QM

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1 Basics

1.1 Pauli Matrix

$$\mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\hat{\sigma} = \sigma^x \hat{\mathbf{X}} + \sigma^y \hat{y} + \sigma^z \hat{z}$, all Pauli matrices are both Hermitian and unitary. $\hat{\sigma} \cdot \hat{\mathbf{n}}$ is also Hermitian and unitary, $\hat{\mathbf{n}}$ is a unit vector.

$$\begin{aligned}
(\sigma^j)^2 &= \mathbb{1} \quad [\sigma^j, \sigma^k] = 2i\varepsilon_{jkl}\sigma^l \quad \{\sigma^j, \sigma^k\} = 2\delta_{jk}\mathbb{1} \\
\hat{\sigma} \cdot \hat{\mathbf{n}} &= \sigma^x n_x + \sigma^y n_y + \sigma^z n_z \\
(\hat{\sigma} \cdot \hat{\mathbf{n}})^2 &= (\sigma^l)^2 n_l^2 + \sum_{j \neq k} \{\sigma^j, \sigma^k\} n_j n_k \\
&= \sum_l n_l^2 \mathbb{1} + 2 \sum_{j \neq k} \delta_{jk} n_j n_k \mathbb{1} \\
&= \mathbb{1} \\
e^{i\theta\hat{\sigma}\cdot\hat{\mathbf{n}}} &= \sum_{k=0} \frac{(i\theta\hat{\sigma} \cdot \hat{\mathbf{n}})^k}{k!} \\
&= \sum_{k=0} \frac{(i\theta\hat{\sigma} \cdot \hat{\mathbf{n}})^{2k}}{(2k)!} + \sum_{l=0} \frac{(i\theta\hat{\sigma} \cdot \hat{\mathbf{n}})^{2l+1}}{(2l+1)!} \\
&= \sum_{k=0} (-1)^k \frac{\theta^{2k}}{(2k)!} \mathbb{1} + i \sum_{l=0} (-1)^l \frac{\theta^{2l+1}}{(2l+1)!} \hat{\sigma} \cdot \hat{\mathbf{n}} \\
&= \cos(\theta)\mathbb{1} + i\sin(\theta)\hat{\sigma} \cdot \hat{\mathbf{n}}
\end{aligned}$$

1.2 Momentum Operator

1.2.1 Momentum Operator Is the Generator of Translation

Set a translation operator $\hat{\mathbf{T}}_{\mathbf{a}} |\mathbf{x}\rangle = |\mathbf{x} + \mathbf{a}\rangle$. It is unitary, since $\langle \mathbf{x}| \hat{\mathbf{T}}_{\mathbf{a}}^\dagger \hat{\mathbf{T}}_{\mathbf{a}} |\mathbf{x}\rangle = \langle \mathbf{x} + \mathbf{a} | \mathbf{x} + \mathbf{a} \rangle = 1 \Rightarrow \hat{\mathbf{T}}_{\mathbf{a}}^\dagger \hat{\mathbf{T}}_{\mathbf{a}} = \mathbb{1}$.

The position operator $\mathbf{x}\left|\mathbf{x}\right\rangle = \mathbf{x}\left|\mathbf{x}\right\rangle$. And $\mathbf{x}\hat{\mathbf{T}}_{\mathbf{a}}\left|\mathbf{x}\right\rangle = (\mathbf{x}+\mathbf{a})\left|\mathbf{x}+\mathbf{a}\right\rangle$. Any unitary vector can be represented as $\hat{\mathbf{T}}_{\mathbf{a}} = e^{-i\hat{\mathbf{O}}\cdot\mathbf{a}/\hbar}$, where $\hat{\mathbf{O}} = \hat{\mathbf{O}}^{\dagger}$. Consider a infinitesimal translation $d\mathbf{x}$

$$\begin{aligned}
\hat{\mathbf{X}}\hat{\mathbf{T}}_{d\mathbf{x}}\left|\mathbf{x}\right\rangle &= (\mathbf{x}+d\mathbf{x})\left|\mathbf{x}+d\mathbf{x}\right\rangle \\
\hat{\mathbf{T}}_{d\mathbf{x}}\hat{\mathbf{X}}\left|\mathbf{x}\right\rangle &= \mathbf{x}\hat{\mathbf{T}}_{d\mathbf{x}}\left|\mathbf{x}\right\rangle = \mathbf{x}\left|\mathbf{x}+d\mathbf{x}\right\rangle
\end{aligned}$$

This leads to

$$\begin{aligned}
&\hat{\mathbf{X}}\hat{\mathbf{T}}_{d\mathbf{x}} - \hat{\mathbf{T}}_{d\mathbf{x}}\hat{\mathbf{X}} = d\mathbf{x} \\
&\hat{\mathbf{X}}e^{-i\hat{\mathbf{O}}\cdot d\mathbf{x}/\hbar} - e^{-i\hat{\mathbf{O}}\cdot d\mathbf{x}/\hbar}\hat{\mathbf{X}} = d\mathbf{x} \\
&\hat{\mathbf{X}}(1-\frac{i}{\hbar}\hat{\mathbf{O}}\cdot d\mathbf{x}) - (1-\frac{i}{\hbar}\hat{\mathbf{O}}\cdot d\mathbf{x})\hat{\mathbf{X}} = d\mathbf{x} \\
&\frac{i}{\hbar}\left(\hat{\mathbf{O}}\cdot d\mathbf{x}\right)\hat{\mathbf{X}} - \frac{i}{\hbar}\hat{\mathbf{X}}\left(\hat{\mathbf{O}}\cdot d\mathbf{x}\right) = \frac{i}{\hbar}[\hat{\mathbf{O}}\cdot d\mathbf{x},\hat{\mathbf{X}}] = d\mathbf{x}
\end{aligned}$$

For each direction,

$$\frac{i}{\hbar}[\hat{\mathbf{O}}\cdot d\mathbf{x},\hat{\mathbf{X}}_j] = d\mathbf{x}_j \Rightarrow \frac{i}{\hbar}[\hat{\mathbf{O}}\cdot d\mathbf{x},\hat{\mathbf{X}}_j] = dx_j$$

Consider an infinitesimal translation along one direction $d\mathbf{x}_j$:

$$\begin{aligned}
\hat{\mathbf{T}}_{d\mathbf{x}_j}\left|\mathbf{x}\right\rangle &= e^{-i\hat{\mathbf{O}}\cdot d\mathbf{x}_j/\hbar}\left|\mathbf{x}\right\rangle = e^{-i\hat{O}_j dx_j/\hbar}\left|\mathbf{x}\right\rangle \\
&= \left|\mathbf{x}+d\mathbf{x}_j\right\rangle
\end{aligned}$$

The commutation relation becomes,

$$\begin{aligned}
&\hat{\mathbf{X}}\hat{\mathbf{T}}_{d\mathbf{x}_j} - \hat{\mathbf{T}}_{d\mathbf{x}_j}\hat{\mathbf{X}} = d\mathbf{x}_j = \frac{i}{\hbar}\hat{O}_j dx_j\hat{\mathbf{X}}_j - \frac{i}{\hbar}\hat{\mathbf{X}}_j\hat{O}_j dx_j \\
&\Rightarrow dx_j = \frac{i}{\hbar}[\hat{O}_j dx_j,\hat{\mathbf{X}}_j] = \frac{i}{\hbar}[\hat{\mathbf{O}}\cdot d\mathbf{x},\hat{\mathbf{X}}_j]
\end{aligned}$$

Thus, $[\hat{\mathbf{X}}_k,\hat{O}_j] = i\hbar\delta_{jk}$. Aligning with classical mechanics (AKA, idk), $\hat{\mathbf{O}}$ is the generator of translation, which should be the momentum operator $\hat{\mathbf{P}}$. The commutation relation between the position operator and the momentum operator:

$$[\hat{\mathbf{X}}_k,\hat{P}_j] = i\hbar\delta_{jk}$$

Consider

$$
\begin{aligned}
\langle \mathbf{x}_j + d\mathbf{x}_j | \psi \rangle = \psi(\mathbf{x}_j + d\mathbf{x}_j) &= \psi(\mathbf{x}_j) + d\mathbf{x}_j \frac{\partial \psi(\mathbf{x}_j)}{\partial \mathbf{x}_j} \\
&= \langle \mathbf{x}_j | T^\dagger_{d\mathbf{x}_j} | \psi \rangle = \langle \mathbf{x}_j | e^{i\hat{P}_j dx_j/\hbar} | \psi \rangle \\
&= \langle \mathbf{x}_j | (1 + \frac{i}{\hbar}\hat{P}_j d_{x_j}) | \psi \rangle = \psi(\mathbf{x}_j) + \frac{i}{\hbar} d_{x_j} \langle \mathbf{x}_j | \hat{P}_j | \psi \rangle \qquad (1)
\end{aligned}
$$

