Derivations II.C

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II.C.2

Show that $c_n = \langle n|\psi\rangle$ if $|\psi\rangle = \sum_n c_n|n\rangle$
OR
Show that $c_n = \int d\vec{r}\,\phi_n^*(\vec{r})\psi(\vec{r})$ if $\psi(\vec{r}) = \sum_n c_n\phi_n(\vec{r})$

Just substitute

$$\int d\vec{r}\,\phi^*(\vec{r})\psi(\vec{r}) = \int d\vec{r}\,\phi_n^*(\vec{r})\left[\sum_m c_m\phi_m(\vec{r})\right] = \sum_m c_m \int d\vec{r}\phi_n^*(\vec{r})\phi_m(\vec{r}) = \sum_m c_m\delta_{m,n} = c_n$$

$$\therefore c_n = \int d\vec{r}\phi^*(\vec{r})\psi(\vec{r}) = \langle n|\psi\rangle$$

Alternate proof

$$\langle n|\psi\rangle = \sum_m \langle n|c_m|m\rangle = \sum_m c_m\langle n|m\rangle = c_n$$

II.C.3.a: The Dirac Delta Function

$\delta(x-x')$ is defined such that

$$\int_{-\infty}^{\infty} dx\, f(x)\delta(x-x') = f(x')$$

II.C.3.b Proof of Closure Relation

Claim

For $\{\phi_n(\vec{r})\}$ to be a basis set spanning the Hilbert space, then

$$\sum_n \phi_n^*(\vec{r}')\phi_n(\vec{r}) = \delta(\vec{r}-\vec{r}')$$

Proof

$$c_n = \langle n|\psi\rangle = \int d\mathbf{r}\phi_n^*(\mathbf{r})\psi(\mathbf{r})$$

$$\psi(\mathbf{r}) = \sum_n \left[\int d\mathbf{r}'\phi_n^*(\mathbf{r}')\psi(\mathbf{r}')\right]\phi_n(\mathbf{r})$$

$$\psi(\mathbf{r}) = \int d\mathbf{r}'\psi(\mathbf{r}')\left[\sum_{\boldsymbol{n}} \phi_n^*(\mathbf{r}')\phi_n(\mathbf{r})\right]$$

$$\psi(\mathbf{r}) = \int d\mathbf{r}'\psi(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \text{ (By definition of delta function)}$$

$$\therefore \sum_n \phi_n^*(\mathbf{r}')\phi_n(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}')$$

Alternate Proof

$$|\psi\rangle = \sum_n c_n|n\rangle \text{ where } c_n = \langle n|\psi\rangle$$

$$|\psi\rangle = \sum_n \langle n|\psi\rangle|n\rangle = \sum_n |n\rangle\langle n|\psi\rangle$$

$\therefore$ This holds iff

$$\sum_n |n\rangle\langle n| = I$$

II.C.4 Matrix Representation of Vectors

$$v(\vec{r}) = \sum_n v_n\phi_n(\vec{r})$$

$$u(\vec{r}) = \sum_n u_n\phi_n(\vec{r})$$

$$\langle v|u\rangle = \int d\vec{r}v^*(\vec{r})u(\vec{r}) = \int d\vec{r}\left(\sum_n v_n^*\phi_n^*(\vec{r})\right)\left(\sum_m u_m\phi_m(\vec{r})\right) = \sum_{n,m} v_n^*u_m\int d\vec{r}\phi_n^*(\vec{r})\phi_m(\vec{r})$$

$$= \sum_{n,m} v_n^*u_m\delta_{n,m} = \sum_n v_n^*u_n$$

Alternate:

$$|v\rangle = \sum_n v_n|n\rangle, \qquad |u\rangle = \sum_n u_n|n\rangle$$

$$\Rightarrow \langle v| = \sum_n \langle n|v_n^*$$

$$\langle v|u\rangle = \left(\sum_n \langle n|v_n^*\right)\left(\sum_m u_n|m\rangle\right) = \sum_{n,m} v_n^*u_m\langle n|m\rangle = \sum_{n,m} v_n^*u_m\delta_{n,m} = \sum_n v_n^*u_n$$

II.C.5.a Matrix Representation of Linear Operators

$\Omega|v\rangle = |v'\rangle$ w.r.t. basis $\{|v\rangle\}$ is $\sum_m \Omega_{nm} v_m = v'_n$

$|v\rangle = \sum_m v_m |m\rangle, \qquad |v'\rangle = \sum_m v'_m |m\rangle$

$\Omega \sum_m v_m |m\rangle = \sum_m v'_m |m\rangle$

$\sum_m v_m \Omega |m\rangle = \sum_m v'_m |m\rangle$

Operate on both sides by $\langle n|$ (In other words, multiply both sides by $\phi_n^*(\boldsymbol{r})$ and then integrate both sides over $\int d\boldsymbol{r}$)

$\langle n| \sum_m v_m \Omega |m\rangle = \langle n| \sum_m v'_m |m\rangle$

$\sum_m v_m \langle n|\Omega|m\rangle = \sum_m v'_m \langle n|m\rangle$

$\sum_m v_m \Omega_{nm} = v'_n$

Example: Identity Operator

$I|v\rangle = v$

$I_{nm} = \langle n|I|m\rangle = \langle n|m\rangle = \delta_{nm}$

II.C.5.b Adjoint of an Operator

Show that $\langle n|\Omega^\dagger|m\rangle = \langle \Omega n|m\rangle$

$\Omega_{nm} = \langle n|\Omega|m\rangle$

$\Omega^\dagger_{nm} = \Omega^*_{mn} = \langle m|\Omega|n\rangle^*$

$\langle m|\Omega|n\rangle^* = \left[\int d\vec{r}\ \phi_m^*(\vec{r})\Omega\phi_n(\vec{r})\right]^* = \int d\vec{r}\ \phi_m(\vec{r})[\Omega\phi_n(\vec{r})]^* = \int d\vec{r}\ [\Omega\phi_n(\vec{r})]^*\phi_m(\vec{r})$

$\langle n|\Omega^\dagger|m\rangle = \langle n|\Omega|m\rangle^\dagger = \langle \Omega n|m\rangle$

Note to self: don't believe that $\langle n|\Omega^\dagger|m\rangle = \langle n|\Omega|m\rangle^\dagger$

In think it should be $\langle n|\Omega^\dagger|m\rangle = \langle m|\Omega|n\rangle^\dagger$

$(1 \quad 0)\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1$

$\left[(1 \quad 0)\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix}\right]^\dagger = 0^\dagger = 0$

Derivations II.D && II.E

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II.D.1 The Eigenvalues of a Hermitian Operator are Real

$\Omega|\omega\rangle = \omega|\omega\rangle$
$\langle\omega|\Omega|\omega\rangle = \langle\omega|\omega|\omega\rangle = \omega\langle\omega|\omega\rangle$
Take the adjoint of both sizes
$\langle\omega|\Omega^\dagger|\omega\rangle = \omega^*\langle\omega|\omega\rangle^* = \omega^*\langle\omega|\omega\rangle$
If Ω is Hermitian then $\Omega = \Omega^\dagger$ so
$\omega\langle\omega|\omega\rangle = \langle\omega|\Omega|\omega\rangle = \langle\omega|\Omega^\dagger|\omega\rangle = \omega^*\langle\omega|\omega\rangle$
$\Rightarrow \omega = \omega^* \Rightarrow \omega \in \mathbb{R}$

