Old Quantum Theory (1900–1925)

$E = hf = \hbar\omega$, $p = h/\lambda = \hbar k$

Quantization Rules : $E = nh$, $\oint_{\text{one period}} p_q \cdot dq = n_q h$

Correspondence Principle : CM is recovered in the limit of large quantum #s ($n \to \infty$)

Probability and some 3D Calculus

for a probability distribution $P(x)$: mean $\langle x\rangle = \int_{x_{\min}}^{x_{\max}} P(x)\, x\, dx$, variance $\sigma_x^2 \equiv \left\langle \left(x - \langle x\rangle\right)^2 \right\rangle = \langle x^2\rangle - \langle x\rangle^2$, $\sigma_x \equiv$ standard deviation

3D operators in Cartesian coord's : $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$ $\quad \vec{\nabla} = \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}$ $\quad \nabla^2 \equiv \vec{\nabla}\cdot\vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

GGS Theorems : $\int_{\vec{a}}^{\vec{b}} \vec{\nabla} f \cdot d\vec{l} = f(\vec{b}) - f(\vec{a})$ $\quad \int_{\text{Surf}} \left(\vec{\nabla}\times\vec{E}\right)\cdot d\vec{A} = \oint_{\partial\text{Surf}} \vec{E}\cdot d\vec{l}$ $\quad \int_{\text{Vol}} \left(\vec{\nabla}\cdot\vec{E}\right) dV = \oint_{\partial\text{Vol}} \vec{E}\cdot d\vec{A}$

Wave Mechanics

The **inner product** of two wavefunctions f & g : $\langle f|g\rangle \equiv \int_{-\infty}^{+\infty} f(\vec{r})^*\, g(\vec{r})\, d^3\vec{r}$

Physical observables Q correspond to **Hermitian operators** $\hat{Q}$ ≡ linear operators with this defining property

(presented in three equivalent forms) : 1. $\langle Q\rangle^* = \langle Q\rangle$ 2. $\langle \Psi | \hat{Q}\Psi\rangle = \langle \hat{Q}\Psi | \Psi\rangle$ i.e. $\hat{Q}$ is **self-adjoint**

3. eigenstates of $\hat{Q}$ are complete over their Hilbert space

Schrödinger Equation : $\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$ $\qquad$ Operators in 3D $\vec{r}$-space : $\hat{\vec{p}} = \frac{\hbar}{i}\vec{\nabla}$, $\hat{\vec{r}} = \vec{r}$, $\hat{H} = \frac{\hat{p}^2}{2m} + V = -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r})$

Eigenfunctions of $\hat{p},\hat{x}$ with Dirac normalization: $\psi_p(x) = e^{ipx/\hbar}/\sqrt{2\pi\hbar}$, $\psi_{x'}(x) = \delta(x - x')$

Boundary Conditions on wavefunctions:

a. Wavefunctions are always **continuous.**
b. Wavefunctions have **continuous derivatives**, **except** at points where $V = \pm\infty$
   where $\lim_{\varepsilon\to 0} \psi'(x+\varepsilon) - \psi'(x-\varepsilon) = \left(2m/\hbar^2\right) \lim_{\varepsilon\to 0} \int_{x-\varepsilon}^{x+\varepsilon} V(x)\psi(x)\, dx$
c. Wavefunctions are **zero** in any region where $V = \infty$.

Probability density $\rho(\vec{r},t)$ $= |\Psi(\vec{r},t)|^2 = \Psi^*\Psi$ $\qquad$ Prob. current density $\vec{j}(\vec{r},t) = \text{Re}\left[\Psi^* \frac{\hat{\vec{p}}}{m}\Psi\right]$ $\qquad$ Continuity Equation : $-\frac{\partial\rho}{\partial t} = \vec{\nabla}\cdot\vec{j}$ $\qquad$ $R,T = \frac{\vec{j}_{\text{re,tr}}\cdot\vec{A}}{\vec{j}_{\text{in}}\cdot\vec{A}}$

Expectation Value $\langle Q\rangle$ of observable $Q(\vec{r},\vec{p})$: $\langle Q\rangle \equiv \langle \Psi|\hat{Q}\Psi\rangle \equiv \int_{-\infty}^{+\infty} \Psi^*\, \hat{Q}\left(\vec{r}, -i\hbar\vec{\nabla}\right)\Psi\, d^3\vec{r}$

