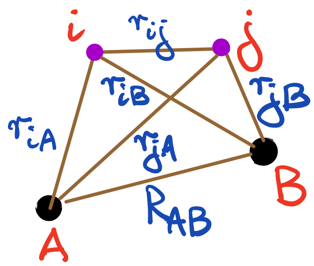
MANY-BODY PROBLEM IN CHEMISTRY

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H} \Psi$$



or

$$\mathcal{H} \Psi = \mathcal{E} \Psi$$

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

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

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

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

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

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

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

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

$$\Psi(\underset{\sim}{x}_1, \dots, \underset{\sim}{x}_N, \underset{\sim}{R}_1, \dots, \underset{\sim}{R}_M)$$

$$\underset{\sim}{x}_1 \to (x_1, y_1, z_1, \sigma_1)$$

$$\underset{\sim}{R}_1 \leftarrow X_1, Y_1, Z_1$$

$$|\sigma\rangle = \begin{cases} |\tfrac{1}{2}, \tfrac{1}{2}\rangle = |\alpha\rangle \\ |\tfrac{1}{2}, -\tfrac{1}{2}\rangle = |\beta\rangle \end{cases}$$

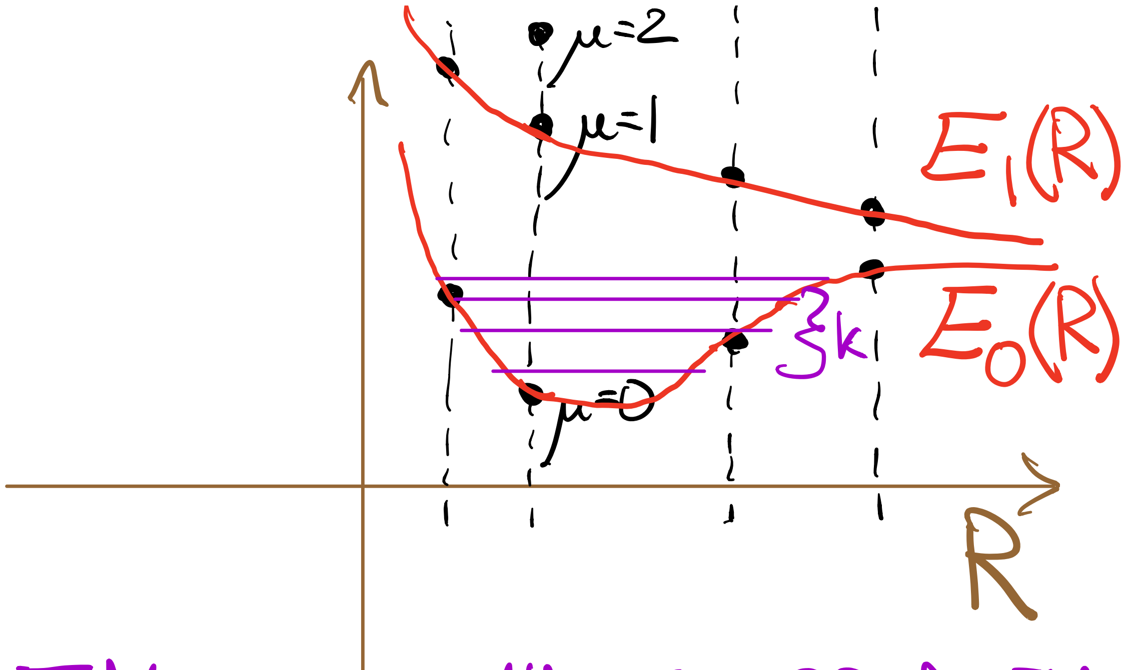
$$\to \Psi(\underset{\sim}{X}, \underset{\sim}{R})$$

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

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

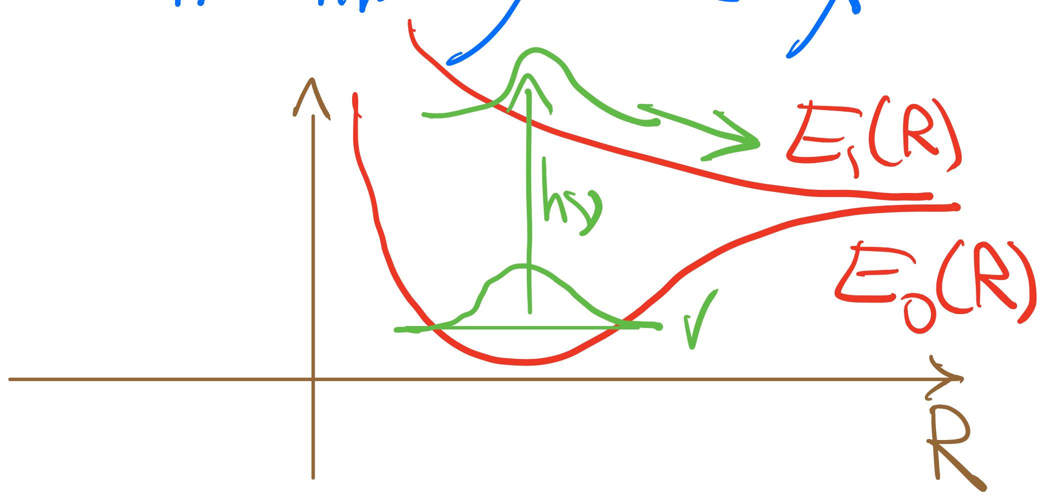
$$\checkmark \quad \Psi(\underset{\sim}{X},\underset{\sim}{R}) = \Psi_{\underset{\sim}{R}}(\underset{\sim}{X})\chi(\underset{\sim}{R})$$

