Second Quantization and Slater Determinants (I)

2/21/10

— Consider a system of N electrons with the Hamiltonian

$$H = \sum_{i=1}^{N} h(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} u(\mathbf{r}_i, \mathbf{r}_j) \tag{1}$$

where the one- and two-body terms are

$$\begin{cases} h(\mathbf{r}) = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial \mathbf{r}^2} + v(\mathbf{r}) & (2) \\[2ex] u(\mathbf{r}, \mathbf{r}') = \dfrac{e^2}{|\mathbf{r} - \mathbf{r}'|} & (3) \end{cases}$$

— The wave function of the system, $\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, t)$, should satisfy the following two conditions:

① It follows the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, t) = H\,\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, t) \tag{4}$$

② It is anti-symmetric

$$\Psi(\cdots \mathbf{r}_i \cdots \mathbf{r}_j \cdots) = -\Psi(\cdots \mathbf{r}_j \cdots \mathbf{r}_i \cdots) \tag{5}$$

– Consider an orthonormal set of single-electron wave functions,

$$\{\psi_\kappa(\mathbf{r}) \mid \kappa = 1, \dots, \infty\} \tag{6}$$

and an anti-symmetric linear combination of the single-electron states, i.e., a Slater determinant,

$$\Phi_{\kappa_1 \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\kappa_1}(\mathbf{r}_1) & \cdots & \psi_{\kappa_1}(\mathbf{r}_N) \\ \vdots & & \\ \psi_{\kappa_N}(\mathbf{r}_1) & \cdots & \psi_{\kappa_N}(\mathbf{r}_N) \end{vmatrix} \tag{7}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{\kappa_{P(1)}}(\mathbf{r}_1) \cdots \psi_{\kappa_{P(N)}}(\mathbf{r}_N) \tag{8}$$

where P denotes permutation. To make the sign unique, we require that the occupied one-electron states are ordered in an ascending order,

$$\kappa_1 < \kappa_2 < \cdots < \kappa_N \tag{9}$$

(Th 1) Slater determinant is anti-symmetric with respect to the interchange of coordinates.

∵

$$\Phi_{\kappa_1 \cdots \kappa_i \cdots \kappa_j \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_j \cdots \mathbf{r}_i \cdots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{\kappa_{P(1)}}(\mathbf{r}_1) \cdots \psi_{\kappa_{P(i)}}(\mathbf{r}_j) \cdots \psi_{\kappa_{P(j)}}(\mathbf{r}_i) \cdots \psi_{\kappa_{P(N)}}(\mathbf{r}_N)$$

$$P' \equiv (i \leftrightarrow j) P \Rightarrow P'(i) = P(j)\,;\ P'(j) = P(i)$$

$$= \frac{1}{\sqrt{N!}} \sum_{P'} (-1)^{P'+1} \psi_{\kappa_{P'(1)}}(\mathbf{r}_1) \cdots \psi_{\kappa_{P'(j)}}(\mathbf{r}_j) \cdots \psi_{\kappa_{P'(i)}}(\mathbf{r}_i) \cdots \psi_{\kappa_{P'(N)}}(\mathbf{r}_N)$$

$$= -\frac{1}{\sqrt{N!}} \sum_{P'} (-1)^{P'} \psi_{\kappa_{P'(1)}}(\mathbf{r}_1) \cdots \psi_{\kappa_{P'(i)}}(\mathbf{r}_i) \cdots \psi_{\kappa_{P'(j)}}(\mathbf{r}_j) \cdots \psi_{\kappa_{P'(N)}}(\mathbf{r}_N)$$

$$= -\Phi_{\kappa_1 \cdots \kappa_i \cdots \kappa_j \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_i \cdots \mathbf{r}_j \cdots \mathbf{r}_N) \;//$$

(Th 2) Slater determinant cannot contain the same state twice; thus the absence of equality in Eq. (9).

∵

Let us assume that rows i and $i+1$ occupy an identical state κ.

$$\Phi_{\kappa_1\cdots\underset{i}{\kappa}\underset{i+1}{\kappa}\cdots\kappa_N}(\mathbb{r}_1\cdots\mathbb{r}_N) = \frac{1}{\sqrt{N!}}\sum_P(-1)^P \psi_{\kappa_{P(1)}}(\mathbb{r}_1)\cdots\underbrace{\psi_{\kappa_{P(i)}}(\mathbb{r}_k)\cdots\psi_{\kappa_{P(i+1)}}(\mathbb{r}_\ell)}_{\text{Let us assume } P(i)=k \text{ \& } P(i+1)=\ell}\cdots\psi_{\kappa_{P(N)}}(\mathbb{r}_N)$$

$$= -\psi_{\kappa_{P(1)}}(\mathbb{r}_1)\cdots\psi_{\underset{\kappa_{P(i)}}{\overset{\kappa_{P(i+1)}}{\|}}}(\mathbb{r}_k)\cdots\psi_{\underset{\kappa_{P(i+1)}}{\overset{\kappa_{P(i)}}{\|}}}(\mathbb{r}_\ell)\cdots\psi_{\kappa_{P(N)}}(\mathbb{r}_N) \quad (\because \text{assumption})$$

$$= -\Phi_{\kappa_1\cdots\underset{i}{\kappa}\underset{i+1}{\kappa}\cdots\kappa_N}(\mathbb{r}_1\cdots\mathbb{r}_N)$$

$$\therefore \Phi_{\kappa_1\cdots\underset{i}{\kappa}\underset{i+1}{\kappa}\cdots\kappa_N}(\mathbb{r}_1\cdots\mathbb{r}_N) = 0 \quad //$$

(Th 3) (Orthonormality)

$$\langle\Phi_{\kappa_1\cdots\kappa_N}|\Phi_{\kappa_1'\cdots\kappa_N'}\rangle \equiv \int d\mathbb{r}_1\cdots d\mathbb{r}_N\, \Phi^*_{\kappa_1\cdots\kappa_N}(\mathbb{r}_1\cdots\mathbb{r}_N)\,\Phi_{\kappa_1'\cdots\kappa_N'}(\mathbb{r}_1\cdots\mathbb{r}_N) \tag{10}$$

$$= \delta_{\kappa_1\kappa_1'}\cdots\delta_{\kappa_N\kappa_N'} \tag{11}$$

∵

If the set of occupied states, $(\kappa_1\cdots\kappa_N)$ and $(\kappa_1'\cdots\kappa_N')$, are not identical, then the inner product contains at least one one-electron integration between dissimilar states,

$$\int d\mathbb{r}_i\, \psi^*_\kappa(\mathbb{r}_i)\,\psi_{\kappa'}(\mathbb{r}_i) = 0,$$

which makes the N-electron inner product, Eq. (10), zero.

On the other hand, if $(k_1 \cdots k_N)$ and $(k'_1 \cdots k'_N)$ are identical,

$$\langle \Phi_{k_1\cdots k_N} | \Phi_{k'_1\cdots k'_N} \rangle = \frac{1}{N!} \sum_{P} \sum_{P'} (-1)^{P+P'}$$

$$\times \underbrace{\underbrace{\int d\mathbf{r}_1 \psi^*_{k_{P(1)}}(\mathbf{r}_1) \psi_{k_{P'(1)}}(\mathbf{r}_1)}_{\delta_{P(1)P'(1)}} \times \cdots \times \underbrace{\int d\mathbf{r}_N \psi^*_{k_{P(N)}}(\mathbf{r}_N) \psi_{k_{P'(N)}}(\mathbf{r}_N)}_{\delta_{P(N)P'(N)}}}_{\prod_i \delta_{P(i)P'(i)} \equiv \delta_{PP'}}$$

$$= \frac{1}{N!} \sum_{P} 1 = \frac{1}{N!} \cdot N! = 1 \quad //$$

In summary, the set of Slater determinants, Eq.(7), with all distinct occupancies is an orthonormal basis sets in $\mathbb{R}^N$.