II.D.2 The Eigenfunctions of a Hermitian Operator are Orthogonal

Let $|\alpha\rangle$ be one eigenfunction of Ω (Hermitian) and $|\beta\rangle$ be another.
$\Omega|\alpha\rangle = \alpha|\alpha\rangle, \qquad \Omega|\beta\rangle = \beta|\beta\rangle$
$\langle\beta|\Omega|\alpha\rangle = \alpha\langle\beta|\alpha\rangle,\ \langle\alpha|\Omega|\beta\rangle = \beta\langle\alpha|\beta\rangle$
(1) (2)
Take the complex conjugate of (2) and subtract it from (1)
$\langle\beta|\Omega|\alpha\rangle - \langle\alpha|\Omega|\beta\rangle^* = \alpha\langle\beta|\alpha\rangle - \beta^*\langle\alpha|\beta\rangle^*$
$\langle\beta|\Omega|\alpha\rangle - \langle\beta|\Omega|\alpha\rangle = \alpha\langle\beta|\alpha\rangle - \beta^*\langle\beta|\alpha\rangle$
$0 = (\alpha - \beta^*)\langle\beta|\alpha\rangle$

Mine:
So either $\alpha = \beta^*$ or $\langle\beta|\alpha\rangle = 0$
If $\alpha = \beta$ then we have a subspace of eigenfunctions with eigenvalues $= \alpha = \beta$. So we can take a basis for that and get orthonormal vectors. In general, two eigenfunctions within that subspace to not have to be orthogonal so the statement is not strictly correct.

More accurately: The eigenspaces of a Hermitian operator are orthogonal.

Note:
Board says: $(\alpha - \beta^*)\langle\alpha|\beta\rangle = 0 \Rightarrow \langle\alpha|\beta\rangle = 0$ but that is wrong.

II.E.1 Continuous Components of a Wavefunction

$$\psi(\vec r) = \int d\vec r'\psi(\vec r')\delta(\vec r - r) = \int d\vec r'\psi(\vec r')\int dx\, w_\alpha(\vec r)w_\alpha^*(\vec r') = \int d\alpha\left[\int dr' w_\alpha^*(\vec r')\psi(\vec r')\right]w_\alpha(\vec r)$$

$$\boxed{\psi(\vec r) = \int d_\alpha\, c(\alpha)w_\alpha(\vec r))}$$

where

$$\boxed{c(\alpha) \equiv \int d\vec r w_\alpha^*(\vec r)\psi(\vec r)}$$

In bra-ket notation:

$$|\psi\rangle = I|\psi\rangle = \int d_\alpha\, |\alpha\rangle\langle\alpha|\psi\rangle = \int d\alpha\, c(\alpha)|\alpha\rangle$$

II.E.2 Scalar Product and Norm in Continuous Components

$$\psi_1(\vec r) = \int d\alpha\, b(\alpha)w_\alpha(\vec r)$$

$$\psi_2(\vec r) = \int d\alpha\, c(\alpha)w_\alpha(\vec r)$$

$$\langle\psi_1|\psi_2\rangle = \int dr\, \psi_1^*(\vec r)\psi_2(\vec r) = \int d\vec r\int d\alpha\, b^*(\alpha)w_\alpha^*(\vec r)\int d\beta\, c(\beta)w_\beta(\vec r)$$

$$= \int d\alpha\int d\beta\, b^*(\alpha)c(\beta)\int d\vec r\, w_\alpha^*(\vec r)w_\beta(\vec r) = \int d\alpha\int d\beta b^*(\alpha)c(\beta)\delta(\alpha-\beta) = \int d\alpha\, b^*(\alpha)c(\alpha)$$

$$\langle\psi|\psi\rangle = \int d\alpha\, c^*(\alpha)c(\alpha) = \int d\alpha\, |c(\alpha)|^2$$

II.E.3.a

1) $\xi_{\vec r'}(\vec r) = \delta(\vec r - \vec r')$ is orthonormal
$$\int d\vec r\, w_\alpha^*(\vec r)w_\beta(\vec r) = \delta(\alpha-\beta) = \int d\vec r\delta(\vec r - \vec r')\delta(\vec r - \vec r'') = \delta(\vec r' - \vec r'') = \langle\vec r'|\vec r''\rangle$$
2) $\xi_{\vec r_0}(\vec r) = \delta(\vec r - \vec r_0)$ spans the space
$$\int d\alpha\, w_\alpha^*(\vec r')w_\alpha(\vec r) = \delta(\vec r - \vec r') = \int d\vec r_0\delta(\vec r' - \vec r_0)\delta(\vec r - \vec r_0) = \delta(\vec r - \vec r')$$

$$\int d\alpha\, w_\alpha^*(\vec r')w_\alpha(\vec r) = \delta(\vec r - \vec r')$$

$$\int d\alpha\, \langle \alpha|\vec{r}'\rangle\langle \vec{r}|\alpha\rangle = \langle \vec{r}|\vec{r}'\rangle$$

$$\int d\alpha\, \langle \vec{r}|a\rangle\langle a|\vec{r}'\rangle = \langle \vec{r}|\vec{r}'\rangle$$

$$I = \int d\alpha\, |\alpha\rangle\langle\alpha|$$

II.E.3.b

$$\langle \boldsymbol{r}|\psi\rangle = \int d\boldsymbol{r}'\xi_{\boldsymbol{r}}^*(\boldsymbol{r}')\psi(\boldsymbol{r}) = \int d\boldsymbol{r}'\delta(\boldsymbol{r}'-\boldsymbol{r})\psi(\boldsymbol{r}') = \psi(\boldsymbol{r})$$

II.E.3.c

$$\langle\psi_1|\psi_2\rangle = \int d\vec{r}\psi_1^*(\vec{r})\psi_2(\vec{r})$$

$$\langle\psi_1|\psi_2\rangle = \langle\psi_1|I|\psi_2\rangle = \int d\vec{r}\langle\psi_1|\vec{r}\rangle\langle\vec{r}|\psi_2\rangle = \int d\vec{r}\ \psi_1^*(\vec{r})\psi_2(\vec{r})$$

II.E.4

$$\langle\psi_1|\psi_2\rangle = \int d\vec{p}\ \bar{\psi}_1^*(\vec{p})\,\bar{\psi}_2(\vec{p})$$

$$\langle\vec{p}|\psi\rangle = \int d\vec{r}\ v_{\vec{p}}^*(\vec{r})\psi(\vec{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{r}\ e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\psi(\vec{r}) = \bar{\psi}(\vec{p})$$

$$\langle\psi_1|\psi_2\rangle = \langle\psi_1|I|\psi_2\rangle = \int d\vec{p}\ \langle\psi_1|\vec{p}\rangle\langle\vec{p}|\psi_2\rangle = \int d\vec{p}\ \bar{\psi}_1^*(\vec{p})\bar{\psi}_2(\vec{p})$$

Derivations II.F

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II.F.1

$$\langle x\rangle = \int d\vec{r}\ \psi^*(\vec{r})x\psi(\vec{r})$$

$$\langle\psi_1|X|\psi_2\rangle = \langle\psi_1|IX|\psi_2\rangle = \int d\vec{r}\ \langle\psi_1|\vec{r}\rangle\langle\vec{r}|X|\psi_2\rangle = \int d\vec{r}\ \ \langle\psi_1|\vec{r}\rangle x\langle\vec{r}|\psi_2\rangle = \int d\vec{r}\psi_1^*(\vec{r})x\psi_2(\vec{r})$$

$$\boxed{\langle X\rangle = \langle\psi|X|\psi\rangle = \int d\vec{r}\ \psi^*(\vec{r})x\psi(\vec{r})}$$