Ehrenfest's Theorem : Expectation values follow classical laws. $\frac{\langle p\rangle}{m} = \frac{d\langle x\rangle}{dt}$, $\frac{d\langle p\rangle}{dt} = \left\langle -\frac{dV}{dx}\right\rangle$ $\qquad$ Virial Theorem : $2\langle T\rangle = \left\langle x\frac{dV}{dx}\right\rangle$

Representations of a state $|\psi\rangle$ & operator $\hat{A}$: In the eigenbasis $\{|e_q\rangle\}$ of any Hermitian operator $\hat{Q}$,

- **Wavefuncⁿ** repres : $\langle f|g\rangle = \int \vec{f}^*(q)\vec{g}(q)\, dq$
  - wavefunction $\psi(q) = \langle e_q|\psi\rangle$
  - & differential operator $\hat{A}(q, \frac{\partial}{\partial q}, \frac{\partial^2}{\partial q^2}, ...)$
- **Matrix** repres : inner product $\langle f|g\rangle = \vec{f}^{*T}\vec{g}$
  - column vector $\vec{\psi} = \begin{pmatrix} \langle e_1|\psi\rangle \\ \langle e_2|\psi\rangle \\ \ldots \end{pmatrix}$ & matrix with elements $\mathbf{A}_{ij} = \langle e_i|\hat{A}|e_j\rangle$

e.g. wavefunction conversion between x- and p-space : $\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{ipx/\hbar}\phi(p)\, dp \Leftrightarrow \phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{-ipx/\hbar}\psi(x)\, dx$

e.g. Operators in 1D p-space : $\hat{p} = p$, $\hat{x} = i\hbar\frac{\partial}{\partial p}$, $\hat{H} = \frac{p^2}{2m} + V\left(i\hbar\frac{\partial}{\partial p}\right)$

Commutator : $\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$ Theorem : Operators that commute share a common set of eigenstates.

Uncertainty Principle : $\sigma_A \sigma_B \geq \left| \frac{1}{2i} \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle \right|$ e.g. $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

Time-dep. of Expec. Value : $\frac{d\langle \hat{Q} \rangle}{dt} = \frac{i}{\hbar} \left\langle \left[\hat{H}, \hat{Q}\right] \right\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle$

Axioms of QM

1. The **STATE** of a QM system is represented by a vector $|\Psi(t)\rangle$ in a Hilbert space (≈ Inner Product Space).

2. **OBSERVABLES** Q are represented by Hermitian operators $\hat{Q}$. In <u>x-space</u> ≡ the eigenbasis of the position operator $\hat{x}$, the phase space operators are $\hat{x} = x$ & $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, and those of dependent observables are $\hat{Q}(\hat{x}, \hat{p})$.

3. **MEASUREMENT** of an observable Q will yield one of its <u>eigenvalues</u> q, and the state of the system will change from $|\psi\rangle$ to the corresponding <u>eigenstate</u> $|e_q\rangle$. Allowed eigenstates are constrained by physical requirements such as boundary conditions and normalizability.

4. The **PROBABILITY** of measuring a particular eigenvalue q from a state $|\psi\rangle$ is $P(q) = \left| \langle e_q | \psi \rangle \right|^2$.

5. The **TIME-EVOLUTION** of a quantum state is given by the <u>Schrödinger Equation</u>, $i\hbar \frac{d}{dt}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$.

6. A multiparticle state containing two **IDENTICAL PARTICLES** is symmetric/anti-symmetric under their exchange if the particles are bosons (integer spin) / fermions (half-integer spin).

Miscellaneous Math

Gaussian prob dist^n : $P(x; x_0, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-x_0)^2/2\sigma^2}$

Sums : $\sum_{j=0}^{\mu} 1 = \mu + 1$, $\sum_{j=0}^{\mu} j = (\mu+1)\frac{\mu}{2}$

Gaussian Integrals: $\int_{-\infty}^{+\infty} e^{-ax^2 - bx}\, dx = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2}{4a}}$ $\int_{-\infty}^{+\infty} x\, e^{-ax^2 - bx}\, dx = -\frac{\sqrt{\pi}\, b}{2a^{3/2}}\, e^{\frac{b^2}{4a}}$ $\int_{-\infty}^{+\infty} x^2\, e^{-ax^2 - bx}\, dx = \frac{\sqrt{\pi}}{4a^{5/2}}\left(2a + b^2\right) e^{\frac{b^2}{4a}}$

