

# 1 Wave Function

$\begin{aligned}\Psi_p &= e^{i(2\pi x/\lambda - 2\pi t/T)} \\ &= e^{i(kx - \omega t)} \\ &= e^{\frac{i}{\hbar}(px - Et)}\end{aligned}$	$\left  \right.$	$\begin{aligned}\hat{P}\Psi_p &= p\Psi_p = \hbar k\Psi_p \\ \hat{P} &= \frac{\hbar}{i}\partial_x \\ \hat{P}\Psi_p &= \frac{\hbar}{i}\partial_x (e^{\frac{i}{\hbar}(px - Et)}) \\ &= p e^{\frac{i}{\hbar}(px - Et)} \\ &= p\Psi_p\end{aligned}$	$\left  \right.$	$\begin{aligned}\hat{E}\Psi_p &= E\Psi_p = \hbar\omega\Psi_p \\ \hat{E} &= -\frac{\hbar}{i}\partial_t \\ \hat{E}\Psi_p &= -\frac{\hbar}{i}\partial_t (e^{\frac{i}{\hbar}(px - Et)}) \\ &= E e^{\frac{i}{\hbar}(px - Et)} \\ &= E\Psi_p\end{aligned}$
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## 1.1 Schrodinger $\Psi$

$$\begin{aligned}\hat{E}\Psi &= \hat{H}\Psi = (\hat{T} + \hat{V})\Psi \\ \hat{E}\Psi &= \left( \frac{\hat{p}^2}{2m} + V(\vec{r}, t) \right) \Psi \\ i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) &= \left( \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right) \Psi(\vec{r}, t)\end{aligned}$$

If  $V = V(x)$

$$\Psi(x, t) = \psi(x)\phi(t) \Rightarrow$$

- $E_n\phi_n(t) = i\hbar \frac{\delta}{\delta t} \phi_n(t) \Rightarrow \boxed{\phi_n(t) = e^{-\frac{i}{\hbar}E_n t}}$

- $E_n\psi_n(x) = \left( \frac{-\hbar^2}{2m} \partial_x^2 + V(x) \right) \psi_n(x)$

-  $\psi$  can be lin. sum of real or complex, so choose real  $\psi$

- Linear:  $\boxed{\Psi(x, t) = \sum_n \psi_n(x) e^{-\frac{i}{\hbar}E_n t}}$

- $\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = 0 \Rightarrow$  measuring stationary state,  $\Psi_n$ , returns one  $E$  (determinate state)

If  $V = V(r)$

$$\Psi(\vec{r}) = R(r)Y_l^m(\theta, \phi) = R(r)\Theta_l^m(\theta)\Phi_m(\phi) \Rightarrow$$

$$Eu = \left( \frac{\hat{p}_r^2}{2m} + V(r) + \frac{\hat{L}^2}{2(mr^2)} \right) u$$

$$\boxed{Eu = \frac{-\hbar^2}{2m} \partial_r^2 u + \left[ V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] u}$$

- $u(r) = rR(r)$

- $\Phi_m(\phi) = e^{im\phi}$

- $\Theta_l^m(\theta) = AP_l^m(\cos \theta)$

$$- A = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}, \quad \epsilon = \begin{cases} (-1)^m & (m \geq 0) \\ 1 & (m \leq 0) \end{cases}$$

$$- P_l^m(x) = \text{Assoc. Legendre Func. (see extra)}$$

- $l \in \mathbb{N}_0, m \in \{-l, \dots, -1, 0, 1, \dots, l\}$

- $\hat{L}_i = (\vec{r} \times \vec{p})_i$

## 1.2 Usage

- $\langle f|g\rangle = \int_{-\infty}^{\infty} f(x)^* g(x) dx$
  - $\langle f|g\rangle_{ab} = \int_a^b f(x)^* g(x) dx$
  - $|f\rangle \equiv f(x)$
  - $\langle f| \equiv \int f(x)^* [\dots] dx$
  - $\langle f|f\rangle = \int_a^b |f|^2 dx < \infty \Rightarrow f \in L_2(a,b)$
  - $\left(\int_a^b |f|^p dx < \infty \Rightarrow f \in L_p(a,b)\right)$
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$$\Psi = \begin{cases} \sum_n c_n f_n \\ \int_n c_n f_n dn \end{cases}, \quad \langle f_m|f_n\rangle = \begin{cases} \delta_{mn} \\ \delta_{(m-n)} \end{cases}, \quad \begin{matrix} \text{(see Born int.)} \\ |c_n|^2 = \begin{cases} P(n) \\ \text{PDF}_{(n)} \end{cases} \end{matrix}$$

$$\Rightarrow \boxed{c_n = \langle f_n|\Psi\rangle}$$

$\forall \{f_n\} \in L_2$ :

$$|\Psi\rangle = \begin{cases} \sum_n c_n |f_n\rangle = \sum_n \langle f_n|\Psi\rangle |f_n\rangle = \left(\sum_n |f_n\rangle \langle f_n|\right) |\Psi\rangle = |\Psi\rangle \\ \int_n c_n |f_n\rangle dn = \int_n \langle f_n|\Psi\rangle |f_n\rangle dn = \left(\int_n |f_n\rangle \langle f_n| dn\right) |\Psi\rangle = |\Psi\rangle \end{cases}$$

$\hat{x}\Psi_y = x\Psi_y = y\Psi_y$ $\Rightarrow \boxed{\Psi_y = \delta_{(x-y)}}$	$\hat{p}\Psi_p = p\Psi_p$ $\Rightarrow \boxed{\Psi_p = A e^{\frac{i}{\hbar} p x}}$	$\hat{H}\Psi_n = E_n \Psi_n$ (See Potential Examples)
$\Psi_{(x,0)} = \int_{-\infty}^{\infty} c_y \Psi_y dy$ $= \int_{-\infty}^{\infty} \Psi_{(y,0)} \delta_{(x-y)} dy$	$\Psi_{(x,t)} = \int_{-\infty}^{\infty} c_p \Psi_p dp$ $= \int_{-\infty}^{\infty} \Phi_{(p,0)} \left( e^{-\frac{i}{\hbar} \frac{p^2}{2m} t} \right) \frac{e^{\frac{i}{\hbar} p x}}{\sqrt{2\pi\hbar}} dp$	$\Psi_{(x,t)} = \int_{-\infty}^{\infty} c_n \Psi_n dn$ $= \int_{-\infty}^{\infty} c_n \left( e^{\frac{-i}{\hbar} E_n t} \right) \Psi_n dn$
$c_y = \langle \Psi_y \Psi\rangle$ $\Psi_{(y,0)} = \int_{-\infty}^{\infty} \delta_{(x-y)} \Psi_{(x,0)} dx$	$c_p = \langle \Psi_p \Psi\rangle$ $\boxed{\Phi_{(p,t)} = \int_{-\infty}^{\infty} \frac{e^{\frac{-i}{\hbar} p x}}{\sqrt{2\pi\hbar}} \Psi_{(x,t)} dx}$	$c_n(t) = \langle \Psi_n \Psi\rangle$ $c_n(t) = \int_{-\infty}^{\infty} \Psi_n^* \Psi_{(x,t)} dx$

Born Interpretation:  $\text{PDF}(x) = |\Psi(x)|^2 = \Psi^* \Psi$

$$P_{(a < x < b)} = \int_a^b |\Psi|^2 dx \equiv \langle \Psi | \Psi \rangle_{ab}$$

Boundary Conditions:

$$\bullet \quad \boxed{\langle \Psi | \Psi \rangle = 1} \quad (\text{physical, bound states only})$$

$$\bullet \quad \Psi(\pm\infty) = 0$$

$$\bullet \quad \text{Min}(V) \leq E_\Psi \in \mathbb{R}$$

$$\bullet \quad \langle \Psi_n | \Psi_n \rangle \rightarrow \infty \Rightarrow \Psi_n \text{ not PHYSICAL}$$

sol. but  $\Psi = \int c_n \Psi_n$  can if  $\langle \Psi | \Psi \rangle = 1$

$$\bullet \quad E[f(x)] = \int_{-\infty}^{\infty} f(x) \text{PDF}(x) dx = \int_{-\infty}^{\infty} f(x) |\Psi(x)|^2 dx = \int_{-\infty}^{\infty} \Psi(x)^* f(x) \Psi(x) dx = \boxed{\langle \Psi | f(x) \Psi \rangle \equiv \langle f(x) \rangle}$$

$$\bullet \quad \int_x \Psi^* \Psi dx = \int_x (\int_n c_n^*(t) \Psi_n^*(x) dn) (\int_{n'} c_{n'}(t) \Psi_{n'}(x) dn') dx$$

$$= \int_n c_n^*(t) \int_{n'} c_{n'}(t) \delta(n-n') dn' dn = \int_n |c_n(t)|^2 dn \Rightarrow \boxed{\text{PDF}(n) = |c_n|^2 = c_n^* c_n}$$

$$\text{Adjoint (herm. adj./herm. conj.): } \{A^\dagger : \langle f | A f \rangle = \langle A^\dagger f | f \rangle\} \Rightarrow \langle h | \hat{A} g \rangle = \langle \hat{A}^\dagger h | g \rangle \quad (\text{let } f=h+g, f=h+ig)$$

Hermitian Operator:  $\{A : \hat{A}^\dagger = \hat{A}\}$

$$\bullet \quad \boxed{\exists \{\Psi_n\} : \hat{A} \Psi_n(x) = a_n \Psi_n(x)} \quad (\text{spectral theorem}) \quad \bullet \quad \langle a \rangle = a \in \mathbb{R} \Rightarrow \hat{A} \text{ can be an observable}$$

$$\bullet \quad \boxed{\langle \Psi_m | \Psi_n \rangle \in \{\delta_{mn}, \delta_{(m-n)}\}} \quad \bullet \quad \boxed{\text{Axiom: } \{\Psi_n\} \text{ for } \hat{A} \text{ are complete}}$$

$$\text{Non-degenerate: } (m \neq n), (a_m \neq a_n) \Rightarrow \langle \Psi_m | \Psi_n \rangle \in \{\delta_{mn}, \delta_{(m-n)}\}$$

$$\text{Degenerate: } (m \neq n), (a_m = a_n), (\Psi_m \neq \Psi_n), \langle \Psi_m | \Psi_n \rangle \neq 0 \Rightarrow \text{Use Gram-Schmidt}$$

$$\text{to find orthogonal } \langle \Psi'_m | \Psi'_n \rangle = \langle a \Psi_m + b \Psi_n | c \Psi_m + d \Psi_n \rangle = 0$$

Expectation:  $E[\hat{A}_{(x,p)}]$

$$\bullet \quad \int_{-\infty}^{\infty} \hat{A}_{(x,p)}^* \Psi^* \Psi dx = \langle \hat{A} \Psi | \Psi \rangle = \boxed{\langle \Psi | \hat{A} \Psi \rangle \equiv \langle \hat{A}_{(x,p)} \rangle} \quad (\text{won't work if } \int A |\Psi|^2 dx)$$

$$\langle \Psi | \hat{A} \Psi \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx = \int_{-\infty}^{\infty} (\int_n c_n^* \Psi_n^* dn) (\int_{n'} c_{n'} \hat{A} \Psi_{n'} dn') dx$$

$$= \int_n a_n |c_n|^2 dn = E[a] \equiv \langle a \rangle \quad c_n = \text{PDF}(n) \quad (\text{see above and see Momentum Space})$$

$$\boxed{\langle a \rangle = \langle \Psi | \hat{A} \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle = \langle A \rangle}$$

$$\bullet \quad \boxed{\langle \sigma_a^2 \rangle = \langle a^2 \rangle - \langle a \rangle^2} \Rightarrow \sigma_A^2 = 0 \quad \text{for } \Psi_n \quad (\text{determinate state})$$

### Matrix Operators:

Given complete  $\{e_n\} : \langle e_m | e_n \rangle = \delta_{mn}$

1.)  $Q_{mn}^{(e)} \equiv \langle e_m | \hat{Q} | e_n \rangle$

$$|\beta\rangle = \hat{Q}|\alpha\rangle = \sum_m |e_m\rangle \left( \begin{array}{l} \langle e_m | \beta \rangle = \langle e_m | \hat{Q} | \alpha \rangle \\ \sum_n b_n \langle e_m | e_n \rangle = \sum_n a_n \cdot \langle e_m | \hat{Q} | e_n \rangle \\ b_m = \sum_n \left( Q_{mn}^{(e)} \right)_n a_n \end{array} \right) = \sum_m b_m |e_m\rangle = \sum_{n,m} \langle e_n | \alpha \rangle Q_{mn}^{(e)} |e_m\rangle = \left( \sum_{n,m} Q_{mn}^{(e)} |e_m\rangle \langle e_n| \right) |\alpha\rangle \Rightarrow \hat{Q} = \sum_{m,n} Q_{mn}^{(e)} |e_m\rangle \langle e_n|$$