II.F.2 The Momentum Operator

i) Show that $P_x\psi(\vec{r}) = \frac{\hbar}{i}\frac{\partial}{\partial x}\psi(\vec{r})$

$$|\vec{p}\rangle \to v_{\vec{p}}(\vec{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \to \langle\vec{r}|\vec{p}\rangle$$

$$\psi(\vec{r}) = \langle\vec{r}|\psi\rangle = \langle\vec{r}|I|\psi\rangle = \int d\vec{p}\ \langle\vec{r}|\vec{p}\rangle\langle\vec{p}|\psi\rangle$$

$$\psi(\vec{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ \bar{\psi}(\vec{p})e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\ \text{ Inverse Fourier Transform}$$

$$\frac{\partial}{\partial x}\psi(\vec{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ \ \bar{\psi}(\vec{p})\left(\frac{ip_x}{\hbar}\right)e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(\vec{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ p_x\bar{\psi}(\vec{p})e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}, \qquad (1)$$

Compare with

$$P_x\psi(\vec{r}) = \langle\vec{r}|P_x|\psi\rangle = \langle\vec{r}|IP_x|\psi\rangle = \int d\vec{p}\ \langle\vec{r}|\vec{p}\rangle\langle\vec{p}|P_x|\psi\rangle$$

$$\langle\vec{r}|P_x|\psi\rangle = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ p_x\langle\vec{p}|\psi\rangle e^{i\vec{p}\cdot\frac{\vec{r}}{\hbar}} = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ \ p_x\bar{\psi}(\vec{p})e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}, \qquad (2)$$

$(1) = (2)$

$$P_x\psi(\vec{r}) = \frac{\hbar}{i}\frac{\partial\psi(\vec{r})}{\partial x}$$

or

$$\langle\vec{r}|P_x|\psi\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\ \langle\vec{r}|\psi\rangle$$

ii) The expectation value

$$\langle\psi_1|P_x|\psi_2\rangle = \langle\psi_1|IP_x|\psi_2\rangle = \int d\vec{r}\ \langle\psi_1|r\rangle\langle\vec{r}|P_x|\psi_2\rangle = \int\ d\vec{r}\psi_1^*(\vec{r})\ \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_2(\vec{r})$$

$$\boxed{\langle P_x\rangle = \langle\psi|P_x|\psi\rangle = \int\ d\vec{r}\ \psi^*(\vec{r})\ \frac{\hbar}{i}\ \frac{\partial\psi(\vec{r})}{\partial x}}$$

$$\langle\vec{r}|P_x|\psi\rangle = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}\ p_r\langle\vec{p}|\psi\rangle e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}} = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int d\vec{p}p_x\bar{\psi}(\vec{p})\ e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

II.F.3.a $[R_i, P_j] = i\hbar\delta_{ij}$

$$\langle\vec{r}|[X,P_x]|\psi\rangle = \langle\vec{r}|XP_x - P_xX|\psi\rangle = \langle\vec{r}|XP_x|\psi\rangle - \langle\vec{r}|P_xX|\psi\rangle$$

Define $|\psi'\rangle = P_x|\psi\rangle,\ |\psi''\rangle = X|\psi\rangle$

$$\langle\vec{r}|[X,P_x]|\psi\rangle = \langle\vec{r}|X|\psi'\rangle - \langle\vec{r}|P_x|\psi''\rangle = x\langle\vec{r}|\psi'\rangle - \frac{\hbar}{i}\frac{\partial}{\partial x}\langle\vec{r}|\psi''\rangle = x\langle\vec{r}|P_x|\psi\rangle - \frac{\hbar}{i}\frac{\partial}{\partial x}\langle\vec{r}|X|\psi\rangle$$

$$= x\frac{\hbar}{i}\frac{\partial}{\partial x}\langle\vec{r}|\psi\rangle - \frac{\hbar}{i}\frac{\partial}{\partial x}[x\langle\vec{r}|\psi\rangle] = \frac{\hbar}{i}\left(x\frac{\partial}{\partial x}\langle\vec{r}|\psi\rangle - x\frac{\partial}{\partial x}\langle\vec{r}|\psi\rangle - \langle\vec{r}|\psi\rangle\right) = -\frac{\hbar}{i}\langle\vec{r}|\psi\rangle = i\hbar\langle\vec{r}|\psi\rangle$$

$$[X,P_x] = i\hbar I$$

Overall,

$$[R_i,R_j] = 0, \qquad [P_i,P_j] = 0, \qquad [R_i,P_j] = i\hbar\delta_{ij}, \qquad i,j = x,y,z$$

II.F.3.b $\Delta p_x\Delta x \geq \frac{\hbar}{2}$

$$\Delta x = \sqrt{\langle X'^2\rangle}, \qquad \text{where } X' = X - \langle X\rangle$$

$$\Delta p = \sqrt{\langle P_x'^2\rangle}, \qquad \text{where } P_x' = P_x - \langle P_x\rangle$$

$$|\psi'\rangle = (X + i\lambda P_x)|\psi\rangle$$

λ is a real parameter

$\langle\psi'|\psi'\rangle = \langle\psi|(X - i\lambda P_x)(X + i\lambda P_x)|\psi\rangle = \langle\psi|X^2|\psi\rangle + \langle\psi|i\lambda X P_x - i\lambda P_x X|\psi\rangle + \lambda^2\langle\psi|P_x^2|\psi\rangle$
$= \langle X^2\rangle + i\lambda\langle[X, P_x]\rangle + \lambda^2\langle P_x^2\rangle = \langle X^2\rangle - \lambda\hbar + \lambda^2\langle P_x^2\rangle$
$\langle\psi'|\psi'\rangle \geq 0$ so $\langle X^2\rangle + i\lambda\langle[X, P_x]\rangle + \lambda^2\langle P_x^2\rangle \geq 0$
$\Rightarrow \hbar^2 - 4\langle P_x^2\rangle\langle X^2\rangle \leq 0$ (discriminant)
$\Rightarrow \langle P_x^2\rangle\langle X^2\rangle \geq \frac{\hbar^2}{4}$

$[X', P_x'] = [X, P_x] = i\hbar$
since
$X'P_x' - P_x'X' = (X - \langle X\rangle)(P_x - \langle P_x\rangle) - (P_x - \langle P_x\rangle)(X - \langle X\rangle) = \cdots = [X, P_x]$
$\langle P_x'^2\rangle\langle X'^2\rangle \leq \frac{\hbar^2}{4}$
$\sqrt{\langle P_x'^2\rangle}\sqrt{\langle X'^2\rangle} \geq \frac{\hbar}{2}$
$\Delta P_x \Delta X \geq \frac{\hbar}{2}$

Derivations III.A & III.B

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III.A.2 The Superposition Principle

$\psi_1 = |\psi_1|e^{i\alpha_1}, \qquad \psi_2 = |\psi_2|e^{i\alpha_2}, \qquad \psi = c_1\psi_1 + c_2\psi_2$

$P = |\psi|^2 = |c_1\psi_1 + c_2\psi_2|^2 = \left|c_1|\psi_1|e^{i\alpha_1} + c_2|\psi_2|e^{i\alpha_2}\right|^2$

$= |c_1\psi_1|^2 + |c_2\psi_2|^2 + c_1c_2^*|\psi_1||\psi_2|e^{i(\alpha_1-\alpha_2)} + \left(c_1c_2^*|\psi_1||\psi_2|e^{i(\alpha_1-\alpha_2)}\right)^*$

$P = |c_1\psi_1|^2 + |c_2\psi_2|^2 + 2\mathrm{Re}\left(c_1c_2^*|\psi_1||\psi_2|e^{i(\alpha_1-\alpha_2)}\right)$

III.B Measurement and Expectation Values

$$\langle c\rangle = \frac{1}{N}\sum_{n=1}^{N} c_n$$

$$\langle c\rangle = \sum_{n=1}^{N} c_n P_n, \qquad \sum_{n=1}^{N} P_n = 1$$

$$\langle c\rangle = \int c(\alpha)P(\alpha)\,d\alpha, \qquad \int P(\alpha)d\alpha = 1$$

$$\langle A\rangle = \langle\psi|A|\psi\rangle, \qquad \langle\psi|\psi\rangle = 1$$