— The N-electron wave function can be expanded as

$$\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, t) = \sum_{n_1, \ldots, n_\infty = 0}^{1} f(n_1 \cdots n_\infty, t)\, \Phi_{n_1 \cdots n_\infty}(\mathbf{r}_1 \cdots \mathbf{r}_N) \tag{12}$$

$$= \sum_{\substack{k_1 < \cdots < k_N \\ (n_1 \cdots n_\infty)}} f(n_1 \cdots n_\infty, t)\, \Phi_{k_1 \cdots k_N}(\mathbf{r}_1 \cdots \mathbf{r}_N) \tag{13}$$

where, for each single-electron state k, we specify the occupation number, $n_k \in \{0, 1\}$, such that

$$\sum_{k=1}^{\infty} n_k = n_1 + \cdots + n_\infty = N \tag{14}$$

and $\sum_{\substack{k_1 < \cdots < k_N \\ (n_1 \cdots n_\infty)}}$ denotes the sum over all states, $k_1 < \cdots < k_N$, of N electrons, which are consistent with the occupation numbers.

Substituting the expansion, Eq.(12), into the time-dependent Schrödinger equation, Eq.(4),

$$i\hbar \sum_{n_1' \cdots n_\infty'} \left[\frac{\partial}{\partial t} f(n_1 \cdots n_\infty, t)\right] \Phi_{n_1' \cdots n_\infty'}(\mathbb{r}_1 \cdots \mathbb{r}_N)$$
$$= \sum_{n_1' \cdots n_\infty'} f(n_1' \cdots n_\infty', t) \sum_{i=1}^{N} h(\mathbb{r}_i) \Phi_{n_1' \cdots n_\infty'}(\mathbb{r}_1 \cdots \mathbb{r}_N)$$
$$+ \sum_{n_1' \cdots n_\infty'} f(n_1' \cdots n_\infty', t) \frac{1}{2}\sum_{i \neq j} u(\mathbb{r}_i, \mathbb{r}_j) \Phi_{n_1' \cdots n_\infty'}(\mathbb{r}_1 \cdots \mathbb{r}_N) \quad (15)$$

$$\int d\mathbb{r}_1 \cdots d\mathbb{r}_N \, \Phi^*_{n_1 \cdots n_\infty}(\mathbb{r}_1 \cdots \mathbb{r}_N) \times \text{Eq.}(15)$$

$$i\hbar \frac{\partial}{\partial t} f(n_1 \cdots n_\infty, t) \quad (\because \text{orthonormality Eq.}(11))$$
$$= \sum_{n_1' \cdots n_\infty'} f(n_1' \cdots n_\infty', t) \sum_{i=1}^{N} \int d\mathbb{r}_1 \cdots d\mathbb{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbb{r}_1 \cdots \mathbb{r}_N) h(\mathbb{r}_i) \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbb{r}_1 \cdots \mathbb{r}_N) \quad (\alpha)$$
$$+ \sum_{n_1' \cdots n_\infty'} f(n_1' \cdots n_\infty', t) \frac{1}{2}\sum_{i \neq j} \int d\mathbb{r}_1 \cdots d\mathbb{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbb{r}_1 \cdots \mathbb{r}_N) u(\mathbb{r}_i \mathbb{r}_j) \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbb{r}_1 \cdots \mathbb{r}_N) \quad (\beta)$$
$$(16)$$

– One-body matrix elements

To evaluate the one-body term (a) in Eq. (16), let us consider a one-body matrix element between 2 Slater determinants,

$$\langle K|O_1|K'\rangle$$

$$= \langle \kappa_1 \cdots \kappa_N | \sum_{i=1}^{N} h(\mathbf{r}_i) | \kappa_1' \cdots \kappa_N' \rangle \tag{17}$$

$$= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_N) \sum_{i=1}^{N} h(\mathbf{r}_i) \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbf{r}_1 \cdots \mathbf{r}_N) \tag{18}$$

The matrix element is nonzero only if $(\kappa_1 \cdots \kappa_N)$ and $(\kappa_1' \cdots \kappa_N')$ differ at most at one place.

<u>Case 1 : $(\kappa_1 \cdots \kappa_N) = (\kappa_1' \cdots \kappa_N')$</u>

Note

$$\langle \kappa_1 \cdots \kappa_N | h(\mathbf{r}_i) | \kappa_1' \cdots \kappa_N' \rangle = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_N) h(\mathbf{r}_i) \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbf{r}_1 \cdots \mathbf{r}_N)$$

$$\mathbf{r}_1 \leftrightarrow \mathbf{r}_i$$

$$= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, \cancel{(-1)} \Phi^*_K(\mathbf{r}_i \cdots \mathbf{r}_1 \cdots \mathbf{r}_N) h(\mathbf{r}_1) \cancel{(-1)} \Phi_{K'}(\mathbf{r}_i \cdots \mathbf{r}_1 \cdots \mathbf{r}_N)$$

Rename $\mathbf{r}_1 \leftrightarrow \mathbf{r}_i$

$$= \langle \kappa_1 \cdots \kappa_N | h(\mathbf{r}_1) | \kappa_1' \cdots \kappa_N' \rangle$$

$$\therefore \langle K | \sum_{i=1}^{N} h(\mathbf{r}_i) | K' \rangle$$

$$= N \langle K | h(\mathbf{r}_1) | K' \rangle \tag{19}$$

$\therefore \langle K|\mathcal{O}_1|K\rangle$

$$= \frac{N}{N!}\sum_P\sum_{P'}(-1)^{P+P'}\int d\mathbf{r}_1\cdots d\mathbf{r}_N\; \psi^*_{\kappa_{P(1)}}(\mathbf{r}_1)\cdots\psi^*_{\kappa_{P(N)}}(\mathbf{r}_N)\, h(\mathbf{r}_1)\,\psi_{\kappa'_{P(1)}}(\mathbf{r}_1)\cdots\psi_{\kappa'_{P(N)}}(\mathbf{r}_N)$$

$$= \frac{1}{(N-1)!}\sum_P\sum_{P'}(-1)^{P+P'}\int d1\cdots dN\; P[\kappa_1^*(1)\cdots\kappa_N^*(N)]\, h(1)\, P'[\kappa_1(1)\cdots\kappa_N(N)] \quad (20)$$

Here, we have denoted $\mathbf{r}_i$ by i and

$$P[\kappa_1(1)\cdots\kappa_N(N)] \equiv \psi_{\kappa_{P(1)}}(\mathbf{r}_1)\cdots\psi_{\kappa_{P(N)}}(\mathbf{r}_N) \quad (21)$$

Equation (20) is nonzero only if $P'=P$, hence $(-1)^{P+P}=1$ (otherwise one-body integration between orthogonal one-election states appear, which is zero).