2.) Find  $\hat{Q}$  as a matrix

$$|f(x)\rangle = \sum_n c_n^{(e)}[f] |e_n(x)\rangle = \begin{pmatrix} \vdots \\ c_n[f] \\ \vdots \end{pmatrix}^{(e)} \cdot \begin{pmatrix} \vdots \\ e_n(x) \\ \vdots \end{pmatrix} \equiv \begin{pmatrix} \vec{c}^{(e)}[f] \cdot \vec{e}(x) \\ \int_n c^{(e)}[f](n) \cdot e(n,x) dn \end{pmatrix}, \quad c_n^{(e)}[f] = \langle e_n | f \rangle$$

$$\hat{Q}|f\rangle$$

$$\begin{aligned} &= \left( \sum_{m,n'} Q_{mn'}^{(e)} |e_m\rangle \langle e_{n'}| \right) \sum_n c_n^{(e)} |e_n\rangle \\ &= \sum_{m,n} \left( \sum_{n'} Q_{mn'}^{(e)} c_n^{(e)} \langle e_{n'} | e_n \rangle \right) |e_m\rangle \\ &= \sum_m \left( \sum_n \left( Q_m^{(e)} \right)_n c_n^{(e)} \right) |e_m\rangle \end{aligned}$$

$$\begin{aligned} \hat{Q} \left[ \begin{pmatrix} | \\ c \\ | \end{pmatrix}^{(e)} \cdot \begin{pmatrix} | \\ e \\ | \end{pmatrix} \right] &= \left[ \begin{pmatrix} - & \vdots & - \\ & Q_m & \\ & \vdots & \end{pmatrix}^{(e)} \begin{pmatrix} | \\ c \\ | \end{pmatrix}^{(e)} \right] \cdot \begin{pmatrix} | \\ e \\ | \end{pmatrix} \\ \hat{Q} |f\rangle &= \hat{Q} [ \vec{c}^{(e)}[f] \cdot \vec{e} ] = [ \overline{Q}^{(e)} \vec{c}^{(e)}[f] ] \cdot \vec{e} \\ \hat{Q}|f\rangle &= \int_m \left[ \overline{Q}^{(\delta)} f \right]_{(m)} \cdot \delta_{(x-m)} dm \\ \text{e.g.} \quad &= \int_m \left[ \int_n Q_m^{(\delta)}(n) \cdot f(n) dn \right] \cdot \delta_{(x-m)} dm = \hat{Q} f(x) \end{aligned}$$

### 3.) Terms

Diagonalizable:  $A \equiv PDP^{-1}$

Conj. Transpose,  $\dagger$ :  $A^\dagger \equiv A^{T*} = A^{*T}$

Hermitian,  $H$ :  $H = H^\dagger$   
 $H = UDU^{-1} = UDU^\dagger$  (spectral theorem)

Unitary,  $U$ :  $U : UU^\dagger = U^\dagger U = 1$   
 $\exists H : U = e^{iH} = (U')e^{iD}(U')^\dagger$

Hermitian Operator  $\leftrightarrow$  Hermitian Matrix

$$\langle Qx|y\rangle = \langle x|Qy\rangle$$

(draw it out)

$$\begin{aligned} \rightarrow (\overline{Qx})^{*T} \cdot y_m |e_m\rangle &= y_m x^{*T} \cdot (\overline{Q}_m^*) \\ &= x^{*T} \cdot \overline{Q}^{*T} y_m |e_m\rangle \\ &= x^{*T} \cdot \overline{Q} y_m |e_m\rangle \end{aligned}$$

$$\rightarrow \overline{Q}^\dagger \equiv \overline{Q}^{*T} = \overline{Q} \quad \square$$

#### 4.) Eigenvalue Equation

General Case:

$$\begin{array}{l} \widehat{Q}|q_i\rangle = q_i|q_i\rangle \\ |q_i\rangle = \sum c_n^{(e)}[q_i]|e_n\rangle \end{array} \quad \left| \begin{array}{l} \overline{Q}^{(e)} = UDU^\dagger \quad (\text{Spectral Theorem}) \\ \\ = \begin{pmatrix} | & | & \\ \vec{c}_0^{[q_0]} & \vec{c}_1^{[q_1]} & \dots \\ | & | & \end{pmatrix}^{(e)} \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} - & \vec{c}_0^*[q_0] & - \\ - & \vec{c}_1^*[q_1] & - \\ \vdots & \vdots & \end{pmatrix}^{(e)} \\ \\ \text{where } \langle \vec{c}_m | \vec{c}_n \rangle = \delta_{mn} \text{ since } Q^\dagger Q = Q Q^\dagger \quad (\text{normal}) \end{array} \right.$$

$$\begin{array}{l} q_i|q_i\rangle = \widehat{Q}|q_i\rangle \\ (q_i \vec{c}^{(e)}[q_i]) \cdot \vec{e}(x) = \left[ \overline{Q}^{(e)} \vec{c}^{(e)}[q_i] \right] \cdot \vec{e}(x) \quad \begin{array}{l} * \forall n \quad (qc)_n |e_n(x)\rangle = (Qc)_n |e_n(x)\rangle \\ \langle e_n(x) | (qc)_n |e_n(x)\rangle = \langle e_n(x) | (Qc)_n |e_n(x)\rangle \\ (qc)_n = (Qc)_n \end{array} \\ \Downarrow^* \\ q_i \vec{c}^{(e)}[q_i] = \overline{Q}^{(e)} \vec{c}^{(e)}[q_i] \\ q_i \begin{pmatrix} | \\ \vec{c}^{[q_i]} \\ | \end{pmatrix}^{(e)} = \begin{pmatrix} | & | & \\ \vec{c}^{[q_0]} & \vec{c}^{[q_1]} & \dots \\ | & | & \end{pmatrix}^{(e)} \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} - & \vec{c}^*[q_0] & - \\ - & \vec{c}^*[q_1] & - \\ \vdots & \vdots & \end{pmatrix}^{(e)} \begin{pmatrix} | \\ \vec{c}^{[q_i]} \\ | \end{pmatrix}^{(e)} \quad \checkmark \\ \Downarrow \\ \boxed{q_i, \vec{c}^{(e)}[q_i]: \quad \det(\overline{Q}^{(e)} - Iq_i) = 0} \end{array}$$

Special Case:

$$\begin{array}{l} |q_n\rangle = |e_n\rangle \\ \widehat{Q}|e_n\rangle = q_n|e_n\rangle \end{array} \quad \left| \begin{array}{l} \widehat{Q}|a\rangle = \sum_n \widehat{Q}|e_n\rangle \langle e_n|a\rangle \\ = \left( \sum_n q_n |e_n\rangle \langle e_n| \right) |a\rangle \Rightarrow \boxed{\widehat{Q} = \sum_n q_n |e_n\rangle \langle e_n|} \Rightarrow \boxed{\overline{Q}^{(e)} = \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & q_i \end{pmatrix}} \\ Q_{mn}^{(e)} = q_n \delta_{mn} \end{array} \right.$$

$$\begin{aligned} \overline{Q}^{(e)} = \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & \end{pmatrix}^{(e)} &= \begin{pmatrix} | & | & \\ \vec{c}^{[q_0]} & \vec{c}^{[q_1]} & \dots \\ | & | & \end{pmatrix}^{(e)} \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} - & \vec{c}^*[q_0] & - \\ - & \vec{c}^*[q_1] & - \\ \vdots & \vdots & \end{pmatrix}^{(e)} \\ &= \begin{pmatrix} 1 & 0 & \dots \\ 0 & 1 & \dots \\ \vdots & \vdots & \end{pmatrix}^{(e)} \begin{pmatrix} q_0 & 0 & \dots \\ 0 & q_1 & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} 1 & 0 & \dots \\ 0 & 1 & \dots \\ \vdots & \vdots & \end{pmatrix}^{(e)} \end{aligned}$$

$$\boxed{\vec{c}^{(e)}[q_i] = (\dots 0 0 0 1_{(i)} 0 0 0 \dots)^T}$$

$\Phi(p, t)$  - Momentum Space (generalizable Born Interpretation):

$$\begin{aligned}
\int_x \Psi^* \Psi dx &= \int_x \int_p c_p^*(t) \Psi_p^*(x) dp \int_{p'} c_{p'}(t) \Psi_{p'}(x) dp' dx & \hat{x} \Phi_x &= \hat{x} e^{\frac{-i}{\hbar} p x} = x e^{\frac{-i}{\hbar} p x} \\
&= \int_p c_p^*(t) \int_{p'} c_{p'}(t) \int_x \Psi_p^*(x) \Psi_{p'}(x) dx dp' dp & \Rightarrow & \boxed{\hat{x}_p = -\frac{\hbar}{i} \partial_p} \\
&= \int_p \Phi^* \int_{p'} \Phi' \delta(p - p') dp' dp & \hat{A}(x, \hat{p}_x) &\rightarrow \hat{A}(\hat{x}_p, p) \\
&= \int_p \Phi^* \Phi dp \Rightarrow \boxed{\text{PDF}(p) = |\Phi|^2 = \Phi^* \Phi} & \rightarrow & \boxed{\langle a \rangle = \langle \Phi | \hat{A}(\hat{x}, p) | \Phi \rangle} \\
\boxed{\langle \Psi | \Psi \rangle} &= \langle \Phi | \Phi \rangle
\end{aligned}$$

Anything in position space can be done in momentum space

(or generalize to any transform,  $c_n$ )

Heisenberg Uncertainty Proof:

$$\begin{aligned}
\langle f | g \rangle &\equiv \langle (\hat{A} - \langle a \rangle) \Psi | (\hat{B} - \langle b \rangle) \Psi \rangle \\
&= \langle \Psi | (\hat{A} - \langle a \rangle) (\hat{B} - \langle b \rangle) | \Psi \rangle \\
&= \langle \hat{A} \hat{B} \rangle - \langle a \rangle \langle b \rangle \\
\sigma_A^2 \sigma_B^2 &= \langle (\hat{A} - \langle a \rangle) \Psi | (\hat{A} - \langle a \rangle) \Psi \rangle \langle (\hat{B} - \langle b \rangle) \Psi | (\hat{B} - \langle b \rangle) \Psi \rangle \\
&\equiv \langle f | f \rangle \langle g | g \rangle \geq \|\langle f | g \rangle\|^2 \quad (\text{see Schwarz Ineq.}) \\
&\geq [\text{Im}(\langle f | g \rangle)]^2 = \left( \frac{1}{2i} [\langle f | g \rangle - \langle f | g \rangle^*] \right)^2 \\
&= \left( \frac{1}{2i} \langle \hat{A} \hat{B} - \hat{B} \hat{A} \rangle \right)^2 = \boxed{\left( \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2}
\end{aligned}$$

Commutator of Hermitian  $\hat{A}, \hat{B}$

- $[A, B]^\dagger = -[A, B]$
- $\exists \Psi_n$  s.t.  $(\hat{A} \Psi_n = a \Psi_n)$  ,  $(\hat{B} \Psi_n = b \Psi_n)$   
 $\Leftrightarrow [\hat{A}, \hat{B}] = 0$   
 $\Rightarrow \boxed{\sigma_A \sigma_B \geq 0} \quad (\text{Both can be measured concurrently})$   
 $\boxed{AB = BA}$

Commutator

- $[\hat{A}, \hat{B}] \equiv \hat{A} \hat{B} - \hat{B} \hat{A}$
- $[A, BC] = [A, B]C + B[A, C]$
- $[AB, C] = A[B, C] + [A, C]B$
- $[x, \hat{p}] = i\hbar$
- $\boxed{\sigma_A \sigma_B \geq \left\| \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right\|}$   
 $\Rightarrow \boxed{\Delta x \Delta p \geq \hbar/2}$
- $[\hat{p}, f] = (\hat{p}f) = \frac{\hbar}{i} \nabla f$

Anti-Hermitian Operators:  $A^\dagger = -A$

- $\langle A \rangle = ai, \quad a \in \mathbb{R}$
- $[A, B]^\dagger = -[A, B]$

## Operator Evolution

$$\frac{d}{dt} \left\langle \Psi(x, t) \left| Q \right| \Psi(x, t) \right\rangle = \left\langle \frac{\partial \Psi}{\partial t} \left| Q \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial Q}{\partial t} \right| \Psi \right\rangle + \left\langle \Psi \left| Q \right| \frac{\partial \Psi}{\partial t} \right\rangle$$

$$\boxed{\frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle} \quad (Q \text{ is conserved when this equals 0!!!})$$

- Conservations:  $\frac{d\langle \Psi | \Psi \rangle}{dt} = 0, \quad \frac{d\langle H \rangle}{dt} = 0$
- Ehrenfest's Theorem:  $m \frac{d\langle x \rangle}{dt} = \langle p \rangle, \quad \frac{d\langle p \rangle}{dt} = - \left\langle \frac{\partial V}{\partial x} \right\rangle \Rightarrow$  other classical eq.
- Virial Theorem:  $\frac{d}{dt} \langle xp \rangle = \frac{i}{\hbar} \langle [H, x]p + x[H, p] \rangle$   
 $= \left\langle \frac{d\langle x \rangle}{dt} p + x \frac{d\langle p \rangle}{dt} \right\rangle$

$$\boxed{\frac{d\langle xp \rangle}{dt} = 2\langle T \rangle - \left\langle x \frac{\partial V}{\partial x} \right\rangle} \rightarrow 0 = \frac{d}{dt} \left\langle \Psi_n(x) \left| Q_{(x,p)} \right| \Psi_n(x) \right\rangle \quad (\text{for stationary states})$$

- Energy-Time Uncertainty:  $\left( \hat{Q} = \hat{Q}(x, \hat{p}) \neq \hat{Q}(x, \hat{p}, t) \right) \Rightarrow \sigma_H \sigma_Q \geq \frac{\hbar}{2} \left| \frac{d\langle Q \rangle}{dt} \right|$

$$\Rightarrow \boxed{\begin{aligned} \sigma_Q &\equiv \frac{d\langle Q \rangle}{dt} \Delta t \approx \Delta \langle Q \rangle \\ \sigma_H \left( \frac{\sigma_Q}{|d\langle Q \rangle/dt|} \right) &\geq \frac{\hbar}{2} \\ \Delta E \Delta t &\geq \frac{\hbar}{2} \end{aligned}} \quad \begin{array}{l} \Delta t \text{ is the amount of time it would} \\ \text{take } \langle Q \rangle \text{ to change "appreciably",} \\ \text{or one std. dev. at the constant} \\ \text{rate } \frac{d}{dt} \langle Q \rangle \end{array}$$