Thus, $\langle \mathbf{x}_j | \hat{P}_j | \psi \rangle \hat{\mathbf{n}}_j = -i\hbar \frac{\partial \psi(\mathbf{x}_j)}{\partial \mathbf{x}_j} \Rightarrow \left(\langle \mathbf{x}_j | \hat{P}_j \right) \hat{\mathbf{n}}_j = -i\hbar \frac{\partial}{\partial \mathbf{x}_j} \langle \mathbf{x}_j |$, and $\left(\langle \mathbf{x}_j | \hat{P}_j \right) = -i\hbar \frac{\partial}{\partial x_j} \langle \mathbf{x}_j |$

In conclusion,

$$
\begin{aligned}
\langle \mathbf{x} | \hat{\mathbf{P}} &= -i\hbar \frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x} | \\
\hat{\mathbf{P}} | \mathbf{x} \rangle &= | \mathbf{x} \rangle \, i\hbar \left(\frac{\partial}{\partial \mathbf{x}} \right)^\dagger
\end{aligned}
$$

What is $\left(\frac{\partial}{\partial \mathbf{x}} \right)^\dagger$? Since $\hat{\mathbf{P}}$ is an observable, it must be Hermitian.

$$
\begin{aligned}
\hat{\mathbf{P}} &= \int d^3\mathbf{x} \, |\mathbf{x}\rangle \langle \mathbf{x}| \hat{\mathbf{P}} = -i\hbar \int d^3\mathbf{x} \, |\mathbf{x}\rangle \frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x}| \\
&= \left(-i\hbar \int d^3\mathbf{x} \, |\mathbf{x}\rangle \frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x}| \right)^\dagger = i\hbar \int d^3\mathbf{x} \, |\mathbf{x}\rangle \left(\frac{\partial}{\partial \mathbf{x}} \right)^\dagger \langle \mathbf{x}| \\
\Rightarrow \left(\frac{\partial}{\partial \mathbf{x}} \right)^\dagger &= -\frac{\partial}{\partial \mathbf{x}}
\end{aligned}
$$

So,

$$
\hat{\mathbf{P}} | \mathbf{x} \rangle = - | \mathbf{x} \rangle \, i\hbar \frac{\partial}{\partial \mathbf{x}}
$$

With this, one can work out the derivative of $|\mathbf{x}\rangle$. From (1), one has (not completely rigorous, but one can show it rigorously)

$$
\begin{aligned}
\langle \mathbf{x} + d\mathbf{x} | \psi \rangle &= \langle \mathbf{x} | \psi \rangle + \frac{i}{\hbar} d\mathbf{x} \langle \mathbf{x} | \hat{\mathbf{P}} | \psi \rangle \\
&= \langle \mathbf{x} | \psi \rangle + d\mathbf{x} \frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x} | \psi \rangle
\end{aligned}
$$

It is true for arbitrary $\mathbf{x}$. Thus,

$$
\begin{aligned}
\langle \mathbf{x} + d\mathbf{x}| &= \langle \mathbf{x}| + d\mathbf{x}\frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x}| \\
\frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x}| &= \lim_{d\mathbf{x}\to 0} \frac{\langle \mathbf{x} + d\mathbf{x}| - \langle \mathbf{x}|}{d\mathbf{x}} \\
\left(\frac{\partial}{\partial \mathbf{x}} \langle \mathbf{x}|\right)^{\dagger} &= \lim_{d\mathbf{x}\to 0} \frac{|\mathbf{x} + d\mathbf{x}\rangle - |\mathbf{x}\rangle}{d\mathbf{x}} \\
-\frac{\partial}{\partial \mathbf{x}} |\mathbf{x}\rangle &= \lim_{d\mathbf{x}\to 0} \frac{|\mathbf{x} + d\mathbf{x}\rangle - |\mathbf{x}\rangle}{d\mathbf{x}} \\
\frac{\partial}{\partial \mathbf{x}} |\mathbf{x}\rangle &= \lim_{d\mathbf{x}\to 0} \frac{|\mathbf{x}\rangle - |\mathbf{x} + d\mathbf{x}\rangle}{d\mathbf{x}}
\end{aligned}
$$

The second last step is little confusing–the order is not inversed after taking ajoint. Just keep in mind the derivative is always acting on the position eigenstate (not completely clear).

1.2.2 Unitary Transformation between Coordinate Space and Momentum Space

Consider the 3-dimensional case. The eigenspectrum of the momentum operator is $\hat{\mathbf{P}} |\mathbf{p}\rangle = \mathbf{p} |\mathbf{p}\rangle$, the eigenspectrum of the position operator is $\hat{\mathbf{X}} |\mathbf{x}\rangle = \mathbf{x} |\mathbf{x}\rangle$.

$$
\begin{aligned}
\langle \mathbf{x}| \hat{\mathbf{P}} |\mathbf{p}\rangle &= \mathbf{p} \langle \mathbf{x}|\mathbf{p}\rangle \\
\left(-i\hbar\frac{\partial}{\partial \mathbf{x}}\right) \langle \mathbf{x}|\mathbf{p}\rangle &= \mathbf{p} \langle \mathbf{x}|\mathbf{p}\rangle \\
\langle \mathbf{x}|\mathbf{p}\rangle &= Ae^{i\mathbf{p}\cdot\mathbf{x}/\hbar}
\end{aligned}
$$

Normalization:

$$
\begin{aligned}
\langle \mathbf{x}'|\mathbf{x}\rangle &= \delta^{(3)}(\mathbf{x} - \mathbf{x}') \\
&= \int d^3\mathbf{p}\, |A|^2 e^{i\mathbf{p}\cdot(\mathbf{x}'-\mathbf{x})/\hbar} \\
&= (2\pi\hbar)^3 |A|^2 \delta^{(3)}(\mathbf{x} - \mathbf{x}')
\end{aligned}
$$

where we have used the Fourier transform of Dirac delta function.

Thus, the momentum eigenstate in the spatial representation is

$$\langle \mathbf{x}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{n/2}} e^{i\mathbf{p}\cdot\mathbf{x}/\hbar}$$

The spatial eigenstate in the momentum representation is

$$\langle \mathbf{p}|\mathbf{x}\rangle = \frac{1}{(2\pi\hbar)^{n/2}} e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}$$

where n is the dimension of space.

1.2.3 Position Operator in Momentum Space

What is the position operator in momentum representation?

$$\begin{aligned}
\langle \mathbf{p}| \hat{\mathbf{X}} |\psi\rangle &= \mathbf{x} \langle \mathbf{p}|\psi\rangle \\
&= \int d^3\mathbf{x} \langle \mathbf{p}| \hat{\mathbf{X}} |\mathbf{x}\rangle \langle \mathbf{x}|\psi\rangle = \int d^3\mathbf{x} \langle \mathbf{p}|\mathbf{x}\rangle\, \mathbf{x} \langle \mathbf{x}|\psi\rangle \\
&= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3\mathbf{x}\, e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} \mathbf{x}\psi(\mathbf{x}) \\
&= -\frac{\hbar}{i}\frac{\partial}{\partial \mathbf{p}} \frac{1}{(2\pi\hbar)^{3/2}} \int d^3\mathbf{x}\, e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} \psi(\mathbf{x}) \\
&= i\hbar \frac{\partial}{\partial \mathbf{p}} \langle \mathbf{p}|\psi\rangle
\end{aligned}$$

Thus, $\langle \mathbf{p}| \hat{\mathbf{X}} = i\hbar \frac{\partial}{\partial \mathbf{p}}$ is a possible representation. According to Stone–von Neumann theorem, $\langle \mathbf{p}| \hat{\mathbf{X}} = i\hbar \frac{\partial}{\partial \mathbf{p}}$.