$\therefore \langle K|\mathcal{O}_1|K\rangle$

$$= \frac{1}{(N-1)!}\sum_P\int d1\cdots dN\; P[\kappa_1^*(1)\cdots\kappa_N^*(N)]\, h(1)\, P[\kappa_1(1)\cdots\kappa_N(N)]$$

The permutation P places each κ_i $(N-1)!$ times (i.e., the combination to place the rest of $(N-1)$ states in coordinates $\mathbf{r}_2\cdots\mathbf{r}_N$), thus

$\langle K|\mathcal{O}_1|K\rangle$

$$= \frac{1}{\cancel{(N-1)!}}\times\cancel{(N-1)!}\sum_{i=1}^{N}\langle\kappa_i|h|\kappa_i\rangle\cdot\underbrace{\prod_{j\neq i}\langle\kappa_j|\kappa_j\rangle}_{=1}$$

$$= \sum_{i=1}^{N}\langle\kappa_i|h|\kappa_i\rangle \quad (22)$$

where

$$\langle k|h|k\rangle \equiv \int d\mathbf{r}\, \varphi_k^*(\mathbf{r})\, h(\mathbf{r})\, \varphi_k(\mathbf{r}) \tag{23}$$

The sum over the occupied states can be replaced by a sum over all one-electron states k weighted by the occupation number:

$$\langle K|O_1|K\rangle = \sum_{k=1}^{\infty} n_k \langle k|h|k\rangle \tag{24}$$

Case 2: $K = |\cdots m \cdots\rangle$
$K' = |\cdots p \cdots\rangle$

(Example)

	1	2	3	4	5 = N
K	1	3	5	7	9
K′	1	8	5	7	9

Again

$\langle K|O_1|K'\rangle$

$= N \langle K|h(\mathbf{r}_1)|K'\rangle$

$$= N \cdot \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P+P'} \int d1 \cdots dN\, P[\cdots m \cdots]\, h(1)\, P'[\cdots p \cdots]$$

The nonzero contribution comes when P' first aligns state p with m (see example), with the sign

$$(-1)^{S_p - S_m}$$

where

$$S_k = n_1 + \cdots + n_{k-1} = \sum_{k'=1}^{k-1} n_{k'} \tag{25}$$

then P and P' work identically to place states m and p in the first place (i.e., P determines P' uniquely). This happens $(N-1)!$ times (to place the $(N-1)$ remaining states in $\mathbf{r}_2 \cdots \mathbf{r}_N$).

$\therefore \langle K | \Theta_1 | K' \rangle$

$$= \cancel{N} \cdot \frac{1}{\cancel{N!}} (-1)^{S_p - S_m} \cdot \cancel{(N-1)!} \langle m | h | p \rangle \tag{26}$$

In summary, one-body matrix elements are

Case 1: $K = K'$

$$\boxed{\langle K | \Theta_1 | K \rangle = \sum_{k=1}^{\infty} n_k \langle k | h | k \rangle} \tag{24}$$

Case 2: $K = |\cdots m \cdots\rangle$
$K' = |\cdots p \cdots\rangle$

$$\boxed{\langle K | \Theta_1 | K' \rangle = (-1)^{S_p - S_m} \langle m | h | p \rangle} \tag{25}$$

where

$$\langle m | h | p \rangle = \int d\mathbf{r}\, \psi_m^*(\mathbf{r})\, h(\mathbf{r})\, \psi_n(\mathbf{r}) \tag{23}$$

Substituting Eqs. (24) and (25) to (16), the one-body contribution to the r.h.s. of the time-dependent Schrödinger equation is

$$(a) = \left(\sum_{k=1}^{\infty} n_k \langle k|h|k\rangle\right) f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{n_1' \cdots n_\infty'} (-1)^{S_p - S_m} \langle m|h|p\rangle f(n_1' \cdots n_\infty', t)$$

In the second m can be any of the occupied state, which can be replaced by any unoccupied state p. Thus the enumeration of all possible K′ amounts to

$$\sum_{n_1' \cdots n_\infty'} \rightarrow \sum_{k} n_k \sum_{k'} (1 - n_{k'})$$

$$\therefore (a) = \left(\sum_{k=1}^{\infty} n_k \langle k|h|k\rangle\right) f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} (-1)^{S_k - S_{k'}} n_k (1 - n_{k'}) \langle k|h|k'\rangle f(\cdots n_k - 1 \cdots n_{k'} + 1 \cdots) \tag{26}$$

– Two-body matrix elements

To evaluate the two-body term (β) in Eq.(16), let us consider a two-body matrix element between 2 Slater determinants,

$$\langle K | \Theta_2 | K' \rangle$$

$$= \langle K | \frac{1}{2} \sum_{i \neq j} \mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) | K' \rangle \qquad (27)$$

It should be noted that $\mathcal{U}(\mathbf{r}, \mathbf{r}')$ is symmetric with respect to the interchange of $\mathbf{r}$ and $\mathbf{r}'$,

$$\mathcal{U}(\mathbf{r}_j, \mathbf{r}_i) = \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = \mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) \qquad (28)$$

The matrix element is nonzero only if $(\kappa_1 \cdots \kappa_N)$ and $(\kappa_1' \cdots \kappa_N')$ differ at most at two places.

<u>Case 1: $(\kappa_1 \cdots \kappa_N) = (\kappa_1' \cdots \kappa_N')$</u>

Note

$$\langle \kappa_1 \cdots \kappa_N | \mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) | \kappa_1' \cdots \kappa_N' \rangle$$

$$= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbf{r}_1 \cdots \mathbf{r}_N) \, \mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) \, \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbf{r}_1 \cdots \mathbf{r}_N)$$

$\mathbf{r}_1 \leftrightarrow \mathbf{r}_i \; ; \; \mathbf{r}_2 \leftrightarrow \mathbf{r}_j$

$$= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, \Phi^*_{\kappa_1 \cdots \kappa_N}(\mathbf{r}_i \mathbf{r}_j \cdots) \, \mathcal{U}(\mathbf{r}_i, \mathbf{r}_j) \, \Phi_{\kappa_1' \cdots \kappa_N'}(\mathbf{r}_i \mathbf{r}_j \cdots)$$ ← Two exchanges; no sign change

Rename $\mathbf{r}_1 \leftrightarrow \mathbf{r}_i$, $\mathbf{r}_2 \leftrightarrow \mathbf{r}_j$

$$= \langle \kappa_1 \cdots \kappa_N | \mathcal{U}(\mathbf{r}_1, \mathbf{r}_2) | \kappa_1' \cdots \kappa_N' \rangle$$

$$\therefore \langle K | \frac{1}{2}\sum_{i\neq j} u(\mathbf{r}_i, \mathbf{r}_j) | K' \rangle$$

$$= \frac{N(N-1)}{2} \langle K | u(\mathbf{r}_1, \mathbf{r}_2) | K' \rangle \tag{29}$$

$$\langle K | \Theta_2 | K \rangle$$

$$= \frac{N(N-1)}{2} \langle K | u(\mathbf{r}_1, \mathbf{r}_2) | K \rangle$$

$$= \frac{N(N-1)}{2} \cdot \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P+P'} \int d1 \cdots dN \, P[\kappa_1^*(1) \cdots \kappa_N^*(N)] \frac{e^2}{r_{12}} P'[\kappa_1(1) \cdots \kappa_N(N)]$$

