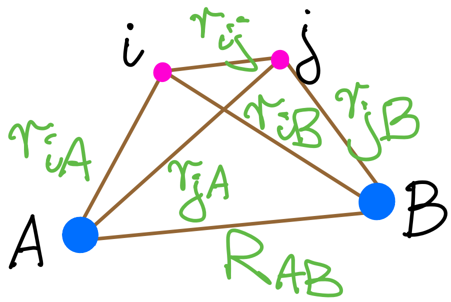
# MANY-BODY PROBLEM IN CHEMISTRY




$$i, j, \ldots = 1, \ldots, N$$

$$A, B, \ldots = 1, \ldots, M$$

$$\boxed{\begin{array}{c} i\hbar \dfrac{\partial \Psi}{\partial t} = \mathcal{H} \Psi \\[2ex] \mathcal{H} \Psi = \mathcal{E} \Psi \end{array}}$$

$$\hbar = \frac{h}{2\pi}$$

$$\mathcal{H} = T_e + T_n + V_{ee} + V_{en} + V_{nn}$$

$$T_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \Delta_i$$

$$\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

$$T_n = -\sum_{A=1}^{M} \frac{\hbar^2}{2M_A} \Delta_A$$

$$\Delta_A = \frac{\partial^2}{\partial X_A^2} + \frac{\partial^2}{\partial Y_A^2} + \frac{\partial^2}{\partial Z_A^2}$$

$$V_{ee} = \sum_{1=i<j}^{N} \frac{e^2}{r_{ij}}$$

$$V_{en} = -\sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A e^2}{r_{iA}}$$

$$V_{nn} = \sum_{1=A<B}^{M} \frac{Z_A Z_B e^2}{R_{AB}}$$

$$\Psi = \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N,\mathbf{R}_1,\dots,\mathbf{R}_M)$$

$(x_1, y_1, z_1, \sigma_1)$

$X_1, Y_1, Z_1$

$$|\sigma\rangle = \begin{cases} |\tfrac{1}{2},\tfrac{1}{2}\rangle = |\alpha\rangle & \text{spin-up}\\ |\tfrac{1}{2},-\tfrac{1}{2}\rangle = |\beta\rangle & \text{spin-down}\end{cases}$$

