EXERCISE: **(1)** Show that $|I_1 I_2 \dots I_{N-1} I_N\rangle$ is normalized.

(2) Let us consider another state $|J_1 J_2 \dots J_{N-1} J_N\rangle$ and assume that at least one of the occupied spin-orbitals (let us denote it φ_{J_k}) is not occupied in $|I_1 I_2 \dots I_{N-1} I_N\rangle$. Show that the two states are orthogonal.

(3) The "counting" operator $\hat{N}$ is defined as $\hat{N} = \sum_I \hat{n}_I$ where $\hat{n}_I = \hat{a}_I^\dagger \hat{a}_I$. Show that

$$\hat{n}_I |I_1 I_2 \dots I_{N-1} I_N\rangle = |I_1 I_2 \dots I_{N-1} I_N\rangle \qquad \text{if } I = I_k \qquad 1 \leq k \leq N$$

$$= 0 \qquad \text{otherwise}$$

and conclude that $\boxed{\hat{N}|I_1 I_2 \dots I_{N-1} I_N\rangle = N|I_1 I_2 \dots I_{N-1} I_N\rangle}$.

(4) Explain why states corresponding to different numbers of electrons are automatically orthogonal.

(5) Explain why any normalized state $|\Psi\rangle$ fulfills the condition $\boxed{0 \leq \langle\Psi|\hat{n}_I|\Psi\rangle \leq 1}$.

EXERCISE:

(1) At the non-relativistic level, real algebra can be used, $\varphi_I(X) = \varphi_{i\sigma}(\mathbf{r},\tau) = \phi_i(\mathbf{r})\delta_{\sigma\tau}$,

$$\hat{h} \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\rm ne}(\mathbf{r})\times \quad \text{and} \quad \hat{w}_{\rm ee} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\times \ .$$

Show that the Hamiltonian, that is here a spin-free operator, can be rewritten in the basis of the molecular orbitals $\Big\{\phi_p(\mathbf{r})\Big\}_p$ as follows

$$\boxed{\hat{H} = \sum_{p,q} h_{pq}\hat{E}_{pq} + \frac{1}{2}\sum_{p,q,r,s}\langle pr|qs\rangle\Big(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\Big)}$$

where $\hat{E}_{pq} = \sum_\sigma \hat{a}^\dagger_{p,\sigma}\hat{a}_{q,\sigma}$, $\quad h_{pq} = \langle\phi_p|\hat{h}|\phi_q\rangle$ and

$$\langle pr|qs\rangle = \int\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\ \phi_p(\mathbf{r_1})\phi_r(\mathbf{r_2})\,\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\phi_q(\mathbf{r_1})\phi_s(\mathbf{r_2}) = (pq|rs)$$

EXERCISE:

For any normalized N-electron wavefunction Ψ, we define the one-electron (1) and two-electron (2) reduced density matrices (RDM) as follows,

$$D_{pq} = \left\langle \Psi \middle| \hat{E}_{pq} \middle| \Psi \right\rangle \quad \text{and} \quad D_{pqrs} = \left\langle \Psi \middle| \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps} \middle| \Psi \right\rangle .$$

(1) Show that the 1RDM is symmetric and that $\forall p$, the occupation $n_p = D_{pp}$ of the orbital p fulfills the inequality $0 \leq n_p \leq 2$. Show that the trace of the 1RDM equals N.

(2) Explain why the expectation value for the energy $\langle \Psi | \hat{H} | \Psi \rangle$ can be determined from the 2RDM.

Hint: show that $D_{pq} = \dfrac{1}{N-1} \sum_r D_{pqrr}$.

(3) Let us consider the particular case $|\Psi\rangle \rightarrow |\Phi\rangle = \prod_{i=1}^{N/2} \prod_{\sigma} \hat{a}^\dagger_{i,\sigma} |\mathrm{vac}\rangle$. Explain why both density matrices are non-zero only in the occupied-orbital space.

Show that $D_{ij} = 2\delta_{ij}$ and $D_{ijkl} = 4\delta_{ij}\delta_{kl} - 2\delta_{jk}\delta_{il}$ and ...

