot e^{\xi^2} \cdot \frac{d^n e^{-\xi^2}}{d\xi^n}$$

$$\mathbf{\Phi}_n(x) = N_n \cdot e^{-\frac{m\omega}{2\hbar}x^2} \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

$$E_n = \hbar\omega \cdot \left(n + \frac{1}{2}\right)$$

The wave equations can alternatively be written:

$$u_n(x) = N\left(\frac{\partial}{\partial x} - ax\right)^n \cdot u_0(x)$$
$$u_0(x) = e^{-ax^2/2}$$

Spherical Symmetric Potential

$$\mathcal{U}(\boldsymbol{r}) = \mathcal{U}(r)$$

$$H = -\frac{\hbar}{2mr^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{L^2}{2mr^2} + \mathcal{U}(r)$$

$$H\boldsymbol{\psi}_{nlm}(\boldsymbol{r}) = E_{nlm}\boldsymbol{\psi}_{nlm}(\boldsymbol{r})$$

$$\boldsymbol{\psi}_{nlm}(\boldsymbol{r}) = \frac{G_{nl}(r)}{r}\Upsilon_l^m(\theta,\phi)$$

Radial equation:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}G(r) + \left[\frac{l(l+1)\hbar^2}{2mr^2} + \mathcal{U}(r)\right]G(r) = EG(r)$$

Hydrogen-like Atom

$$\mathcal{U}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The Schrödinger equation simplifies to:

$$\left[\Delta + \frac{2Z}{a_0 r} + \frac{2mE}{\hbar^2}\right]\boldsymbol{\Phi}(r) = 0$$

Radial wave functions of hydrogenic atoms:

n	l	$R_{nl}(r)$
1	0	$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2	0	$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2	1	$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}$
3	0	$R_{30}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-6\rho+\rho^2\right)e^{-\rho/2}$
3	1	$R_{31}(r) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho(4-\rho)e^{-\rho/2}$
3	2	$R_{32}(r) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/2}$

$$E-n = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2\hbar^2n^2} = -\frac{Z^2\hbar^2}{2a_0^2mn^2} = -13.6\frac{Z^2}{n^2}\text{eV}$$

$$S(x,t) = \frac{\hbar}{2im}\left[\boldsymbol{\psi}^*\cdot\frac{\partial\boldsymbol{\psi}}{\partial x} - \boldsymbol{\psi}\frac{\partial}{\partial x}\boldsymbol{\psi}^*\right]$$

Disturbance Calculations

Time independent disturbance:

$$\left.\begin{array}{l}\left(H^0+H'\right)\boldsymbol{\psi}'_m = E'_m\boldsymbol{\psi}'_m \\ H^0\boldsymbol{\psi}_n = E_n^0\boldsymbol{\psi}_n\end{array}\right\} \Longrightarrow$$

$$E'_m = E_m^0 + \langle m|H'|m\rangle + \sum_{n\neq m}\frac{|\langle m|H'|n\rangle|^2}{E_m^0 - E_n^0}$$

$$\boldsymbol{\psi}'_m = \boldsymbol{\psi}_m + \sum_{n\neq m}\frac{\int\boldsymbol{\psi}_n^* H'\boldsymbol{\psi}_m\,d^3r}{E_m^0 - E_n^0}\boldsymbol{\psi}_n$$

Time dependent disturbance:

$$\left.\begin{array}{l}H = H^0 + H' \\ H^0 \text{ Time independent} \\ H^0\boldsymbol{\psi}_n = E_n^0\boldsymbol{\psi}_n \\ H\boldsymbol{\psi}' = i\hbar\frac{\partial}{\partial t}\boldsymbol{\psi}'\end{array}\right\} \Longrightarrow$$

$$\boldsymbol{\psi}'_m = \sum_n a_{mn}(t)\boldsymbol{\psi}_n$$

$$\dot{a}_{mn} = -\frac{i}{\hbar} e^{-i(E_m - E_n)t/\hbar} \cdot H'_{nm}$$

"Golden Rule"

The transition probability per unit of time $w_{f\leftarrow i}$ for a transition from the state $\boldsymbol{\psi}_i$ to a group of states $F = \{\boldsymbol{\psi}_f\}$ with energy sin E_i^0 for a system characterized by the state density $\rho(E)$ is given by:

$$w_{f\leftarrow i} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2_{E_i^0 \approx E_f^0} \cdot \rho(E_f^0)$$

Dispersion (Born Approximation)

$$\frac{d\sigma}{d\Omega} = |f(\xi, \eta)|^2$$

$$f(\xi, \eta) = \frac{m}{2\pi\hbar^2} \int e^{i(\boldsymbol{k}_i - \boldsymbol{k}_f)\cdot\boldsymbol{r}} \cdot v(\boldsymbol{r})\, d^3r$$

For spherical symmetrical potential:

$$f(\xi, \eta) = \frac{2m}{\hbar^2 K} \int_0^\infty \sin(Kr)\cdot r\cdot v(r) dr, \qquad |K| = 2k\cdot\sin\left(\frac{\xi}{2}\right)$$

Spherical box-potential:

$$V(r) = \begin{cases} -V_0 & r \le a \\ 0 & r > a \end{cases}$$

$$f(\xi, \eta) = -\frac{2mV_0}{\hbar^2} \cdot \frac{\sin(Ka) - Ka\cos(Ka)}{K^3}$$

Screened Coulomb Potential:

$$v(r) = -\frac{A}{r} \cdot e^{-\alpha r}$$

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mA}{\hbar^2\left(\alpha^2 + 4k^2\sin^2(\xi/2)\right)}\right)^2$$

$$\sigma = \left(\frac{Am}{\hbar^2}\right)^2 \frac{16\pi}{\alpha^2\left(\alpha^2 + 4k^2\right)}$$

When $\alpha \to 0$, $\quad \dfrac{d\sigma}{d\Omega} \to \left(\dfrac{Am}{\hbar^2}\right)^2 \dfrac{1}{4\left(k\sin(\xi/2)\right)^4}$

Periodic Potential

$$V(x) = \left.\begin{matrix} 0 & n(a+b) < x < n(a+b) + a \\ V_0 & n(a+b) + a < x < (n+1)(a+b) \end{matrix}\right\}$$

Continuity Requirements:

$$\cos k_1a\cdot\cos k_2b - \frac{k_1^2 + k_2^2}{2k_1k_2}\sin k_1a\cdot\sin k_2b = \cos(k(a+b)), \quad V_0 < E$$

$$\cos k_1a\cdot\cosh \kappa b - \frac{k_1^2 + \kappa^2}{2k_1\kappa}\sin k_1a\cdot\sinh \kappa b = \cos(k(a+b)), \quad V_0 < E$$

Phase and group speed:

$$v_f = \frac{\omega}{k}, \quad v_g = \frac{d\omega}{dk} = \frac{dE}{dp}$$

Effective mass:

$$m^* = \left(\frac{1}{\hbar^2}\frac{d^2E}{dk^2}\right)^{-1}$$