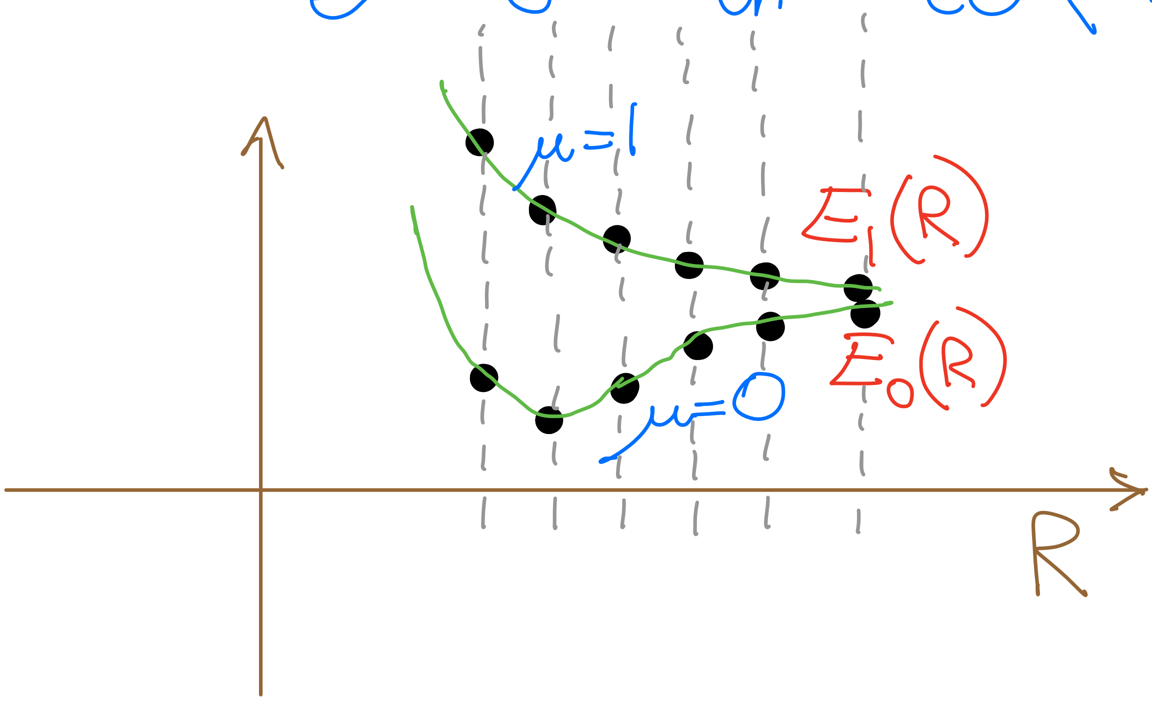
$$\Psi = \Psi(\mathbf{X},\mathbf{R})$$

$$\checkmark\checkmark \quad \Psi(\underset{\sim}{X},\underset{\sim}{R}) = \underbrace{\Psi_{\underset{\sim}{R}}(\underset{\sim}{X})}_{\text{electronic}}\,\underbrace{\chi(\underset{\sim}{R})}_{\text{nuclear}}$$

$$\chi(\underset{\sim}{R}) \to \chi(\underset{\sim}{R},t)$$

$$\checkmark \quad H_e\,\Psi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X}) = E_\mu(\underset{\sim}{R})\,\Psi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X})$$

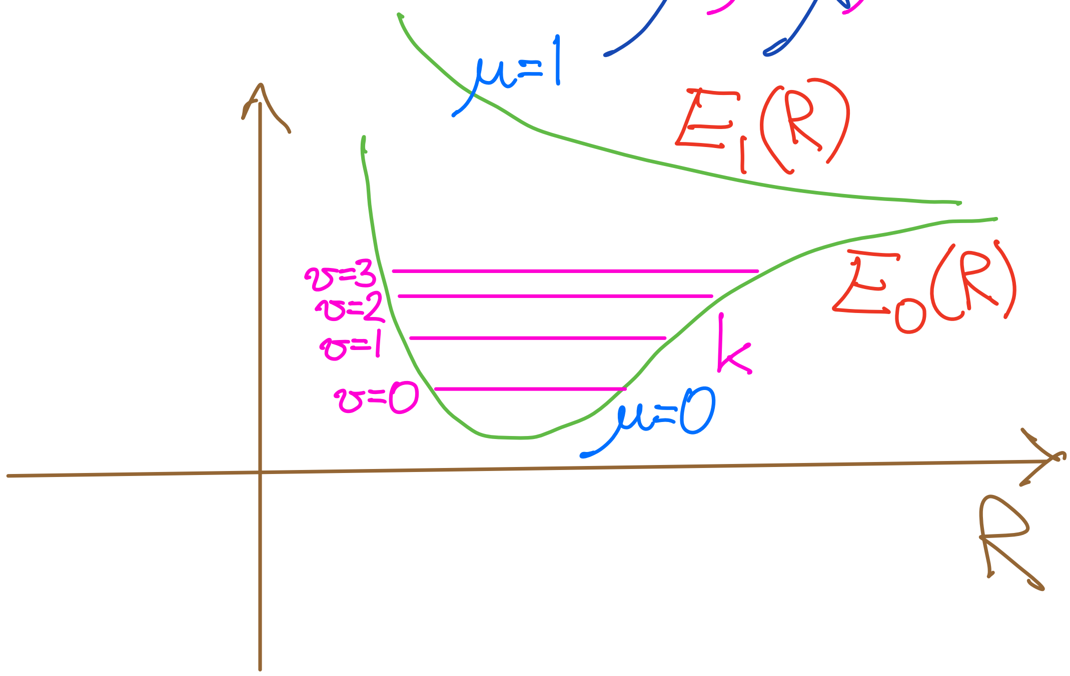
$$H_e = T_e + V_{en} + V_{ee}\;(+V_{nn})$$