... deduce the corresponding energy expression:

$$\langle \Phi | \hat{H} | \Phi \rangle = 2 \sum_{i=1}^{N/2} h_{ii} + \sum_{i,j=1}^{N/2} \Big(2\langle ij|ij \rangle - \langle ij|ji \rangle \Big).$$

(4) Let i, j and a, b denote occupied and unoccupied (virtuals) orbitals in Φ, respectively. Explain why $\hat{E}_{ai}$ and $\hat{E}_{ai}\hat{E}_{bj}$ are referred to as single excitation and double excitation operators, respectively.

Hint: derive simplified expressions for $|\Phi_i^a\rangle = \frac{1}{\sqrt{2}} \hat{E}_{ai} |\Phi\rangle$ and $|\Phi_{ij}^{ab}\rangle = \frac{1}{2} \hat{E}_{ai}\hat{E}_{bj} |\Phi\rangle$ with $i < j$, $a < b$.

Ex: p 11

(1) $\langle I_1 I_2 \dots I_N | I_1 I_2 \dots I_N \rangle = \langle \hat{a}^+_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} vac | \hat{a}^+_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} | vac \rangle$

$= \langle vac | \hat{a}_{I_N} \dots \hat{a}_{I_2} \underbrace{\hat{a}_{I_1} \hat{a}^+_{I_1}}_{1 - \hat{a}^+_{I_1} \hat{a}_{I_1}} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} | vac \rangle$

$= \langle vac | \hat{a}_{I_N} \dots \hat{a}_{I_2} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} | vac \rangle$

since $\hat{a}_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} | vac \rangle = (-1)^{N-1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} \underbrace{\hat{a}_{I_1} | vac \rangle}_{0}$

Using $\hat{a}_{I_2} \hat{a}^+_{I_2} = 1 - \hat{a}^+_{I_2} \hat{a}_{I_2}$ and so on

we finally obtain $\boxed{\langle I_1 I_2 \dots I_N | I_1 I_2 \dots I_N \rangle = \langle vac | vac \rangle = 1}$

(2) $\langle J_1 J_2 \dots J_k \dots J_N | I_1 I_2 \dots I_N \rangle = \langle vac | \hat{a}_{J_N} \dots \hat{a}_{J_k} \dots \hat{a}_{J_2} \hat{a}_{J_1} \hat{a}^+_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} | vac \rangle$

$= (-1)^{k-1} \times (-1)^N \langle vac | \hat{a}_{J_N} \dots \hat{a}_{J_{k+1}} \hat{a}_{J_{k-1}} \dots \hat{a}_{J_2} \hat{a}_{J_1} \hat{a}^+_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_N} \underbrace{\hat{a}_{J_k} | vac \rangle}_{= 0}$

since $J_k \neq I_p$ with $1 \leq p \leq N$

thus leading to $\boxed{\langle J_1 J_2 \dots J_k \dots J_N | I_1 I_2 \dots I_N \rangle = 0}$

(3) $\hat{N} = \sum_I \hat{n}_I$. If $I = I_k$ $1 \leq k \leq N$ then $\hat{n}_I | I_1 I_2 \dots I_N \rangle = \hat{n}_{I_k} | I_1 I_2 \dots I_N \rangle$

$= \hat{a}^+_{I_k} \hat{a}_{I_k} \hat{a}^+_{I_1} \hat{a}^+_{I_2} \dots \hat{a}^+_{I_k} \dots \hat{a}^+_{I_N} | vac \rangle$

$$\Rightarrow \hat{n}_{I_k} |I_1 I_2 \ldots I_N\rangle = \hat{a}^{+}_{I_1} \left(\hat{a}^{+}_{I_k} a_{I_k} \right) \hat{a}^{+}_{I_2} \ldots \hat{a}^{+}_{I_k} \ldots \hat{a}^{+}_{I_N} |vac\rangle$$