1.2.4 Function of Position and Momentum

First, consider 1D case, $F(\hat{P}) = \sum_n \frac{1}{n!} \left.\frac{\partial^n F(\hat{P})}{\partial \hat{P}^n}\right|_0 \hat{P}^n$. Claim that in 3D case,

$$F(\hat{\mathbf{P}}) = \sum_{n,j} \left.\frac{\partial^n F(\hat{\mathbf{P}})}{\partial \hat{P}_j^n}\right|_0 \frac{\hat{P}_j^n}{n!}$$

where j is the summation over x, y, z.

$$[\hat{X}_i, F(\hat{\mathbf{P}})] = \sum_{n,i} \frac{\partial^n F(\hat{\mathbf{P}})}{\partial \hat{P}_i^n}\bigg|_0 \frac{1}{n!}[\hat{X}_i, \hat{P}_i^n]$$
$$= \sum_{n} \frac{\partial^n F(\hat{\mathbf{P}})}{\partial \hat{P}_i^n}\bigg|_0 \frac{1}{n!}[\hat{X}_i, \hat{P}_i^n]$$

The commutator

$$[\hat{X}_i, \hat{P}_i^n] = \hat{X}_i \hat{P}_i^n - \hat{P}_i^n \hat{X}_i$$

Evaluate with an arbitrary state,

$$[\hat{X}_i, \hat{P}_i^n] |\psi\rangle = \int dp_i \; |p_i\rangle \langle p_i| \hat{X}_i \hat{P}_i^n |\psi\rangle - \int dx_i \; |x_i\rangle \langle x_i| \hat{P}_i^n \hat{X}_i |\psi\rangle$$
$$= \int dp_i \; |p_i\rangle \, i\hbar \frac{\partial}{\partial p_i} \left(p_i^n \langle p_i|\psi\rangle\right) - \int dx_i \; |x_i\rangle \, (-i\hbar)^n \frac{\partial^n}{\partial x_i^n} \left(x_i \langle x_i|\psi\rangle\right)$$
$$= i\hbar n \int dp_i \, p_i^{n-1} |p_i\rangle \langle p_i|\psi\rangle + i\hbar \int dp_i \, p_i^n \frac{\partial}{\partial p_i} \langle p_i|\psi\rangle$$
$$- (-i\hbar)^n \int dx_i \, x_i \, |x_i\rangle \frac{\partial^n}{\partial x_i^n} \langle x_i|\psi\rangle$$
$$= i\hbar \frac{\partial}{\partial p_i} p_i^n + (i\hbar)^n \frac{\partial^n}{\partial \hat{X}_i^n} \hat{X}_i$$
$$= n i\hbar p_i^{n-1}$$

One has

$$[\hat{X}_i, F(\mathbf{p})] = \sum_{n=0} \frac{\partial^n F(\mathbf{p})}{\partial p_i^n}\bigg|_0 \frac{1}{n!} n i\hbar p_i^{n-1}$$
$$= \sum_{n=1} \frac{\partial^n F(\mathbf{p})}{\partial p_i^n}\bigg|_0 \frac{1}{n!} n i\hbar p_i^{n-1}$$
$$= i\hbar \frac{\partial}{\partial p_i} \sum_{n=1} \frac{\partial^{n-1} F(\mathbf{p})}{\partial p_i^{n-1}}\bigg|_0 \frac{1}{(n-1)!} p_i^{n-1}$$
$$= i\hbar \frac{\partial}{\partial p_i} \sum_{n=0} \frac{\partial^n F(\mathbf{p})}{\partial p_i^n}\bigg|_0 \frac{1}{n!} p_i^n$$
$$= i\hbar \frac{\partial F(\mathbf{p})}{\partial p_i}$$

2 Simple Harmonic Oscillator

$$
\begin{aligned}
H &= \frac{P^2}{2m} + \frac{m\omega^2 X^2}{2} \\
m\omega^2 X^2 \to X^2, \frac{P^2}{2m} &\to \frac{P^2}{2} \\
\Rightarrow H &= \frac{P^2}{2} + \frac{X^2}{2}
\end{aligned}
$$

Construct ladder operators,

$$
\begin{aligned}
a =&(X + iP)/\sqrt{2} \\
a^\dagger =&(X - iP)/\sqrt{2}
\end{aligned}
$$

One has,

$$
\begin{aligned}
X &= (a + a^\dagger)/\sqrt{2} \\
P &= (a - a^\dagger)/i\sqrt{2}
\end{aligned}
$$

The commutator of a and $a^\dagger$:

$$
\begin{aligned}
[a, a^\dagger] &= \frac{1}{2}[X + iP, X - iP] \\
&= \frac{1}{2}(-i[X, P] + i[P, X]) \\
&= 1
\end{aligned}
$$

Given that $[\hat{\mathbf{X}}, \hat{P}] = i$ is equivalent to

$$\hat{P} = -i\frac{\partial}{\partial \hat{\mathbf{X}}} \text{ and } \hat{\mathbf{X}} = i\frac{\partial}{\partial \hat{P}}$$

One has

$$\hat{a} = \frac{\partial}{\partial \hat{a}^\dagger} \text{ and } \hat{a}^\dagger = -\frac{\partial}{\partial \hat{a}}$$

Substituting into the Hamiltonian:

$$H = a^\dagger a + \frac{1}{2}$$

Take the eigenstates to be $a^\dagger a |n\rangle = n|n\rangle$, one has

$$\begin{aligned}
a^\dagger a a|n\rangle &= (aa^\dagger - 1)a|n\rangle = (n-1)a|n\rangle \\
\Rightarrow a|n\rangle &\propto |n-1\rangle, a^\dagger|n\rangle \propto |n+1\rangle \\
a|n\rangle &= c|n-1\rangle \\
\langle n| a^\dagger a |n\rangle &= |c|^2 \langle n-1|n-1\rangle \\
n &= |c|^2 \\
|c| &= \sqrt{n}e^{i\theta}
\end{aligned}$$

where $e^{i\theta}$ is the phase factor. $a|n\rangle = \sqrt{n}|n-1\rangle, a^\dagger = \sqrt{n+1}|n+1\rangle$

3 Composite System

Tensor product

$$\begin{pmatrix} a_0 & b_0 \\ c_0 & d_0 \end{pmatrix} \otimes \begin{pmatrix} a_1 & b_1 \\ c_1 & d_1 \end{pmatrix} = \begin{pmatrix} a_0a_1 & a_0b_1 & b_0a_1 & b_0b_1 \\ a_0c_1 & a_0d_1 & b_0c_1 & b_0d_1 \\ c_0a_1 & c_0b_1 & d_0a_1 & d_0b_1 \\ c_0c_1 & c_0d_1 & d_0c_1 & d_0d_1 \end{pmatrix}$$

4 Density Matrix

Claim $\langle \hat{O} \rangle = \mathrm{Tr}\Big[|\psi\rangle\langle\psi|\hat{O}\Big]$. $\mathrm{Tr}\,\hat{\Omega} = \sum_i \langle\phi_i|\hat{\Omega}|\phi_i\rangle$. $|\phi_i\rangle$ is arbitrary basis set.