Example: Position operator X

$$\langle X\rangle = \langle\psi|X|\psi\rangle = \langle\psi|IX|\psi\rangle, \qquad I = \int dx\ |x\rangle\langle x|$$

$$\langle X\rangle = \int dx\ \ \langle\psi|x\rangle\langle x|X|\psi\rangle = \int dx\ \langle\psi|x\rangle x\langle x|\psi\rangle = \int dx\ \psi^*(x)x\psi(x)$$

$$\boxed{\langle X\rangle = \int x|\psi(x)|^2 dx}$$

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \langle\psi|IA|\psi\rangle, \qquad I = \int d\alpha\ |\alpha\rangle\langle\alpha|$$

$$\langle A\rangle = \int d\alpha\ \langle\psi|\alpha\rangle\langle\alpha|A|\psi\rangle$$

Need $\langle\alpha|A|\psi\rangle = a(\alpha)\langle\alpha|\psi\rangle \Rightarrow \langle\alpha|A = a(\alpha)\langle\alpha|,\ A^\dagger|\alpha\rangle = a^*(\alpha)|\alpha\rangle$

$$\langle A\rangle = \int d\alpha\ \langle\psi|\alpha\rangle a(\alpha)\langle\alpha|\psi\rangle = \int a(\alpha)|\psi(\alpha)|^2\, d\alpha$$

III.C.1 The Schrodinger Equation

$$i\hbar\frac{\partial\psi(\vec r,t)}{\partial t} = H\psi(\vec r,t)$$

$$H = \frac{p^2}{2m} + V(\vec r,t)$$

$$p = \frac{\hbar}{i}\vec\nabla = -i\hbar\vec\nabla$$

Not right:

(1) $\quad c\dfrac{d^2}{dt^2}\psi(\vec r,t) = -\dfrac{\hbar^2}{2m}\nabla^2\,\psi(\vec r,t) + V(\vec r,t)\psi(\vec r,t)$

This is the wave equation. But does not describe particles

Need $\int d\vec r\ |\psi(\vec r,t)|^2 = 1$ (2)

(1) does not guarantee this

Diffusion equation:

$$\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t) \quad (3)$$

(3) guarantees (2) but it is not a wave equation. So (3) is no good.

$$\psi(x,t) = Ae^{-i(ux-\omega t)} \quad (4), \qquad c = \frac{\hbar^2 k^2}{2m\omega^2}$$

$$\hbar\omega = \frac{i\hbar^2 k^2}{2m} \quad (5)$$

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t)$$

Combines (1) and (2)

III.C.2 The Time Independent Schrodinger Equation

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = H\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t)$$

Assume $V(\vec{r},t) = V(\vec{r})$

$\psi(\vec{r},t) = \phi(\vec{r})f(t)$

$$i\hbar\,\phi(\vec{r})\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}f(t)\nabla^2\phi(\vec{r}) + V(\vec{r})\phi(\vec{r})f(t)$$

Divide by $\phi(\vec{r})f(t)$

$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\phi(t)}\nabla^2\phi(\vec{r}) + V(\vec{r})$$

Each side is equal to the same constant. Call it E.

L.H.S $i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E, \frac{df(t)}{df} = -\frac{iE}{\hbar}f(t) \Rightarrow \boxed{f(t) = e^{-\frac{iEt}{\hbar}}}$

R.H.S.

$$-\frac{\hbar^2}{2m}\frac{1}{\phi(\vec{r})}\nabla^2\phi(\vec{r}) + V(\vec{r}) = E$$

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})(+V(\vec{r})\phi(\vec{r}) = E\phi(\vec{r})$$

$$\boxed{H\phi(\vec{r}) = E\phi(\vec{r})}$$

Eigenvalue equation (H is operator)

$$\psi(\vec{r},t) = \phi(\vec{r})f(t) = \phi(\vec{r})e^{-\frac{iEt}{\hbar}}$$

$$|\psi(\vec{r},t)|^2 = \psi^*(\vec{r},t)\psi(\vec{r},t) = \phi^*(\vec{r})e^{\frac{iEt}{\hbar}}\phi(\vec{r})e^{-\frac{iEt}{\hbar}} = |\phi(\vec{r})|^2$$

$$\langle X\rangle = \langle\psi|X|\psi\rangle = \int d\vec{r}\,\phi^*(\vec{r})e^{\frac{iEt}{\hbar}}Xe^{-\frac{iEt}{\hbar}}\phi(\vec{r}) = \int d\vec{r}\,\phi^*(\vec{r})X\phi(\vec{r}) = \langle\phi|X|\phi\rangle$$

$$H\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$$

$$\psi_n(\vec{r},t) = \phi_n(\vec{r})e^{-\frac{iE_n t}{\hbar}}$$

$$\boxed{\phi(\vec{r},t) = \sum_{n=1}^{\infty} c_n\phi_n(\vec{r})e^{-\frac{iE_n t}{\hbar}}}$$

Derivations IV.A

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IV.A.1 The Harmonic Oscillator

$H\psi(x) = E\psi(x)$

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

$-\frac{\hbar^2}{2m}\cdot\frac{d^2}{dx^2}\phi\psi(x) + \frac{1}{2}mw^2X^2\psi(x) = E\psi(x)$

$\frac{1}{2m}\left(P^2 + (mwX)^2\right)\psi(x) = E\psi(x)$

$P^2 + (mwx)^2 = (ip + mwx)(-ip + mwx)$

$a_{\mp} \equiv \frac{1}{\sqrt{2\hbar mw}}(\pm iP + mwX)$

$a_+a_- = \frac{1}{2\hbar mw}(-iP + mwX)(+iP + mwX) = \frac{1}{2\hbar mw}[P^2 + (mwX)^2 + imw(XP - PX)]$

$= \frac{1}{2\hbar mw}[P^2 + (xwX)^2] + \frac{i}{2\hbar}[X, P] = \frac{1}{\hbar w}H - \frac{1}{2} \Rightarrow \boxed{H = \hbar w\left(a_+a_- + \frac{1}{2}\right)}$

$a_-a_+ = \frac{1}{\hbar w}H + \frac{1}{2}$

$[a_-, a_+] = a_-a_+ - a_+a_- = \frac{1}{\hbar w}H + \frac{1}{2} - \frac{1}{\hbar w}H + \frac{1}{2} = 1$

Therefore, if $\psi(x)$ satisfies $H\psi(x) = E\psi(x)$, then $a_+\psi(x)$ will satisfy $Ha_+\psi(x) = (E + \hbar w)a_+\psi(x)$ and $Ha_-\psi(x) = (E - \hbar w)a_-\psi(x)$

Proof

$Ha_+\psi(x) = \hbar w\left(a_+a_- + \frac{1}{2}\right)a_+\psi(x) = \hbar w\left(a_+a_-a_+ + \frac{1}{2}a_+\right)\psi(x) = \hbar w a_+\left(a_-a_+ + \frac{1}{2}\right)\psi(x)$

$= a_+\left[\hbar w\left(a_+a_- + 1 + \frac{1}{2}\right)\psi(x)\right] = a_+\left[\hbar w\left(a_+a_- + \frac{1}{2}\right) + \hbar w\right]\psi(x) = a_+(H + \hbar w)\psi(x)$

$= a_+(E + \hbar w)\psi(x)$

$Ha_+\psi(x) = (E + \hbar w)\left(a_+\psi(x)\right)$

IV.A.3 Normalization with Operators

$\int |\psi_n(x)|^2 dx = 1$

$\langle\psi_n|\psi_n\rangle = 1, \qquad \langle n|n\rangle = 1$

Assume $\psi_0(x)$ is normalized.