The contribution is nonzero only when two of the occupied states, $\kappa_i < \kappa_j$, are placed in the first two places by both P and P', and for each case they place the remaining $(N-2)$ states at $\mathbf{r}_3 \cdots \mathbf{r}_N$ in $(N-2)!$ ways.

$$\therefore \langle K | \Theta_2 | K \rangle$$

$$= \frac{\cancel{N(N-1)}}{2} \sum_{\kappa_i < \kappa_j} \frac{1}{\cancel{N!}} \int d1 d2 \Big\{ \kappa_i^*(1)\kappa_j^*(2) \frac{e^2}{r_{12}} [\kappa_i(1)\kappa_j(2) - \kappa_j(1)\kappa_i(2)]$$

$$+ \underbrace{\kappa_j^*(1)\kappa_i^*(2) \frac{e^2}{r_{12}} [\kappa_j(1)\kappa_i(2) - \kappa_i(1)\kappa_j(2)]}_{\text{dummy } 1 \leftrightarrow 2} \Big\}$$

$$\times \cancel{(N-2)!}$$

$$= \cancel{\frac{1}{2}} \sum_{\kappa_i < \kappa_j} \int d1 d2 \, \kappa_i^*(1)\kappa_j^*(2) \frac{e^2}{r_{12}} [\kappa_i(1)\kappa_j(2) - \kappa_j(1)\kappa_i(2)] \times \cancel{2}$$

$$= \frac{1}{2} \sum_{\kappa_i \neq \kappa_j} \int d1\, d2\, \kappa_i^*(1) \kappa_j^*(2) \frac{e^2}{r_{12}} \left[\kappa_i(1) \kappa_j(2) - \kappa_j(1) \kappa_i(2) \right]$$

Since $\kappa_i(1)\kappa_j(2) - \kappa_j(1)\kappa_i(1) = 0$ for $i \neq j$, we can remove the restriction $\kappa_i \neq \kappa_j$ in the summation, and hence

$$\langle K | O_2 | K \rangle = \frac{1}{2} \sum_{\kappa_i=1}^{N} \sum_{\kappa_j=1}^{N} \int d1\, d2\, \kappa_i^*(1) \kappa_j^*(2) \frac{e^2}{r_{12}} \left[\kappa_i(1) \kappa_j(2) - \kappa_j(1) \kappa_i(2) \right]$$

We further replace the sum over occupied states by a sum over all states weighted by the occupation number.

$$\therefore \langle K | O_2 | K \rangle = \frac{1}{2} \sum_{\kappa=1}^{\infty} \sum_{\kappa'=1}^{\infty} n_\kappa n_{\kappa'} \left(\langle \kappa\kappa' | \kappa\kappa' \rangle - \langle \kappa\kappa' | \kappa'\kappa \rangle \right) \qquad (30)$$

$$= \frac{1}{2} \sum_{\kappa=1}^{\infty} \sum_{\kappa'=1}^{\infty} n_\kappa n_{\kappa'} \langle \kappa\kappa' || \kappa\kappa' \rangle \qquad (31)$$

where the two-electron integral is defined as

$$\langle ij | kl \rangle = \int d\mathbf{r}\, d\mathbf{r}'\, \varphi_i^*(\mathbf{r})\, \varphi_j^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_k(\mathbf{r})\, \varphi_l(\mathbf{r}') \qquad (32)$$

and the antisymmetrized two-election integral is

$$\langle ij || kl \rangle = \int d\mathbf{r}\, d\mathbf{r}'\, \varphi_i^*(\mathbf{r})\, \varphi_j^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \left[\varphi_k(\mathbf{r})\, \varphi_l(\mathbf{r}') - \varphi_l(\mathbf{r})\, \varphi_k(\mathbf{r}') \right]$$

(33)

Case 2 : $|K\rangle = |\cdots m \cdots\rangle$
$|K'\rangle = |\cdots p \cdots\rangle$

$\langle K|O_2|K'\rangle$

$$= \frac{N(N-1)}{2}\frac{1}{N!}\sum_P\sum_{P'}(-1)^{P+P'}\int d1\cdots dN\, P[\cdots m\cdots]\frac{e^2}{r_{12}}P'[\cdots p\cdots]$$

Since m is orthogonal to any state in K', it has to be placed at either $\mathbf{r}_1$ and $\mathbf{r}_2$; once m is placed at $\mathbf{r}_1|\mathbf{r}_2$, any of the $(N-1)$ states common to K and K', κ_i, should be placed at $\mathbf{r}_2|\mathbf{r}_1$. P' should first aligns P with state m, with sign $(-1)^{S_p-S_m}$, and should place p and κ_i in the first 2 places. For each of the state choices for $\mathbf{r}_1$ and $\mathbf{r}_2$, the remaining $(N-2)$ states should be identically placed by P and P' at $\mathbf{r}_3\cdots\mathbf{r}_N$ in $(N-2)!$ ways.

$\langle K|O_2|K'\rangle$

$$= \frac{\cancel{N(N-1)}}{2}\cancel{\frac{1}{N!}}\sum_{\kappa_i\neq m}(-1)^{S_p-S_m}\big[\langle m\kappa_i|p\kappa_i\rangle - \langle m\kappa_i|\kappa_i p\rangle + \langle\kappa_i m|\kappa_i p\rangle - \langle\kappa_i m|p\kappa_i\rangle\big] \times \cancel{(N-2)!}$$

note p is none of κ_i

equal by $1\leftrightarrow 2$

$$= \frac{1}{\cancel{2}}\sum_{\kappa_i\neq m}(-1)^{S_p-S_m}\,\langle m\kappa_i||p\kappa_i\rangle \times \cancel{2}$$

If $\kappa_i = m$,

$$\langle mm||pm\rangle = \langle mm|pm\rangle - \underbrace{\overset{\text{dummy } 1\leftrightarrow 2}{\langle mm|mp\rangle}}_{=\langle mm|pm\rangle} = 0$$

Thus the condition $\kappa_i \neq m$ can be removed. By replacing the occupied-state sum over κ_i by the infinite state sum weighted with the occupation number,

$$\langle K|\Theta_2|K'\rangle = \sum_{\kappa=1}^{\infty} (-1)^{S_p - S_m} n_\kappa \langle m\kappa \| p\kappa \rangle \qquad (34)$$

Case 3: $|K\rangle = |\cdots m \cdots n \cdots\rangle$
$|K'\rangle = |\cdots p \cdots q \cdots\rangle$

$\langle K|\Theta_2|K'\rangle$

$$= \frac{N(N-1)}{2} \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P+P'} \int d1 \cdots dN \, P[\cdots m \cdots n \cdots] \frac{e^2}{r_{12}} P'[\cdots p \cdots q \cdots]$$

The permutations P and P' should place m and n and p and q, respectively, at $\mathbf{r}_1$ and $\mathbf{r}_2$, and otherwise identical. For each choice, they place the remaining (N-2) states at $\mathbf{r}_3 \cdots \mathbf{r}_N$ identically in (N-2)! ways.