Proof for $\operatorname{Tr}\hat{\Omega} = \sum_i \langle\phi_i|\,\hat{\Omega}\,|\phi_i\rangle$:

$$
\begin{aligned}
\operatorname{Tr}\hat{\Omega} &= \operatorname{Tr} U^\dagger \hat{\Omega} U \text{ (where U is the unitary matrix of eigenvectors of } \Omega) \\
&= \sum_i \lambda_i \\
&= \sum_i \langle i|\,\hat{\Omega}\,|i\rangle \\
&\text{Insert arbitrary basis } \{|\phi_n\rangle\} \\
&= \sum_{m,n,i} \langle i|\phi_m\rangle \langle\phi_m|\,\hat{\Omega}\,|\phi_n\rangle \langle\phi_n|i\rangle \\
&= \sum_{m,n} \langle\phi_n|\phi_m\rangle \langle\phi_m|\,\hat{\Omega}\,|\phi_n\rangle \\
&= \sum_i \langle\phi_i|\,\hat{\Omega}\,|\phi_i\rangle \qquad \text{Q.E.D}
\end{aligned}
$$

Proof for $\langle\hat{O}\rangle = \operatorname{Tr}\Big[|\psi\rangle\langle\psi|\,\hat{O}\Big]$:

Choose $|\psi\rangle$ to be one of the eigenvectors, and $\{|\phi_i\rangle\}$ to be the eigenbasis.

$$
\operatorname{Tr}\Big[|\psi\rangle\langle\psi|\,\hat{O}\Big] = \sum_i \langle\phi_i|\psi\rangle\langle\psi|\,\hat{O}\,|\phi_i\rangle = \langle\hat{O}\rangle \qquad \text{Q.E.D}
$$

4.1 Density Matrix ρ

$$
\hat{\rho} = |\psi\rangle\langle\psi|
$$

$$
\Rightarrow \langle\hat{O}\rangle = \operatorname{Tr}\Big[\hat{\rho}\cdot\hat{O}\Big] \text{ (pure state)}
$$

For mixed state, $\hat{\rho} \equiv \sum_i P_i\,|\psi_i\rangle\langle\psi_i|$.

If ρ has only one nonzero eigenvalue, it is a pure state. $Eigen(\rho) = \{\lambda, 0, 0...\}$.

$$\begin{aligned}
\langle \hat{O} \rangle &= \sum_i P_i \langle \psi_i | \hat{O} | \psi_i \rangle \\
&= \sum_i P_i \operatorname{Tr}\Big[|\psi_i\rangle \langle \psi_i | \hat{O} \Big] \\
&= \operatorname{Tr}\left[\hat{O} \sum_i P_i |\psi_i\rangle \langle \psi_i | \right] \\
&= \operatorname{Tr}\Big[\hat{O} \cdot \hat{\rho} \Big] (\text{Recall that } \operatorname{Tr}[AB] = \operatorname{Tr}[BA])
\end{aligned}$$

$\operatorname{Tr}[\rho] = 1$ for all states, $\operatorname{Tr}[\rho^2] = 1$ for pure states, $\operatorname{Tr}[\rho^2] < 1$ for mixed states.

4.2 Von Neumann Entanglement

$S_A = -\operatorname{Tr}_{\bar{A}}[\rho_{\bar{A}} \log \rho_{\bar{A}}] = -\sum_i \lambda_{i\bar{A}} \log \lambda_{i\bar{A}}$, $\lambda_{i\bar{A}}$ is the eigenvalue of $\rho_{\bar{A}}$. $\bar{A}$ denotes the complement of Hilbert space A. For two Hilbert spaces, A, B, $\bar{A}$ represents Hilbert space B.

The maximum value of S_A: $\operatorname{Max}(S_A) = \log(|\mathscr{H}_A|)$, where $|\mathscr{H}_A|$ is the dimension of $\mathscr{H}_A$.

Proof for n-dimensional Hilbert space:

5 Quantum Dynamics

Starting with TDSE, and assuming H is time-independent,

$$\begin{aligned}
i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} &= H |\psi(t)\rangle \\
\Rightarrow |\psi(t)\rangle &= e^{-i\frac{H}{\hbar}t} |\psi(t=0)\rangle
\end{aligned}$$

where $e^{-i\frac{H}{\hbar}t} |\psi(t=0)\rangle$ is called **Schr$\ddot{o}$dinger Evolved State**, $e^{-i\frac{H}{\hbar}t}$ is the **Time Evolution Operator**. To make life easier, ignore $\hbar$, $|\psi(t)\rangle =$

$e^{-iHt}|\psi(t=0)\rangle$. Thinking of the evolution from the point of Schr$\ddot{o}$dinger evolved state is called **Schr$\ddot{o}$dinger's Picture**

Given arbitrary observable $\hat{O}$,

$$\begin{aligned}\langle\hat{O}\rangle(t) &= \langle\psi(t)|\,\hat{O}\,|\psi(t)\rangle \\ &= \langle\psi(t=0)|\,e^{iHt}\hat{O}e^{-iHt}\,|\psi(t=0)\rangle\end{aligned}$$

which gives another way to think about the evolution, from the point of operator. This is **Heisenberg's Picture**. **Heisenberg Evolved Operator** is defined as:

$$\hat{O}(t) \equiv e^{iHt}\hat{O}e^{-iHt}$$

An important equation can be derived:

$$\begin{aligned}\frac{d\hat{O}(t)}{dt} =&(iH)e^{iHt}\hat{O}e^{-iHt} + e^{iHt}\hat{O}e^{-iHt}(-iH) \\ =&i[H,\hat{O}(t)]\end{aligned}$$

which is the **Heisenberg's equation of motion** (EOM).

Naturally, we have

$$\frac{d\hat{H}(t)}{dt} = i[H,H(t)] = 0$$

Note that commutation relation does not change with time, which can be easily verified.

Power of EOM:

For SHO,

$$\frac{d\hat{\mathbf{X}}(t)}{dt} = \hat{P}(t), \frac{d\hat{P}(t)}{dt} = -\hat{\mathbf{X}}(t)$$
$$\frac{d\hat{a}(t)}{dt} = -\hat{a}(t)$$
$$\Rightarrow a(t) = e^{-it}a(0) = [\hat{\mathbf{X}}(t) + i\hat{P}(t)]/\sqrt{2}$$
$$\Rightarrow a^\dagger(t) = e^{it}a^\dagger(0) = [\hat{\mathbf{X}}(t) - i\hat{P}(t)]/\sqrt{2}$$
$$\Rightarrow \hat{\mathbf{X}}(t) = \hat{\mathbf{X}}(0)\cos(t) + \hat{P}(0)\sin(t)$$
$$\Rightarrow \hat{P}(t) = \hat{P}(0)\cos(t) - \hat{\mathbf{X}}(0)\sin(t)$$

6 Generator

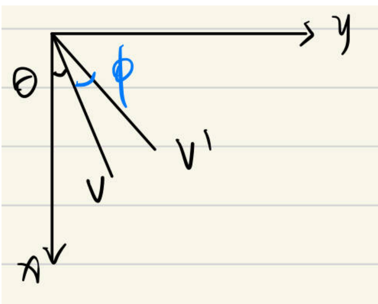
Translation generator

$$\hat{P} \text{ is the generator of translation}$$
$$e^{-i\hat{P}a}|\mathbf{x}\rangle = |x + a\rangle$$
$$e^{i\hat{P}a}\hat{\mathbf{X}}e^{-i\hat{P}a} = \hat{\mathbf{X}} + a$$

Rotation generator

First, deriving rotation matrix.

For rotation by z-axis.



One has

$$V = V'$$

$$V_x = V\cos\theta$$

$$V_y = V\sin\theta$$

$$V_x' = V'\cos(\theta+\phi) = V'(\cos\theta\cos\phi - \sin\theta\sin\phi) = V_x\cos\phi - V_y\sin\phi$$

$$V_y' = V'\sin(\theta+\phi) = V'(\sin\theta\cos\phi + \cos\theta\sin\phi) = V_x\sin\phi + V_y\cos\phi$$

$$\Rightarrow R_z(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Similarly, } R_x(\phi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{pmatrix} R_y(\phi) = \begin{pmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{pmatrix}$$

$$\hat{D}(R) = e^{-i\theta\vec{n}\cdot\hat{L}},\ \hat{L} = \hat{r}\times\hat{P}$$

7 Angular Momentum

7.1 Definition

$$
\begin{aligned}
J_{\pm} &= J_x \pm i j_y \\
J^2 &= J_x^2 + J_y^2 + J_z^2
\end{aligned}
$$

7.2 Commutation relation

$$[J_i, J_j] = i\varepsilon_{ijk} J_k$$

$$[J_+, J_-] = [J_x + iJ_y, J_x - iJ_y] = -2i[J_x, J_y] = 2J_z$$

$$[J_z, J_+] = [J_z, J_x + iJ_y] = iJ_y + J_x = J_+$$

$$[J_z, J_-] = [J_z, J_x - iJ_y] = iJ_y - J_x = -J_-$$

$$
\begin{aligned}
[J^2, J_j] &= [\sum_i J_i^2, J_j] = [J_i^2, J_j] + [J_k^2, J_j] \\
&= i\varepsilon_{ijk}(J_i J_k + J_k J_i) + i\varepsilon_{kji}(J_i J_k + J_k J_i) \\
&= 0
\end{aligned}
$$

ε_{ijk} equals $-\varepsilon_{kji}$.