$\psi_1(x) = A_1 a_+ \psi_0(x)$

$|1\rangle = A_1 a_+|0\rangle, \qquad \langle 1|1\rangle = 1$

$\langle 1|1\rangle = |A_1|^2\langle 0|a_-a_+|0\rangle$

Note: $a_-^\dagger = a_+$

Proof: observe

$a_{\mp} = \frac{1}{\sqrt{2\hbar mw}}(\pm iP + mwX)$

$[a_-, a_+] = 1, \qquad a_-a_+ - a_+a_- = 1, \qquad a_-a_+ = 1 + a_+a_-$

$\langle 1|1\rangle = |A_1|^2\langle 0|a_+a_- + 1|0\rangle = |A_1|^2(\langle 0|a_+a_-|0\rangle + \langle 0|0\rangle)$

$a_-|0\rangle = 0$ since $|0\rangle$ is already the lowest level

So $\langle 1|1\rangle = |A_1|^2 = 1 \Rightarrow \boxed{A_1 = 1}$

Next, $|2\rangle = A_2 a_+|1\rangle$

$\langle 2|2\rangle = |A_2|^2\langle 1|a_- a_+|1\rangle = |A_2|^2\langle 1|a_+ a_- + 1|1\rangle = |A_2|^2(\langle 1|a_+ a_-|1\rangle + \langle 1|1\rangle),$
$a_+ a_- = N, N|1\rangle = 1|1\rangle$

$$= |A_2|^2(\langle 1|1\rangle + \langle 1|1\rangle) = 2|A_2|^2 = 1 \Rightarrow \boxed{A_2 = \frac{1}{\sqrt{2}}}$$

$\langle n-1|n-1\rangle = |A_n|^2 = \langle n-1|a_- a_+|n-1\rangle = |A_n|^2\langle n-1|a_+ a_- + 1|n-1\rangle$
$= |A_n|^2(\langle n-1|N|n-1\rangle + \langle n-1|n-1\rangle) = |A_n|^2\big((n-1)\langle n|n\rangle + \langle n|n\rangle\big) = n|A_n|^2 = 1$
$\Rightarrow \boxed{A_n = \frac{1}{\sqrt{n}}}$

$\boxed{a_+\psi_n(x) = \sqrt{n+1}\psi_{n+1}(x)}$
$\boxed{a_{\psi_n(x)} = \sqrt{n}\psi_{n-1}(x)}$

Derivations IV.B

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IV.B.1.a Angular and Radial Equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})+E\psi(\vec{r})$$

$$-\frac{\hbar}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right)+V(r)\psi+E\psi$$

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

$$-\frac{\hbar^2}{2m}\left(\frac{Y}{r^2}\frac{d}{dr}\left(r^3\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{dY}{d\theta}\right)+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)+VRY=ERY$$

Divide through by RY and multiply by $-\frac{2mr^2}{\hbar^2}$

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]\right\}+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0$$

depends only on r depends only on θ and ϕ

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar}(V(r)-E)=l(l+1)$$

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)=-l(l+1)$$

IV.B.1.b Angular Equations

Multiply by $Y\sin^2\theta$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)\sin^2\theta\, Y$$

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

$$\Phi\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\Theta\frac{d^2\Phi}{d\phi^2}=-l(l+1)\sin^2\theta\,\Theta\Phi$$

Divide by $\Theta\Phi$

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

$$\frac{1}{\Theta}\left(\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right)+l(l+1)\sin^2\theta=m^2$$

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

$\Phi(\phi)=e^{im\phi}$

$\Phi(\phi)=\Phi(\phi+2\pi)$

$e^{im\phi}=e^{im(\phi+2\pi)}=e^{im\phi}e^{im2\pi}$

$e^{im2\pi}=1$

$\cos m2\pi+i\sin m2\pi=1$

$\Rightarrow m=0,\pm1,\pm2,\pm3,\ldots$

Magnetic quantum number

$\Theta(\theta)=AP_l^m(\cos\theta)$

Only has solution for $l=0,1,2,3,\ldots$

$|m|\le l$

IV.B.1.c Radial Equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]R=l(l+1)R$$

Let $u(r) = rR(r), R = \frac{U(r)}{r}$

$$\frac{dR}{dr} = \left(r\frac{du}{dr} - u\right)\frac{1}{r^2}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{d}{dr}\left(r\frac{du}{dr} - u\right) = r\frac{d^2u}{dr^2} + \frac{du}{dr} - \frac{du}{dr}$$

$$r\frac{d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}[V(r) - E]\frac{u}{r} = l(l+1)\frac{u}{r}$$

Multiply by $-\frac{\hbar^2}{2mr}$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + [V(r) - E]u = -\frac{\hbar^2}{2m}l(l+1)\frac{u}{r^2}$$

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

For normalization, we should have $\int |\psi(\vec{r})|^2 d\vec{r} = 1$

$d\vec{r} = r^2 \sin\theta \, dr \, d\theta \, d\phi$

$$\int |\psi(r,\theta,\phi)|^2 r^3 \sin\theta \, dr \, d\theta \, d\phi = 1$$

$\psi(r,\theta,\psi) = R(r)Y(\theta,\phi)$

$$\int |R|^2 r^2 dr \int |Y|^2 \sin\theta \; d\theta d\phi = 1$$

Require $\int |Y|^2 \sin\theta \; d\theta d\phi = 1$ not justified in this class

$$\int |R|^2 r^2 = 1, \qquad u(r) = rR, \qquad |U|^2 = r^2|R|^2$$

$$\int |U|^2 dr = 1$$

IV.B.2.a The Radial Equation for Hydrogen

$$\frac{d^2u}{dr^2} + \left[\frac{me^2}{2\pi\epsilon_0\hbar^2}\frac{1}{r} - \frac{l(l+1)}{r^2}\right]u = -\frac{2mE}{\hbar^2 u}, \qquad \mathrm{K} = \sqrt{-\frac{2mE}{\hbar^2}}$$

$$\frac{1}{\mathrm{K}^2}\frac{d^2u}{dr^2} + \left[\frac{me^2}{2\pi\epsilon_0\hbar^2}\frac{1}{\mathrm{K}r} - \frac{l(l+1)}{(\mathrm{K}r)^2}\right]u = u$$

Let $\rho = \mathrm{K}r$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

IV.B.2.b The Radial Equation of Hydrogen some More

Define $v(\rho)$ such that

$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^3}\right]u$$

$$\frac{d^2u}{d\rho^2} = u \text{ for } \rho \to \infty, \qquad u(\rho) = Ae^{-\rho} + Be^{\rho}, \text{require } B = 0 \text{ since } e^{\rho} \to \infty \text{ as } \rho \to \infty$$

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{u^2}u \text{ for } \rho \to 0, \qquad u(\rho) = C\rho^{l+1} + D\rho^{-l}, \text{require } D = 0 \text{ since } \rho^{-1} \to \infty \text{ as } \rho \to 0$$

Finding the derivatives

$$\frac{du}{d\rho} = \rho^{l+1}e^{-\rho}\frac{dv}{d\rho} + v\left[-\rho^{l+1}e^{-\rho} + (l+1)e^{-\rho}\rho^l\right] = \rho^l e^{-\rho}\left[(l+1-\rho)v + \rho\frac{dv}{d\rho}\right]$$

$$\frac{d^2u}{d\rho^2} = \rho^l e^\wedge - \rho\left(\left(-2 - 2l + \rho + \frac{l(l+1)}{\rho}\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right)$$

Substituting

$$\rho^l e^{-\rho}\left(\left(-2-2l+\rho+\frac{l(l+1)}{\rho}\right)v+2(l+1-\rho)\frac{dv}{d\rho}+\rho\frac{d^2v}{d\rho^2}\right)=\left(1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right)\rho^{l+1}e^{-\rho}v$$