$$= \hat{a}^{+}_{I_1} \hat{a}^{+}_{I_2} \ldots \hat{a}^{+}_{I_{k-1}} \underbrace{\left(\hat{a}^{+}_{I_k} \hat{a}_{I_k} \right) \hat{a}^{+}_{I_k}}_{\text{rule 3}} \hat{a}^{+}_{I_{k+1}} \ldots \hat{a}^{+}_{I_N} |vac\rangle$$

$$\hat{a}^{+}_{I_k} \left(1 - \hat{a}^{+}_{I_k} \hat{a}_{I_k} \right) = \hat{a}^{+}_{I_k} - \underbrace{\hat{a}^{+}_{I_k} \hat{a}^{+}_{I_k}}_{\overset{\shortparallel}{0} \ (\text{rule } 2)} \hat{a}_{I_k}$$

Therefore $\hat{n}_{I_k} |I_1 I_2 \ldots I_N\rangle = |I_1 I_2 \ldots I_N\rangle$

- if $I \notin \{I_1, I_2, \ldots, I_N\}$ then $\hat{n}_I |I_1 I_2 \ldots I_N\rangle = \hat{a}^{+}_{I} \hat{a}_{I} \hat{a}^{+}_{I_1} \hat{a}^{+}_{I_2} \ldots \hat{a}^{+}_{I_N} |vac\rangle$

$$= \hat{a}^{+}_{I_1} \hat{a}^{+}_{I_2} \ldots \hat{a}^{+}_{I_N} \hat{a}^{+}_{I} \underbrace{\hat{a}_{I} |vac\rangle}_{0}$$

Conclusion:

$$\boxed{\hat{n}_I |I_1 I_2 \ldots I_N\rangle = n_I |I_1 I_2 \ldots I_N\rangle}$$

$(= 0)$

occupation of spin-orbital φ_I (zero or 1) in $|I_1 I_2 \ldots I_N\rangle$

$$\hat{N} |I_1 I_2 \ldots I_N\rangle = \sum_I \hat{n}_I |I_1 I_2 \ldots I_N\rangle = \sum_I n_I |I_1 I_2 \ldots I_N\rangle = \underbrace{\left(\sum_I n_I \right)}_{n_{I_1} + n_{I_2} + \ldots n_{I_N}} |I_1 I_2 \ldots I_N\rangle$$

$$n_{I_1} \to 1, \quad n_{I_2} \to 1, \quad \ldots, \quad n_{I_N} \to 1$$

$$\Rightarrow \boxed{\hat{N} |I_1 I_2 \ldots I_N\rangle = N |I_1 I_2 \ldots I_N\rangle}$$

number of electrons!

Let us consider $|\Psi^N\rangle$ and $|\Psi^M\rangle$ N- and M-electron states, respectively

$$\hat{N}|\Psi^N\rangle = N|\Psi^N\rangle \qquad \text{with } N \neq M$$
$$\hat{N}|\Psi^M\rangle = M|\Psi^M\rangle$$

so that we have

$$\left.\begin{array}{l} \langle\Psi^M|\hat{N}|\Psi^N\rangle = N\langle\Psi^M|\Psi^N\rangle \\ \quad \parallel \\ \langle\hat{N}^\dagger\Psi^M|\Psi^N\rangle \\ \quad \parallel \\ \langle\hat{N}\Psi^M|\Psi^N\rangle = M\langle\Psi^M|\Psi^N\rangle \end{array}\right\} \Rightarrow \underbrace{(N-M)}_{\neq 0}\underbrace{\langle\Psi^M|\Psi^N\rangle}_{\overset{\parallel}{0}} = 0$$

(5) We conclude from question (3) that the eigenvalues of $\hat{n}_I$ are 0 or 1.