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



TIME-DEPENDENT PROBLEM

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



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

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

$$H_e = Z + V$$

$$Z = \sum_{i=1}^{N} \hat{z}(\underset{\sim}{x}_i)$$

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

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

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

MANY-FERMION WAVE FUNCTIONS

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

anti-symmetric

$$\Psi(x_2, x_1, x_3, \ldots, x_N)$$

$$= -\Psi(x_1, x_2, x_3, \ldots, x_N)$$

$$H\Psi = E\Psi$$

$$P, R, S, \ldots \in \mathcal{S}_N$$

sign of P

$$\Psi(x_{P_1}, \ldots, x_{P_N}) = (-1)^P \times$$

$$\times \Psi(x_1, \ldots, x_N)$$

$$P = \begin{pmatrix} 1 & \ldots & N \\ P_1 & \ldots & P_N \end{pmatrix}$$

Single-particle states

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

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

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

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

$$c_p = \langle\psi_p|\psi\rangle$$

$$= \int \psi_p^*(x)\psi(x)\,dx$$

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

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

In QC (typically):

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

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

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

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

$$\times\, \psi_{p_1}(x_1) \times \dots \times \psi_{p_N}(x_N)$$

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

$$= \int \psi_{p_1}^*(x_1) \dots \psi_{p_N}^*(x_N)$$

$$\times\, \Psi(x_1, \dots, x_N)\, dx_1 \dots dx_N$$

Idempotent anti-symmetrizer

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

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

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

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

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

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

$$|\Phi_{p_1 \ldots p_N}\rangle$$ Slater determinant

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{p_1}(x_1) & \cdots & \chi_{p_1}(x_N) \\ \chi_{p_2}(x_1) & \cdots & \chi_{p_2}(x_N) \\ & \cdots & \\ \chi_{p_N}(x_1) & \cdots & \chi_{p_N}(x_N) \end{vmatrix} \checkmark$$

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

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

$N=2$:

$|\Phi_{12}\rangle, |\Phi_{13}\rangle, |\Phi_{14}\rangle, \ldots,$

$|\Phi_{23}\rangle, |\Phi_{24}\rangle, \ldots$

$$|\Phi_{p_1 p_2}\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_{p_1}(x_1) & \chi_{p_1}(x_2) \\ \chi_{p_2}(x_1) & \chi_{p_2}(x_2) \end{vmatrix}$$

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

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

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

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

$$= \delta_{p_1 q_1} \cdots \delta_{p_N q_N}$$

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

OCCUPATION NUMBER REPRESENTATION

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

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

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

$\left(|p_1 \cdots p_N\rangle = |p_1\rangle \otimes \cdots |p_N\rangle \right)$

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

$$|n_1 n_2 \ldots n_p \ldots \rangle$$

$$n_p = 0 \text{ or } 1$$

FOCK SPACE

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

N-fermion Hilbert space:

$$\mathcal{H}_N = \mathrm{Span}\{|n_1 \ldots n_p \ldots\rangle, \sum_p n_p = N\}$$

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

$$|\Phi_{1,2,7,10}\rangle = |\{\varphi_1 \varphi_2 \varphi_7 \varphi_{10}\}\rangle$$

$= |1110000100100\ldots\rangle$

CREATION & ANNIHILATION OPERATORS

Annihilation operators

$$X_p|\ldots \overset{0 \text{ or } 1}{n_p} \ldots\rangle$$

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

$$m = \sum_{k=1}^{p-1} n_k$$

(number of occupied single-particle states preceding p)

An alternative notation:

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

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

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

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

example:

$$X_5 |\underbrace{0010}_{m=1}1010110\ldots\rangle$$

$$= (-1)^1 |1001000110\ldots\rangle$$

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

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

Yet another definition ...

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

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

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

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

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

Vacuum state:

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

(all n_p's are 0)

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

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

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

$n_p = 1$ single-particle states

$\forall p$

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

$$X_p|0\rangle = 0$$

Creation operators:

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

$$\langle p|X_p^\dagger = \langle 0| \quad / \quad |0\rangle$$

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

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

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

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

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

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

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

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

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

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

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

$$X_p^\dagger | \ldots n_p \ldots \rangle$$
$$= (-1)^m (1-n_p) | \ldots (1-n_p) \ldots \rangle$$
$$(n_p = 0, 1)$$

Number operator

$$N_p = X_p^\dagger X_p \quad (N_p^\dagger = N_p)$$

$$\hat{N}_p | \ldots n_p \ldots \rangle = n_p | \ldots n_p \ldots \rangle$$
$$(n_p = 0, 1)$$

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

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

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

$$\langle\ |\ldots n_p \ldots\rangle$$

anticommutator

$$\{A, B\} = AB + BA$$

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

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