Mass Lifetime:

$$\Delta(mc^2) \Delta t \geq \frac{\hbar}{2} \quad \checkmark$$

Orthogonal Time Example:

$$\Psi(x, \tau) = \frac{\sqrt{2}}{2} (\Psi_1 e^{-\frac{i}{\hbar} E_1 \tau} + \Psi_2 e^{-\frac{i}{\hbar} E_2 \tau})$$

$$\left\langle \Psi(x, 0) \left| \Psi(x, \tau) \right\rangle = 0 = \frac{1}{2} (e^{-\frac{i}{\hbar} E_1 \tau} + e^{-\frac{i}{\hbar} E_2 \tau})$$

$$\Rightarrow \tau \frac{E_2 - E_1}{2} = \frac{\pi}{2} \hbar \left( \frac{1}{2} + n \right) \geq \frac{\hbar}{2} \quad \checkmark$$

## Translation Operator

$$\begin{aligned}
 f(x + \Delta x) &\approx f(x) + \frac{df}{dx} \Delta x \\
 &= f(x) + f'(x) \Delta x + \frac{f''(x)}{2!} (\Delta x)^2 + \dots = \left\{ \begin{aligned} f(x') &= \sum_n \frac{f^{(n)}(a)}{n!} (x' - a)^n \\ (x' = x + \Delta x), \quad (a = x) \end{aligned} \right\} \\
 &= \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!} (\Delta x)^n = \sum_{n=0}^{\infty} \frac{(\Delta x \nabla)^n}{n!} f(x) \\
 \boxed{f(x + \Delta x) = e^{\frac{i}{\hbar}(\Delta x)\hat{p}} f(x)} &\Leftrightarrow \boxed{f(x) = e^{\frac{i}{\hbar}x\hat{p}} f(0)}
 \end{aligned}$$

$$\begin{array}{l}
 \text{Time Translation:} \\
 \left| \begin{array}{l}
 f(t + \Delta t) = f(t) + f'(t)\Delta t + \dots = \sum_n \frac{(\Delta t)^n}{n!} \left( \frac{\partial}{\partial t} \right)^n f(t) \\
 \\
 i\hbar \frac{\partial}{\partial t} = \hat{H} \quad \Rightarrow \quad \left\{ \begin{array}{l}
 \dots = \sum_n \frac{(\Delta t)^n}{n!} \left( \frac{\partial}{\partial t} \right)^n f(t) \\
 \\
 \boxed{f(t + \Delta t) = e^{\frac{-i}{\hbar}(\Delta t)\hat{H}} f(t)} \Leftrightarrow \\
 \\
 \boxed{f(0 + t) = e^{\frac{-i}{\hbar}t\hat{H}} f(0) = f(t)}
 \end{array} \right.
 \end{array} \right.
 \end{array}$$

Pictures:  $\langle Q \rangle_{(t)} = \langle \Psi_{(x,t)} | Q_{(x,p,t)} | \Psi_{(x,t)} \rangle$

- Schrodinger Picture:  $\langle Q \rangle_{(t)} = \left\langle e^{\frac{-i}{\hbar}t\hat{H}} \Psi_{(x,0)} \mid Q_{(x,p,t)} \mid e^{\frac{-i}{\hbar}t\hat{H}} \Psi_{(x,0)} \right\rangle$

$$Q = Q(x, p) \Rightarrow \langle Q \rangle_{(t)} = \left\langle \sum e^{\frac{-i}{\hbar}E_n t} c_n \Psi_{n(x)} \mid Q \mid \sum e^{\frac{-i}{\hbar}E_n t} c_n \Psi_{n(x)} \right\rangle \quad (\text{nice for stationary states})$$

- Heisenberg Picture:  $\langle Q \rangle_{(t)} = \left\langle \Psi_{(x,0)} \mid e^{\frac{i}{\hbar}t\hat{H}} Q_{(x,p,t)} e^{\frac{-i}{\hbar}t\hat{H}} \mid \Psi_{(x,0)} \right\rangle$

- Dirac Picture:  $\langle Q \rangle_{(t)} = \left\langle e^{\frac{-i}{\hbar}t\hat{H}_0} \Psi_{(x,0)} \mid e^{\frac{i}{\hbar}t\hat{H}_1} Q_{(x,p,t)} e^{\frac{-i}{\hbar}t\hat{H}_1} \mid e^{\frac{-i}{\hbar}t\hat{H}_0} \Psi_{(x,0)} \right\rangle$

$$\begin{aligned}
 \langle Q \rangle_{(t+\Delta t)} &= \langle Q \rangle_{(t)} + \frac{d\langle Q \rangle}{dt} \Delta t + \dots \Rightarrow \text{A 1st order approximation of } \langle Q \rangle_{(t+\Delta t)} \\
 &\text{should yield } \frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar} \left\langle [H, Q] \right\rangle + \frac{\partial Q}{\partial t}
 \end{aligned}$$



### 1.3 Extra

$L_2 \subset$  Hilbert Space = complete inner product space

$$P(t) = \langle \Psi(x, t) | \Psi(x, t) \rangle, \quad P_{ab}(t) = \langle \Psi(x, t) | \Psi(x, t) \rangle_{ab}$$

- $(V \in \mathbb{R}) \Rightarrow \frac{d}{dt}P = 0 \Rightarrow P(t) \equiv 1$
- $(V = V_0 - i\Gamma) \Rightarrow \frac{d}{dt}P = \frac{-2\Gamma}{\hbar}P \Rightarrow P(t) = e^{-2(\Gamma/\hbar)t}$
- $\frac{d}{dt}P_{ab} = J(a, t) - J(b, t)$
- $J(x, t) = \frac{1}{2m}(\Psi^* \hat{p} \Psi - \Psi \hat{p} \Psi^*)$  (Probability Current)
- $\langle \Psi_n | \Psi_n \rangle, \langle \Psi_m | \Psi_m \rangle = 1 \Rightarrow \frac{d}{dt} \langle \Psi_n | \Psi_m \rangle = 0$

Schwarz Inequality:  $\left\| \int_a^b f^* g \, dx \right\|^2 \leq \left\| \int_a^b f^* f \, dx \right\| \left\| \int_a^b g^* g \, dx \right\|$

$$\|\langle f | g \rangle_{ab}\|^2 \leq \|\langle f | f \rangle_{ab}\| \|\langle g | g \rangle_{ab}\|$$

$$[V(x) = V(-x)] \Rightarrow [\Psi(x) \Rightarrow \Psi(-x)] \Rightarrow [\Psi(-x) = \Psi(x)] \cup [\Psi(-x) = -\Psi(x)]$$

Discontinuity in  $\Psi$  means the possibility of  $\sigma_p \rightarrow \infty$

$$\text{Prob 3.29: } \Psi(x, 0) = \begin{cases} \frac{1}{\sqrt{2n\lambda}} e^{2\pi i x / \lambda}, & -n\lambda < x < n\lambda \\ 0 & \text{else} \end{cases}$$

$\sigma_p \rightarrow \infty$  because the integral of  $\delta^2(x)$  is infinite

$$\int_{-\infty}^{\infty} f(x) D_1(x) dx = \int_{-\infty}^{\infty} f(x) D_2(x) dx \Rightarrow \delta(cx) = \frac{1}{|c|} \delta(x)$$

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dx \Rightarrow F[\delta(x)] = \frac{1}{2\pi}$$

Associated Legendre Functions:  $P_l^m \equiv \sqrt{1-x^2}^{|m|} \left(\frac{d}{dx}\right)^{|m|} P_l(x)$  (not a polynomial if odd)

Legendre Polynomials:  $P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2 - l)^l$

Associated Laguerre Polynomials:  $L \equiv$

Laguerre Polynomials:  $L_{\equiv}$

## 2 Simple Potentials

### 2.1 Infinite Square Well (1-D)

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin k_n x$$

$$k_n = \frac{2\pi}{\lambda} = \frac{2\pi}{2a/n} = \frac{n\pi}{a} \quad \forall n = 1, 2, 3, \dots \quad \boxed{!! \hat{p}\Psi_n \neq p\Psi_n !!} \quad \text{wave isn't infinite}$$

$$E_n = \frac{p^2}{2m} = \frac{\hbar^2 k_n^2}{2m}$$

#### 2.1.1 3-D Rectangular Box

$$\Psi_{n_x n_y n_z}(x, y, z) = \Psi_{n_x}(x) \Psi_{n_y}(y) \Psi_{n_z}(z) = \sqrt{\frac{8}{a_x a_y a_z}} (\sin k_{n_x} x) (\sin k_{n_y} y) (\sin k_{n_z} z)$$

$$k_{n_i} = \frac{n_i \pi}{a_i} \quad \forall n_x, n_y, n_z = 1, 2, 3, \dots$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m} (k_{n_x}^2 + k_{n_y}^2 + k_{n_z}^2)$$

## 2.2 Harmonic Oscillator (1-D)

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

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = \frac{1}{2m}(p^2 + m^2\omega^2x^2) = \frac{1}{2m}(-ip + m\omega x)(ip + m\omega x) \sim E \sim \hbar\omega \quad \Rightarrow$$

$$a = a_- = \frac{1}{\sqrt{2m}} \frac{1}{\sqrt{\hbar\omega}} (i\hat{p} + m\omega x)$$

$$H = \hbar\omega(aa^\dagger - 1/2) = \hbar\omega(a^\dagger a + 1/2) \quad \rightarrow \quad [a, a^\dagger] = 1$$

$$\begin{aligned} H(a\Psi_n) &= \hbar\omega(aa^\dagger - 1/2)a\Psi_n & H(a^\dagger\Psi_n) &= \hbar\omega(a^\dagger a + 1/2)a^\dagger\Psi_n \\ &= a\hbar\omega(a^\dagger a + 1/2 - 1)\Psi_n & &= a^\dagger\hbar\omega(aa^\dagger - 1/2 + 1)\Psi_n \\ &= a(H - \hbar\omega)\Psi_n & &= a^\dagger(H + \hbar\omega)\Psi_n \\ &= (E_n - \hbar\omega)(a\Psi_n) & &= (E_n + \hbar\omega)(a^\dagger\Psi_n) \\ &\Rightarrow & &\Rightarrow \\ E_{n-1}\Psi_{n-1} &= (E_n - \hbar\omega)\Psi_{n-1} & E_{n+1}\Psi_{n+1} &= (E_n + \hbar\omega)\Psi_{n+1} \end{aligned}$$

$$\begin{aligned} H(a^\dagger)^n\Psi_0 &= (E_0 + n\hbar\omega)(a^\dagger)^n\Psi_0 \\ E_n\Psi_n &= (E_0 + n\hbar\omega)\Psi_n \end{aligned}$$

$$E_n \geq \text{Min}(V) \Rightarrow a\Psi_0 = 0 \quad (\text{else let it be un-normalizable})$$

$$\begin{aligned} 0 &= (ip + m\omega x)\Psi_0 & H\Psi_0 &= \hbar\omega(a^\dagger a + 1/2)\Psi_0 \\ -m\omega x\Psi_0 &= \hbar\frac{d}{dx}\Psi_0 & E_0\Psi_0 &= \frac{1}{2}\hbar\omega\Psi_0 \end{aligned}$$

$$\Psi_0 = Ae^{-\frac{m\omega}{2\hbar}x^2}, \quad A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

$$E_n = (n + 1/2)\hbar\omega, \quad \forall n = 0, 1, 2, 3, \dots$$

$$H\Psi_n = E_n\Psi_n$$

$$\hbar\omega(a^\dagger a + 1/2)\Psi_n = (n + 1/2)\hbar\omega\Psi_n$$

$$\boxed{a^\dagger a\Psi_n = n\Psi_n}$$

$$\begin{aligned}\langle\Psi_n|a^\dagger a\Psi_n\rangle &= n = \langle a\Psi_n|a\Psi_n\rangle \\ &= \langle c_n\Psi_{n-1}|c_n\Psi_{n-1}\rangle\end{aligned}$$

$$\boxed{a\Psi_n = \sqrt{n}\Psi_{n-1}}$$

$$H\Psi_n = E_n\Psi_n$$

$$\hbar\omega(aa^\dagger - 1/2)\Psi_n = (n + 1/2)\hbar\omega\Psi_n$$

$$\boxed{aa^\dagger\Psi_n = (n + 1)\Psi_n}$$

$$\begin{aligned}\langle\Psi_n|aa^\dagger\Psi_n\rangle &= n + 1 = \langle a^\dagger\Psi_n|a^\dagger\Psi_n\rangle \\ &= \langle c_n\Psi_{n+1}|c_n\Psi_{n+1}\rangle\end{aligned}$$

$$\boxed{a^\dagger\Psi_n = \sqrt{n + 1}\Psi_{n+1}}$$

$$\boxed{\Psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^n\Psi_0}$$

### 2.2.1 Position/Momentum Operators

$$\boxed{x = \frac{1}{2}\frac{\sqrt{2m}\sqrt{\hbar\omega}}{m\omega}(a + a^\dagger)}$$

$$\boxed{\hat{p} = \frac{1}{2}\frac{\sqrt{2m}\sqrt{\hbar\omega}}{i}(a - a^\dagger)}$$