$\therefore \langle K|\Theta_2|K'\rangle$

$$= \frac{N\cancel{(N-1)}}{2} \frac{1}{\cancel{N!}} \cancel{(N-2)!} \cdot (-1)^{S_p - S_m + S_q - S_n} [\langle mn|pq\rangle - \langle mn|qp\rangle$$

$$+ \underbrace{\langle nm|qp\rangle - \langle nm|pq\rangle}_{1 \leftrightarrow 2;\ \text{the same as above}}]$$

$$= \frac{1}{\cancel{2}} (-1)^{S_p + S_q - S_m - S_n} \langle mn\|pq\rangle \times \cancel{2}$$

$$\therefore \langle K|\Theta_2|K'\rangle = (-1)^{S_p + S_q - S_m - S_n} \langle mn\|pq\rangle \qquad (35)$$

In summary, two-body matrix elements are

$$\boxed{\begin{aligned}
&\text{Case 1: } K = K' \\
&\langle K|\Theta_2|K\rangle = \frac{1}{2}\sum_{\kappa=1}^{\infty}\sum_{\kappa'=1}^{\infty} n_\kappa n_{\kappa'} \langle \kappa\kappa' \| \kappa\kappa' \rangle \qquad (31) \\
&\text{Case 2: } K = |\cdots m \cdots\rangle \\
&\qquad\quad\;\; K' = |\cdots p \cdots\rangle \\
&\langle K|\Theta_2|K'\rangle = \sum_{\kappa=1}^{\infty} (-1)^{S_p - S_m} n_\kappa \langle m\kappa \| p\kappa \rangle \qquad (34) \\
&\text{Case 3: } K = |\cdots m \cdots n \cdots\rangle \\
&\qquad\quad\;\; K' = |\cdots p \cdots q \cdots\rangle \\
&\langle K|\Theta_2|K'\rangle = (-1)^{S_p + S_q - S_m - S_n} \langle mn \| pq \rangle \qquad (35)
\end{aligned}}$$

where the two-electron integrals are

$$\begin{cases}
\langle ij|kl\rangle = \int d\mathbf{r}\, d\mathbf{r}'\, \varphi_i^*(\mathbf{r})\, \varphi_j^*(\mathbf{r}')\, \dfrac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, \varphi_k(\mathbf{r})\, \varphi_l(\mathbf{r}') & (32) \\[2ex]
\langle ij\|kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle & (33)
\end{cases}$$

Substituting Eqs. (31), (34), (35) to (16), the two-body contribution to the r.h.s. of the time-dependent Schrödinger equation is

$$(\beta) = \left[\frac{1}{2}\sum_{k}\sum_{k'} n_k n_{k'} \langle kk' \| kk' \rangle\right] f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{n_1' \cdots n_\infty'} \sum_{k=1}^{\infty} (-1)^{S_p - S_m} n_k \langle mk \| pk \rangle f(n_1' \cdots n_\infty', t) \qquad (\beta 1)$$

$$+ \sum_{n_1' \cdots n_\infty'} (-1)^{S_p + S_q - S_m - S_n} \langle mn \| pq \rangle f(n_1' \cdots n_\infty', t) \qquad (\beta 2)$$

(β1) The $(n_1' \cdots n_\infty')$ sum picks up all occupied m and unoccupied p.

$$\therefore (\beta 1) = \sum_k \sum_m \sum_p (-1)^{S_p - S_m} n_k n_m (1 - n_p) \langle mk \| pk \rangle$$

$$\times f(\cdots n_m - 1 \cdots n_p + 1 \cdots)$$

(β2) The $(n_1' \cdots n_\infty')$ sum picks up all occupied states m & n and unoccupied p & q.

$$\therefore (\beta 2) = \sum_m \sum_n \sum_p \sum_q (-1)^{S_p + S_q - S_m - S_n} n_m n_n (1 - n_p)(1 - n_q) \langle mn \| pq \rangle$$

$$\times f(\cdots n_m - 1 \cdots n_n - 1 \cdots n_p + 1 \cdots n_q + 1 \cdots)$$

Note any index collision of $m = n$ or $p = q$ will make the matrix element zero, so no need to enforce the conditions, $m \neq n$ and $p \neq q$, in the sum.

$$\therefore (\beta) = \left[\frac{1}{2} \sum_{k}^{\infty} \sum_{k'}^{\infty} n_k n_{k'} \langle kk' \| kk' \rangle \right] f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{k}^{\infty} \sum_{m}^{\infty} \sum_{p}^{\infty} (-1)^{S_p - S_m} n_k n_m \overline{n}_p \langle mk \| pk \rangle f(\cdots n_m - 1 \cdots n_p + 1 \cdots)$$

$$+ \sum_{m}^{\infty} \sum_{n}^{\infty} \sum_{p}^{\infty} \sum_{q}^{\infty} (-1)^{S_p + S_q - S_m - S_n} n_m n_n \overline{n}_p \overline{n}_q \langle mn \| pq \rangle$$

$$\times f(\cdots n_{m-1} \cdots n_n - 1 \cdots n_p + 1 \cdots n_q + 1 \cdots) \tag{36}$$

where

$$n_p \equiv 1 - n_p \tag{37}$$

Substituting Eqs. (26) and (36) in (16),

$$i\hbar \frac{\partial}{\partial t} f(n_1 \cdots n_\infty, t) =$$

$$\left(\sum_{k=1}^{\infty} n_k \langle k | h | k \rangle \right) f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{m=1}^{\infty} \sum_{p=1}^{\infty} (-1)^{S_p - S_m} n_m \overline{n}_p \langle m | h | p \rangle f(\cdots n_m - 1 \cdots n_p + 1 \cdots)$$

$$+ \left(\frac{1}{2} \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} n_k n_{k'} \langle kk' \| kk' \rangle \right) f(n_1 \cdots n_\infty, t)$$

$$+ \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} \sum_{p=1}^{\infty} (-1)^{S_p - S_m} n_k n_m \overline{n}_p \langle mk \| pk \rangle f(\cdots n_m - 1 \cdots n_p + 1 \cdots)$$

$$+ \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} (-1)^{S_p + S_q - S_m - S_n} n_m n_n \overline{n}_p \overline{n}_q \langle mn \| pq \rangle$$

$$\times f(\cdots n_m - 1 \cdots n_n - 1 \cdots n_p + 1 \cdots n_q + 1 \cdots) \tag{38}$$

Second Quantization and Slater Determinants (II)

2/24/10

– Let us define creation $\{\hat{a}_k^\dagger | k = 1 \cdots \infty\}$ and annihilation $\{\hat{a}_k | k = 1 \cdots \infty\}$ operators, which satisfy anticommutation relations

$$\begin{cases} \{\hat{a}_k, \hat{a}_{k'}^\dagger\} = \delta_{kk'} & (1) \\ \{\hat{a}_k, \hat{a}_{k'}\} = \{\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger\} = 0 & (2) \end{cases}$$

where the anticommutator is defined as

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} \tag{3}$$

(Pauli exclusion)

For $k = k'$, Eq. (2) implies

$$\hat{a}_k^2 = (\hat{a}_k^\dagger)^2 = 0 \tag{4}$$

(Number representation)