$$\left[T_n + V_{nn} + E_\mu(\underset{\sim}{R})\right]\chi_{\mu,k}(\underset{\sim}{R})$$

vibrations, rotations

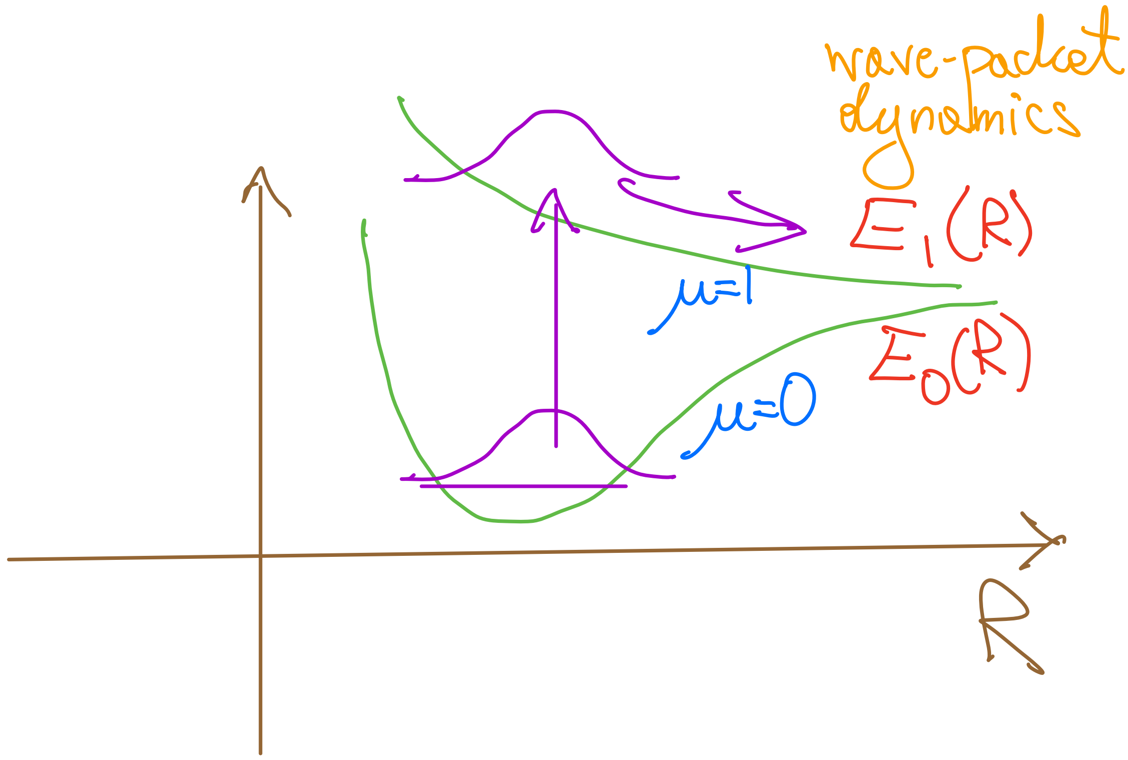
$$= \mathcal{E}_{\mu,k}\,\chi_{\mu,k}(\underset{\sim}{R})$$




TIME-DEPENDENT PROBLEM

$$i\hbar\,\frac{\partial \chi_\mu(\underset{\sim}{R},t)}{\partial t}$$

$$= \left[T_n + V_{nn} + E_\mu(\underset{\sim}{R})\right]\chi_\mu(\underset{\sim}{R},t)$$