Show Virial Theorem Works

$$2\langle T \rangle = N\langle V \rangle$$

$$\begin{aligned} E_n &= 2\langle V \rangle_n \\ &= 2\langle \Psi_n | V | \Psi_n \rangle \\ &= 2 \left\langle \Psi_n \left| \frac{1}{2} m \omega^2 \frac{2m\hbar\omega}{(2m\omega)^2} (a + a^\dagger)^2 \right| \Psi_n \right\rangle \\ &= \frac{2m^2\hbar\omega^3}{(2m\omega)^2} (0 + \langle \Psi_n | (aa^\dagger + a^\dagger a) | \Psi_n \rangle + 0) \end{aligned}$$

$$E_n = (n + 1/2)\hbar\omega \quad \checkmark$$

Test the Uncertainty Principle

$$\sigma_x \sigma_p \geq \frac{1}{2} \left| \langle [x, p] \rangle \right|$$

$$\begin{aligned} xp - px &= \frac{2m\hbar\omega}{4m\omega i} \begin{pmatrix} a^2 - aa^\dagger + a^\dagger a - (a^\dagger)^2 \\ -a^2 + a^\dagger a - aa^\dagger + (a^\dagger)^2 \end{pmatrix} \\ &= \frac{\hbar}{i} (a^\dagger a - aa^\dagger) \\ &= i\hbar(n + 1 - n) \\ \Rightarrow \sigma_x \sigma_p &\geq \frac{\hbar}{2} \quad \checkmark \end{aligned}$$

$$\begin{aligned} \sigma_x^2 &= \langle x^2 \rangle - \langle x \rangle^2 & \sigma_p^2 &= \langle p^2 \rangle - \langle p \rangle^2 \\ &= \frac{2m\hbar\omega}{4m^2\omega^2} \begin{bmatrix} \langle (a + a^\dagger)^2 \rangle \\ -\langle a + a^\dagger \rangle^2 \end{bmatrix} & &= \frac{2m\hbar\omega}{-4} \begin{bmatrix} \langle (a - a^\dagger)^2 \rangle \\ -\langle a - a^\dagger \rangle^2 \end{bmatrix} \\ &= \frac{\hbar}{2m\omega} \langle aa^\dagger + a^\dagger a \rangle & &= \frac{\hbar m\omega}{2} \langle aa^\dagger + a^\dagger a \rangle \\ &= \frac{\hbar}{m\omega} (n + \frac{1}{2}) & &= \hbar m\omega (n + \frac{1}{2}) \end{aligned}$$

$$\Rightarrow \sigma_x \sigma_p = \hbar(n + \frac{1}{2}) \geq \frac{\hbar}{2} \quad \checkmark$$

### 2.2.2 Coherent States

$$a|\alpha\rangle = \alpha|\alpha\rangle$$

$$\sigma_x \sigma_p = \frac{\hbar}{2}$$

$$\begin{aligned} \langle \alpha | \alpha \rangle &= \langle \alpha | \left( \sum_{n=0}^{\infty} \langle \Psi_n | \alpha \rangle | \Psi_n \rangle = \sum_{n=0}^{\infty} \left\langle \frac{(a^\dagger)^n}{\sqrt{n!}} \Psi_0 \middle| \alpha \right\rangle | \Psi_n \rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \langle \Psi_0 | \alpha \rangle | \Psi_n \rangle \right) \\ &= \langle \Psi_0 | \alpha \rangle^2 \sum_{n=0}^{\infty} \frac{(\alpha^2)^n}{n!} \langle \Psi_n | \Psi_n \rangle \\ &= \langle \Psi_0 | \alpha \rangle^2 e^{\alpha^2} = 1 \end{aligned} \Rightarrow \begin{aligned} &\boxed{|\alpha\rangle = e^{-\alpha^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |\Psi_n\rangle} \rightarrow |\alpha=0\rangle = |\Psi_0\rangle \\ &a|\alpha(x,t)\rangle = e^{-\frac{\alpha^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{\frac{-i}{\hbar} E_n t} a |\Psi_n\rangle \\ &= e^{-\frac{\alpha^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{\frac{-i}{\hbar} \hbar \omega (\frac{1}{2}+n)t} \sqrt{n} |\Psi_{n-1}\rangle \\ &= \left( \alpha e^{\frac{-i}{\hbar} \hbar \omega t} \right) e^{-\frac{\alpha^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{\frac{-i}{\hbar} \hbar \omega (\frac{1}{2}+n)t} |\Psi_n\rangle \\ &\boxed{a|\alpha(x,t)\rangle = \left( \alpha e^{-i\omega t} \right) |\alpha(x,t)\rangle} \end{aligned}$$

$|\alpha\rangle$  are obviously not orthogonal. They are an overcomplete basis.

### 2.2.3 Analytic Method

$$\Psi_n = A \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$

$$A = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4}$$

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x$$

$$H_n(x) = (-1)^n e^{-x^2} \left( \frac{d}{dx} \right)^n e^{x^2}$$

Hermite Polynomials:

$$e^{-z^2+2zx} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(x)$$

### 2.2.4 3-D Harmonic Potential

$$V(r) = \frac{1}{2} k r^2$$

$$\boxed{E_{n_x n_y n_z} = \hbar \omega \left( n_x + n_y + n_z + \frac{3}{2} \right)}$$

## 2.3 Free Particle (1-D)

$$V(x) = 0$$

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(x, 0) e^{\frac{i}{\hbar}px - Et} dp$$

$$\Phi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{\frac{-i}{\hbar}px} dx$$

( $E < 0 \rightarrow \Psi = e^{\pm kx}$  is possible and also not normalizable, but solution above is already a complete set)

$$E(p) = \frac{p^2}{2m}$$

$$v_{\text{wave}} = \boxed{v_{\text{phase}} = \frac{\omega(k)}{k}} = \frac{E}{p} = \frac{v_{\text{classical}}}{2}$$

$$v_{\text{particle}} \approx \boxed{v_{\text{group}} = \frac{d\omega(k)}{dk}} = 2v_{\text{wave}} \quad (\text{dispersion relation})$$

## 2.4 Delta Potential (1-D)

Potential Well:

$$V(x) = -\alpha\delta(x)$$

( $\alpha \rightarrow -\alpha$  for potential wall)

Bound State ( $E < 0$ ) [only for Well]:

$$\Psi = \sqrt{k}e^{k|x|} = \begin{cases} \sqrt{k}e^{kx} & x \leq 0 \\ \sqrt{k}e^{-kx} & x \geq 0 \end{cases}$$

$$k = \frac{m\alpha}{\hbar^2}$$

$$E = -\frac{(\hbar k)^2}{2m}$$

Scattering State ( $E > 0$ ) [for both]:

$$\Psi = \begin{cases} Ae^{iKx} + Be^{-iKx} & x < 0 \\ Fe^{iKx} & x > 0 \end{cases}$$

$$E = \frac{(\hbar K)^2}{2m},$$

$$\beta \equiv \frac{k}{K} = \frac{m\alpha/\hbar^2}{K}$$

$$B = \frac{i\beta}{1 - i\beta}A,$$

$$F = \frac{1}{1 - i\beta}A$$

$$R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2},$$

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}$$

Can't normalize. All free particles have ranges of  $p$  and thus  $E$ , so  $R$  and  $T$  are approx. in the vicinity of  $E$ .



## 2.5 Finite Square Potential (1-D)

**2.5.1 Potential Well**  $V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & \text{otherwise} \end{cases}$  ( $V_0 \rightarrow -V_0$  for wall and do cases for  $E > V_0, E = V_0, E < V_0$ , and change to sinh, cosh if needed)

$$\begin{aligned} k; K : \quad E &= \frac{-(\hbar k)^2}{2m} = \frac{(\hbar K)^2}{2m} \\ l : \quad E + V_0 &= \frac{(\hbar l)^2}{2m} \\ v : \quad V_0 &= \frac{\hbar^2 v^2}{2m} = \frac{\hbar^2 (l^2 + k^2)}{2m} = \frac{\hbar^2 (l^2 - K^2)}{2m} \end{aligned} \quad \left| \quad \begin{aligned} \frac{k_a}{l_a} &\equiv \sqrt{\frac{(ka)^2}{(la)^2}} = \sqrt{\frac{(la)^2 + (ka)^2}{(la)^2}} - 1 \\ \frac{k_a}{l_a} &\equiv \sqrt{\left(\frac{v_a}{l_a}\right)^2 - 1}, \quad v_a^2 = \begin{cases} l_a^2 + k_a^2 \\ l_a^2 - K_a^2 \end{cases} \end{aligned}$$

Bound State ( $E_n < 0$ ) [only for well]:

$$\Psi_{\text{even}}(x) = \begin{cases} \Psi(-x) & x < 0 \\ D \cos(lx) & 0 < x < a \\ F e^{-kx} & a < x \end{cases} \quad \Psi_{\text{odd}}(x) = \begin{cases} -\Psi(-x) & x < 0 \\ C \sin(lx) & 0 < x < a \\ F e^{-kx} & a < x \end{cases}$$

- $F = D \cos(la) e^{ka}$
- $\frac{-(\partial_x \Psi)(a)}{\Psi(a)} = k = l \tan(la) \Rightarrow$   
 $\tan(la) = \sqrt{(v_a/l_a)^2 - 1}$   
 $\text{big } v_a \rightarrow l \approx \frac{n\pi}{2a} \rightarrow E_n + V_0 = \frac{\hbar^2 l^2}{2m} ; \underline{n \text{ odd}}$
- $n_{\text{max}} = \left\lfloor \frac{v_a}{\pi} \right\rfloor + 1$

- $F = D \sin(la) e^{ka}$
- $\frac{-(\partial_x \Psi)(a)}{\Psi(a)} = k = -l \cot(la) \Rightarrow$   
 $-\cot(la) = \sqrt{(v_a/l_a)^2 - 1}$   
 $\text{big } v_a \rightarrow l \approx \frac{n\pi}{2a} \rightarrow E_n + V_0 = \frac{\hbar^2 l^2}{2m} ; \underline{n \text{ even}}$
- $n_{\text{max}} = \left\lfloor \frac{v_a + \frac{\pi}{2}}{\pi} \right\rfloor$

Scattering State ( $E > 0$ ) [for both]:

$$\Psi = \begin{cases} A e^{iKx} + B e^{-iKx} & x < -a \\ C \sin lx + D \cos lx & -a < x < a \\ F e^{iKx} & a < x \end{cases} \quad \frac{d\Psi}{dx} = \begin{cases} iK A e^{iKx} - iK B e^{-iKx} & x < -a \\ lC \cos lx - lD \sin lx & -a < x < a \\ iK F e^{iKx} & a < x \end{cases}$$

$$B = i \sin(2la) \left( \frac{l_a^2 - K_a^2}{2K_a l_a} \right) F$$

$$F = \frac{e^{-2iKa}}{\cos(2la) - i \left( \frac{l_a^2 + K_a^2}{2K_a l_a} \right) \sin(2la)} A$$

(Can't normalize. See delta potential.)

$$T^{-1} = 1 + \left( \frac{l_a^2 - K_a^2}{2K_a l_a} \right)^2 \sin^2(2la)$$

$$= 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left( 2a \sqrt{\frac{E + V_0}{\hbar^2/2m}} \right)$$

(full transmission at inf. sq. well  $E_n + V_0 = \frac{\hbar^2 l^2}{2m} ; l = \frac{n\pi}{2a}$ )

## 2.6 Hydrogen Atom

$$Eu = \left( \frac{\hat{p}_r^2}{2m} + V(r) + \frac{\hat{L}^2}{2(mr^2)} \right) u \quad u(r) = rR(r)$$

$$Eu = \frac{-\hbar^2}{2m} \partial_r^2 u + \left[ -\frac{ke^2}{r} + \frac{\hbar^2 l(l+1)}{2mr^2} \right] u$$

$$\Psi_{nlm}(\vec{r}) = R_{nl}(r) Y_l^m(\theta, \phi) = R_{nl}(r) \Theta_l^m(\theta) \Phi_m(\phi)$$

- $\Phi_m(\phi) = e^{im\phi}$
- $\Theta_l^m(\theta) = AP_l^m(\cos \theta)$
- $A = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}$ ,  $\epsilon = \begin{cases} (-1)^m & (m \geq 0) \\ 1 & (m \leq 0) \end{cases}$
- $P_l^m(x)$  Assoc. Legendre Func. (see extra)
- $R_{nl}(r) = \frac{B}{r} \rho^{l+1} e^{-\rho} \nu(\rho)$
- $\rho = k_n r$ ,  $k_n = \frac{1}{a_0 n}$  (fine structure below)
- $\nu(\rho) = L_{n-l-1}^{2l+1}(2\rho)$  Assoc. Laguerre Poly. (see extra)
- $B = \sqrt{2k_n \frac{(n-l-1)!}{2n[(n+l)!]^3}} 2^{l+1}$

$$\alpha \equiv \frac{kq q}{\hbar c} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

$$a_0 \equiv \frac{\hbar^2}{m(kq q)} = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

$$E_n = -\frac{\hbar^2 k_n^2}{2m} \Rightarrow E_n = -\frac{\hbar^2}{2ma_0^2} \frac{1}{n^2} = -\frac{1}{2} \alpha^2 (mc^2) \frac{1}{n^2} \approx -13.6 \frac{1}{n^2} [\text{eV}]$$

$$\frac{1}{\lambda} = \frac{\alpha^2 (mc^2)}{2\hbar c} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad R = 1.097 \text{ E7 } [\text{m}^{-1}]$$

Quantum Numbers -  $n, l, m$ :

- $(n \in \{1, 2, 3, \dots\}), (l \in \{0, 1, 2, \dots, n-1\}), (m \in \{-l, \dots, -1, 0, 1, \dots, l\})$
- Degeneracy is  $n^2$

(outdated) Bohr Model:

- $L = (\vec{r})(\vec{p}) = (a_0 n^2)(\hbar k_n) = n\hbar$  (not correct!!)
- Electrons don't radiate about the nucleus
- Energy diff. follows Rydberg formula

### 3 Spin and $L$

#### 3.1 Hydrogen Atom

Angular Momentum:

$$\widehat{L}_i \equiv (\vec{r} \times \vec{p})_i$$

$$\widehat{L}_{\pm} \equiv \widehat{L}_x \pm i\widehat{L}_y$$

$$\widehat{L}^2 \equiv L_x^2 + L_y^2 + L_z^2$$

$$= L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z$$

Commutation Relations:

$$[L_x, L_y] = i\hbar L_z \quad (\text{can't measure concurrently})$$

$$[H, L^2] = [H, L_i] = [L^2, L_i] = 0 \quad (\text{can measure concurrently})$$

$$\rightarrow \begin{pmatrix} L_z Y_{m'} = m' Y_{m'} \\ L^2 Y_{m'} = \lambda_{m'} Y_{m'} \end{pmatrix} \Rightarrow \begin{aligned} \langle L^2 \rangle = \lambda_{m'} &\geq (m')^2 = \langle L_z \rangle^2 \\ \bullet \sqrt{\lambda_{m'}} &\geq m' \geq -\sqrt{\lambda_{m'}} \end{aligned}$$