Exponential Integrals: $\int_0^{\infty} x^n\, e^{-x}\, dx = \Gamma(n+1) = n!$ $\int x\, e^{-ax}\, dx = -\frac{e^{-ax}}{a^2}(ax+1)$ $\int x^2\, e^{-ax}\, dx = -\frac{e^{-ax}}{a^3}\left(a^2x^2 + 2ax + 2\right)$

Sinusoidal Integrals: $\int_0^{\pi} \begin{matrix} \sin^2(a\phi) \\ \cos^2(a\phi) \end{matrix}\, d\phi = \frac{\pi}{2} \mp \frac{\sin(2\pi a)}{4a}$ $\int_0^{\pi} \begin{matrix} \sin(n\phi)\sin(m\phi) \\ \cos(n\phi)\cos(m\phi) \end{matrix}\, d\phi = \delta_{nm}$ $\int_0^{\pi} \sin(n\phi)\cos(m\phi)\, d\phi = 0$

Fourier Integrals: $f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} A(k) e^{ikx}\, dk$ where $A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx}\, dx$

Dirac δ function : $\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{iqx}\, dq$

Defining Properties :
1. $\delta(x) = 0$ when $x \neq 0$
2. $\delta(x) = \infty$ when $x = 0$ OR $\int_{-\infty}^{+\infty} \delta(x) f(x)\, dx = f(0)$
3. $\int_{-\infty}^{+\infty} \delta(x)\, dx = 1$

Classical Mechanics security blanket ☺

$L(q_i, \dot{q}_i, t) = T - U$ Lagrange EOM: $\frac{\partial L}{\partial q_i} = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)$

$H \equiv \dot{q}_i (\partial L / \partial \dot{q}_i) - L$ equals $T+U$ when $\vec{r}_a = \vec{r}_a(q_i)$

$dH/dt = -\partial L / \partial t$

Common Forces : $F_{\text{grav}} = \frac{Gm_1 m_2}{r^2}$, $F_{\text{elec}} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$, $F_{\text{cf}} = \frac{mv^2}{r}$

Generalized momentum $p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$, force $Q_i \equiv \frac{\partial L}{\partial q_i}$

Hamilton's EOM: $-\frac{\partial H}{\partial q_i} = \frac{dp_i}{dt}$, $\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}$

Special Relativity: $E^2 = (pc)^2 + (mc^2)^2$

$\gamma = \frac{1}{\sqrt{1 - (v/c)^2}}$, $E = \gamma mc^2$, $p = \gamma mv$, $v = \frac{pc^2}{E}$

Constants : $m_e c^2 = 0.511$ MeV $\qquad \hbar c \; \begin{matrix} = 197 \text{ MeV}\cdot\text{fm} \\ \approx 200 \text{ MeV}\cdot\text{fm} \end{matrix} \qquad \alpha \equiv \dfrac{e^2}{4\pi\varepsilon_0 \hbar c} = \dfrac{1}{137} \qquad a_0 \equiv \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \dfrac{(\hbar c)}{\alpha\,(m_e c^2)}$

Angular Momentum $\quad \hat{L}^2 = \left|\vec{r}\times\frac{\hbar}{i}\vec{\nabla}\right|^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

$$\hat{L}_x = +i\hbar\left(\sin\phi\frac{\partial}{\partial\theta}+\frac{\cos\theta}{\sin\theta}\cos\phi\frac{\partial}{\partial\phi}\right), \quad \hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta}-\frac{\cos\theta}{\sin\theta}\sin\phi\frac{\partial}{\partial\phi}\right), \quad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Spin & Angular Momentum : L, l can be replaced by S, s $\qquad [L^2, L_{x,y,z}] = 0$, $\qquad \left[L_x, L_y\right] = i\hbar L_z$, etc

$$L^2|l\,m\rangle = \hbar^2 l(l+1)|l\,m\rangle, \quad L_z|l\,m\rangle = \hbar m|l\,m\rangle, \quad L_\pm = L_x \pm iL_y, \quad L_\pm|l\,m\rangle = \hbar\sqrt{l(l+1)-m(m\pm1)}\,|l(m\pm1)\rangle$$

Pauli Spin Matrices $\left\{S_x, S_y, S_z\right\} = \frac{\hbar}{2}\left\{\sigma_x, \sigma_y, \sigma_z\right\}$ where $\sigma_x, \sigma_y, \sigma_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Spherical Harmonics $Y_l^m(\theta,\phi)$, $m = -l,\ldots,l$ in steps of 1

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_2^{\pm2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta \qquad Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$$

$$Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi} \qquad Y_3^{\pm1} = \mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1) \qquad Y_3^{\pm2} = \left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm2i\phi}$$

$$Y_2^{\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{\pm i\phi} \qquad Y_3^{\pm3} = \mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm3i\phi}$$