In general,

$$\Psi(\underset{\sim}{X},\underset{\sim}{R}) = \sum_{\mu,k} \Phi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X})\,\chi_{\mu,k}(\underset{\sim}{R})$$

$\downarrow$ Born-Oppenheimer

$$\Phi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X})\,\chi_{\mu,k}(\underset{\sim}{R})$$

$$H_e \Psi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X}) = E_\mu(\underset{\sim}{R}) \Psi_{\mu,\underset{\sim}{R}}(\underset{\sim}{X})$$

$$H_e = T_e + V_{en} + V_{ee}$$

$$H_e = Z + V$$

$$Z = \sum_{i=1}^{N} \hat{z}(\underset{\sim}{x}_i) \quad \leftarrow \text{1-body}$$

$$\hat{z}(x_i) = -\frac{\hbar^2}{2m_e}\Delta_i - \sum_{A=1}^{M} \frac{Z_A e^2}{r_{iA}}$$

$$V = \sum_{1=i<j}^{N} \hat{v}(\underset{\sim}{x}_i, \underset{\sim}{x}_j)$$

$$\hat{v}(\underset{\sim}{x}_i, \underset{\sim}{x}_j) = \frac{e^2}{r_{ij}}$$

# MANY-FERMION WAVE FUNCTIONS

$$\Psi(\underset{\sim}{X}) = \Psi(\underset{\sim}{x}_1, \dots, \underset{\sim}{x}_N)$$

$$\Psi(\underset{\sim}{x}_2, \underset{\sim}{x}_1, \underset{\sim}{x}_3, \dots, \underset{\sim}{x}_N)$$

$$= -\Psi(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \underset{\sim}{x}_3, \dots, \underset{\sim}{x}_N)$$

$P, R, S, \dots \in S_N$ (group of permutations)

$$P = \begin{pmatrix} 1 & \dots & N \\ P_1 & \dots & P_N \end{pmatrix}$$ ← permutation

$$\Psi(x_{P_1}, \dots, x_{P_N})$$

$$= (-1)^P \, \Psi(x_1, \dots, x_N)$$

↑ sign of permutation P

✓

Example:

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 3 & 1 & 5 & 4 \end{pmatrix} = \underbrace{(123)}_{\text{even},+}\underbrace{(45)}_{\text{odd},-}$$

odd number

even number

$$(-1)^P \to -1$$ (minus: odd permutation)

## Single-particle states

$$\psi_p(x) = \langle x | \psi_p \rangle = \langle x | p \rangle$$

$$\{ |\psi_p\rangle \} \text{ or } \{ |p\rangle \}$$

$$\langle \psi_p | \psi_q \rangle \equiv \langle p | q \rangle = \delta_{pq}$$

$$\int \psi_p^*(x) \psi_q(x) \, dx$$

$$\psi(x) = \sum_p c_p \psi_p(x)$$

$$c_p = \langle \psi_p | \psi \rangle = \int \psi_p^*(x) \psi(x) \, dx$$

$$|\chi\rangle = \sum_p c_p |p\rangle$$

$$c_p = \langle p|\chi\rangle$$

In quantum chemistry, $|p\rangle$s are called spin-orbitals,

$|\alpha\rangle$ or $|\beta\rangle$

$$|\chi_p\rangle = |\varphi_p\rangle \otimes |\sigma_p\rangle$$

$$\chi_p(x) = \varphi_p(\vec{r})\,\sigma_p$$

$$\Psi(x_1,\dots,x_N) = \sum_{p_1,\dots,p_N} d_{p_1\dots p_N} \times \chi_{p_1}(x_1)\times\dots\times\chi_{p_N}(x_N)$$

$$d_{p_1\dots p_N} = \langle \chi_{p_1}\dots\chi_{p_N}|\Psi\rangle$$

$$= \int \chi_{p_1}^*(x_1)\dots\chi_{p_N}^*(x_N)\,\Psi(x_1,\dots,x_N)\,dx_1\dots dx_N$$