**Let**  $(L_{\pm})^n Y_{\mu} \equiv |m\rangle$

$$[L_z, (L_{\pm})^n] = \pm n\hbar (L_{\pm})^n$$

(Proof By Ind.)

$$\text{- } [L_z, L_{\pm}] = \pm \hbar L_{\pm}$$

$$\text{- } [L_z, (L_{\pm})^{n+1}] = \pm(n+1)\hbar (L_{\pm})^{n+1}$$

$$\Rightarrow L_z [(L_{\pm})^n Y_{\mu}] = (\mu \pm n\hbar) [(L_{\pm})^n Y_{\mu}]$$

$$\bullet L_z |m\rangle = (\mu \pm n\hbar) |m\rangle$$

$$[L^2, L_{\pm}] = 0 \Rightarrow [L^2, (L_{\pm})^n] = 0 \Rightarrow$$

$$L^2 [(L_{\pm})^n Y_{\mu}] = \lambda_{\mu} [(L_{\pm})^n Y_{\mu}]$$

$$\bullet L^2 |m\rangle = \lambda_{\mu} |m\rangle$$

**Then**  $(\sqrt{\lambda_{\mu}} \geq (\mu \pm n\hbar) \geq -\sqrt{\lambda_{\mu}}) \Rightarrow \text{Let}$  (else un-normalizable solution)

$$\begin{aligned} \overline{L_+ |m_t\rangle} &= 0, \quad L_z |m_t\rangle = \hbar l, \\ L^2 |m_t\rangle &= \lambda, \quad L^2 = L_- L_+ + L_z^2 + \hbar L_z \end{aligned}$$

$$\bullet L^2 |m_t\rangle = \hbar^2 l(l+1) |m_t\rangle = \lambda |m_t\rangle$$

$$\begin{aligned} \overline{L_- |m_b\rangle} &= 0, \quad L_z |m_b\rangle = \hbar l', \\ L^2 |m_b\rangle &= \lambda, \quad L^2 = L_+ L_- + L_z^2 - \hbar L_z \end{aligned}$$

$$\bullet L^2 |m_b\rangle = \hbar^2 l'(l'-1) |m_b\rangle = \lambda |m_b\rangle$$

$$\left( \lambda = \hbar^2 l'(l'-1) = \hbar^2 l(l+1) \right) \Rightarrow (l' = -l) \Rightarrow \begin{pmatrix} L_z |m_t\rangle = \hbar l |m_t\rangle \\ L_z |m_b\rangle = -\hbar l |m_b\rangle \end{pmatrix} \quad (\text{Spherical Harmonics do not allow half-integer } l)$$

Schrodinger  $Y_l^m$ :

$$\begin{aligned} l &\in \{0, 1, 2, \dots\} \\ m &\in \{-l, -l+1, \dots, l-1, l\} \end{aligned}$$

$$\begin{aligned} L_z |Y_l^m\rangle &= \hbar m |Y_l^m\rangle \\ L^2 |Y_l^m\rangle &= \hbar^2 l(l+1) |Y_l^m\rangle \\ L_{\pm} |Y_l^m\rangle &= \hbar \sqrt{l(l+1)-m(m\pm 1)} |Y_l^{m\pm 1}\rangle \end{aligned}$$

### 3.2 Generalized

Angular Momentum:

$$\hat{L}_i \equiv ???$$

$$L_{\pm} \equiv L_x \pm iL_y$$

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2$$

$$= L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z$$

Commutation Relations:

$$[L_i, L_j] = i\hbar L_k \quad \epsilon_{ij} \quad (\text{can't measure concurrently})$$

$$[L^2, L_z] = 0 \quad (\text{can measure concurrently})$$

General:

$$\left. \begin{array}{l} l \in \{0, \frac{1}{2}, 1, \frac{3}{2}, \dots\} \\ m \in \{-l, -l+1, \dots, l-1, l\} \end{array} \right\} \begin{array}{l} L_z |l \ m\rangle = \hbar m |l \ m\rangle \\ L^2 |l \ m\rangle = \hbar^2 l(l+1) |l \ m\rangle \\ L_{\pm} |l \ m\rangle = \hbar \sqrt{l(l+1)-m(m\pm 1)} |l \ m\rangle \end{array}$$

### 3.3 1 Particle w/ Spin, $s = \frac{1}{2}$

\*Find the Eigenvectors,  $e_i$ , of  $S_z$  and  $S^2$  in the form of  $|\chi\rangle$

$$* \quad e_i \in \left\{ \begin{array}{l} |\frac{1}{2} \ \frac{1}{2}\rangle \equiv |\uparrow\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad |\frac{1}{2} \ \frac{-1}{2}\rangle \equiv |\downarrow\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{array} \right\}$$

$$\left. \begin{array}{l} S^2 |\uparrow\rangle = \frac{3\hbar^2}{4} |\uparrow\rangle \\ S^2 |\downarrow\rangle = \frac{3\hbar^2}{4} |\downarrow\rangle \end{array} \right\} \Rightarrow S^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = * \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{3\hbar^2}{4} & 0 \\ 0 & \frac{3\hbar^2}{4} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{T*}$$

$$\left. \begin{array}{l} S_- |\uparrow\rangle = \hbar |\downarrow\rangle \\ S_+ |\downarrow\rangle = \hbar |\uparrow\rangle \\ S_+ |\uparrow\rangle = S_- |\downarrow\rangle = 0 \end{array} \right\} \Rightarrow S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (\text{can't measure})$$

$$\left. \begin{array}{l} S_z |\uparrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \\ S_z |\downarrow\rangle = \frac{\hbar}{2} |\downarrow\rangle \end{array} \right\} \Rightarrow S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2} \sigma_z = * \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{T*}$$

$$\left. \begin{array}{l} S_x = \frac{1}{2}(S_+ + S_-) \\ S_y = \frac{1}{2i}(S_+ - S_-) \end{array} \right\} \Rightarrow S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2} \sigma_x \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2} \sigma_y$$

### 3.4 2 Objects w/ Spin

Objects could be orbital momentum, another particle spin, etc.

#### 3.4.1 2 Objects w/ Spin $\frac{1}{2}$

\*Find Eigenvectors,  $e_i$ , of  $(S^{(1,2)})_z$  and  $(S^{(1,2)})^2$  in the form of  $|\chi_i \chi_j\rangle$  ( using  $(S^{(1,2)})_{\pm}$  )

$$\boxed{|\chi_i \chi_j\rangle \equiv \chi_i \chi_j \equiv |\chi_i\rangle |\chi_j\rangle \equiv |\chi_i\rangle \otimes |\chi_j\rangle}$$

Choose  $|\chi_i\rangle \equiv S_z$ -Eigenvector w/ Spin  $\frac{1}{2}$  (e.g,  $|\frac{1}{2} \frac{-1}{2}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ , as opposed to  $\begin{pmatrix} .6 \\ .8 \end{pmatrix}$ )

$$S^{(i)} \equiv \begin{pmatrix} S_x^{(i)} \\ S_y^{(i)} \\ S_z^{(i)} \end{pmatrix}$$

$$S^{(1,2)} \equiv (S^{(1)} + S^{(2)}) \equiv \begin{pmatrix} S_x^{(1)} + S_x^{(2)} \\ S_y^{(1)} + S_y^{(2)} \\ S_z^{(1)} + S_z^{(2)} \end{pmatrix}$$

$$\bullet S_z^{(2)} S_x^{(1)} (|\chi_1\rangle \otimes |\chi_2\rangle) = (S_x^{(1)} |\chi_1\rangle) \otimes (S_z^{(2)} |\chi_2\rangle)$$

$$\bullet (S^{(1,2)})^2 = (S^{(1)} + S^{(2)}) \cdot (S^{(1)} + S^{(2)})$$

$$\bullet S^{(i)} \cdot S^{(j)} \equiv S_x^{(i)} S_x^{(j)} + S_y^{(i)} S_y^{(j)} + S_z^{(i)} S_z^{(j)}$$

$$(S^{(i)})^2 \equiv S^{(i)} \cdot S^{(i)}$$

#### 1. $(S^{(1,2)})_z$

$$(S^{(1,2)})_z \chi_1 \chi_2 = (S_z^{(1)} + S_z^{(2)}) |\chi_1\rangle |\chi_2\rangle$$

$$= S_z^{(1)} |\chi_1\rangle \otimes |\chi_2\rangle + |\chi_1\rangle \otimes S_z^{(2)} |\chi_2\rangle$$

$$(S^{(1,2)})_z |\chi_1 \chi_2\rangle = \hbar(m_1 + m_2) |\chi_1 \chi_2\rangle$$

$$\Rightarrow \underline{e_i = a_i |\uparrow\uparrow\rangle + b_i |\uparrow\downarrow\rangle + c_i |\downarrow\uparrow\rangle + d_i |\downarrow\downarrow\rangle}$$

$$|\uparrow\uparrow\rangle = |\frac{1}{2} \frac{1}{2}\rangle \otimes |\frac{1}{2} \frac{1}{2}\rangle$$

$$|\uparrow\downarrow\rangle = |\frac{1}{2} \frac{1}{2}\rangle \otimes |\frac{1}{2} \frac{-1}{2}\rangle$$

$$|\downarrow\uparrow\rangle = |-\frac{1}{2} \frac{1}{2}\rangle \otimes |\frac{1}{2} \frac{1}{2}\rangle$$

$$|\downarrow\downarrow\rangle = |\frac{1}{2} \frac{1}{2}\rangle \otimes |\frac{1}{2} \frac{-1}{2}\rangle$$

2. Use  $(S^{(1,2)})_{\pm}$  on  $|\uparrow\rangle \otimes |\uparrow\rangle$  to GUESS  $e_i$  from "nice" behavior

$S_-  \uparrow\uparrow\rangle = \frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle)$ $S_- \left[ \frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle) \right] =  \downarrow\downarrow\rangle$ $S_-  \downarrow\downarrow\rangle = 0$ <p><math>S_+</math> works too</p> <p>If <math>\frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle)</math> then maybe  <math>\frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle)</math> works (try <math>S_{\pm}</math> on it).</p>	<p>Guess for <math>\{e_i\}</math>:</p> $ 1\ 1\rangle \equiv \left  \frac{1}{2}\frac{1}{2} \right\rangle \left  \frac{1}{2}\frac{1}{2} \right\rangle =  \uparrow\uparrow\rangle$ $ 1\ 0\rangle \equiv \frac{1}{\sqrt{2}} \left( \left  \frac{1}{2}\frac{1}{2} \right\rangle \left  \frac{1}{2}\frac{-1}{2} \right\rangle + \left  \frac{1}{2}\frac{-1}{2} \right\rangle \left  \frac{1}{2}\frac{1}{2} \right\rangle \right) = \frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle)$ $ 1\ -1\rangle \equiv \left  \frac{1}{2}\frac{-1}{2} \right\rangle \left  \frac{1}{2}\frac{-1}{2} \right\rangle =  \downarrow\downarrow\rangle$ $ 0\ 0\rangle \equiv \frac{1}{\sqrt{2}} \left( \left  \frac{1}{2}\frac{1}{2} \right\rangle \left  \frac{1}{2}\frac{-1}{2} \right\rangle - \left  \frac{1}{2}\frac{-1}{2} \right\rangle \left  \frac{1}{2}\frac{1}{2} \right\rangle \right) = \frac{\sqrt{2}}{2}( \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle)$
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3. Check if the guesses are eigenvectors of  $(S^{(1,2)})^2$  [and do  $(S^{(1,2)})_z$  to see eigenvalues]

(work has been skipped, do it yourself, check answer below)

$S^2 1\ 1\rangle = \hbar^2(1)(1+1) 1\ 1\rangle$	$(s=1)$	$S_z 1\ 1\rangle = \hbar(1) 1\ 1\rangle$	$(m=1)$
$S^2 1\ 0\rangle = \hbar^2(1)(1+1) 1\ 0\rangle$	$(s=1)$	$S_z 1\ 0\rangle = \hbar(0) 1\ 0\rangle$	$(m=0)$
$S^2 1\ -1\rangle = \hbar^2(1)(1+1) 1\ -1\rangle$	$(s=1)$	$S_z 1\ -1\rangle = \hbar(-1) 1\ -1\rangle$	$(m=-1)$
$S^2 0\ 0\rangle = \hbar^2(0)(0+1) 0\ 0\rangle$	$(s=0)$	$S_z 0\ 0\rangle = \hbar(0) 0\ 0\rangle$	$(m=0) \quad \square$

$$* \quad e_i \in \left\{ \begin{array}{l} |1\ 1\rangle = \left| \frac{1}{2}\frac{1}{2} \right\rangle \left| \frac{1}{2}\frac{1}{2} \right\rangle = |\uparrow\uparrow\rangle \\ |1\ 0\rangle = \frac{1}{\sqrt{2}} \left( \left| \frac{1}{2}\frac{1}{2} \right\rangle \left| \frac{1}{2}\frac{-1}{2} \right\rangle + \left| \frac{1}{2}\frac{-1}{2} \right\rangle \left| \frac{1}{2}\frac{1}{2} \right\rangle \right) = \frac{\sqrt{2}}{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1\ -1\rangle = \left| \frac{1}{2}\frac{-1}{2} \right\rangle \left| \frac{1}{2}\frac{-1}{2} \right\rangle = |\downarrow\downarrow\rangle \end{array} \right\} \quad \text{Triplet : } s=1$$

$$\left\{ \begin{array}{l} |0\ 0\rangle = \frac{1}{\sqrt{2}} \left( \left| \frac{1}{2}\frac{1}{2} \right\rangle \left| \frac{1}{2}\frac{-1}{2} \right\rangle - \left| \frac{1}{2}\frac{-1}{2} \right\rangle \left| \frac{1}{2}\frac{1}{2} \right\rangle \right) = \frac{\sqrt{2}}{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{array} \right\} \quad \text{Singlet : } s=0$$

### 3.4.2 2 Objects w/ Any Spin

- $|\chi_1\rangle$  has spin,  $s_1$ ; and  $|\chi_2\rangle$  has spin,  $s_2$
- $s_{\max} = s_2 + s_1$  and  $s_{\min} = s_2 - s_1$
- Possible total  $|s\ m\rangle$  must satisfy (not proven here)
  - 1.)  $s_{\min} \leq s \leq s_{\max}$ ,
  - 2.)  $-s \leq m \leq s$ ,
  - 3.) have integer differences

In general,

$$|s\ m\rangle = \sum_{1'2'} C_{s m s_1' m_1' s_2' m_2'} |s_1' m_1'\rangle \otimes |s_2' m_2'\rangle$$

where the sum is over all poss. int. diff. values that satisfy

$$s_1' + s_2' = s, \quad 0 \leq s_1' \leq s_1, \quad 0 \leq s_2' \leq s_2,$$

$$m_1' + m_2' = m, \quad -s_1' \leq m_1' \leq s_1', \quad -s_2' \leq m_2' \leq s_2',$$

and  $C$  are the corresponding Clebsh-Gordan coefficients, whose squared value is the probability of measuring the  $\chi_1 \otimes \chi_2$  state represented by that term.

