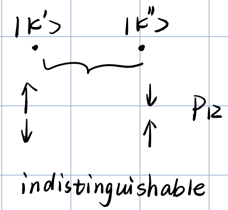
Many Particle Systems

Permatation Operation $\overset{1}{o}$ $\overset{2}{o}$

particle 1. particle 2.

$$P_{12}|k'\rangle|k''\rangle$$ 定
$$=|k''\rangle|k'\rangle$$ 义



$$=\alpha|k'\rangle|k''\rangle$$

$$P_{12}^2|k'\rangle|k''\rangle=|k'\rangle|k''\rangle$$
$$=\alpha^2|k'\rangle|k''\rangle$$

$\alpha^2=1$.
$\alpha=\pm1$.

$\alpha=1$ $P_{12}|k'\rangle|k''\rangle=|k'\rangle|k''\rangle$, boson Symmetric

$\alpha=-1$. $P_{12}|k'\rangle|k''\rangle=-|k'\rangle|k''\rangle$. Fermion. Anti-Symmetric

$$|\psi\rangle=\frac{1}{\sqrt{2}}(|k'\rangle|k''\rangle+|k''\rangle|k'\rangle)$$

$P_{12}|\psi\rangle=|\psi\rangle$ boson

$$|\psi\rangle=\frac{1}{\sqrt{2}}(|k'\rangle|k''\rangle-|k''\rangle|k'\rangle)$$

$P_{12}|\psi\rangle=-|\psi\rangle$. Fermion.

Many particles.

P_{ij} | N identical bosons > = | N identical bosons >

P_{ij} | N identical Fermions > = − | N identical Fermions >

$$\psi(x_1,x_2,\cdots,x_n)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1)\\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2)\\ \vdots & \vdots & & \vdots\\ \chi_i(x_n) & \chi_j(x_n) & & \chi_k(x_n)\end{vmatrix}$$

$$=|\chi_i(x_1)\rangle|\chi_j(x_2)\rangle$$

$$\psi(x_1,x_2,\cdots,x_n)=-\psi(x_1,x_2,\cdots,x_n).$$

Second quantization

$P_{ij} | \varphi_1 \varphi_2 \cdots \varphi_i \cdots \varphi_j \cdots \rangle = | \varphi_1 \varphi_2 \cdots \varphi_j \cdots \varphi_i \cdots \rangle$

$H = \hbar w (a^+ a + \frac{1}{2})$ $\qquad [a, a^+] = 1$

$a^+ |0\rangle = |1\rangle$

$a|0\rangle = |0\rangle$

$a^+ . a$ are boson creation and annilation Operators, i.e. $[a, a^+] = 1$.

$H = \sum_i \hbar w_i (a_i^+ a_i + \frac{1}{2})$

a_i^+ , a^+ ———— for $\underline{\text{ith}}$ boson.

第i个.

$[a_i^+ , a_j] = \delta_{ij}$.

$|\vec{0}\rangle = |0, 0, 0, \cdots, 0\rangle$ Vacuum State

$a_i^+ |\vec{0}\rangle = |0, 0, \cdots, \overset{\text{ith.}}{1}, \cdots, 0\rangle$

$(a_i^+)^2 |\vec{0}\rangle = \frac{1}{\sqrt{2}} |0, 0, \cdots, 2, \cdots, 0\rangle$

$|n_1, n_2, \cdots, n_i, \cdots\rangle$ Fock Space

$a_i^+ |n_1, n_2, \cdots, n_i, \cdots\rangle = \frac{1}{\sqrt{n_i + 1}} |n_1, n_2, \cdots, n_i + 1, \cdots\rangle$

$a_i |\vec{0}\rangle = 0$.

indistinguishable

$a_i^+ a_j^+ |\vec{0}\rangle = |0, 0, \cdots, n_i = 1, \cdots, n_j = 1, \cdots 0\rangle$

$a_j^+ a_i^+ |\vec{0}\rangle = P_{ij} (a_i^+ a_j^+ |\vec{0}\rangle) = P_{ij} |0, 0, \cdots, n_i = 1, \cdots, n_j = 1, \cdots, 0\rangle$

$P_{ij} (a_i^+ a_j^+) = a_j^+ a_i^+$ $\qquad P_{ij} = \pm 1$ $\qquad P_{ij}^2 = 1$

$a_j^+ a_i^+ - a_i^+ a_j^+ = [a_j^+, a_i^+] = 0$ $\qquad P_{ij} = 1$ boson

$a_j^+ a_i^+ + a_i^+ a_j^+ = \{a_j^+, a_i^+\} = 0$ $\qquad P_{ij} = -1$. Fermion.