Idempotent anti-symmetrizer

$$\mathcal{A} = \frac{1}{N!} \sum_{Q \in S_N} (-1)^Q Q$$

$$\mathcal{A}^2 = \mathcal{A}, \quad \mathcal{A}^\dagger = \mathcal{A}$$

$$\mathcal{A} |\Psi\rangle = |\Psi\rangle$$

✓ $$|\Psi\rangle = \sum_{p_1 < \dots < p_N} c_{p_1 \dots p_N} |\Phi_{p_1 \dots p_N}\rangle$$

$$|\Phi_{p_1 \dots p_N}\rangle = \sqrt{N!}\, \mathcal{A} \underbrace{|\chi_{p_1} \cdots \chi_{p_N}\rangle}_{|\chi_{p_1}\rangle \otimes \dots \otimes |\chi_{p_N}\rangle}$$

✓ $$c_{p_1 \dots p_N} = \langle \Phi_{p_1 \dots p_N} | \Psi \rangle$$

$$|\Phi_{p_1 \dots p_N}\rangle = |\{p_1 \dots p_N\}\rangle$$

Slater determinant

$$|\Phi_{p_1 \cdots p_N}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{p_1}(x_1) & \cdots & \psi_{p_N}(x_N) \\ \psi_{p_2}(x_1) & \cdots & \psi_{p_2}(x_N) \\ & \cdots & \\ \psi_{p_N}(x_1) & \cdots & \psi_{p_N}(x_N) \end{vmatrix}$$

$|p\rangle$: $|1\rangle, |2\rangle, |3\rangle, \ldots$

$p = 1, 2, 3, \ldots$

$N=2$:

$$|\Phi_{12}\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) \\ \psi_2(x_1) & \psi_2(x_2) \end{vmatrix},$$

$|\Phi_{13}\rangle, |\Phi_{14}\rangle, \ldots, |\Phi_{23}\rangle,$

$|\Phi_{24}\rangle, \ldots, |\Phi_{34}\rangle, \ldots$

$$|\Phi_{p_2 p_1 p_3 \cdots p_N}\rangle = -|\Phi_{p_1 p_2 p_3 \cdots p_N}\rangle,$$

etc.

$$c_{p_2 p_1 p_3 \cdots p_N} = -c_{p_1 p_2 p_3 \cdots p_N}$$

$$\langle \Phi_{p_1 \cdots p_N} | \Phi_{q_1 \cdots q_N} \rangle = \delta_{p_1 q_1} \cdots \delta_{p_N q_N}$$

for $p_1 < \cdots < p_N$, $q_1 < \cdots < q_N$

$$|\Phi_{p p p_3 \cdots p_N}\rangle = -|\Phi_{p p p_3 \cdots p_N}\rangle = 0$$

$$c_{p p p_3 \cdots p_N} = 0$$

# OCCUPATION NUMBER REPRESENTATION

$|1\rangle, |2\rangle, |3\rangle, \ldots$

$p = 1, 2, 3, \ldots$

$$|\Phi_{p_1 \ldots p_N}\rangle \equiv |\{p_1 \ldots p_N\}\rangle$$

$$|0 \ldots 0 \underset{\underset{p_1}{\uparrow}}{1} 0 \ldots 0 \underset{\underset{p_2}{\uparrow}}{1} 0 \ldots 0 \underset{\underset{p_N}{\uparrow}}{1} 0 \ldots\rangle$$

$$|n_1 n_2 \ldots n_p \ldots\rangle, \quad n_p = 0 \text{ or } 1$$

$$\mathcal{F} = \mathrm{Span}\{|n_1 \ldots n_p \ldots\rangle, n_p = 0, 1\}$$

FOCK SPACE

N-fermion Hilbert space:

$$\mathcal{H}_N = \text{Span}\{|n_1 \ldots n_p \ldots\rangle, n_p = 0,1, \sum_{n_p} n_p = N\}$$