Possible Combined  $|s\ m\rangle$

$$(2s_{\max} + 1) \left\{ \begin{array}{l} |s_{\max} \ s_{\max}\rangle \\ |s_{\max} \ s_{\max}-1\rangle \\ \dots \\ |s_{\max} \ -s_{\max}\rangle \end{array} \right.$$

$$\left\{ \begin{array}{l} |s_{\max}-1 \ s_{\max}-1\rangle \\ |s_{\max}-1 \ s_{\max}-2\rangle \\ \dots \end{array} \right.$$

...

$$(2s_{\min} + 1) \left\{ \begin{array}{l} |s_{\min} \ s_{\min}\rangle \\ \dots \\ |s_{\min} \ -s_{\min}\rangle \end{array} \right.$$

More easily, if  $m_1$  and  $m_2$  are also known from the start, then  $m = m_1 + m_2$ , and

$$|s_1\ m_1\rangle \otimes |s_2\ m_2\rangle = \sum_s C'_{s m s_1 m_1 s_2 m_2} |s\ (m_1+m_2)\rangle$$

where the sum is only over all possible  $s$  as satisfied above - **1.), 2.) and 3.)**. The coefficient  $C'$  also takes the same 6 variables as  $C$  but the numbers and their primes are swapped (e.g.,  $s_1 \leftrightarrow s_1'$ ). In this case, the total z-component,  $m$ , is known. The only unknown is the total spin,  $s$ , whose probability when measured is  $(C')^2$ .

### 3.5 Electron in Magnetic Field

$$\mu_{\text{clas.}} = IA = \frac{q}{2\pi r} v(\pi r^2) = \frac{q}{2\pi r} \frac{L}{mr} (\pi r^2) = \left(\frac{q}{2m}\right) L$$

$$\mu_{\text{quan.}} = \left(\frac{geq}{2m}\right) S = \left(\frac{q}{m}\right) S = \gamma S$$

$$\begin{aligned} \tau_\mu &= \mu \times B & H &= -\mu \cdot B \\ F_\mu &= \nabla(\mu \cdot B) & &= -\gamma S \cdot B \end{aligned},$$

#### Larmor Precession

$$\begin{aligned} \chi(t) &= \cos(\alpha/2) \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-\frac{i}{\hbar} E_1 t} + \sin(\alpha/2) \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-\frac{i}{\hbar} E_2 t} \\ B &= B_0 \hat{k} \\ H &= -\gamma B_0 S_z \\ &= -\gamma B_0 \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \end{aligned} \Rightarrow \begin{aligned} &= \begin{pmatrix} \cos(\alpha/2) e^{-\frac{i}{\hbar} E_1 t} \\ \sin(\alpha/2) e^{-\frac{i}{\hbar} E_2 t} \end{pmatrix} \\ \begin{pmatrix} \langle S_x \rangle \\ \langle S_y \rangle \\ \langle S_z \rangle \end{pmatrix} &= \begin{pmatrix} \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B_0 t) \\ -\frac{\hbar}{2} \sin(\alpha) \sin(\gamma B_0 t) \\ \frac{\hbar}{2} \cos(\alpha) \end{pmatrix} \quad (\text{torque from } B \text{ with } S \text{ leads to precession}) \end{aligned}$$

#### Stern-Gerlach



## 4 Bosons and Fermions

Distinguishable Particles:  $\boxed{\psi(r_1, r_2) \equiv \psi_a(r_1)\psi_b(r_2)}$

Indistinguishable Particles:

$$\underline{P_x f(x_1, x_2; y_1, y_2; \dots) = \pm f(x_2, x_1; y_1, y_2; \dots)}$$

Boson:

$$(s \in \{0, 1, 2, \dots\}) \quad \psi_+(r_1, r_2) \equiv \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) + \psi_b(r_1)\psi_a(r_2)]$$

$$\boxed{\psi(r_1, r_2) = \psi(r_2, r_1)} \rightarrow \boxed{P_i \Psi = \Psi} \quad (\text{symmetric})$$

Fermion:

$$(s \in \{\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots\}) \quad \psi_-(r_1, r_2) \equiv \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2)]$$

$$\boxed{\psi(r_1, r_2) = -\psi(r_2, r_1)} \rightarrow \boxed{P_i \Psi = -\Psi} \quad (\text{antisymmetric})$$

### 4.1 Exchange Forces: $\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

Dist. Part. :	$\langle (\Delta x)^2 \rangle = \langle (\Delta x)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$
Symmetric:	$\langle (\Delta x)^2 \rangle = \langle (\Delta x)^2 \rangle_d - 2 \parallel \langle \psi_b   x   \psi_a \rangle \parallel^2 \quad (\text{attractive if overlap})$
Antisymmetric:	$\langle (\Delta x)^2 \rangle = \langle (\Delta x)^2 \rangle_d + 2 \parallel \langle \psi_b   x   \psi_a \rangle \parallel^2 \quad (\text{repulsive if overlap})$

$$\begin{aligned}
 \bullet \langle x_1 x_2 \rangle &= \frac{1}{2} \int [\psi_a(r_1)^* \psi_b(r_2)^* \pm \psi_b(r_1)^* \psi_a(r_2)^*] x_1 x_2 [\psi_a(r_1) \psi_b(r_2) \pm \psi_b(r_1) \psi_a(r_2)] dx_1 dx_2 \\
 &= \frac{1}{2} \langle x \rangle_a \langle x \rangle_b + \frac{1}{2} \langle x \rangle_b \langle x \rangle_a \\
 &\quad \pm \frac{1}{2} \langle \psi_b(r_1) | x_1 | \psi_a(r_1) \rangle \langle \psi_a(r_2) | x_2 | \psi_b(r_2) \rangle \pm \frac{1}{2} \langle \psi_a(r_1) | x_1 | \psi_b(r_1) \rangle \langle \psi_b(r_2) | x_2 | \psi_a(r_2) \rangle \\
 &= \langle x \rangle_a \langle x \rangle_b \pm \parallel \langle \psi_b | x | \psi_a \rangle \parallel^2
 \end{aligned}$$

Two Electrons:

$$\psi(r_1, r_2) \chi(m_1, m_2) = \begin{cases} \text{(singlet)} & \Rightarrow \chi \text{ is antisymmetric so } \Rightarrow \text{Attractive} \\ -\psi(r_1, r_2) \chi(m_2, m_1) & \Rightarrow \psi \text{ is symmetric} \\ \text{(triplet)} & \Rightarrow \chi \text{ is symmetric so } \Rightarrow \text{Repulsive} \\ -\psi(r_2, r_1) \chi(m_1, m_2) & \Rightarrow \psi \text{ is antisymmetric} \end{cases}$$

## 4.2 Statistics

Sterling's Approx:  $\log(z!) \approx z \log(z) - z \quad z \gg 1 \text{ or } z = 0$

$$\frac{d}{dz} \log(z!) \approx \log(z)$$

Lagrange Multiplier:  $G(X, \alpha, \beta) = \log(Q(X)) + \alpha f_1(X) + \beta f_2(X)$

$$\frac{\partial G}{\partial \alpha}[Q_{\max}] = 0, \quad \frac{\partial G}{\partial \beta}[Q_{\max}] = 0, \quad \frac{\partial G}{\partial N_n}[Q_{\max}] = 0$$


---

$$\sum_n N_n = N \quad \sum_n N_n E_n = E$$

$$f_1(X) = N - \sum_n N_n = 0 \quad f_2(X) = E - \sum_n N_n E_n = 0$$

Let there be  $N_n$  particles in the  $E_n$  energy level having  $d_n$  degeneracies, and  $Q(N_1, N_2, \dots)$  be the number of possible configurations for such a state given  $X = (N_1, N_2, \dots, N_n)$ .

Dist.	$\left\{ \begin{array}{l} \text{1.) } Q(X) = \prod_n \binom{N - N_1 - \dots - N_{n-1}}{N_n} d_n^{N_n} \\ \quad = N! \prod_n \frac{d_n^{N_n}}{N_n!} \\ \text{2.) } \log(Q) = \log(N!) + \sum_n N_n \log(d_n) \\ \quad \quad - \log(N_n!) \end{array} \right.$	$\begin{array}{l} \text{3.) } \frac{\partial G}{\partial N_n} \approx \frac{\log(d_n) - \log(N_n)}{-\alpha - \beta E_n} = 0 \\ \text{4.) } N_n = \frac{d_n}{e^{\beta E_n + \alpha}} \end{array}$
Fermion	$\left\{ \begin{array}{l} \text{1.) } Q(X) = \prod_n \binom{d_n}{N_n} \\ \text{2.) } \log(Q) = \sum_n \log(d_n!) - \log(N_n!) \\ \quad \quad - \log[(d_n - N_n)!] \end{array} \right.$	$\begin{array}{l} \text{3.) } \frac{\partial G}{\partial N_n} \approx \frac{-\log(N_n) + \log(d_n - N_n)}{-\alpha - \beta E_n} = 0 \\ \text{4.) } N_n = \frac{d_n}{e^{\beta E_n + \alpha} + 1} \end{array}$
Boson	$\left\{ \begin{array}{l} \text{1.) } Q(X) = \prod_n \binom{N_n + d_n - 1}{N_n} \\ \text{2.) } \log(Q) = \sum_n \log[(N_n + d_n - 1)!] \\ \quad \quad - \log(N_n!) \\ \quad \quad - \log[(d_n - 1)!] \end{array} \right.$	$\begin{array}{l} \text{3.) } \frac{\partial G}{\partial N_n} \approx \frac{\log(N_n + d_n - 1) - \log(N_n)}{-\alpha - \beta E_n} = 0 \\ \text{4.) } N_n = \frac{d_n - 1}{e^{\beta E_n + \alpha} - 1} \approx \frac{d_n}{e^{\beta E_n + \alpha} - 1} \end{array}$

Given some substance in thermal equilibrium,

$$\beta = \frac{1}{k_b T} \quad \mu(T) \equiv -\frac{\alpha}{k_b T}$$

where  $\mu$  depends on the situation.

$$\frac{N_n}{d_n} : \quad n(\epsilon) = \begin{cases} \frac{1}{e^{(\epsilon-\mu)/k_b T}} & \text{Maxwell-Boltzmann} \\ \frac{1}{e^{(\epsilon-\mu)/k_b T} + 1} & \text{Fermi-Dirac} \\ \frac{1}{e^{(\epsilon-\mu)/k_b T} - 1} & \text{Bose-Einstein} \end{cases}$$

## 5 Perturbation Theory

$$H^{(0)}\psi_n = E_n\psi_n$$

$$\downarrow$$

$$H\psi'_n = E'_n\psi'_n$$

$$\left(H^{(0)} + \lambda H^{(1)}\right)\left(\psi_n + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots\right) = \left(E_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\right)\left(\psi_n + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots\right)$$

$$\begin{array}{ccc} \cancel{\lambda^0 H^{(0)}\psi_n} & \cancel{\lambda^0 E_n\psi_n} & \\ + \lambda^1 (H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n) & + \lambda^1 (E_n\psi_n^{(1)} + E_n^{(1)}\psi_n) & \\ + \lambda^2 (H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)}) & + \lambda^2 (E_n\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n) & \\ + \dots & + \dots & \end{array} \quad (\lambda=1)$$

### 5.1 Non-Degenerate Theory

$$\underline{E_n^{(1)}, \psi_n^{(1)}} : \quad H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n = E_n\psi_n^{(1)} + E_n^{(1)}\psi_n$$

$$\begin{aligned} \langle \psi_m | (-H^{(1)} + E_n^{(1)}) | \psi_n \rangle &= \langle \psi_m | (H^{(0)} - E_n) | \psi_n^{(1)} \rangle \\ &= \langle \psi_m | (H^{(0)} - E_n) \sum c_i | \psi_i \rangle \\ &= \sum c_i (E_i - E_n) \langle \psi_m | \psi_i \rangle \end{aligned}$$

$$-\langle \psi_m | H^{(1)} | \psi_n \rangle + E_n^{(1)} \langle \psi_m | \psi_n \rangle = c_m (E_m - E_n)$$

$$\boxed{E_n^{(1)} = \langle \psi_n | H^{(1)} | \psi_n \rangle}$$

$$\boxed{\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m | H^{(1)} | \psi_n \rangle}{E_n - E_m} \psi_m + (0) \psi_n}$$

$$\begin{aligned} \underline{E_n^{(2)}} : \quad \cancel{E_n \langle \psi_n | \psi_n^{(2)} \rangle} + E_n^{(1)} \cancel{\langle \psi_n | \psi_n^{(1)} \rangle} &= \cancel{\langle H^{(0)} \psi_n | \psi_n^{(2)} \rangle} + \langle \psi_n | H^{(1)} | \psi_n^{(1)} \rangle \\ + E_n^{(2)} \langle \psi_n | \psi_n \rangle &= \sum_{m \neq n} \frac{\langle \psi_m | H^{(1)} | \psi_n \rangle}{E_n - E_m} \langle \psi_n | H^{(1)} | \psi_m \rangle \end{aligned}$$

$$\boxed{E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m | H^{(1)} | \psi_n \rangle|^2}{E_n - E_m}}$$