$\underbrace{a_i^+ , a_j^+ , \cdots}_{\text{可以给出real function}} |\vec{0}\rangle$

$a_i^+ a_i^+ + a_i^+ a_i^+ = 0$

$\{a_i, a_j\} = 0$ $\qquad a_i^+ a_i^+ |\vec{0}\rangle = 0$. $\qquad$ pauli exclusion principle

$\hat{N}=\sum_i a_i^\dagger a_i$ Number Operator

$\hat{H}=\sum_i k_i a_i^\dagger a_i$ 二次量子化 This is the 1 particle Hamitonion in the second quantization Form.

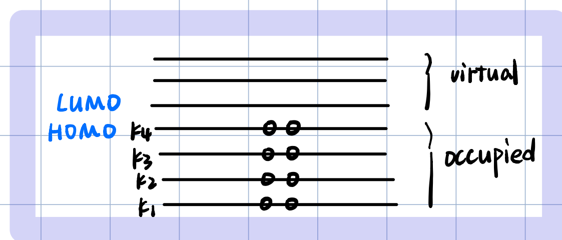
$=\sum_i \frac{\nabla_i^2}{2m_i}$

$V=\frac{e^2}{|r_i-r_j|}$

$=\sum_{ijkl} V_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k$ 2 particle intevations Hamiltonian.

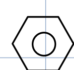
$H=\sum_{ij} h_{ij}\, a_i^\dagger a_j + \frac{1}{2}\sum_{ijkl} V_{ijkl}\, a_i^\dagger a_j^\dagger a_k a_l$

$|HF\rangle = |\underbrace{111111}_{\text{occupied}}\underbrace{00000}_{\text{virtual}}\rangle$



(考虑 spin)

$\langle HF|\hat{N}|HF\rangle = n$ electrons



C_6H_6 : $6\times6+6=42$.

$E=\langle HF|\hat{H}|HF\rangle=\sum_i k_i n_i$.

$n_i=\langle HF|a_i^\dagger a_i|HF\rangle$

$\therefore E=\sum_{i\in Occ} k_i$.

$h_{ij}=\int d\vec{r}\, \chi_i^*(\vec{r})\cdot\frac{-\nabla^2}{2m}\chi_j(\vec{r})$

$V_{ijkl}=\int d\vec{r}\, d\vec{r}'\, \frac{\chi_i^*(\vec{r})\,\chi_j^*(\vec{r}')\,\chi_k(\vec{r}')\,\chi_l(\vec{r})}{|\vec{r}-\vec{r}'|}$

$S_{ij}=\int d\vec{r}\, \chi_i^*(\vec{r})\,\chi_j(\vec{r})$

$\{a_i, a_j^\dagger\}=S_{ij}$

$\sigma_{ij}=tr(\rho a_i^\dagger a_j)=\langle a_i^\dagger a_j\rangle$ $\quad \rho=|\psi\rangle\langle\psi|$

$i=j$: $\langle\psi|a_i^\dagger a_i|\psi\rangle=n_i$.

HF : Mean Field

$a_i^\dagger a_j^\dagger a_k a_l = a_i^\dagger \sigma_{jk} a_l - a_i^\dagger a_k \langle a_j^\dagger a_l\rangle$ correlation

$\bar{H}=\sum_{ij} h_{ij}\, a_i^\dagger a_j + \frac{1}{2}\sum_{ijkl} V_{ijkl}\, a_i^\dagger a_l \sigma_{jk} - \frac{1}{2}\sum_{ijkl} V_{ijkl}\, a_i^\dagger a_k \sigma_{jl}$ Exchange.

$=\sum (h_{ij} + V_{ij}^{c} - V_{ij}^{ex})$ quadric.

$V_{ij}^{c} = \sum_{kl} V_{ijkl}\sigma_{kl}$

$V_{ij}^{ex} = \sum_{kl} V_{ijkl}\sigma_{lk}$ self-constistank.

$\bar{H} = \sum_i \kappa_i b_i^{\dagger} b_i$. $b_i^{\dagger} = \sum_j C_{ij} a_j^{\dagger}$.

$\bar{\sigma}_{ij} = n_i \delta_{ij}$. σ unchange.

Hartree-Fock Method.