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N$$

$$|\Phi_{1,2,7,10}\rangle = |\{\chi_1 \chi_2 \chi_7 \chi_{10}\}\rangle$$

$$= |1100000100100\ldots\rangle$$

# CREATION AND ANNIHILATION OPERATORS

Annihilation operators

$$X_p |\ldots n_p \ldots\rangle$$

$$= (-1)^m n_p |\ldots (1-n_p) \ldots\rangle$$

$$n_p = 0, 1$$

$$m = \sum_{k=1}^{p-1} n_k \quad \text{(number of occupied single-particle states preceding } p\text{)}$$

An alternative notation:

$$|\ldots p \ldots\rangle, \quad n_p = 1$$

$$|\ldots \cancel{p} \ldots\rangle, \quad n_p = 0$$

$$X_p |\ldots \overset{n_p=1}{p} \ldots\rangle = (-1)^m |\ldots \underset{n_p=0}{\cancel{p}} \ldots\rangle$$

$$X_p |\ldots \overset{n_p=0}{\cancel{p}} \ldots\rangle = 0$$

Example:

$$X_5 |\underbrace{0010}_{m=1}10110\ldots\rangle$$

$$= -|001000110\ldots\rangle$$

$$X_5 |\{3578\}\rangle$$

$$= - |\{378\}\rangle$$

Yet another definition:

$$X_p |\{p\, p_2 \cdots p_N\}\rangle$$

$$= |\{p_2 \cdots p_N\}\rangle$$

$$X_p |\{p_1\, p\, p_3 \cdots p_N\}\rangle$$

$$= - X_p |\{p\, p_1\, p_3 \cdots p_N\}\rangle$$

$$= - |\{p_1\, p_3 \cdots p_N\}\rangle$$

# Vacuum state

(TRUE VACUUM STATE)

$$|0\rangle = |000\ldots\rangle$$

$$\forall_p \quad n_p = 0 \quad \text{(all } n_p\text{s are zero)}$$

$$\langle 0|0\rangle = 1$$

$$\text{Span}\{|0\rangle\} = \mathcal{H}_0$$

single-particle states

$$|00\ldots 0p0\ldots\rangle \equiv |p\rangle$$

$$n_p = 1, \quad n_q = 0, \quad q \neq p$$

$$\forall_p \quad X_p|p\rangle = |0\rangle$$

$$X_p|0\rangle = 0$$

## Creation operators:

$$X_p|p\rangle = |0\rangle$$

$$\langle p|X_p^\dagger = \langle 0| \qquad |0\rangle$$

$$\langle p|\underbrace{X_p^\dagger|0\rangle}_{|p\rangle} = \langle 0|0\rangle = 1$$

(since $\langle p|q\rangle = \delta_{pq}$)

$$X_p^\dagger|0\rangle = |p\rangle$$

$$X_p^\dagger|\{p_1 p_2 \ldots p_N\}\rangle$$

$$= |\{p\, p_1 p_2 \ldots p_N\}\rangle$$

$$p < p_1 < p_2 < \ldots$$

$$X_p^\dagger |\{p_1 p_2 \cdots p_N\}\rangle$$

$$= |\{p\, p_1 p_2 \cdots p_N\}\rangle$$

$$= -|\{p_1\, p\, p_2 \cdots p_N\}\rangle$$

$$p_1 < p < p_2 < p_3 < \cdots$$

$$X_p^\dagger |\cdots \underset{n_p=0}{\cancel{p}} \cdots\rangle = (-1)^m |\cdots \underset{n_p=1}{p} \cdots\rangle$$

$$X_p^\dagger |\cdots \underset{n_p=1}{p} \cdots\rangle = 0$$

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$$X_p^\dagger |\cdots n_p \cdots\rangle$$