We introduce the number operator as

$$\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k \tag{5}$$

Then

$$\begin{aligned} \hat{n}_k^2 &= \hat{a}_k^\dagger \hat{a}_k \hat{a}_k^\dagger \hat{a}_k \\ &= \hat{a}_k^\dagger (1 - \hat{a}_k^\dagger \hat{a}_k) \hat{a}_k \quad (\because \text{Eq.}(1)) \\ &= \hat{n}_k - \underbrace{(\hat{a}_k^\dagger)^2 (\hat{a}_k)^2}_{=0} \quad (\because \text{Eq.}(4)) \end{aligned}$$

$$\therefore \hat{n}_k^2 = \hat{n}_k \tag{6}$$

Consider the eigenvalues n_k and the corresponding eigenvectors $|n_k\rangle$ of the number operator $\hat{n}_k$,

$$\hat{n}_k |n_k\rangle = n_k |n_k\rangle \tag{7}$$

From Eq. (6)

$$0 = (\hat{n}_k^2 - \hat{n}_k)|n_k\rangle = (n_k^2 - n_k)|n_k\rangle = n_k(1-n_k)|n_k\rangle$$

$$\therefore\ n_k = 0 \text{ or } 1 \tag{8}$$

or

$$\begin{cases} \hat{a}_k^\dagger \hat{a}_k |1_k\rangle = |1_k\rangle & (9) \\ \hat{a}_k^\dagger \hat{a}_k |0_k\rangle = 0 & (10) \end{cases}$$

Note

$$\begin{cases} \hat{a}_k^\dagger |0_k\rangle = |1_k\rangle & (11) \\ \hat{a}_k |1_k\rangle = |0_k\rangle & (12) \\ \hat{a}_k |0_k\rangle = 0 & (13) \\ \hat{a}_k^\dagger |1_k\rangle = 0 & (14) \end{cases}$$

∵

(11) $\hat{n}_k(\hat{a}_k^\dagger|0_k\rangle) = \hat{a}_k^\dagger \hat{a}_k \hat{a}_k^\dagger |0_k\rangle$

$= \hat{a}_k^\dagger(1 - \hat{a}_k^\dagger \hat{a}_k)|0_k\rangle$ (∵ Eq. (1))

$= \hat{a}_k^\dagger|0_k\rangle - \cancel{(\hat{a}_k^\dagger)^2}\hat{a}_k|0_k\rangle$ (∵ Eq. (4))

$\therefore\ \hat{a}_k^\dagger|0_k\rangle = |1_k\rangle$ (∵ Eq. (9))

(12) $0 = (1 - \hat{a}_k \hat{a}_k^\dagger)|0_k\rangle \Rightarrow |0_k\rangle = \hat{a}_k(\underbrace{\hat{a}_k^\dagger|0_k\rangle}_{|1_k\rangle})$ (∵ Eq. (11))

(∵ Eqs. (1) & (10))

$$(13)\quad \hat{a}_n|0_n\rangle \overset{(\because\ \text{Eq.}(12))}{=} \underbrace{\hat{a}_n^2}_{=0\ (\because\ \text{Eq.}(4))}|1_n\rangle = 0$$

$$(14)\quad \hat{a}_n^\dagger|1_n\rangle \overset{(\because\ \text{Eq.}(11))}{=} \underbrace{(\hat{a}_n^\dagger)^2}_{=0\ (\because\ \text{Eq.}(4))}|0_n\rangle = 0$$

//

(Adjoincy and orthonormality)

By defining the creation and annihilation operators adjoint, the orthonormality of the basis set can be algebraically derived.

$$\begin{cases} \langle 0_n|0_n\rangle = \langle 1_n|1_n\rangle = 1 & (15) \\ \langle 0_n|1_n\rangle = \langle 1_n|0_n\rangle = 0 & (16) \end{cases}$$

∵

We can prove $(\hat{a}_n^\dagger)^\dagger = \hat{a}_n \Rightarrow \langle 1_n|1_n\rangle = \langle 0_n|0_n\rangle$

$$\begin{aligned} \because\ \langle 1_n|1_n\rangle &= \langle 0_n|(\hat{a}_n^\dagger)^\dagger\hat{a}_n^\dagger|0_n\rangle && (\because\ \text{Eq.}(11)) \\ &= \langle 0_n|\hat{a}_n\hat{a}_n^\dagger|0_n\rangle && (\because\ \text{assumption}) \\ &= \langle 0_n|1-\underbrace{\cancel{\hat{a}_n^\dagger\hat{a}_n}}_{(\because\ \text{Eq.}(13))}|0_n\rangle && (\because\ \text{Eq.}(1)) \\ &= \langle 0_n|0_n\rangle \end{aligned}$$

$$\begin{aligned} (16)\quad \langle 0_n|1_n\rangle &= \langle 0_n|\hat{a}_n^\dagger|0_n\rangle && (\because\ \text{Eq.}(11)) \\ &= \langle 0_n|(\hat{a}_n^\dagger)^\dagger|0_n\rangle^* \\ &= \langle 0_n|\underbrace{\hat{a}_n|0_n\rangle}_{=0}{}^* && (\because\ \text{assumption}) \end{aligned}$$

//

For many states, we define the direct-product state

$$|n_1 \cdots n_\infty\rangle = (\hat{a}_1^+)^{n_1} \cdots (\hat{a}_\infty^+)^{n_\infty} |0\rangle \tag{17}$$

where the vacuum vector $|0\rangle$ is defined as

$$\hat{n}_k |0\rangle = \hat{a}_k |0\rangle = 0 \quad (k = 1 \cdots \infty) \tag{18}$$

Then

$$\begin{cases} \hat{a}_k |\cdots n_k \cdots\rangle = (-1)^{S_k} n_k |\cdots n_k - 1 \cdots\rangle & (19) \\ \hat{a}_k^+ |\cdots n_k \cdots\rangle = (-1)^{S_k} \bar{n}_k |\cdots n_k + 1 \cdots\rangle & (20) \\ \hat{n}_k^+ |\cdots n_k \cdots\rangle = n_k \quad |\cdots n_k \cdots\rangle & (21) \end{cases}$$

where the phase factor is

$$S_k = 1 + \cdots + n_{k-1} \tag{22}$$

and

$$\bar{n}_k = 1 - \bar{n}_k \tag{23}$$

∵

(19) If $n_k = 0$, $\hat{a}_k$ can be permuted all the way to the right, where $\cdots \hat{a}_k |0\rangle = 0$. Else, $n_k = 1$ and

$$\hat{a}_k (\hat{a}_1^+)^{n_1} \cdots (\hat{a}_{k-1}^+)^{n_{k-1}} \hat{a}_k^+ \cdots |0\rangle$$

$$= (-1)^{S_k} \cdots \underbrace{\hat{a}_k \hat{a}_k^+}_{1 - \hat{a}_k^+ \hat{a}_k} \cdots |0\rangle$$