## 5.2 Degenerate Perturbation Theory (see Matrix Operators)

$$\begin{aligned}
 \Psi &= \sum_i \left( c_i^{(\psi)} [\Psi] \right) \psi_i & \bullet \quad H^{(0)} \psi_i &= E_n \psi_i \quad (\psi_n \text{ are degenerate eigenfunctions of } H^{(0)}) \\
 &\equiv \sum_i c_i^{(\psi)} \psi_i & \bullet \quad \langle \psi_i | \psi_j \rangle &= \delta_{ij} \\
 &= c_0^{(\psi)} \psi_0 + c_1^{(\psi)} \psi_1 + \dots & \bullet \quad \langle \psi_i | \hat{Q} | \psi_j \rangle &\equiv Q_{ij}
 \end{aligned}$$

$$E_n \Psi^{(1)} + E^{(1)} \Psi = H^{(0)} \Psi^{(1)} + H^{(1)} \Psi \quad (\text{first order})$$

$$\begin{aligned}
 \cancel{E_n \langle \psi_i | \Psi^{(1)} \rangle} + E^{(1)} \langle \psi_i | \Psi \rangle &= \cancel{\langle H^{(0)} \psi_i | \Psi^{(1)} \rangle} + \langle \psi_i | H^{(1)} | \Psi \rangle \\
 &= \langle \psi_i | H^{(1)} | c_0 \psi_0 + c_1 \psi_1 + \dots \rangle \\
 c_i E^{(1)} &= c_0 \langle \psi_i | H^{(1)} | \psi_0 \rangle + c_1 \langle \psi_i | H^{(1)} | \psi_1 \rangle + \dots
 \end{aligned}$$

$$E^{(1)} \begin{pmatrix} c_0[\Psi] \\ c_1[\Psi] \\ \vdots \end{pmatrix}^{(\psi)} = \begin{pmatrix} H_{00}^{(1)} & H_{01}^{(1)} & \dots \\ H_{10}^{(1)} & H_{11}^{(1)} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}^{(\psi)} \begin{pmatrix} c_0[\Psi] \\ c_1[\Psi] \\ \vdots \end{pmatrix}^{(\psi)} \Rightarrow \boxed{\begin{aligned} &(\text{solve for } E^{(1)}, \vec{c}^{(\psi)}[\Psi]) \\ &\left\| \begin{pmatrix} H_{aa}^{(1)} - E^{(1)} & H_{ab}^{(1)} & \dots \\ H_{ba}^{(1)} & H_{bb}^{(1)} - E^{(1)} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \right\| = 0 \end{aligned}}$$

In general,

$$\begin{aligned}
 E_i^{(1)} \vec{c}^{(\psi)}[\Psi_i] &= \overline{H^{(1)}}^{(\psi)} \vec{c}^{(\psi)}[\Psi_i] \quad (i\text{th eigen-}) \\
 E_i^{(1)} \begin{pmatrix} | \\ \vec{c}[\Psi_i] \\ | \end{pmatrix}^{(\psi)} &= \begin{pmatrix} | & | & | \\ \vec{c}[\Psi_i] & \vec{c}[\Psi_i] & \dots \\ | & | & | \end{pmatrix}^{(\psi)} \begin{pmatrix} E_0^{(1)} & 0 & \dots \\ 0 & E_1^{(1)} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} - & \vec{c}^*[\Psi_i] & - \\ - & \vec{c}^*[\Psi_i] & - \\ \vdots & \vdots & \ddots \end{pmatrix}^{(\psi)} \begin{pmatrix} | \\ \vec{c}[\Psi_i] \\ | \end{pmatrix}^{(\psi)}
 \end{aligned}$$

Instead of solving the characteristic polynomial, it would be wise to choose a basis  $\{\psi\}$  such that  $\vec{c}^{(\psi)}[\Psi_i] = (\dots 0 \ 0 \ 1_{(i)} \ 0 \ 0 \ \dots)^T \Leftrightarrow \Psi_i = \psi_i$ , making  $\overline{H^{(1)}}^{(\psi)}$  diagonal with eigenvalue entries. These are the energy eigenvalues,  $E_i^{(1)} = (H^{(1)})_{ii}^{(\psi)} = \langle \psi_i | H^{(1)} | \psi_i \rangle$ , which is just like first-order non-Perturbation energy. This also means  $|\psi_i\rangle$  are eigenfunctions of  $H^{(1)}$  (see Matrix Operators).

It is best to find a hermitian operator,  $\hat{A}$ , that commutes with  $H^{(0)}$  and  $H^{(1)}$ , whose eigenvalues within the degenerate basis are unique. The corresponding eigenfunctions will be a basis that makes  $H^{(1)}$  diagonal. This will also make them eigenfunctions of  $H^{(1)}$ .

1.  $A = A^\dagger$
2.  $[A, H^{(0)}] = 0 \rightarrow \left\{ \exists \{\Psi\} \mid (A\Psi_n = a_n \Psi_n), (H^{(0)}\Psi_n = E_n \Psi_n) \right\}$
3.  $\{\psi\} \subset \{\Psi\}$  s.t.  $\forall \psi_i : \begin{cases} (H^{(0)}\psi_i = E_n \psi_i), & \leftarrow \text{degenerate} \\ (A\psi_i = a_i \psi_i), & (\forall (i \neq j) \ a_i \neq a_j) \end{cases}$
4.  $[A, H^{(1)}] = 0 \Rightarrow \begin{aligned} 0 &= \langle A\psi_i | H^{(1)} | \psi_j \rangle - \langle \psi_i | H^{(1)} | A\psi_j \rangle \\ 0 &= (a_i - a_j) H_{ij}^{(1)} \\ 0 &= H_{ij}^{(1)} \quad \square \end{aligned}$

## 5.3 Hydrogen Energy Corrections

### 5.3.1 Fine Structure - $\alpha^4 mc^2$

The Dirac Equation can derive the total fine structure correction with a  $\alpha^4$  order approx.

#### 1. Relativistic, $\hat{p}^4$

$$\begin{aligned}
 T &= \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \\
 &= \frac{(\frac{1}{2})}{1!} \left( \frac{p}{mc} \right) + \frac{(\frac{1}{2})(1 - \frac{1}{2})}{2!} \left( \frac{p}{mc} \right)^2 + \dots \\
 &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots \\
 &\downarrow \\
 H_r^{(1)} &= -\frac{p^4}{8m^3 c^2} \quad \text{(For some reason } \hat{p}^4 \text{ needs to be hermitian to use perturbation theory. It only isn't when } l = 0, \text{ while } \hat{p}^2 \text{ always is hermitian. See Prob. 6.15)}
 \end{aligned}$$

$L^2$  and  $L_z$  should commute with  $p^4$  because the perturbation is spherically symmetric, meaning  $l$  and  $m_l$  should be conserved (see Operator Evolution). Their eigenvalues are also distinct (taking the eigenfunctions of  $nlm_l$  together) within each set of  $n^2$  degeneracies, so their eigenvectors and eigenvalues can be used.  $n, l$  and  $m_l$  the "good" numbers.

$$\left. \begin{aligned}
 \langle r^{-1} \rangle &= \frac{1}{n^2 a_0} \\
 \langle r^{-2} \rangle &= \frac{1}{(l+1/2)n^3 a_0^2}
 \end{aligned} \right| \begin{aligned}
 \langle \psi_{nlm_l} | H_r^{(1)} | \psi_{nlm_l} \rangle &= \frac{-1}{8m^3 c^2} \langle \psi_{nlm_l} | p^4 | \psi_{nlm_l} \rangle \\
 &= \frac{-1}{8m^3 c^2} \langle p^2 \psi_{nlm_l} | p^2 | \psi_{nlm_l} \rangle \\
 &= \frac{-1}{8m^3 c^2} \langle [2m(E_n - V)]^2 \rangle \\
 &= \frac{-4m^2}{8m^3 c^2} \langle E_n^2 - 2E_n V + V^2 \rangle \\
 &= -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l+1/2} - 3 \right]
 \end{aligned}$$

#### 2. Spin-Orbit Coupling, $\mathbf{S}_e \cdot \mathbf{L}_e$

In the electron's frame of reference, the proton is spinning around it, creating a  $B$ -field affecting its magnetic dipole moment. The non-inertial reference frame requires multiplying by the Thomas precession correction, which in this case is  $C_T = g_e - 1 = 1/2$ . In the lab frame, the moving electron's magnetic dipole moment creates an electric dipole moment, which is affected by the proton charge. The latter is much harder to calculate.

$$\begin{aligned}
H_{so}^{(1)} &= -C_T \mu_e \cdot B(L_e) \quad (\text{See Electron in Magnetic Field}) \\
&= \frac{kqq}{2} \frac{1}{m^2 c^2 r^3} S_e \cdot L_p \\
&= \frac{kqq}{2m} \frac{1}{mc^2} \frac{S \cdot L}{r^3} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \frac{S \cdot L}{r^3}
\end{aligned}$$

$S \cdot L$  does not commute with  $L$  or  $S$  (meaning  $m_l$  and  $m_s$  are bad), but  $[S \cdot L, S^2] = [S \cdot L, L^2] = 0$ . The sum of the two,  $J \equiv L + S$ , and  $J^2$  also commute with the perturbation. They are all conserved, and their unique eigenvalues per set of degeneracies -  $l, s=1/2, j, m_j$  - are the "good" numbers (along with  $n$ ).

$$\left. \begin{aligned}
S \cdot L &= \frac{1}{2} (J^2 - L^2 - S^2) \\
\langle r^{-3} \rangle &= \frac{1}{l(l+1/2)(l+1)n^3 a_0^3}
\end{aligned} \right| \begin{aligned}
\langle n l j m_j | H_{so}^{(1)} | n l j m_j \rangle &= \frac{kqq}{2m} \frac{1}{mc^2} \frac{\hbar^2 [j(j+1) - l(l+1) - s(s+1)]}{2l(l+1/2)(l+1)n^3 a_0^3} \\
&= \frac{kqq}{4mn^4} \frac{\hbar^2 \alpha^3 m^3 c^3}{\hbar^3 mc^2} \frac{n[j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)} \\
&= \frac{kqq}{4\hbar c n^4} \frac{\alpha^3 m^2 c^4}{mc^2} \frac{n[j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)} \\
&= \frac{E_n^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right\}
\end{aligned}$$

3. Darwin Term (correction for  $H_{so}^{(1)}$  when  $l = 0$ ) skipped

#### 4. Total Correction

$$\begin{aligned}
E_{fs}^{(1)} &= E_r^{(1)} + E_{so}^{(1)} \\
&= -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + \frac{1}{2}} - 3 \right] + \frac{E_n^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right\} \\
&= \frac{E_n^2}{2mc^2} \left( 3 - \frac{4n}{j + 1/2} \right) \quad (j=l\pm 1/2) \\
&\downarrow \\
E_{nj} &= E_n + E_{fs}^{(1)} \\
&= E_n \left[ 1 - \frac{E_n}{2mc^2} \left( \frac{4n}{j + 1/2} - 3 \right) \right] \\
&= -\frac{\alpha^2 mc^2}{2n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + 1/2} - 3/4 \right) \right]
\end{aligned}$$

Fine structure splits the  $l$  energy degeneracies. However, since  $j = l \pm 1/2$ , there are still two  $j$  degeneracies if  $n > 2$ . Overall, the good numbers to use for stationary state solutions to the hydrogen atom w/ fine structure correction are  $n, l, s=1/2, j, m_j$ . Note,  $J^2, L^2$ , and  $S^2$  always commute(?)