$$= (-1)^m (1-n_p) |\cdots (1-n_p) \cdots\rangle$$

$$(n_p = 0, 1)$$

# Number operator

$$\hat{N}_p = X_p^\dagger X_p$$

$$\hat{N}_p^\dagger = \hat{N}_p$$

$$\hat{N}_p | \ldots n_p \ldots \rangle = n_p | \ldots n_p \ldots \rangle$$

$n_p = 0, 1$

$$\sum_p \hat{N}_p = \hat{N} \leftarrow \text{total number operator}$$

$$\hat{N} | \Phi_{p_1 \ldots p_N} \rangle = N | \Phi_{p_1 \ldots p_N} \rangle$$

$$\hat{N} | \ldots n_p \ldots \rangle = \left( \sum_p n_p \right) \times | \ldots n_p \ldots \rangle$$

anticommutator $\rightarrow \{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$

$$\{X_p, X_q\} = X_p X_q + X_q X_p = 0$$

$$\{X_p^\dagger, X_q^\dagger\} = X_p^\dagger X_q^\dagger + X_q^\dagger X_p^\dagger = 0$$

$$\{X_p, X_q^\dagger\} = X_p X_q^\dagger + X_q^\dagger X_p = \delta_{pq}$$

Other properties:

- $X_p^2 = 0$, $(X_p^\dagger)^2 = 0$ (nilpotent)
- $$X_p X_q = - X_q X_p$$
  $$X_p^\dagger X_q^\dagger = - X_q^\dagger X_p^\dagger$$

In general,

$$X_{p_{R_1}} \cdots X_{p_{R_N}} = (-1)^R X_{p_1} \cdots X_{p_N}$$

$$R = \begin{pmatrix} 1 & \dots & N \\ R_1 & \cdots & R_N \end{pmatrix}$$

Similarly for $X^\dagger$s.

- $N_p^2 = N_p$, (idempotent)

$$N_p = X_p^\dagger X_p$$

$$N_p | \cdots n_p \cdots \rangle = n_p | \cdots n_p \cdots \rangle$$

$$n_p = 0, 1.$$

- $[N_p, N_q] = 0$

- $[X_p, N_q] = \delta_{pq} X_p$

$$[X_p^\dagger, N_q] = -\delta_{pq} X_p^\dagger$$

Example:

$$\langle \Phi_{pq} | \Phi_{rs} \rangle = \langle \{pq\} | \{rs\} \rangle$$

$$|\Phi_{pq}\rangle = |\{pq\}\rangle = X_p^\dagger |\{q\}\rangle = X_p^\dagger X_q^\dagger |0\rangle$$

$$|\Phi_{rs}\rangle = X_r^\dagger X_s^\dagger |0\rangle .$$

$$\langle \Phi_{pq} | \Phi_{rs} \rangle$$

try to relocate to the right-most position, since $X_p|0\rangle = 0$

$$= \langle 0 | X_q X_p X_r^\dagger X_s^\dagger |0\rangle$$

$$= \overset{\text{anticommutation rules}}{\cdots} = \langle p|r\rangle\langle q|s\rangle - \langle q|r\rangle\langle p|s\rangle$$

$$(\delta_{pr}\delta_{qs} - \delta_{qr}\delta_{ps})$$

$$= \begin{vmatrix} \langle p|r\rangle & \langle p|s\rangle \\ \langle q|r\rangle & \langle q|s\rangle \end{vmatrix}$$

If $p<q$ and $r<s$,

$$\langle \Phi_{pq} | \Phi_{rs} \rangle = \delta_{pr}\delta_{qs}$$

# OPERATORS IN SECOND QUANTIZATION:

In 1st quantization,

$$\hat{O} = \sum_{k=0}^{N} \hat{O}_k$$

k-body component

$$\hat{O}_k = \sum_{1=i_1<\dots<i_k}^{N} \hat{o}_k(x_{i_1},\dots,x_{i_k})$$

$$[\hat{O}, R] = 0 \quad \forall_{R \in S_N}$$

In particular,

$$\hat{o}_k(x_{i_{R_1}}, \dots, x_{i_{R_k}}) = \hat{o}_k(x_{i_1}, \dots, x_{i_k})$$