$\chi_1(r_1)$. $\chi_2(r_2)$

$$|\varphi\rangle = \frac{1}{\sqrt{2}}\left(|\chi_1(r_1)\chi_2(r_2)\rangle - |\chi_2(r_1)\chi_1(r_2)\rangle\right)$$

$$\left.\begin{aligned}\langle\varphi|V|\varphi\rangle = &\int d\vec{r}_1 d\vec{r}_2 \frac{\chi_1(r_1)\chi_2(r_2)\chi_1(r_1)\chi_1(r_2)}{|\vec{r}_1-\vec{r}_2|} \\ &+\int d\vec{r}_1 d\vec{r}_2 \frac{\chi_2(r_1)\chi_1(r_2)\chi_2(r_1)\chi_1(r_2)}{|\vec{r}_1-\vec{r}_2|}\end{aligned}\right\}\text{correlation energy}$$

$$-\int d\vec{r}_1 d\vec{r}_2 \frac{\chi_1(r_1)\chi_2(r_2)\chi_2(r_1)\chi_1(r_2)}{|r_1-r_2|}$$ exchange energy.

HF - DFT

Excied State $E_{HF} + E_{LUMO} - E_{HOMO}$

$|\varphi_i^a\rangle = a_a a_i^{\dagger}|HF\rangle$ Configuration interaction Singles.
CIS

$i \in Vir$
$a \in occ$

$|\varphi\rangle = \sum_{ia} C_i^a |\varphi_i^a\rangle$ $H|\varphi\rangle = E|\varphi\rangle$

$|\varphi|V|\varphi\rangle$

Doubles $|\varphi\rangle = \sum_{ijab} C_{ij}^{ab} a_i^{\dagger} a_j^{\dagger} a_a a_b |HF\rangle$

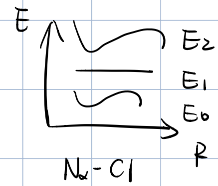
CISDTQ $\longrightarrow$ Full CI.
双 三 四.

Acative Space

Born - Oppenheimer Approximation

$$H = H_e + \sum_I -\frac{\nabla_I^2}{2M_I}$$

$$H_e = T_e + V_{e-e} + V_{e-N} + V_{N-N}$$



$$H_e(\vec{R})\,|\varphi_I\rangle = E_I(\vec{R})\,|\varphi_I\rangle$$

$$|\Psi| = |\chi_I\rangle \varphi_I\rangle$$

$$H|\Psi| = E_I(R)\,|\chi_I\rangle|\varphi_I\rangle$$

$$-\frac{\nabla_I^2}{2M_I}|\chi_I\rangle|\varphi_I\rangle \quad = E|\chi_I\rangle|\varphi_I\rangle$$

$$\langle\varphi_I|\left(-\frac{\nabla_I^2}{2M_I} + E_I(R)\right)|\chi_I\rangle = E|\chi_I\rangle$$

$$M_I \ddot{X} = -\frac{\partial E_I}{\partial X}.$$

$$|\Psi\rangle = \sum_I |\chi_I\rangle|\Psi_I\rangle$$

$$H|\Psi\rangle = E|\Psi\rangle$$

$$\left(H_e + \frac{-\nabla^2}{2M}\right)\sum_I |\chi_I\rangle|\varphi_I\rangle = E\sum_I |\chi_I\rangle|\varphi_I\rangle$$

$$\sum_I E_I|\chi_I\rangle|\varphi_I\rangle - \sum_I \frac{\nabla^2}{2M}|\chi_I\rangle|\varphi_I\rangle = E\sum_I |\chi_I\rangle|\varphi_I\rangle$$

$\langle\varphi_J|$.

$$E_I|\chi_I\rangle - \langle\varphi_J|\frac{\nabla^2}{2m}|\varphi_I\rangle\,|\chi_I\rangle$$

$$-\sum_I \langle\varphi_J|\nabla|\varphi_I\rangle \cdot \frac{\nabla}{2M}|\chi_I\rangle$$

$$-\quad \frac{\nabla^2}{2M}|\chi_J\rangle \qquad\qquad = E|\chi_J\rangle$$

$$d_{IJ} = \langle\varphi_I|\nabla|\varphi_J\rangle$$

$$-\frac{\nabla^2}{2m}|\chi_J\rangle + \frac{\sum_I d_{IJ}}{2m}\nabla|\chi_I\rangle - \sum_I D_{IJ}|\chi_I\rangle = E|\chi_J\rangle$$

$$D_{IJ} = \langle\varphi_I|\frac{\nabla^2}{2m}|\varphi_J\rangle$$

Nonadiabetic Coupling