CB2070 Ex session 3

① One-electron operator

$$\hat{\Omega} = \sum_i^N \hat{\omega}(i)$$

SD reference

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_j^{N!} (-1)^{p_i} P_i \{\psi_1(\bar{r}_1), \dots, \psi_i(\bar{r}_i), \dots, \psi_N(\bar{r}_N)\} d\bar{r}_1 \dots d\bar{r}_N$$

$$|\Psi_i^s\rangle = \frac{1}{\sqrt{N!}} \sum_k^{N!} (-1)^{p_k} P_k \{\psi_1(\bar{r}_1), \dots, \psi_s(\bar{r}_s), \dots, \psi_N(\bar{r}_N)\} d\bar{r}_1, \dots, d\bar{r}_N$$

indistinguishable particles

$$\sum_i^N \langle \Psi_i^s | \hat{\omega}(i) | \Psi \rangle = N \langle \Psi_i^s | \hat{\omega}(1) | \Psi \rangle$$

$$= \frac{N}{N!} \sum_{j,k}^{N!} \int (-1)^{p_j} (-1)^{p_k} P_k \{\dots, \psi_s^*(\bar{r}_s), \dots\}^{+} \hat{\omega}(1) P_j \{\dots, \psi_i(\bar{r}_i), \dots\} d\bar{r}_1 \dots d\bar{r}_N$$

In order to be nonzero, the permutations must be identical due to orthonormality.
ψ_s must be occupied by electron 1 in order to be associated with $\hat{\omega}(1)$ and thus give a nonzero result.
ψ_i must also be occupied by electron 1 with the same reasoning
⇒ factor of $(N-1)!$ because having that electron constellation can happen in ↑ many ways

Integrating over all other electrons give factor of 1

$$N \langle \Psi_i^s | \hat{\omega}(1) | \Psi \rangle = \frac{1}{(N-1)!} \sum_k^{N!} \int (-1)^{2p_k} P_k \{\dots, \psi_s^*(1), \dots\} \hat{\omega}(1) P_k \{\dots, \psi_i(1), \dots\} d\bar{r}_1 \dots d\bar{r}_N$$

$$= \frac{(N-1)!}{(N-1)!} \int \psi_s(1) \hat{\omega}(1) \psi_i(1) d\bar{r}_1 = \langle \psi_s | \hat{\omega} | \psi_i \rangle$$

② $$\langle \Psi_{ij}^{st} | \hat{\Omega} | \Psi \rangle = \frac{N}{N!} \sum_{k,l} \int (-1)^{p_k} (-1)^{p_l} P_k \{\dots, \psi_s^*(1), \psi_t^*(2), \dots\}^{+} \hat{\omega}(1) P_l \{\dots, \psi_i(1), \psi_j(2)\} d\bar{r}_1 \dots$$

Again, the permutations must be identical to give nonzero. ψ_s and ψ_t are orthogonal to any spin orbital in the other determinant, they must both be occupied by electron 1 to associate w $\hat{\omega}(1)$, but this is impossible. Hence:

$$\langle \Psi_{ij}^{st} | \hat{\Omega} | \Psi \rangle = 0 \quad \text{for } \hat{\Omega} \text{ being one-electron operator}$$

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① Reflection on the case of spin-independent/pure-orbital operator
Spin-orbitals ψ_s and ψ_i must have the same spin in order to give non-zero

CB2070 ex 3 cont'd

(3) Derive explicit HF energy

N-electron Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \sum_{j>i}^{N} \hat{g}(i,j)$$

$$E^{HF} = \langle\Psi|\hat{H}|\Psi\rangle = \sum_{i}^{N} \langle\Psi|\hat{h}(i)|\Psi\rangle + \sum_{j>i}^{N} \langle\Psi|\hat{g}(i,j)|\Psi\rangle$$

We have the case for matrix elements where the bra- and ket states are the same

One-elec part

$$\underbrace{\sum_{i}^{N}}_{\text{sum over elecs}} \langle\Psi|\hat{h}(i)|\Psi\rangle = \frac{N}{N!} \underbrace{\sum_{i,j}^{N!}}_{\text{sum over orbital permutations}} \int (-1)^{P_i}(-1)^{P_j} P_i\{\psi_m^*(1)\psi_n^*(2)\ldots\} \hat{h}(1) P_j\{\psi_m(1)\psi_n(2)\ldots\} \ldots d\bar{r}_N$$

P_i and P_j must be identical for non-zero and electron 1 (which is operated on by $\hat{h}(1)$ is there in the same orbital in each permutation. There are $(N-1)!$ ways of arranging the remaining orbitals.
Integration over $d\bar{r}_2 \ldots d\bar{r}_N$ gives factor of 1

$$\sum_{i}^{N} \langle\Psi|\hat{h}|\Psi\rangle = \frac{(N-1)!}{(N-1)!} \underbrace{\sum_{i}^{N}}_{\text{sum over occupied orbitals}} \psi_i^*(1)\hat{h}(1)\psi_i^*(1) = \sum_{i}^{N} \langle i|\hat{h}|i\rangle$$