$R_1, \dots, R_k$: permutation of $1, \dots, k$

Examples:

$k=1$

$$\hat{Z} = \sum_{i=1}^{N} \hat{z}(x_i)$$

$k=2$

$$\hat{V} = \sum_{1 \leq i < j}^{N} \hat{v}(x_i, x_j)$$

$$[\hat{v}(x_j, x_i) = \hat{v}(x_i, x_j)]$$

$$\hat{H} = \hat{Z} + \hat{V}$$ ← example of $\hat{O} = \hat{O}_1 + \hat{O}_2$

Derivation of the second-quantized forms of many-body operators requires the following four lemmas:

Lemma 1:

$$|\Phi_{p_1 \ldots p_N}\rangle \equiv |\{p_1 \ldots p_N\}\rangle$$
$$= X^\dagger_{p_1} \ldots X^\dagger_{p_N} |0\rangle,$$
$$p_1 < \ldots < p_N$$

(ordered set of indices)

Lemma 2:

$$|\Phi_{q_1 \ldots q_N}\rangle \equiv |\{q_1 \ldots q_N\}\rangle$$
$$= X^\dagger_{q_1} \ldots X^\dagger_{q_N} |0\rangle$$

(ordered or not)

Isomorphism between

$\Phi_{p_1 \cdots p_N}(x_1, \ldots, x_N)$

and

$$X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$$

Lemma 3:

$$X_q X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$$

$$= \sum_{i=1}^{N} (-1)^{i-1} \delta_{q p_i}$$

$$\times X^\dagger_{p_1} \cdots X^\dagger_{p_{i-1}} X^\dagger_{p_{i+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$\prod X^\dagger |0\rangle = X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$$

$$\prod^{p_i} X^\dagger |0\rangle = X^\dagger_{p_1} \cdots X^\dagger_{p_{i-1}} X^\dagger_{p_{i+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$X^\dagger_{p_i}$ removed

$$X_q \prod X^\dagger |0\rangle = \sum_{i=1}^{N} (-1)^{i-1} \delta_{q p_i} \prod^{p_i} X^\dagger |0\rangle$$

Lemma 4:

Discussed in video 4.

(to be discussed during the next Zoom meeting)

Answers to questions:

Proof of lemma 1:

$$|\Phi_{p_1 p_2 \cdots p_N}\rangle = |\{p_1 p_2 \cdots p_N\}\rangle$$

$$= X^\dagger_{p_1} |\{p_2 \cdots p_N\}\rangle$$

$$= X^\dagger_{p_1} X^\dagger_{p_2} |\{p_3 \cdots p_N\}\rangle$$

$$= \cdots = X^\dagger_{p_1} X^\dagger_{p_2} \cdots X^\dagger_{p_{N-1}} |\{p_N\}\rangle$$

$$= X^\dagger_{p_1} X^\dagger_{p_2} \cdots X^\dagger_{p_{N-1}} X^\dagger_{p_N} |0\rangle$$

for $p_1 < p_2 < \cdots < p_N$

Proof of lemma 2:

$$|\Phi_{q_1 \cdots q_N}\rangle = |\Phi_{p_{R_1} \cdots p_{R_N}}\rangle$$

$$R = \begin{pmatrix} p_1 & \cdots & p_N \\ q_1 & \cdots & q_N \end{pmatrix} \quad (p_1 < p_2 < \cdots < p_N)$$

$$= (-1)^R |\Phi_{p_1 \cdots p_N}\rangle$$

$$\overset{\text{lemma 1}}{=} (-1)^R X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$$

$$= X^\dagger_{q_1} \cdots X^\dagger_{q_N} |0\rangle ,$$

since $X^\dagger_p X^\dagger_q = -X^\dagger_q X^\dagger_p$.