$\hat{a}_k$ permuted to the right, producing 0

$\hat{a}_k^+$ eliminated $\Rightarrow n_k = 0$

$$= (-1)^{S_k} |\cdots n_k - 1 \cdots\rangle$$

(20) If $n_k = 1$, $\hat{a}_k^\dagger$ is permuted to the k-th place to produce $(\hat{a}_k^\dagger)^2 = 0$. Else, $n_k = 0$ and

$$\hat{a}_k^\dagger (\hat{a}_1^\dagger)^{n_1} \cdots (\hat{a}_{k-1}^\dagger)^{n_{k-1}} (\hat{a}_{k+1}^\dagger)^{n_{k+1}} \cdots |0\rangle$$

$$= (-1)^{S_k} (\hat{a}_1^\dagger)^{n_1} \cdots (\hat{a}_{k-1}^\dagger)^{n_{k-1}} \hat{a}_k^\dagger (\hat{a}_{k+1}^\dagger)^{n_{k+1}} \cdots |0\rangle$$

$$= (-1)^{S_k} |\cdots n_k + 1 \cdots\rangle$$

(21) If $n_k = 0$, $\hat{a}_k$ in $\hat{n}_k$ can be permuted all the way next to $|0\rangle$ to produce $\cdots \hat{a}_k|0\rangle = 0$. Else, note that

$$[\hat{n}_k, \hat{a}_{k'}^\dagger] = [\hat{a}_k^\dagger \hat{a}_k, \hat{a}_{k'}^\dagger]$$

$$= \underbrace{\hat{a}_k^\dagger \hat{a}_k \hat{a}_{k'}^\dagger}_{-\hat{a}_k^\dagger \hat{a}_{k'}^\dagger \hat{a}_k} - \hat{a}_{k'}^\dagger \hat{a}_k^\dagger \hat{a}_k$$

$$= \hat{a}_{k'}^\dagger \hat{a}_k^\dagger \hat{a}_k$$

$$= 0$$

$$\therefore \hat{n}_k (\hat{a}_1^\dagger)^{n_1} \cdots (\hat{a}_{k-1}^\dagger)^{n_{k-1}} \hat{a}_k^\dagger \cdots |0\rangle$$

$$= (\hat{a}_1^\dagger)^{n_1} \cdots (\hat{a}_{k-1}^\dagger)^{n_{k-1}} \underbrace{\hat{n}_k \hat{a}_k^\dagger}_{\hat{a}_k^\dagger \hat{a}_k \hat{a}_k^\dagger} \cdots |0\rangle$$

$$= \hat{a}_k^\dagger (1 - \hat{a}_k^\dagger \hat{a}_k)$$

$$= \hat{a}_k^\dagger - \underbrace{(\hat{a}_k^\dagger)^2}_{=0} \hat{a}_k$$

$$= 1 \cdot |\cdots \underset{n_k}{1} \cdots\rangle$$

//

— We consider an abstract vector space spanned by the orthonormal set

$$\{ |n_1 \cdots n_\infty\rangle \mid n_1, \ldots, n_\infty \in \{0, 1\} \} \tag{24}$$

which satisfies the following two properties.

(Orthonormality)

$$\langle n_1 \cdots n_\infty | n_1' \cdots n_\infty' \rangle = \delta_{n_1 n_1'} \cdots \delta_{n_\infty n_\infty'} \tag{25}$$

(Completeness)

$$\sum_{n_1, \ldots, n_\infty = 0}^{1} |n_1 \cdots n_\infty\rangle\langle n_1 \cdots n_\infty| = 1 \tag{26}$$

— We introduce a vector in this vector space as

$$|\Psi(t)\rangle = \sum_{n_1, \ldots, n_\infty = 1}^{\infty} f(n_1 \cdots n_\infty, t)\, |n_1 \cdots n_\infty\rangle \tag{27}$$

and define its time variation as governed by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}\, |\Psi(t)\rangle \tag{28}$$

where the second-quantized Hamiltonian operator is

$$\hat{H} = \sum_{mn} \hat{a}_m^{\dagger} \langle m|h|n\rangle \hat{a}_n + \frac{1}{2} \sum_{mnpq} \hat{a}_m^{\dagger} \hat{a}_n^{\dagger} \langle mn|v|pq\rangle \hat{a}_q \hat{a}_p \tag{29}$$

$$\begin{cases} \langle m|h|n\rangle = \int d\mathbf{r}\, \psi_m^*(\mathbf{r})\, h(\mathbf{r})\, \psi_n(\mathbf{r}) & (30) \\ \langle mn|v|pq\rangle = \int d\mathbf{r}\, d\mathbf{r}'\, \psi_m^*(\mathbf{r})\, \psi_n^*(\mathbf{r}')\, v(\mathbf{r}, \mathbf{r}')\, \psi_p(\mathbf{r})\, \psi_q(\mathbf{r}') & (31) \end{cases}$$

$$= [m^* p | v | n^* q] \quad \text{(Chemist's notation)}$$

— (Jh) The time dependence of $f(n_1 \cdots n_\infty, t)$ governed by Eq. (27) is identical to that followed by the expansion coefficients of the N-electron wave function in terms of Slater determinants (i.e., Eq. (38) in 2/21/10 note).

Below, we will prove that the Hamiltonian operator Eq. (29) has the same matrix element as Eqs. (24), (25), (31), (34), (35) in 2/21/10 note.

– (One-body term)

$$\langle K|H_1|K'\rangle = \langle n_1 \cdots n_\infty| \sum_{mn} \hat{a}_m^\dagger \langle m|h|n\rangle a_n |n_1' \cdots n_\infty'\rangle \tag{32}$$

The one-body matrix element is nonzero only if K and K′ differ at most for one occupation.

<u>Case 1 : K = K′</u>

For each index n, $a_n|K\rangle = 0$ if it is not occupied.
Similarly, m should be occupied, otherwise $\langle K|a_m = 0$.

$$\therefore \langle K|H_1|K\rangle = \sum_{m,n} n_m n_n \langle K|\underbrace{a_m^\dagger a_n}_{\delta_{mn} - a_n a_m^\dagger}|K\rangle \langle m|h|n\rangle$$

↳ $a_m^\dagger|K\rangle = 0$ since m is occupied

$$= \sum_n \underbrace{(n_n)^2}_{= n_n \ (\because \text{ Eq. } (6))} \langle n|h|n\rangle$$

$$\therefore \langle K|H_1|K\rangle = \sum_{n=1}^{\infty} n_n \langle n|h|n\rangle \tag{33}$$

This is identical to Eq. (24) in 2/21/10.

Case 2: $K = |\cdots m \cdots>$

$K' = |\cdots p \cdots>$

$$\langle K|H_1|K'\rangle = \sum_{ab} \langle K|a_a^+ a_b|K'\rangle \langle a|h|b\rangle$$

The matrix element is nonzero only if $b = p$ and $a = m$, othewise the orthonormality makes it zero

$$\therefore \langle K|H_1|K'\rangle = \langle K|a_m^+ a_p|K'\rangle \langle m|h|p\rangle$$

$$= (-1)^{S_p - S_m} \langle 0|\cdots \underbrace{a_m a_m^+}_{1-\cancel{a_m^+ a_m}} \cdots|\cdots \underbrace{a_p a_p^+}_{1-\cancel{a_p^+ a_p}} \cdots|0\rangle \langle m|h|p\rangle$$

$$= (-1)^{S_p - S_m} \underbrace{\langle 0|a_N \cdots \cancel{a_m} \cdots a_1 \, a_1^+ \cdots \cancel{a_p^+} \cdots a_N^+|0\rangle}_{1} \langle m|h|p\rangle$$

$$\therefore \langle K|H_1|K'\rangle = (-1)^{S_p - S_m} \langle m|h|p\rangle \qquad (34)$$

This is identical to Eq.(25) in 2/21/10.

– (Two-body term)

$$\langle K|H_2|K'\rangle = \langle n_1 \cdots n_\infty | \frac{1}{2}\sum_{mnpq} a_m^\dagger a_n^\dagger \langle mn|u|pq\rangle a_q a_p \qquad (35)$$

The two-body matrix element is nonzero only if K and K′ differ at most for 2 occupations.