7.3 Eigenvalue

According to the commutation relations, one can only simultaneously take the eigenvalue of J^2 and one of J_i or $J_{\pm}$, since J^2 commutes with all of them, but they do not commute with each other. Choose:

$$J_z |j,m\rangle = m |j,m\rangle$$
$$J^2 |j,m\rangle = j(j+1) |j,m\rangle$$

One can derive:

$$\begin{aligned} J_z J_\pm |j,m\rangle &= (J_\pm J_z \pm J_\pm) |j,m\rangle \\ &= (m\pm 1) J_\pm |j,m\rangle \end{aligned}$$

$J_\pm |j,m\rangle$ acts as $|j, m\pm 1\rangle$, $J_\pm |j,m\rangle = C_\pm(j,m) |j,m\pm 1\rangle$. Since $(J_+)^\dagger = J_-$,

$$\begin{aligned} \langle j,m| J_\mp J_\pm |j,m\rangle &= |C_\pm(j,m)|^2 \\ &= \langle j,m| (J_x^2 + J_y^2 \pm i[J_x, J_y]) |j,m\rangle \\ &= \langle j,m| (J^2 - J_z^2 \mp J_z) |j,m\rangle \\ &= j(j+1) - m(m\pm 1) \end{aligned}$$

$$\Rightarrow C_\pm(j,m) = \sqrt{j(j+1) - m(m\pm 1)}$$
$$\Rightarrow J_\pm |j,m\rangle = \sqrt{j(j+1) - m(m\pm 1)}\, |j, m\pm 1\rangle$$

7.4 Angular Momentum Addition

Add angular momentum j_1 to j_2, it forms complete basis of $(2j_1+1)(2j_2+1)$ states.

$|j_1, m_1, j_2, m_2\rangle$ also eigenstates of J_z but usually not eigenstates of J^2.

Let $j = j_1 + j_2$ be the total angular momentum, it takes values of $|j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2$

First, we can uniquely determine two states:

$$|j_1 + j_2, j_1 + j_2\rangle = |j_1, j_1\rangle \otimes |j_2, j_2\rangle$$
$$|j_1 + j_2, -j_1 - j_2\rangle = |j_1, -j_1\rangle \otimes |j_2, -j_2\rangle$$

Then, act J_- on both sides of the first equation:

$$\sqrt{j(j+1)-m(m-1)}\,|j=j_1+j_2, m=j_1+j_2-1\rangle =$$
$$\sqrt{j_1(j_1+1)-m_1(m_1-1)}\,|j_1, j_1-1\rangle \otimes |j_2, j_2\rangle$$
$$+\sqrt{j_2(j_2+1)-m_2(m_2-1)}\,|j_1, j_1\rangle \otimes |j_2, j_2-1\rangle$$

Repeat this procedure, one can calculate to $m = |j_1 - j_2|$

Now, one has calculated all the states of $j = j_1 + j_2$. Let's move on to $j = j_1 + j_2 - 1$. $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$ must be orthogonal to $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$. So, one can directly write down the expression of it

$|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle = \frac{\sqrt{j_2(j_2+1)-m_2(m_2-1)}}{\sqrt{j(j+1)-m(m-1)}}\,|j_1, j_1-1\rangle \otimes |j_2, j_2\rangle - \frac{\sqrt{j_1(j_1+1)-m_1(m_1-1)}}{\sqrt{j(j+1)-m(m-1)}}\,|j_1, j_1\rangle \otimes |j_2, j_2-1\rangle$

Using J_- procedure, one can write all other states with $j = j_1 + j_2 - 1$.

A technique to simply the calculation is that one can use symmetry to obtain the corresponding states.

Let's say,

$|j_1 + j_2, j_1 + j_2 - 1\rangle = c_1\,|j_1, j_1 - 1\rangle \otimes |j_2, j_2\rangle + c_2\,|j_1, j_1\rangle \otimes |j_2, j_2 - 1\rangle$.

Via symmetry,

$|j_1 + j_2, -(j_1 + j_2 - 1)\rangle = c_1\,|j_1, -(j_1 - 1)\rangle \otimes |j_2, -j_2\rangle + c_2\,|j_1, -j_1\rangle \otimes |j_2, -(j_2 - 1)\rangle$

Mind the sign change, if there is minus sign in the equation.

8 Tensor Operator

8.1 Vector operator

Satisfy $[\hat{V}_i, \hat{J}_j] = i\varepsilon_{ijk}\hat{V}_k$, let $\hat{V}_0 = \hat{V}_z, \hat{V}_{\pm 1} = \mp(\hat{V}_x \pm i\hat{V}_y)/\sqrt{2}$.

$$
\begin{aligned}
[\hat{J}_z, \hat{V}_m] &= m\hat{V}_m \\
[\hat{J}_\pm, \hat{V}_m] &= \sqrt{j(j+1) - m(m \pm 1)}\hat{V}_{m\pm 1}
\end{aligned}
$$

where $j = 1$ and $m = 0, \pm 1$. $\hat{V}_{m_1} |j_2, m_2\rangle$ for any j_2 and m_2 transform under rotation in the same way as a state $|j_1 = 1, m_1\rangle \otimes |j_2, m_2\rangle$. This directly follows from the above commutation relation:

$$
\begin{aligned}
&\hat{J}_z\hat{V}_{m_1} |j_2, m_2\rangle \\
=&(\hat{V}_{m_1}\hat{J}_z + m_1\hat{V}_{m_1}) |j_2, m_2\rangle \\
=&(m_1 + m_2)\hat{V}_{m_1} |j_2, m_2\rangle
\end{aligned}
$$

The result is the same as $\hat{J}_z |j_1 = 1, m_1\rangle \otimes |j_2, m_2\rangle$. Similar result can be found with acting $\hat{J}_\pm$ on $\hat{V}_{m_1} |j_2, m_2\rangle$.
$\Rightarrow$ Acting with $\hat{V}_m$ on $|j_2, m_2\rangle$ is akin to adding angular momentum of unit 1 to the state $|j_2, m_2\rangle$.

8.2 Tensor Operator

A set of operators $\hat{O}_{j,m}$ with $m = -j, -j+1, \ldots, j-1, j$ that satisfy,

$$
\begin{aligned}
[\hat{J}_z, \hat{O}_{j,m}] &= m\hat{O}_{j,m} \\
[\hat{J}_\pm, \hat{O}_{j,m}] &= \sqrt{j(j+1) - m(m+1)}\hat{O}_{j,m\pm 1}
\end{aligned}
$$

Therefore, a vector operator is just a special case of a tensor operator with $j = 1$. Similarly, $\hat{O}_{j_1,m_1} |j_2, m_2\rangle$ transforms under rotation in the same way as $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$.

8.3 Wigner-Eckart Theorem

9 Perturbation Theory

9.1 Non-degenerate perturbation theory

If the "target" state is separated from any nearby state $|\beta\rangle$ by a gap, $\Delta = |E_\beta - E_\alpha| >> \lambda \langle\alpha| H_1 |\beta\rangle$, it can be dealt with non-degenerate perturbation theory.

System Hamiltonian $H = H_0 + \lambda H_1$, λ is a small number. Unperturbed states $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$, corresponding perturbed states are $|a\rangle, |b\rangle, |c\rangle$.

$$|a\rangle = c_\alpha |\alpha\rangle + \sum_{\alpha\neq\beta} d_\beta |\beta\rangle \qquad \text{(eq.8.1.1)}$$

$$H_0 |\alpha\rangle = E_\alpha |\alpha\rangle$$

$$H |a\rangle = E_a |a\rangle \qquad \text{(eq.8.1.2)}$$

And $\lambda \to 0$,

$$|a\rangle \to |\alpha\rangle$$

$$E_a \to E_\alpha$$

Here, $|\beta\rangle$ represents all the states in addition to $|\alpha\rangle$. One can expect c_α to be much larger than d_β, since $|a\rangle$ is just the perturbated state of $|\alpha\rangle$, which should be mainly composed of $|\alpha\rangle$.