### 5.3.2 Zeeman Effect (Ext. $B$ -Field)

$$\begin{aligned}
H_B^{(1)} &= -(\mu_s + \mu_l) \cdot B_{\text{ext}} && \text{(see Electron in Magnetic Field)} \\
&= -\left(\frac{g_e q}{2m} S + \frac{q}{2m} L\right) \cdot B_{\text{ext}} \\
&= \frac{e}{2m} (2S + L) \cdot B_{\text{ext}}
\end{aligned}$$

Weak Zeeman ( $B_{\text{ext}} \ll B_{\text{int}}$ )

$$\begin{aligned}
H_{WZ}^{(1)} &= \frac{e}{2m} B_{\text{ext}} \cdot (2S + L) \\
&= \frac{e}{2m} B_{\text{ext}} \cdot (J + S)
\end{aligned}$$

Fine structure effects dominate the Zeeman effect, so the fine structure numbers are the good ones:  $n, l, s=1/2, j$ , and  $m_j$ .  $m_s$  can't be used for  $\langle S \rangle$ , so instead use the fact that the "vector"  $J = L + S$  is conserved, so a **time-averaged**  $S$ -component to the  $J$  "vector" can be defined as  $S_{\text{ave}} = \frac{S \cdot J}{J^2} J$ , where  $S \cdot J = \frac{1}{2} (J^2 + S^2 - L^2)$ .

$$\begin{aligned}
E_{WZ}^{(1)} &= \frac{e}{2m} B_{\text{ext}} \cdot \langle n l j m_j | J + S_{\text{ave}} | n l j m_j \rangle \\
&= \frac{e}{2m} B_{\text{ext}} \cdot \left\langle J \left( 1 + \frac{S \cdot J}{J^2} \right) \right\rangle \\
&= \frac{e}{2m} B_{\text{ext}} \cdot \langle J \rangle \left( 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right) \\
&= \frac{e\hbar}{2m} B_{\text{ext}} m_j \left( 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right) && \text{(let } B_{\text{ext}} \text{ be parallel to the z-axis)} \\
&= \mu_B B_{\text{ext}} m_j g_j && \begin{aligned} \mu_B &= \text{Bohr magneton} = 5.788 \times 10^{-5} \text{ eV/T} \\ g_j &= \text{Lande g-factor} \end{aligned}
\end{aligned}$$

Strong Zeeman ( $B_{\text{ext}} \gg B_{\text{int}}$ )

For a strong magnetic field parallel to the z-axis,  $m_l$  and  $m_s$  are stuck in the same place, making them and  $l$  conserved. The external torque, however, means that the total angular momentums,  $j$  and  $m_j$  are not. Though unneeded, obviously  $s=1/2$ .

$$\begin{aligned}
E_{SZ}^{(1)} &= \frac{e}{2m} B_{\text{ext}} \langle 2S_z + L_z \rangle \\
&= \mu_B B_{\text{ext}} (2m_s + m_l)
\end{aligned}$$

The spin-orbit correction must be changed with respect to the new good numbers,  $m_l$  and  $m_s$ . The relativistic correction uses the same numbers, so it stays the same.



$$\begin{aligned}
E_{\text{so}}^{(1)} &= \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \left\langle \frac{S_x L_x + S_y L_y + S_z L_z}{r^3} \right\rangle \rightarrow E_{\text{fs}}^{(1)} = E_{\text{so}}^{(1)} + E_{\text{r}}^{(1)} \\
&= \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \frac{0 + 0 + \hbar^2 m_s m_l}{l(l+1/2)(l+1)n^3 a_0^3} = \frac{E_n^2}{2mc^2} \frac{4nm_s m_l}{l(l+1/2)(l+1)} + \frac{E_n^2}{2mc^2} \left[ 3 - \frac{4n}{l+1/2} \right] \\
&= \frac{kqq}{2m^2 c^2} \frac{\hbar^2}{(\hbar/\alpha mc)^3 n^3} \frac{m_s m_l}{l(l+1/2)(l+1)} = \frac{4nE_n^2}{2mc^2} \left[ \frac{m_s m_l}{l(l+1/2)(l+1)} + \frac{3}{4n} - \frac{1}{l+1/2} \right] \\
&= \frac{kqq}{2\hbar c} \frac{\alpha^3 m^2 c^4}{4mc^2 n^4} \frac{4nm_s m_l}{l(l+1/2)(l+1)} \downarrow \\
&= \frac{E_n^2}{2mc^2} \frac{4nm_s m_l}{l(l+1/2)(l+1)} E_{nlm_l m_s} = E_n + E_{\text{SZ}}^{(1)} + E_{\text{fs}}^{(1)}
\end{aligned}$$

### Intermediate Zeeman ( $B_{\text{ext}} \sim B_{\text{int}}$ )

There are no good numbers here (see Degenerate Perturbation Theory). The basis is chosen to be  $|j m_j\rangle = \sum_i C_i |l m_l\rangle \otimes |s m_s\rangle$  (see 2 Objects w/ Any Spin), as it makes  $\overline{H^{(1)}}^{(e)}$  easier (instead of using  $l, m_l, m_s$ ).

$$\begin{aligned}
1.) \psi_i &= |j m_j\rangle_i & 2.) \left( |l m_l\rangle \langle s m_s| \right)_x \left( |l m_l\rangle |s m_s\rangle \right)_y &= \delta_{xy} \\
3.) Q_{rc}^{(\psi)} &= \langle \psi_r | \hat{Q} | \psi_c \rangle & 4.) \psi_i \text{ s.t. } &\begin{cases} 0 \leq l < n \\ j_{(l\pm)} = l \pm 1/2, \\ 2l^2 < i \leq 2(l+1)^2 \end{cases}
\end{aligned}$$

$$\begin{aligned}
\langle j m_j | H_{fs}^{(1)} | j m_j \rangle &= \frac{E_n^2}{2mc^2} \left( 3 - \frac{4n}{j+1/2} \right) \\
&\equiv \gamma_n \left( 3 - \frac{4n}{j+1/2} \right) \\
\langle j m_j | H_{IZ}^{(1)} | j m_j \rangle &= \langle j m_j | H_{IZ}^{(1)} (C_i |l m_l\rangle \otimes |s m_s\rangle) \\
&= \mu_B B_{\text{ext}} (2m_s + m_l) C_i^2 \\
&\equiv \beta (2m_s + m_l) C_i^2
\end{aligned}
\quad \left| \quad \begin{aligned}
\overline{H^{(1)}}^{(jm_j)} &= \overline{H_{fs}^{(1)}}^{(jm_j)} + \overline{H_{IZ}^{(1)}}^{(jm_j)} \\
\text{See Griffith Prob. 6.25 for example with } n &= 2
\end{aligned}
\right.$$

### 5.3.3 Stark Effect (Small Ext. $E$ -Field)

- $H^{(1)} = -\mathbf{p} \cdot \mathbf{E} = e\mathbf{E} \cdot \mathbf{r}$  (small  $r$ )
- $n = 1 \rightarrow H^{(1)} = 0$
- $n = 2 \rightarrow \begin{cases} H^{(1)} = 0 & m = \pm 1 \\ H^{(1)} = ke|E|a_0 & m = 0 \end{cases}$  ( $k$  is some constant)

### 5.3.4 Lamb Shift (quantitized $E$ -field) - $\alpha^5 mc^2$ (skipped)

### 5.3.5 Hyperfine (Spin-Spin), $\mathbf{S}_p \cdot \mathbf{S}_e$ - $m/m_p \alpha^4 mc^2$

(Coupling between the electron magnetic moment and the magnetic field from the proton magnetic moment)

$$\left. \begin{aligned} \mu_e &= -\frac{g_e e}{2m_e} S_e = -\frac{e}{m_e} S_e, & \mu_p &= \frac{g_p e}{2m_p} S_p \\ B(\mu_p) &= \frac{\mu_0}{4\pi r^3} [3(\vec{\mu}_p \cdot \hat{r})\hat{r} - \vec{\mu}_p] + \frac{2\mu_0}{3} \vec{\mu}_p \delta^3(r) \end{aligned} \right| \begin{aligned} H_{hf}^{(1)} &= -\mu_e \cdot B(\mu_p) \\ &= \dots \\ &\downarrow \\ E_{hf}^{(1)} &= \left(\frac{e}{m_e}\right) \left(\frac{2\mu_0}{3} \frac{g_p e}{2m_p}\right) \langle S_e \cdot S_p \rangle |\psi_{nlm}(0)|^2 \end{aligned}$$

In the ground state,  $|\psi_{100}(0)|^2 = 1/(\pi a_0^3)$ .  $S_e^2, S_p^2$ , and the sum  $S = S_e + S_p$  commute with  $S_e \cdot S_p$ , so  $s_e, s_p, m_s, s^2$  are the good numbers.  $S_e$  and  $S_p$  do not, so  $m_{se}$  and  $m_{sp}$  are not good numbers.

$$\begin{aligned} E_{hf}^{(1)} &= \left(\frac{e}{m_e}\right) \left(\frac{2}{3\epsilon_0 c^2} \frac{g_p e}{2m_p}\right) \frac{1}{2\pi a_0^3} \langle S^2 - S_e^2 - S_p^2 \rangle \\ &= \frac{g_p e^2}{4\pi\epsilon_0 c^2 m_p m_e} \frac{4\alpha^3 m_e^3 c^3 \hbar^2}{3\hbar^3} \left[ \frac{s(s+1)}{2} - 3/4 \right] \\ &= \frac{4}{3} g_p \frac{m_e}{m_p} \alpha^4 m_e c^2 \left[ \frac{s(s+1)}{2} - 3/4 \right] \\ &= \frac{4}{3} g_p \frac{m_e}{m_p} \alpha^4 m_e c^2 \cdot \begin{cases} \frac{1}{4} & s = 1 \text{ (triplet)} \\ \frac{-3}{4} & s = 0 \text{ (singlet)} \end{cases} \rightarrow \begin{aligned} \Delta E &= 5.88 \times 10^{-6} \text{ eV} \\ \lambda &= 21 \text{ cm}, \quad \nu = 1420 \text{ MHz} \end{aligned} \end{aligned}$$

## 5.4 Variation Principle - Approx. Ground State Energy

$$\psi = \sum c_n \psi_n \rightarrow E(\psi) > E_0 = E(\psi_0)$$

$$\psi \equiv f(b, x), \quad \langle H \rangle = \langle T \rangle + \langle V \rangle$$

$$b_{\min} : \frac{d}{db} \langle H \rangle = 0$$

$$E_{\text{gs}} \approx \left\langle f(b_{\min}, x) \left| H \right| f(b_{\min}, x) \right\rangle$$

## 5.5 Adiabatic Theorem - Slow Changing of Potential

$$H(t=\tau) = H'$$

$$H(t=0) = H_0$$

$$t = \tau \rightarrow \psi(t=\tau) = \psi_n^{(H')} \quad t = 0 \rightarrow \psi(t=0) = \psi_n^{(H_0)}$$

$$E(\psi) = E_n^{(H')}$$

$$E(\psi) = E_n^{(H_0)}$$

## 5.6 Selection Rules - Orbital Transitions

Electric Dipole Approximation ONLY:  $\lambda_\gamma \gg$  atom length  $\rightarrow E, B$  feels homogenously oscillating to the atom

$$\psi_{nlm} \rightarrow \psi_{n'l'm'}:$$

- $\Delta m \in \{-1, 0, 1\}$   
 $s(\gamma) = 1 \rightarrow m_s(\gamma) \in \{-\hbar, 0, \hbar\}$   
 $E = E_z \rightarrow \Delta m = 0$
- $\Delta l = \pm 1$   
 $1s \leftrightarrow 2p$   
 Exception: ( $2s \rightarrow 1s$ ) through two-photon emission
- $\Delta j \in \{-1, 0, 1\}$   
 Exception: ( $j = 0 \rightarrow j = 0$ ) not allowed

## 6 Blackbody Radiation

- Power Spectrum :  $I'(\omega) = \frac{\hbar^3 \omega^3}{h^2 c^2} \frac{1}{e^{\hbar \omega / k_b T} - 1} \left[ \frac{I}{\Omega \cdot f} \right]$  ( $\mu = 0$  for photons since photon number isnt conserved)
- Stefan-Boltzmann Law :  $I = \frac{dP}{dA} \propto T^4$  !! important !!
- Wien's Displacement Law :  $\lambda_{\max} = \frac{2.9 \times 10^{-3}}{T} [\text{m}]$  (mode of spectrum)

## 7 Klein-Gordon Equation (Free Particle)

$$\begin{aligned}
 (p^2 c^2 + m^2 c^4) \psi &= E^2 \psi \\
 (-E^2 + p^2 c^2 + m^2 c^4) \psi &= 0 \\
 [-(E/c)^2 + p^2 + (mc)^2] \psi &= 0 \\
 \frac{[-(E/c)^2 + p^2 + (mc)^2]}{\hbar^2} \psi &= 0 \\
 \left[ \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 + \left( \frac{mc}{\hbar} \right)^2 \right] \psi &= 0 \\
 \boxed{(\square^2 + \mu^2) \psi = 0}
 \end{aligned}$$

## 8 Dirac Equation

$$\begin{aligned}
 \mu^2 &= -\square^2 \\
 \mu &= \sqrt{\nabla^2 - \frac{1}{c^2} \partial_t^2} = A \partial_x + B \partial_y + C \partial_z + \frac{i}{c} D \partial_t \\
 \partial_x^2 + \partial_y^2 + \partial_z^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} &= (A \partial_x + B \partial_y + C \partial_z + \frac{i}{c} D \partial_t)^2 \\
 &= A^2 \partial_x^2 + B^2 \partial_y^2 + C^2 \partial_z^2 - D^2 \frac{1}{c^2} \partial_t^2 \\
 &\quad + [AB + BA] \partial_x \partial_y + [AC + CA] \partial_x \partial_z + [AD + DA] \frac{i}{c} \partial_x \partial_t \\
 &\quad + [BC + CB] \partial_y \partial_z + [BD + DB] \frac{i}{c} \partial_y \partial_t \\
 &\quad + [CD + DC] \frac{i}{c} \partial_z \partial_t
 \end{aligned}$$

$$D = \gamma^0, \quad A = i\gamma^1, \quad B = i\gamma^2, \quad C = i\gamma^3$$

$$\gamma^\mu = \left[ \begin{pmatrix} I_2 & 0 \\ 0 & I_2 \end{pmatrix}, \begin{pmatrix} 0 & \sigma_x \\ -\sigma_x & 0 \end{pmatrix}, \begin{pmatrix} 0 & \sigma_y \\ -\sigma_y & 0 \end{pmatrix}, \begin{pmatrix} 0 & \sigma_z \\ -\sigma_z & 0 \end{pmatrix} \right]$$

$$\boxed{
 \begin{aligned}
 (i\hbar \gamma^\mu \partial_\mu - mc) \psi &= 0 \\
 (i\not{\partial} - m) \psi &= 0 \quad (\text{natural units})
 \end{aligned}
 }$$

## 9 Integral Form

$$\begin{aligned}\psi(r) &= \psi_0(r) + \int g(r-r_0)V(r_0)\psi(r_0) \, d^3r & g(r) &= -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \\ &= \psi_0 + \int gV\psi(r_0) \\ &= \psi_0 + \int gV\psi_0 + \int \int gVgV\psi(r_0) \\ &= \psi_0 + \int gV\psi_0 + \int \int gVgV\psi_0 + \int \int gVgVgV\psi_0 + \dots\end{aligned}$$