Simplifying,

$$\boxed{\rho\frac{d^2v(\rho)}{d\rho^2}+2(l+1-\rho)\frac{dv(\rho)}{d\rho}+\big(\rho_0-2(l+1)\big)v(\rho)=0}$$

IV.B.2.c Recursion Relation

$$v(\rho)=\sum_{j=0}^{\infty}c_j\rho^j, \qquad \text{power series}$$

$$\frac{dv}{d\rho}=\sum_{j=0}^{\infty}jc_j\rho^{j-1}=\sum_{j=-1}^{\infty}(j+1)c_{j+1}\rho^j=\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j, \qquad \text{since } (-1+1)=0$$

$$\frac{d^2v}{d\rho^2}=\sum_{j=0}^{\infty}j(j+1)c_{j+1}\rho^{j-1}$$

Substituting,

$$\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}+\big(\rho_0-2(l+1)\big)v=0$$

$$\sum_{j=0}^{\infty}j(j+1)c_{j+1}\rho^j+2(l+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j-2\sum_{j=0}^{\infty}jc_j\rho^j+\big(\rho_0-2(l+1)\big)\sum_{j=0}^{\infty}c_j\rho^j=0$$

Equate coefficients of like powers

$$j(j+1)c_{j+1}+2(l+1)(j+1)c_{j+1}-2jc_j+\big(\rho_0+2(l+1)\big)c_j=0$$

$$\big(j(j+1)+2(l+1)(j+1)\big)c_{j+1}=(2(l+1)-\rho_0+2j)c_j$$

$$c_{j+1}=\left(\frac{(2j+l+1)-\rho_0}{j^2+j+2lj+2l+2j+2}\right)c_j$$

$$\boxed{c_{j+1}=\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j}$$

Derivations V

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V.A.2 Angular Momentum Eigenvalues

$L^2 f = \lambda f, \qquad L_z f = \mu f$

Define $L_\pm = L_x + \pm i L_y$

$[L_z, L_\pm] = [L_z, L_x \pm i L_y] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm (-i\hbar L_x) = i\hbar L_y \pm \hbar L_x = \pm\hbar L_x + i\hbar L_y$
$= \pm\hbar(L_x \pm i L_y) = \pm\hbar L_\pm$

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

$[L^2, L_\pm] = [L^2, L_x \pm i L_y] = [L^2, L_x] \pm i[L^2, L_y] = 0$

Since f is an eigenfunction of L^2 and L_z, $(L_\pm f)$ is also an eigenfunction of L^2 and and L_z

$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f)$

$L_z(L_\pm f) = L_z L_\pm f - L_\pm L_z f + L_\pm L_z f = [L_z, L_\pm]f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm \mu f = \pm\hbar L_\pm f + \mu L_\pm f$
$= (\pm\hbar + \mu)(L_\pm f) = (\mu \pm h)(L_\pm f)$

Since L_z is just one of three components of $\vec{L}$, it can't have a magnitude than the total angular momentum of $\vec{L}$

So there is a "top" angular momentum component

$L_t f_t = 0$

Let the eigenvalue of f_t be $\hbar l$

$L_z f_t = \hbar l f_t, \qquad \mu = \hbar l, \qquad L^2 f f_t = \lambda f_t$

$L_\pm, L_\mp = (L_x \pm i L_y)(L_x \pm i L_y) = L_x^2 \mp i L_x L_y \pm i L_y L_x + L_y^2 = L_x^2 + L_y^2 + L_z^2 - L_z^2 \pm i[L_x, L_y]$
$= L^2 - L_z^2 \mp i(i\hbar L_z) = L^2 - L_z \pm \hbar L_z$

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

$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = L - (L_t f_t) + L_z(L_z f_t) + \hbar L_z f_t = \hbar l L_z f_t + \hbar^2 l f_t$

V.A.Extra Complete Set of Commuting Observables (CSCO)

a) Observables that share eigenfunctions commute

$A\phi_n = a_n \phi_n, \qquad \beta\phi_n = b_n \phi_n$

$AB\phi_n = Ab_n\phi_n = b_n a_n \phi_n$

Similarly, $BA\phi_n = Ba_n\phi_n = a_n b_n \phi_n = b_n a_n \phi_n$

$\therefore AB\phi_n = BA\phi_n \ \forall n$

$$\psi = \sum_n c_n \phi_n$$

$$(AB - BA)\psi = \sum_n c_n (AB - BA)\phi_n = 0$$

$\therefore AB - BA = [A, B] = 0$

b) If $[A, B] = 0$ (A and B are observabalse)

assume a_n are non-degenrate (ϕ_n are the eigenfunctions of A)

$[A, B]\phi_n = 0 \Rightarrow AB\phi_n - BA\phi_n = 0 \Rightarrow AB\phi_n = BA\phi_n = Ba_n\phi_n = a_n B\phi_n$

So $B\phi_n$ is an eigenfunction of A with eigenvalue a_n

$\therefore B\phi_n$ can differ from ϕ_n only by a multiplicative constant, call it b_n

$\therefore B\phi_n = b_n\phi_n$

VI Derivations

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VI.C.1 Symmetric and Antisymmetric States

Single state to observe $x_1 = a, x_2 = b$ and $x_1 = b, x_2 = a$
$|\psi\rangle \Leftrightarrow \alpha|\psi\rangle$
$|\psi(a,b)\rangle = \alpha|\psi(b,a)\rangle$ upon echange of particles.
$|\psi\rangle = \beta|ab\rangle + \gamma|ba\rangle = \alpha[\beta|ba\rangle + \gamma|ab\rangle] \Rightarrow \beta = \alpha\gamma$ and $\gamma = \alpha\beta$
$\beta = \alpha^2\beta \Rightarrow \alpha^2 = 1 \Rightarrow \alpha = \pm 1$
For $\alpha = 1, \beta = \gamma \Rightarrow |\psi\rangle = \beta|ab\rangle + \beta|ba\rangle$
$\boxed{|\psi\rangle = |ab\rangle + |ba\rangle}$

For $\alpha = -1 \Rightarrow \beta = -\gamma \Rightarrow |\psi\rangle = \beta|ab\rangle - \beta|ba\rangle$
$\boxed{|\psi\rangle = |ab\rangle - |ba\rangle}$

VI.C.2 Pauli Exclusion Principle

$|\psi\rangle = |\omega_1\omega_2\rangle - |\omega_2\omega_1\rangle$
If particles are in the same state: $\omega_1 = \omega_2 = \omega$
$|\psi\rangle = |\omega\omega\rangle - |\omega\omega\rangle = 0$

VII Derivations

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VII.A.3 First Order Perturbation Theory

a) Energy correction

$H|n\rangle = E_n|n\rangle$

$(H^0 + H^1)\,(|n^0\rangle + |n^1\rangle + \cdots) = (E_n^0 + E_n^1 + \cdots)(|n^0\rangle + |n^1\rangle + \cdots)$

$H^0|n^0\rangle + H^0|n^1\rangle + H^1|n^0\rangle + H^1|n^1\rangle + \cdots = E_n^0|n^0\rangle + E_n^0|n^1\rangle + E_n^1|n^0\rangle + E_n^1|n^1\rangle + \cdots$

Ignore anything 2nd order and above

$H^0|n^0\rangle = E_n^0|n^0\rangle$ so

$H^0|n^1\rangle + H^1|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$

Multiply on left by $\langle n^0|$

$\langle n^0|H^0|n^1\rangle + \langle n^0|H^1|n^0\rangle = E_n^0\langle n^0|n^1\rangle + E_n^1\langle n^0|n^0\rangle$