Two-elec part. The two SDs are the same

For two-elec operator $\sum_{i,j}^{N} \hat{g}(i,j) = \frac{N(N-1)}{2} \hat{g}(1,2)$ due to indistinguishable electrons.

$$\frac{N(N-1)}{2} \langle\Psi|\hat{g}(1,2)|\Psi\rangle = \frac{N(N-1)}{2\,N!} \sum_{i,j}^{N!} (-1)^{P_i}(-1)^{P_j} \int P_i\{\psi_m^*(1)\psi_n^*(2)\ldots\} \hat{g}(1,2) P_j\{\ \} \ldots d\bar{r}_N$$

Again, permutations must be the same to give nonzero, and electrons 1 and 2 must be in either of the two same orbitals:
- If $\psi_m(1)\psi_n(2)$ in P_i, then it must either be $\psi_m(1)\psi_n(2)$ or $\psi_m(2)\psi_n(1)$ in P_j to give nonzero

Integrating over electrons $3, \ldots, N$ and multiplying by $(N-2)!$ since we fixed electrons 1 and 2

$\frac{1}{2} \longrightarrow$

$$\underbrace{\frac{N(N-1)(N-2)!}{2N!}}_{=\frac{1}{2}\frac{N!}{N!}=\frac{1}{2}} \sum_{m\neq n}^{N} \int \psi_m^*(1)\psi_n^*(2)\hat{g}(1,2)[\psi_m(1)\psi_n(2) - \psi_m(2)\psi_n(1)]\, d\bar{r}_1\, d\bar{r}_2$$

$$= \frac{1}{2}\sum_{m,n}^{N} \underbrace{\langle mn|\hat{g}|mn\rangle - \langle mn|\hat{g}|nm\rangle}_{\langle mn||mn\rangle}$$

p. 83 in MQM book

③ cont'd: Closed-shell HF ground state. Simplify result

We have
$$E^{HF} = \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j}^{N} \langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle$$

We assume that $\hat{h}$ and $\hat{g}$ do not depend on spin.

Introduce the following notation for the spinorbitals

$\psi_1 = \phi_1(\vec{r})\alpha(\omega) = \phi_1 \quad , \quad \psi_2 = \phi_1(\vec{r})\beta(\omega) = \bar{\phi}_1$

where ϕ_i refers to the spatial orbital and "bar" indicates β spin.

We then write the closed-shell restricted HF wave function

$|\Psi_0\rangle = |\phi_1\bar{\phi}_1, \dots, \phi_{N/2}\bar{\phi}_{N/2}\rangle$

with this notation, we can split the summation over all spin orbitals into two sums over $N/2$ α/β spins respectively.

For one-electron part:
$$\sum_i^N \langle\psi_i|\hat{h}|\psi_i\rangle = \sum_i^{N/2}\langle\phi_i|\hat{h}|\phi_i\rangle + \sum_i^{N/2}\langle\bar{\phi}_i|\hat{h}|\bar{\phi}_i\rangle = 2\sum_i^{N/2}\langle\phi_i|\hat{h}|\phi_i\rangle$$
where the last sum is purely over spatial orbitals.

For two-electron part

* after integration over spin variable

$$\frac{1}{2}\sum_{i,j}^{N}\langle\psi_i\psi_j|\hat{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\hat{g}|\psi_j\psi_i\rangle$$

equal*

$$= \frac{1}{2}\sum_i^{N/2}\sum_j^{N/2}\Big[\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle + \langle\bar{\phi}_i\bar{\phi}_j|\hat{g}|\bar{\phi}_i\bar{\phi}_j\rangle - \langle\bar{\phi}_i\bar{\phi}_j|\hat{g}|\bar{\phi}_j\bar{\phi}_i\rangle$$

equal*

$$+ \langle\phi_i\bar{\phi}_j|\hat{g}|\phi_i\bar{\phi}_j\rangle - \underbrace{\langle\phi_i\bar{\phi}_j|\hat{g}|\bar{\phi}_j\phi_i\rangle}_{=0} + \langle\bar{\phi}_i\phi_j|\hat{g}|\bar{\phi}_i\phi_j\rangle - \underbrace{\langle\bar{\phi}_i\phi_j|\hat{g}|\phi_j\bar{\phi}_i\rangle}_{=0}\Big]$$

$$= \frac{1}{2}\sum_{i,j}^{N/2} 4\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - 2\langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle = \sum_{i,j}^{N/2} 2\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle$$

The HF energy of closed-shell ground state becomes
$$E_{HF} = 2\sum_i^{N/2}\langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{i,j}^{N/2} 2\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle$$