<u>Case 1: $K = K'$</u>

$\langle K| a_m^\dagger a_n^\dagger$ and $a_q a_p |K\rangle$ restrict that m, n, p, q be occupied.

$$\therefore \langle K|H_2|K\rangle = \frac{1}{2}\sum_{mnpq} n_m n_n n_p n_q \langle mn|pq\rangle$$

↑ we adopt two-electron integral notation in 2/21/10

$$\times \langle K| \underbrace{a_m^\dagger a_n^\dagger a_q a_p}_{a_m^\dagger(\delta_{nq} - a_q a_n^\dagger) a_p} |K\rangle$$

$$= \delta_{nq} a_m^\dagger a_p - a_m^\dagger a_q a_n^\dagger a_p$$

$$= \delta_{nq}(\delta_{mp} - \cancel{a_p a_m^\dagger}) - (\delta_{mq} - \cancel{a_q a_m^\dagger}) a_n^\dagger a_p$$

$(\because a_m^\dagger |K\rangle = 0) \qquad (\because \langle K| a_q = 0)$

$$= \delta_{nq}\delta_{mp} - \delta_{mq}(\delta_{np} - \cancel{a_p a_n^\dagger})$$

$(\because \langle K| a_p = 0)$

$$= \delta_{mp}\delta_{nq} - \delta_{mq}\delta_{np}$$

$$= \frac{1}{2}\sum_{mn} \underbrace{n_m^2 n_n^2}_{= n_m n_n \ (\because \text{Eq.}(6))} [\underbrace{\langle mn|mn\rangle - \langle mn|nm\rangle}_{= \langle mn||mn\rangle}]$$

$$\therefore \langle K|H_2|K\rangle = \frac{1}{2}\sum_{mn} n_m n_n \langle mn||mn\rangle \qquad (36)$$

This is identical to Eq. (31) in 2/21/10.

Case 2: $K = |\cdots m \cdots\rangle$
$K' = |\cdots p \cdots\rangle$

$$\langle K|H_2|K'\rangle = \frac{1}{2}\sum_{ab\,rs} \langle K| a_a^\dagger a_b^\dagger a_s a_r |K'\rangle \langle ab|rs\rangle$$

Let n be one of the occupied states, then (r,s) should be (p,n) or (n,p), and (a,b) should be (m,n) or (n,m).

$$\langle K|H_2|K'\rangle = \frac{1}{2}\sum_{n} n_n \Big[\underbrace{\langle K|a_m^\dagger a_n^\dagger a_n a_p|K'\rangle}_{①} \langle mn|pn\rangle + \underbrace{\langle K|a_m^\dagger a_n^\dagger a_p a_n|K'\rangle}_{②} \langle mn|np\rangle + \underbrace{\langle K|a_n^\dagger a_m^\dagger a_p a_n|K'\rangle}_{③} \langle nm|np\rangle + \underbrace{\langle K|a_n^\dagger a_m^\dagger a_n a_p|K'\rangle}_{④} \langle nm|pn\rangle \Big]$$

$$① = \langle K|a_m^\dagger (1-\cancel{a_n a_n^\dagger}) a_p|K'\rangle \quad (\because\ a_n^\dagger|K'\rangle = 0)$$
$$= \langle K|a_m^\dagger a_p|K'\rangle$$
$$= (-1)^{S_p - S_m} \langle 0| \cdots \underbrace{a_m a_m^\dagger}_{1-\cancel{a_m^\dagger a_m}} \cdots | \cdots \underbrace{a_p a_p^\dagger}_{1-\cancel{a_p^\dagger a_p}} \cdots |0\rangle$$
$$= (-1)^{S_p - S_m}$$

$$② = -\langle K|a_m^\dagger a_p a_n^\dagger a_n|K'\rangle$$
$$= -\langle K|a_m^\dagger a_p (1-\cancel{a_n a_n^\dagger})|K'\rangle$$
$$= -\langle K|a_m^\dagger a_p|K'\rangle$$
$$= -(-1)^{S_p - S_m}$$

$$③ = \langle K| a_k^{\dagger} a_m^{\dagger} a_p a_k |K'\rangle$$
$$= \langle K| a_m^{\dagger} a_p a_k^{\dagger} a_k |K'\rangle$$
$$= \langle K| a_m^{\dagger} a_p (1 - \cancel{a_k a_k^{\dagger}}) |K'\rangle$$
$$= (-1)^{S_p - S_m}$$

$$④ = \langle K| a_k^{\dagger} a_m^{\dagger} a_k a_p |K'\rangle$$
$$= -\langle K| a_m^{\dagger} (1 - \cancel{a_k a_k^{\dagger}}) a_p |K'\rangle$$
$$= -(-1)^{S_p - S_m}$$

$$\therefore \langle K|H_2|K'\rangle = \frac{1}{2}\sum_k n_k (-1)^{S_p - S_m} \Big[\langle mk|pk\rangle - \langle mk|kp\rangle + \langle km|kp\rangle - \langle km|pk\rangle \Big]$$

(☺ dummy $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$)

$$= \cancel{\frac{1}{2}} \sum_k n_k (-1)^{S_p - S_m} \times \cancel{2} \langle mk||pk\rangle$$

$$\therefore \langle K|H_2|K'\rangle = \sum_k n_k (-1)^{S_p - S_m} \underbrace{\langle mk||pk\rangle} \tag{37}$$

$$\langle mk|pk\rangle - \langle mk|kp\rangle$$
$$= \langle mk|u|pk\rangle - \langle mk|u|kp\rangle$$

This is identical to Eq. (34) in 2/21/10.

Case 3: $K = |\cdots m \cdots n \cdots\rangle$

$K' = |\cdots p \cdots q \cdots\rangle$

$$\langle K|H_2|K'\rangle = \frac{1}{2}\sum_{abrs} \langle K|a_a^\dagger a_b^\dagger a_s a_r|K'\rangle \langle ab|rs\rangle$$

(a,b) should be (m,n) or (n,m) and (r,s) should be (p,q) or (q,p)

$$\langle K|H_2|K'\rangle = \frac{1}{2}\Big[\langle K|a_m^\dagger a_n^\dagger a_q a_p|K\rangle \langle mn|pq\rangle$$
$$+ \langle K|a_m^\dagger a_n^\dagger a_p a_q|K\rangle \langle mn|qp\rangle$$
$$+ \langle K|a_n^\dagger a_m^\dagger a_p a_q|K'\rangle \langle nm|qp\rangle$$
$$+ \langle K|a_n^\dagger a_m^\dagger a_q a_p|K'\rangle \langle nm|pq\rangle\Big]$$

$$= \frac{1}{2}\Big[\langle K|a_m^\dagger a_n^\dagger a_q a_p|K\rangle \langle mn||pq\rangle$$
$$+ \langle K|a_n^\dagger a_m^\dagger a_p a_q|K\rangle \langle nm||qp\rangle\Big]$$

dummy $r_1 \leftrightarrow r_2$

$$= \langle K|a_m^\dagger a_n^\dagger a_q a_p|K'\rangle \langle mn||pq\rangle$$
$$= (-1)^{S_p - S_m} \langle K|a_n^\dagger a_q|K'\rangle \langle mn||pq\rangle$$
$$= (-1)^{S_p + S_q - S_m - S_n} \langle mn||pq\rangle$$

$$\therefore \langle K|H_2|K'\rangle = (-1)^{S_p + S_q - S_m - S_n} \langle mn||pq\rangle \qquad (38)$$

This is identical to Eq. (35) in 2/21/10. //