$\langle n^0|n^0\rangle = 1, \qquad \langle n^0|H^0|n^1\rangle = E_n^0\langle n^0|n^1\rangle$

$\boxed{E_n^1 = \langle n^0|H^1|n^0\rangle}$

b) Wave function correction

$H^0|n^1\rangle + H^1|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$

Multiply on left by $\langle m^0|$

$\langle m^0|H^0|n^1\rangle + \langle m^0|H^1|n^0\rangle = E_n^0\langle m^0|n^1\rangle + E_n^1\langle m^0|n^0\rangle$

$E_m^0\langle m^0|n^1\rangle + \langle m^0|H^1|n^0\rangle + E_n^0\langle m^0|n^1\rangle$

$$\langle m^0|n^1\rangle = \frac{\langle m^0|H^1|n^0\rangle}{E_n^0 - E_m^0}$$

$$|n^1\rangle = I|n^1\rangle = \sum_m |m^0\rangle\langle m^0|n^1\rangle = \sum_m \langle m^0|n^1\rangle|m^0\rangle$$

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

VII.A.4 Griffiths problem 6.1

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

Solution: (PHYS 234 - Griffiths 2.2)

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad \psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

Now with spike: $H^1 = \alpha\delta\left(x - \frac{a}{2}\right)I$

a) $E_n^1 = \langle n^0|H^1|n^0\rangle = \int dx\langle n^0|x\rangle\langle x|H^1|n^0\rangle = \int dx\,\psi_n^*(x)H^1\psi_n(x)$

$$= \frac{\alpha 2}{a}\int dx\,\sin\left(\frac{n\pi}{a}x\right)\delta\left(x - \frac{a}{2}\right)\sin\left(\frac{n\pi}{a}x\right) = \frac{2}{a}\alpha\int dx\,\delta\left(x - \frac{a}{2}\right)\sin^2\left(\frac{n\pi}{a}x\right)$$

$$= \frac{2}{a}\alpha\sin^2\left(\frac{n\pi}{a}\frac{a}{2}\right) = \frac{2}{a}\alpha\sin^2\left(\frac{n\pi}{2}\right)$$

$$E_n^1 = \begin{cases} 0 & \text{for } n \text{ even} \\ \dfrac{2\alpha}{a} & \text{for } n \text{ odd} \end{cases}$$

VII.B.2 First Order Degenerate Energy Correction

Diagonalizing H^1

$E_n^1 = \langle n^0|H^1|n^0\rangle$

$E_n^1 = \langle \bar{n}|H^1|\bar{n}\rangle$ Hypothesizing

$\{|\bar{n}\rangle\}$ is orthonormal
$H^1|\bar{n}\rangle = E_n^1|\bar{n}\rangle$
$\langle\bar{n}|H^1|\bar{n}\rangle = E_n^1\langle\bar{n}|\bar{n}\rangle = E_n^1$

$H^0|n^0\rangle = E_n|n^0\rangle$
$H|n\rangle = E_n|n\rangle$
$\langle m|H|n\rangle = E_{n\langle m|n\rangle} \Rightarrow H_{mn} = E_n\delta_{mn}$ diagonal

$$|\bar{n}\rangle = \sum_i a_i|i^0\rangle$$

$$H^1\sum_i a_{in}|i^0\rangle = E_n^1\sum_i a_{in}|i^0\rangle$$

$$\sum_i a_{in}H^1|i^0\rangle = E_n^1\sum_i a_{in}|i^0\rangle$$

Operate with $\langle p^0|$

$$\sum_i a_{in}\langle p^0|H^1|i_0\rangle = E_n^1\sum_i a_{in}\langle p^0|i^0\rangle$$

$$\sum_i a_{in}H_{pi}^1 = E_n^1 a_{np}$$

$$\sum_i \left(H_{pi}^1 - E_n^1\delta_{pi}\right)a_{ni} = 0$$

$$\begin{pmatrix} H_{11}^1 - E_n^1 & H_{12}^1 & \cdots \\ H_{21}^1 & H_{22}^1 - E_n^1 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} a_{n1} \\ a_{n2} \\ \vdots \end{pmatrix} = 0$$

$$\det\left(H_{pi}^1 - E_n^1\delta_{pi}\right) = 0$$

VII.B.3 Griffiths Example 6.2

$$\langle\vec{r}|n^0\rangle = \psi_n^0(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{a}\right)\sin\left(\frac{n_z\pi z}{a}\right)$$

$$E_{n_x n_y n_z}^0 = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$E_n^1 = \langle n^0|H^1|\, n^0\rangle = \int d\vec{r}\psi_n^{0^*}(\vec{r})H^1\psi_n^0(\vec{r})$$

$n_x = n_y = n_z = 1$ ground state

$$E_{111}^1 = \int d\vec{r}\psi_{111}^{0\ *}(\vec{r})\psi_{111}^0(\vec{r}) = \left(\frac{2}{a}\right)^3 V_0\int_0^{\frac{a}{2}}\sin^2\left(\frac{\pi x}{a}\right)dx\int_0^{\frac{a}{2}}\sin^2\left(\frac{\pi y}{a}\right)dy\int_0^{a}\sin^2\left(\frac{\pi z}{a}\right)dz$$

$$E_{111}^1 = \left(\frac{2}{a}\right)^3 V_0\frac{a^3}{32} = \frac{V_0}{4}$$

$$E_{111} = E_{111}^0 + \frac{V_0}{4}$$

$$E_{112}^0 = E_{121}^0 = E_{221}^0 = \frac{3\pi^2\hbar^2}{ma^2}$$

VII.C

November-22-13 8:49 AM

VII.C.2 Spin Orbit Correction

(a)

$$B = \frac{\mu I}{2r}, \qquad I = \frac{e}{T}$$
$$|\vec{L}| = |\vec{r} \times \vec{p}| = rmv \sin\theta$$
$$v = \frac{2\pi r}{T}$$
$$L = \frac{2\pi m_e r^2}{T}, \qquad T = \frac{2\pi m_e r^2}{L}$$
$$B = \frac{\mu_0 e}{2rT} = \frac{\mu_0 eL}{4\pi m r^3}$$
$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}} \text{ or } \mu_0 = \frac{1}{c^2 \epsilon_0}$$
$$B = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} L$$
$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}$$

(b) Solid ring, rotating with period T
Define magnetic dipole moment as current * area

$$\boxed{\vec{\mu} = -\left(\frac{e}{2m}\right)\vec{S}}$$

VII.C.2.d

$$E'_{\text{so}} = \langle H'_{\text{so}} \rangle = \langle jm_j ls | H'_{\text{so}} | jm_j ls \rangle = \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \langle jm_j ls | \frac{\vec{S}\cdot\vec{L}}{R} R^3 | \, jm_j ls \rangle$$
$$\vec{J} = \vec{L} + \vec{S}$$
$$J^2 = L^2 + S^2 + \vec{S}\cdot\vec{L} + \vec{L}\cdot\vec{S} = L^2 + S^2 + 2\vec{S}\cdot\vec{L}$$
$$\vec{S}\cdot\vec{L}|jm_j ls\rangle = \frac{1}{2}(J^2 - L^2 - S^2)|jm_j ls\rangle = \frac{J^2}{2}|jm_j ls\rangle - \frac{L^2}{2}|jm_j ls\rangle - \frac{S^2}{2}|jm_j ls\rangle$$
$$L^2|l\rangle = \hbar^2 l(l+1)|l\rangle$$
$$\therefore \vec{S}\cdot\vec{L}|jm_j ls\rangle = \frac{\hbar^2}{2} j(j+1)|jm_j ls\rangle - \frac{\hbar^2}{2} l(l+1)|jm_j ls\rangle - \frac{\hbar^2}{2} s(s+1)|jm_j ls\rangle$$
$$= \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right)|jm_j ls\rangle, \qquad \left[s = \frac{1}{2}\right]$$
$$E^1_{\text{so}} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right)\left\langle jm_j ls \left| \frac{1}{r^3} \right| jm_j ls \right\rangle$$