Act $\langle\beta| H$ on both sides of (Eq. 8.1.1),

$$\langle\beta| (H_0 + \lambda H_1) |a\rangle = \langle\beta| (H_0 + \lambda H_1) \left(c_\alpha |\alpha\rangle + \sum_{\beta'\neq\alpha} d_{\beta'} |\beta'\rangle \right)$$

$$d_\beta E_a = d_\beta E_\beta + \lambda c_\alpha \langle\beta| H_1 |\alpha\rangle + \lambda \sum_{\beta'\neq\alpha} d_{\beta'} \langle\beta| H_1 |\beta'\rangle$$

d_β for $\beta \neq \alpha$ is $O(\lambda)$, the last term on RHS is $O(\lambda^2)$

$$\begin{aligned} d_\beta &= \frac{\lambda c_\alpha \langle\beta| H_1 |\alpha\rangle}{E_a - E_\beta} + \frac{\lambda \sum_{\beta' \neq \alpha} d_{\beta'} \langle\beta| H_1 |\beta'\rangle}{E_a - E_\beta} \\ &= \frac{\lambda c_\alpha \langle\beta| H_1 |\alpha\rangle}{E_a - E_\beta} + O(\lambda^2) \end{aligned}$$

$|c_\alpha^2| + \sum_{\beta' \neq \alpha} d_{\beta'}^2 = 1$, $\Rightarrow |c_\alpha| = 1 - O(\lambda^2)$. One may choose $c_\alpha = 1$.

$$\begin{aligned} &\Rightarrow d_\beta = \frac{\lambda \langle\beta| H_1 |\alpha\rangle}{E_a - E_\beta} + O(\lambda^2) \\ &\Rightarrow |a\rangle = |\alpha\rangle + \lambda \sum_{\beta \neq \alpha} |\beta\rangle \frac{\langle\beta| H_1 |\alpha\rangle}{E_a - E_\beta} + O(\lambda^2) \end{aligned}$$

Combining eq.8.1.2

$$\Rightarrow E_a |a\rangle = (H_0 + \lambda H_1)(c_\alpha |\alpha\rangle + \lambda \sum_{\beta \neq \alpha} |\beta\rangle \frac{\langle\beta| H_1 |\alpha\rangle}{E_a - E_\beta} + O(\lambda^2))$$

Choose $c_\alpha = 1$, and act $\langle\alpha|$ on both sides

$$\Rightarrow E_a = E_\alpha + \lambda \langle\alpha| H_1 |\alpha\rangle + \lambda^2 \sum_{\beta \neq \alpha} \frac{|\langle\beta| H_1 |\alpha\rangle|^2}{E_a - E_\beta}$$

Since $E_a = E_\alpha + O(\lambda)$, replace E_a by E_α in the denominator on RHS.

$$\begin{aligned} E_a &= E_\alpha + \lambda \langle\alpha| H_1 |\alpha\rangle + \lambda^2 \sum_{\beta \neq \alpha} \frac{|\langle\beta| H_1 |\alpha\rangle|^2}{E_\alpha - E_\beta} + O(\lambda^3) \\ |a\rangle &= |\alpha\rangle + \lambda \sum_{\beta \neq \alpha} |\beta\rangle \frac{\langle\beta| H_1 |\alpha\rangle}{E_\alpha - E_\beta} + O(\lambda^2) \end{aligned}$$

9.2 Example

$$H = \frac{X^2 + P^2}{2} - FX$$

9.3 Degenerate Perturbation Theory

If $\lambda \langle\alpha| H_1 |\beta\rangle$ is of the same of order of $E_\alpha - E_\beta$, state $|\alpha\rangle$ and state $|\beta\rangle$ are close.

Interested degenerate states belong to sub-Hilbert space D, labeled as $\{|\alpha\rangle, |\beta\rangle, \cdots\}$. The degenerate states far away from interested states are called $\{|\mu\rangle, |\Delta\rangle, |\lambda\rangle \cdots\}$. Perturbed states are $\{|a\rangle, |b\rangle, \cdots\}$.

$$\text{Perturbed states: } |a\rangle = \sum_{\alpha\in D} c_\alpha |\alpha\rangle + \sum_{\mu\notin D} d_\mu |\mu\rangle$$

Deriving d_μ

$$\begin{aligned}
\langle\mu| E_a |a\rangle &= \langle\mu| H |a\rangle \\
d_\mu E_a &= \langle\mu| (H_0 + \lambda H_1)(\sum_{\alpha\in D} c_\alpha |\alpha\rangle + \sum_{\mu'\notin D} d_{\mu'} |\mu'\rangle) \\
d_\mu E_a &= d_\mu E_\mu + \lambda \sum_{\alpha\in D} \langle\mu| H_1 |\alpha\rangle c_\alpha + \lambda \sum_{\mu'\notin D} \langle\mu| H_1 |\mu'\rangle d_{\mu'}
\end{aligned}$$

Keeping $O(\lambda)$ term,

$$\Rightarrow d_\mu = \frac{\lambda \sum_{\alpha\in D} c_\alpha \langle\mu| H_1 |\alpha\rangle}{E_a - E_\mu}$$

To the leading order, E_a =mean energy of levels within D $\equiv \bar{E}_D$.

$$\Rightarrow d_\mu = \frac{\lambda \sum_{\alpha\in D} c_\alpha \langle\mu| H_1 |\alpha\rangle}{\bar{E}_D - E_\mu}$$

Deriving c_β

$$\begin{aligned}
\langle\beta| E_a |a\rangle &= \langle\beta| H |a\rangle \\
c_\beta E_a &= \langle\beta| (H_0 + \lambda H_1)(\sum_{\alpha\in D} c_\alpha |\alpha\rangle + \sum_{\mu\notin D} d_\mu |\mu\rangle) \\
c_\beta E_a &= c_\beta E_\beta + \lambda \sum_{\alpha\in D} \langle\beta| H_1 |\alpha\rangle c_\alpha + \lambda \sum_{\mu\notin D} \langle\beta| H_1 |\mu\rangle d_\mu \\
c_\beta E_a &= c_\beta E_\beta + \lambda \sum_{\alpha\in D} \langle\beta| H_1 |\alpha\rangle c_\alpha + \lambda^2 \sum_{\alpha\in D} c_\alpha \sum_{\mu\notin D} \frac{\langle\beta| H_1 |\mu\rangle \langle\mu| H_1 |\alpha\rangle}{\bar{E}_D - E_\mu}
\end{aligned}$$

Effective Hamiltonian for subspace D

$$\langle\beta| H_{eff} |\alpha\rangle = \langle\beta| H_0 |\alpha\rangle + \lambda \langle\beta| H_1 |\alpha\rangle + \lambda^2 \sum_{\mu \notin D} \frac{\langle\beta| H_1 |\mu\rangle \langle\mu| H_1 |\alpha\rangle}{\bar{E}_D - E_\mu}$$

H_{eff} has eigenstates $|\psi\rangle = \sum_\alpha c_\alpha |\alpha\rangle$, corresponding Schrodinger equation is $H_{eff} |\psi\rangle = E_a |\psi\rangle$

10 Hydrogen Atom

The Hamiltonian under relative coordinate:

$$H_0 = \frac{P^2}{2m} - \frac{e^2}{r}$$

where m is the reduced mass, r is the distance between electron and nuclear.

$$\begin{aligned}
&\text{Born radius: } a_0 = \frac{\hbar^2}{me^2} \sim 53 \text{ pm} \\
&\text{Energy: } E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} \\
&\text{Fine structure constant: } \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \\
&\frac{e^2}{2a_0} = \frac{me^4}{2\hbar^2} = \frac{m\alpha^2 c^2}{2} \\
&\Rightarrow E_n = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{n^2} \\
&P \sim \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = m(\alpha c)
\end{aligned}$$

10.1 Fine Structure

10.1.1 Pauli Equation

Magnetic momentum $\vec{\mu}$ of an electron:

$$\vec{\mu} = g\frac{e}{2mc}\vec{S}$$

For electrons, $g = 2$

$$\vec{\mu} = 2\left(-\frac{e}{2mc}\right)\frac{\hbar}{2}\hat{\sigma} = -\frac{e\hbar}{2mc}\hat{\sigma}$$