H-like atom : radial e-functions $R_{nl}(r)$

$Ze \equiv$ nuclear charge (Z=1 is hydrogen)

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Zr}{a_0}\right)$$

$$R_{20} = \left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)$$

$$E_n = -\frac{(Z\alpha)^2}{2n^2}\left(m_e c^2\right) \text{ for } n = 1,2,3,\ldots$$

Spherical Coordinates $\qquad$ *Line Element:* $d\vec{l} = dr\;\hat{r} + r\,d\theta\;\hat{\theta} + r\sin\theta\,d\phi\;\hat{\phi}$

$$x = r\sin\theta\cos\phi \qquad \hat{x} = \sin\theta\cos\phi\;\hat{r} + \cos\theta\cos\phi\;\hat{\theta} - \sin\phi\;\hat{\phi}$$

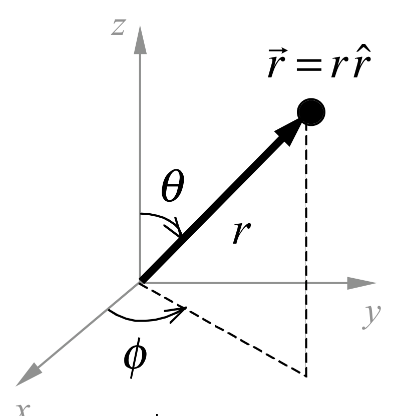
$$y = r\sin\theta\sin\phi \qquad \hat{y} = \sin\theta\sin\phi\;\hat{r} + \cos\theta\sin\phi\;\hat{\theta} + \cos\phi\;\hat{\phi}$$

$$z = r\cos\theta \qquad \hat{z} = \cos\theta\;\hat{r} - \sin\theta\;\hat{\theta}$$

$$r = \sqrt{x^2+y^2+z^2} \qquad \hat{r} = \sin\theta\cos\phi\;\hat{x} + \sin\theta\sin\phi\;\hat{y} + \cos\theta\;\hat{z}$$

$$\theta = \tan^{-1}(\sqrt{x^2+y^2}\,/\,z) \qquad \hat{\theta} = \cos\theta\cos\phi\;\hat{x} + \cos\theta\sin\phi\;\hat{y} - \sin\theta\;\hat{z}$$

$$\phi = \tan^{-1}(y\,/\,x) \qquad \hat{\phi} = -\sin\phi\;\hat{x} + \cos\phi\;\hat{y}$$



Gradient: $\quad \vec{\nabla}V = \frac{\partial V}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial V}{\partial\theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial V}{\partial\phi}\hat{\phi}$

Laplacian: $\quad \nabla^2 V = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial V}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial V}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 V}{\partial\phi^2}$

Divergence: $\quad \vec{\nabla}\cdot\vec{E} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 E_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\;E_\theta) + \frac{1}{r\sin\theta}\frac{\partial E_\phi}{\partial\phi}$

	∂_r	∂_θ	∂_ϕ
$\hat{r}$	0	$\hat{\theta}$	$\sin\theta\hat{\phi}$
$\hat{\theta}$	0	$-\hat{r}$	$\cos\theta\hat{\phi}$
$\hat{\phi}$	0	0	$-\sin\theta\hat{r}$ $-\cos\theta\hat{\theta}$

Curl: $\quad \vec{\nabla}\times\vec{E} = \frac{\hat{r}}{r\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta\;E_\phi) - \frac{\partial E_\theta}{\partial\phi}\right] + \frac{\hat{\theta}}{r}\left[\frac{1}{\sin\theta}\frac{\partial E_r}{\partial\phi} - \frac{\partial}{\partial r}(rE_\phi)\right] + \frac{\hat{\phi}}{r}\left[\frac{\partial}{\partial r}(rE_\theta) - \frac{\partial E_r}{\partial\theta}\right]$

Acceleration: $\quad \vec{a} = \hat{r}\left[\ddot{r} - r\dot{\theta}^2 - r\dot{\phi}^2\sin^2\theta\right] + \hat{\theta}\left[r\ddot{\theta} + 2\dot{r}\dot{\theta} - r\dot{\phi}^2\sin\theta\cos\theta\right] + \hat{\phi}\left[\sin\theta(r\ddot{\phi} + 2\dot{r}\dot{\phi}) + \cos\theta(2r\dot{\theta}\dot{\phi})\right]$