Problem 6.35.c) in Griffith's:

$$\left\langle \frac{1}{R^3} \right\rangle = \frac{1}{l\left(l + \frac{1}{2}\right)(l+1) n^3 a^3}$$
$$E'_{\text{so}} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \frac{\hbar^2}{2} \frac{\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}{l\left(l + \frac{1}{2}\right)(l+1) n^3 a^3}$$
$$E'_{\text{so}} = \frac{(E_n)^2}{mc^2}\left\{\frac{n\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}{l\left(l + \frac{1}{2}\right)(l+1)}\right\}$$
$$E_n = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

VIII.A.2

$\langle H\rangle = \langle T\rangle + \langle V\rangle$

$\langle T\rangle = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx\,\psi^*(x)\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2}{2m}\sqrt{\frac{2b}{\pi}}\int_{\infty}^{\infty} e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right)dx = \frac{b\hbar^2}{2m}$

$\langle V\rangle = \langle\psi|V|\psi\rangle = \frac{1}{2}m\omega^2\sqrt{\frac{2b}{\pi}}\int_{-\infty}^{\infty} e^{-bx^2}x^2e^{-bx^2}dx = \frac{1}{2}m\omega^2\sqrt{\frac{2b}{\pi}}\frac{\sqrt{2\pi}}{2b\sqrt{b}}$

$\langle H\rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{2b}$

$E_{\text{gs}} \le \langle H\rangle$

$\frac{d\langle H\rangle}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0$

Solving for b: $b = \frac{m\omega}{2\hbar}$

$\langle H\rangle_{\min} = \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{2b^2}\left(\frac{2\hbar}{m\omega}\right) = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}$

$\therefore E_{\text{gs}} \le \frac{\hbar\omega}{2}$

It turns out that this is exact: $E_{\text{gs}} = \frac{\hbar\omega}{2}$

VIII.A.3 Griffiths Example 7.2

$\langle H\rangle = \langle T\rangle + \langle V\rangle, \qquad \psi(x) = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}} e^{-bx^2}$

$\langle T\rangle = \frac{\hbar^2 b}{2m}$

as before

$\langle V\rangle = \langle\psi|V|\psi\rangle = \int_{-\infty}^{\infty}\psi^*(x)V(x)\psi(x)\,dx = -\alpha\int_{-\infty}^{\infty}\psi^*(x)\delta(x)\psi(x)dx = -\alpha|\psi(0)|^2 = -\alpha\sqrt{\frac{2b}{\pi}}$

$\langle H\rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}} \ge E_{\text{gs}}\ \forall b$

$\frac{\partial}{\partial b}\langle H\rangle = 0 = \frac{\hbar^2}{2m} - \frac{\alpha}{2}\sqrt{\frac{2}{\pi}}\frac{1}{\sqrt{b}} \Rightarrow b = \frac{2\alpha^2 m^2}{\pi\hbar^4}$

$E_{\text{gs}} \le \frac{\hbar^2}{2m}\left(\frac{2\alpha^2 m^2}{\pi\hbar^4}\right) - \alpha\sqrt{\frac{2}{\pi}}\sqrt{\frac{2}{\pi}}\frac{\alpha m}{\hbar^2} = -\frac{\alpha^2 m}{\pi\hbar^2}$

VIII.B.1 Simplest Approximation for Helium

$H = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2}\right) + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

The third term is dropped in this approximation

Hydrogenic charge $2e$ instead of e ($2e^2$ instead of e^2)

$\psi_{100} = \frac{1}{\sqrt{\pi a^3}}\,e^{-\frac{r}{a}}$ with $a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$

$E_{100} = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6eV$

Ground state of Hydrogenic atom:

$$\psi_{100} = \frac{1}{\sqrt{\pi\left(\frac{a}{2}\right)^3}} e^{-\frac{2r}{a}}$$

∴ Ground state for Helium:

$$\psi_{\mathrm{gs}}(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2(r_1+r_2)}{a}}$$

Ground state energy of Hydrogenic atom

$$E_{100} = -4\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = 4E_1 = 4\times -13.6eV = -54.4eV$$

$$E_{\mathrm{gs}} = 2\times(-54.4eV) = -108.8eV \cong 109eV$$

VIII.B.2 A Better Approximation for One Helium Atom

$$H = H_1 + H_2 + V_{22}$$

$$\langle H\rangle = \langle H_1\rangle + \langle H_2\rangle + \langle V_{22}\rangle$$

$$\langle\psi_{\mathrm{gs}}|H_1|\psi_{\mathrm{gs}}\rangle = 4E_1\langle\psi_{\mathrm{gs}}|\psi_{\mathrm{gs}}\rangle = 4E_1$$

$$\langle H\rangle = 4E_1 + 4E_1 + \langle V_{ee}\rangle$$

$$\langle V_{ee}\rangle = \langle\psi_{\mathrm{gs}}|V_{ee}|\psi_{\mathrm{gs}}\rangle = \iint d\vec{r}_1 d\vec{r}_2\, \langle\psi_{\mathrm{gs}}|\vec{r}_1\vec{r}_2\rangle\langle\vec{r}_1\vec{r}_2|V_{ee}|\psi_{\mathrm{gs}}\rangle$$

$$= \iint d\vec{r}_1 d\vec{r}_2\, \psi^*_{\mathrm{gs}}(\vec{r}_1,\vec{r}_2)\, V_{ee}(\vec{r}_1,\vec{r}_2)\, \psi_{\mathrm{gs}}(\vec{r}_1,\vec{r}_2)$$

$$= \left(\frac{8}{\pi a^3}\right)^2 \frac{e^2}{4\pi\epsilon_0}\iint d\vec{r}_1 d\vec{r}_2 \frac{e^{\frac{-4(r_1+r_2)}{a}}}{|\vec{r}_1 - \vec{r}_2|}$$

…

$$\langle V_{ee}\rangle = \frac{8}{\pi a^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{5a^2}{128}4\pi = \frac{5}{4a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5}{2}E_1 = 34eV$$

$$\langle H\rangle = 8E_1 - \frac{5}{2}E_1 = -109eV + 34eV = -75eV$$

VIII.B.3 An Even Better Solution

$$H = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_2}\right) + \frac{e}{4\pi\epsilon_0}\frac{Z-2}{r_1} + \frac{e}{4\pi\epsilon_0}\frac{(Z-2)}{r_2} + \frac{e}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$$e^2 \to Ze^2 \to E_{\mathrm{gs}}Z^2E_1 \times 2 \times 2Z^2E_1$$

$$\left\langle\frac{1}{r}\right\rangle \to \frac{1}{a}, \qquad \left\langle\frac{1}{r}\right\rangle \to \frac{Z}{a}$$

$$\langle V_{ee}\rangle = -\frac{5}{2}E_1, \qquad \langle V_{ee}\rangle = -\frac{5}{4}ZE_1$$

$$\langle H\rangle = 2Z^2E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle = 2Z^2E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{Z}{a} - \frac{5}{4}ZE_1$$

$$\langle H\rangle = \left(-2Z^2 + \frac{27}{4}Z\right)E_1$$

$$\frac{d}{dZ}\langle H\rangle = \left(-4Z - \frac{27}{4}\right)E_1 = 0 \Rightarrow Z = \frac{27}{16} = 1.69$$

$$\langle H\rangle_{\min} = \left[-2\left(\frac{27}{16}\right)^2 + \frac{27}{4}\left(\frac{27}{16}\right)\right] = 77.5eV$$