With an external magnetic field B_{ext},

$$H = -\vec{\mu}\cdot\vec{B} = \frac{e\hbar}{2mc}\hat{\sigma}\cdot\vec{B}$$

10.1.2 Darwin Term

It is caused by charge distribution. One cannot continue regarding electron as an pure point charge. It only affects $l = 0$.

$$\frac{\hbar^2}{8m^2c^2}\nabla^2 V$$

10.1.3 Relativistic Term

The Hamiltonian is

$$H = \sqrt{\hat{\mathbf{P}}^2 c^2 + m^2 c^4} \sim H_0 - \frac{\hat{\mathbf{P}}^4}{8m^3c^2}$$

Evaluation of the correction on total energy,

$$\begin{aligned}
E_{nlm_l}^{(1)\,rel} &= -\frac{1}{8m^3c^2}\left\langle \psi_{nlm_l}\right| \hat{\mathbf{P}}^4 \left|\psi_{nlm_l}\right\rangle \\
&= -\frac{1}{8m^3c^2}\left\langle \hat{\mathbf{P}}^2\psi_{nlm_l}\middle|\hat{\mathbf{P}}^2\psi_{nlm_l}\right\rangle \\
&= -\frac{1}{2mc^2}\left\langle (E_n - V(r))\psi_{nlm_l}\middle|(E_n - V(r))\psi_{nlm_l}\right\rangle
\end{aligned}$$

in the second step we use the fact that $\hat{\mathbf{P}}^2$ is Hermitian. In the last step, using the fact that $(\frac{\hat{\mathbf{P}}^2}{2m} + V(r))\psi_{nlm_l} = E_n\psi_{nlm_l}$.

It is diagonal, since $[\hat{\mathbf{P}}^4, \vec{L}^2] = 0$ and $[\hat{\mathbf{P}}^4, L_z] = 0$.

Further write as

$$E_{nlm_l}^{(1)\,rel} = -\frac{1}{8}\alpha^4(mc^2)\left[\frac{4n}{l+\frac{1}{2}} - 3\right]$$

Uncoupled basis: $\{|nlm_l m_s\rangle\}$

Coupled basis: $\{|nljm_j\rangle\}$

10.1.4 Spin-Orbit Coupling Term

Leading by the interaction between the magnetic field generated by proton and the electron's magnetic dipole. The Hamiltonian is

$$H_{spin-orbit} = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$

Notice that $\frac{\vec{S}\cdot\vec{L}}{r^3}$ commutes with $\vec{L}^2$, $\vec{J}^2$, J_z. One can use coupled basis to diagonalize the Hamiltonian. Energy correction:

$$\begin{aligned}
E^{(1)}_{nljm_j} &= \frac{e^2}{2m^2c^2}\langle nljm_j|\frac{\vec{S}\cdot\vec{L}}{r^3}|nljm_j\rangle \\
&= \frac{e^2\hbar^2}{4m^2c^2}\left(j(j+1)-l(l+1)-\frac{3}{4}\right)\underbrace{\langle nljm_j|\frac{1}{r^3}|nljm_j\rangle}_{\frac{1}{n^3a_0^3l(l+1)(l+\frac{1}{2})}} \\
&= \frac{(E^{(0)}_n)^2}{mc^2}\frac{n[j(j+1)-l(l+1)-\frac{3}{4}]}{l(l+\frac{1}{2})(l+1)}
\end{aligned}$$

10.1.5 Fine-Structure Corrections

$$E^{(1)}_{nljm_j} = -\alpha^4(mc^2)\frac{1}{2n^4}\left[\frac{n^7}{j+\frac{1}{2}}-\frac{3}{4}\right]$$

$\vec{J}^2 = (\vec{L}+\hat{\sigma})^2$

$[\vec{L},\hat{\sigma}] = 0$

$[\vec{L}_z,\hat{\sigma}_z] \neq 0$

An additional quantum number n compare with addition of angular momentum.

$$H = \sum_{n,j,l,m_J} E(n,j)\,|n,j,l,m_J\rangle\langle n,j,l,m_J|$$

This is called fine structure.

$$E(n,j) = -\frac{\alpha^2 m_e}{n^2} - \frac{\alpha^4 m_e}{2n^3}[\frac{-3}{4n}+\frac{1}{j+\frac{1}{2}}]$$

Contributions: (1). $\frac{P^2}{2m}$(non-relativistic) $\rightarrow \sqrt{p^2+m^2}$(relativistic), (2). $\hat{\sigma}\cdot\vec{L}$(spin-orbit coupling), (3). $l=0$(Darwin-term)$\propto|\Psi(r=0)|^2$

Correction due to dispersion:

$$H = \sqrt{p^2 + m^2} - m - \frac{e^2}{r} \approx \frac{p^2}{2m} - \frac{e^2}{r} - \frac{p^4}{8m^3} + \ldots \text{(expansion in } \frac{1}{m})$$

$$\delta E(nlm_l m_s) = \frac{-1}{8m^3} \langle nlm_l m_s | P^4 | nlm_l m_s \rangle$$

$$\propto \frac{-1}{m} \langle (\frac{P^2}{2m})^2 \rangle \propto \ldots$$

$$\delta E_{Spin-orbit} \propto \langle (\frac{\hat{\sigma} \cdot \vec{L}}{r^3}) \rangle e^2$$

$$\propto \langle (\frac{1}{r^3}) \alpha \rangle$$

$$\langle (\frac{-e^2}{r}) \rangle \propto \alpha^2 m$$

$$\Rightarrow \langle (\frac{1}{r}) \rangle \propto \alpha m$$

$$\langle \frac{P^2}{2m} - \frac{-e^2}{r} \rangle \propto \frac{\alpha^2 m}{n^2}$$

$[\vec{J}^2, \hat{\sigma} \cdot \vec{L}] = 0 = [\hat{\sigma}^2, \hat{\sigma} \cdot \vec{L}]$, which makes $\hat{\sigma} \cdot \vec{L}$ a good quantum number.

10.2 Zeeman effect

The Zeeman effect is the effect of splitting of a spectral line into several components in the presence of a static magnetic field. The Hamiltonian of Zeeman effect is composed of two parts (the magnetic momentum associated with the orbital motion and the magnetic momentum associated with the spin motion):

$$H_{\text{Zeeman}} = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B} = \frac{e}{2mc}(\vec{L} + 2\vec{S}) \cdot \vec{B}$$

Take the direction of magnetic field as the z-axis.

$$H_{\text{Zeeman}} = \frac{e}{2mc}(L_z + 2S_z)B$$

The full Hamiltonian of Hydrogen atom becomes:

$$H = H_0 + H_{\text{fs}} + H_{\text{Zeeman}}$$

where H_{fs} is the fine structure term, composed of relativistic term, the Darwin term and the spin-orbit coupling term.

From fine structure, one knows there is something like an internal magnetic field, responsible for spin-orbit coupling.

First, consider the case that the external field is much weaker than that, weak Zeeman effect case, which means H_{fs} weighs larger than H_{Zeeman}. H_{Zeeman} is treated as perturbation. $H_0 + H_{\text{fs}}$ should be thought as known Hamiltonian.

On the contrary, if $B \gg B_{\text{int}}$. $H_0 + H_{\text{Zeeman}}$ now is the known Hamiltonian, and H_{fs} becomes the perturbation.

10.2.1 Weak Field Zeeman

The approximate eigenstates of $H_0 + H_{\text{Zeeman}}$ are $|nljm_j\rangle$, with eigenvalue $E(n, j)$. Degeneracy occurs among the states with the same n and j but different l and m_j.

So, one may need to consider matrix element $\langle nljm_j| H_{\text{Zeeman}} \left|nl'jm_j'\right\rangle$

$\vec{L}^2$ commutes with L_z and obviously commutes with S_z

$$\Rightarrow [\vec{L}^2, H_{\text{Zeeman}}] = 0$$

$$\langle nljm_j|\vec{L}^2 \left|nl'jm_j'\right\rangle = l(l+1)\delta_{l,l'} \Rightarrow l = l'$$

Similarly, $J_z = L_z + S_z$ commutes with H_{Zeeman}

$\Rightarrow m_j = m_j'$

Only diagonal terms left.

$$\begin{aligned} E^{(1)}_{nljm_j} =& \frac{e}{2mc} B \langle nljm_j| (L_z + 2S_z) |nljm_j\rangle \\ =& \frac{e}{2mc} B \langle nljm_j| (J_z + S_z) |nljm_j\rangle \\ =& \frac{e}{2mc} B(\hbar m_j + \langle nljm_j| S_z |nljm_j\rangle) \end{aligned}$$

Recap the concept of vector operator.

Obviously, $[J_i, S_j] = i\hbar\varepsilon_{ijk}S_k$, indicating that $\vec{S}$ is a vector operator under $\vec{J}$. An important property of vector operator is:

$$\frac{1}{\alpha}[\vec{J}^2, [\vec{J}^2, \vec{S}]] = (\vec{S} \cdot \vec{J})\vec{J} - \frac{1}{2}(\vec{J}^2\vec{S} + \vec{S}\vec{J}^2)$$

where α is some constant (I think it is $-4\hbar^2$). With this, one can derive projection lemma. First consider LHS.

$$\begin{aligned}
\langle jm_j| LHS |jm_j\rangle &= \langle jm_j| [\vec{J}^2, [\vec{J}^2, \vec{S}]] |jm_j\rangle \\
&= \langle jm_j| \vec{J}^2[\vec{J}^2, \vec{S}] |jm_j\rangle - \langle jm_j| [\vec{J}^2, \vec{S}]\vec{J}^2 |jm_j\rangle \\
&= \langle jm_j| [\vec{J}^2, \vec{S}] |jm_j\rangle (j(j+1)\hbar^2 - j(j+1)\hbar^2) = 0
\end{aligned}$$

Here, the constant is ignored, which is irrelevant.

$$\begin{aligned}
\langle jm_j| RHS |jm_j\rangle = 0 &= \langle jm_j| (\vec{S} \cdot \vec{J})\vec{J} |jm_j\rangle - \frac{1}{2}\langle jm_j| (\vec{J}^2\vec{S} + \vec{S}\vec{J}^2) |jm_j\rangle \\
&= \langle jm_j| (\vec{S} \cdot \vec{J})\vec{J} |jm_j\rangle - \hbar^2 j(j+1) \langle jm_j| \vec{S} |jm_j\rangle
\end{aligned}$$

where $\hbar^2 j(j+1) = \langle J^2\rangle_j$, and $\langle jm_j| \vec{S} |jm_j\rangle$ is just $\langle \vec{S}\rangle_j$

$$\Rightarrow \langle \vec{S}\rangle_j = \frac{\langle(\vec{S} \cdot \vec{J})\vec{J}\rangle_j}{\langle J^2\rangle_j}$$

This relation is valid for any vector operator over $\vec{J}$. And,

$$\vec{S} \cdot \vec{J} = \frac{1}{2}(J^2 + S^2 - L^2)$$

One can deduce,

$$\begin{aligned}
\langle nljm_j| S_z |nljm_j\rangle &= \frac{\hbar m_j}{\hbar^2 j(j+1)} \langle nljm_j| \vec{S} \cdot \vec{J} |nljm_j\rangle \\
&= \frac{\hbar m_j}{\hbar^2 j(j+1)} \frac{\hbar^2}{2}[j(j+1) + \frac{3}{4} - l(l+1)] \\
&= \frac{\hbar m_j[j(j+1) + \frac{3}{4} - l(l+1)]}{2j(j+1)}
\end{aligned}$$

Put it back to the energy,

$$
\begin{aligned}
E^{(1)}_{nljm_j} &= \frac{e}{2mc}B(\hbar m_j + \langle nljm_j|\, S_z\, |nljm_j\rangle) \\
&= \frac{e\hbar m_j}{2mc}B\underbrace{\left[1 + \frac{j(j+1)+\frac{3}{4}-l(l+1)}{2j(j+1)}\right]}_{g_J(e)\text{ Lande g factor}} \\
&= \frac{e\hbar}{2mc}g_J(e)Bm_j
\end{aligned}
$$

10.2.2 Strong Field Zeeman

The Hamiltonian becomes:

$$H = \underbrace{H_0 + \frac{e}{2mc}(\hat{L}_z + 2\hat{S}_z)B}_{H^{(0)}} + \underbrace{H_f s}_{H^{(1)}}$$

Since H_0 is invariant under rotation, it commutes with any angular momentum. $[H_0, \hat{L}_z + 2\hat{S}_z] = 0$, they can be diagonalized simultaneously.

Take the eigenstates:

$$|nlm_l m_s\rangle$$

With eigenvalues:

$$E^{(0)}_n + \frac{e\hbar}{2mc}B(m_l + m_s)$$

$$
\begin{aligned}
n = 1 \quad l = 0 \quad \vec{J} = \hat{\sigma} + \vec{L} = 0 \\
\left| n = 1, j = \frac{1}{2}, l = 0, m_J = \pm\frac{1}{2} \right\rangle \\
\Delta E = 2\mu_B B m_J
\end{aligned}
$$

$$
\begin{aligned}
&n = 2 \qquad l = 0, 1, \ldots, n-1 \\
&\left| n = 2, l = 0, j = \frac{1}{2}, m_J = \pm\frac{1}{2} \right\rangle \\
&\left| n = 2, l = 1, j = \frac{1}{2}, m_J = \pm\frac{1}{2} \right\rangle \\
&\left| n = 2, l = 1, j = \frac{3}{2}, m_J = \pm\frac{3}{2},\ \pm\frac{1}{2} \right\rangle
\end{aligned}
$$

$$
\begin{aligned}
&\langle l, j, m_J|\, 2\hat{\sigma}_z + \hat{L}_z \,|l', j', m_J'\rangle \\
&= m_J ... wtf
\end{aligned}
$$

Selection rules:

$$m_J = m_J'$$

$|l - l'|$ must be even, i.e. 0, 2, 4...

$|j - j'|$ must be 0 or 1

10.3 Stark Effect

$H_1 = e\varepsilon\hat{z}$ for z direction electric field.

Selection rules $|l - l'| = 1 \mod 2$, i.e. 1, 3, 5..., $m_j = m_j'$

11 Variational Principle

Consider an arbitrary state $|\Psi\rangle$ in the Hilbert space

$|\Psi\rangle H |\Psi\rangle \geq E_0$

when equality is taken $|\Psi\rangle = |E_0\rangle$

$|\Psi\rangle = \sum C_n |E_n\rangle$

$$\begin{aligned}
&\frac{\langle\Psi| H |\Psi\rangle}{\langle\Psi|\Psi\rangle} - E_0 \\
=&\frac{\sum |C_n|^2 E_n}{\sum |C_n|^2} - E_0 \\
=&\frac{\sum |C_n|^2 (E_n - E_0)}{\sum |C_n|^2} \geq 0
\end{aligned}$$

$$\begin{aligned}
&\langle\Psi_v| H |\Psi_v\rangle = xE_0 \\
=&|C_0|^2 E_0 + \sum_{n=1} |C_n|^2 E_1 \\
=&|C_0|^2 E_0 + (1 - |C_0|^2) E_1 \\
=&-|C_0|^2 (E_1 - E_0) + E_1 \\
\Rightarrow&|C_0|^2 = \frac{E_1 - xE_0}{E_1 - E_0} \geq 0
\end{aligned}$$

12 Landau Level

Two-dimensional particle in magnetic field (z-direction) question.

$H = \frac{(\hat{\mathbf{P}} - e\mathbf{a})^2}{2m}$, $\vec{D} \times \mathbf{a} = \vec{B}$

Energy difference: $\omega_c = \frac{B}{m}$, degeneracy: $N = \frac{BL_xL_y}{\phi_0}$, $\phi_0 = \frac{h}{e}$

Good basis $\{|n, m\rangle\}$(m, angular momentum; n, Landau level).

Choose $\mathbf{a} = B(-y, 0) = -B_y\hat{\mathbf{X}}$

$\Rightarrow H = \frac{1}{2m}[(P_x + B_y)^2 + P_y^2]$