General problem: Let $\hat{A}$ be a hermitian operator, A its highest eigenvalue and a its lowest eigenvalue. We consider the basis of eigenvectors $\{|u_i\rangle\}_i$ with $\hat{A}|u_i\rangle = \alpha_i|u_i\rangle$ and $a \leq \alpha_i \leq A$

normalized eigenvalue

For any normalized state $|\Psi\rangle$, $|\Psi\rangle = \sum_i c_i|u_i\rangle$ and $\langle\Psi|\Psi\rangle = 1 = \sum_i |c_i|^2$

and $\langle\Psi|\hat{A}|\Psi\rangle = \sum_i c_i\langle\Psi|\hat{A}|u_i\rangle = \sum_i c_i\alpha_i\langle\Psi|u_i\rangle = \sum_i |c_i|^2\alpha_i$

Since $\forall i$ $|c_i|^2 a \leq |c_i|^2\alpha_i \leq |c_i|^2 A \rightarrow \sum_i a|c_i|^2 \leq \sum_i |c_i|^2\alpha_i \leq \sum_i |c_i|^2 A$

$$\rightarrow \boxed{a \leq \langle\Psi|\hat{A}|\Psi\rangle \leq A}$$

In our case $\hat{A} \rightarrow \hat{n}_I$, $a \rightarrow 0$, $A \rightarrow 1$ $\rightarrow \boxed{0 \leq \langle\Psi|\hat{n}_I|\Psi\rangle \leq 1}$

EX p 17

(1) $$\hat{H} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}^+_P \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_R | \hat{w}_{ee} | \varphi_Q \varphi_S \rangle \hat{a}^+_P \hat{a}^+_R \hat{a}_S \hat{a}_Q$$

$$= \sum_{p,q,\sigma,\tau} \langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle \hat{a}^+_{p,\sigma} \hat{a}_{q,\tau} + \frac{1}{2} \sum_{pqrs} \sum_{\sigma_1\sigma_2\tau_1\tau_2} \langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle \hat{a}^+_{p,\sigma_1} \hat{a}^+_{r,\sigma_2} \hat{a}_{s,\tau_2} \hat{a}_{q,\tau_1}$$

where $\langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle = \int dx\, \varphi^*_{p\sigma}(x) (\hat{h} \varphi_{q\tau})(x) = \int d\vec{r} \sum_{\mu=\alpha,\beta} \varphi^*_{p\sigma}(\vec{r},\mu) (\hat{h} \varphi_{q\tau})(\vec{r},\mu)$

spin-free

$$= \int d\vec{r} \sum_{\mu=\alpha,\beta} \phi_p(\vec{r})\, \delta_{\mu\sigma}\, (\hat{h} \phi_q)(\vec{r})\, \delta_{\tau\mu}$$

real algebra!

$$\rightarrow \boxed{\langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle = \delta_{\sigma\tau}\, h_{pq}}$$

and $\langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle = \int dx_1 \int dx_2\, \varphi^*_{p\sigma_1}(x_1) \varphi^*_{r\sigma_2}(x_2) \frac{1}{r_{12}} \varphi_{q\tau_1}(x_1) \varphi_{s\tau_2}(x_2)$ where $r_{12} = |\vec{r}_1 - \vec{r}_2|$

$$= \int d\vec{r}_1 \int d\vec{r}_2 \sum_{\mu=\alpha,\beta} \sum_{\nu=\alpha,\beta} \phi_p(\vec{r}_1)\, \delta_{\sigma_1\mu}\, \phi_r(\vec{r}_2)\, \delta_{\sigma_2\nu} \frac{1}{r_{12}} \phi_q(\vec{r}_1)\, \delta_{\tau_1\mu}\, \phi_s(\vec{r}_2)\, \delta_{\tau_2\nu}$$

$$\rightarrow \boxed{\langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle = \delta_{\sigma_1\tau_1} \delta_{\sigma_2\tau_2} \langle pr | qs \rangle}$$

Therefore $\hat{H} = \sum_{pq\sigma\tau} h_{pq} \delta_{\sigma\tau} \hat{a}^+_{p,\sigma} \hat{a}_{q,\tau} + \frac{1}{2} \sum_{pqrs} \sum_{\sigma_1\sigma_2\tau_1\tau_2} \langle pr|qs\rangle \delta_{\sigma_1\tau_1} \delta_{\sigma_2\tau_2} \hat{a}^+_{p,\sigma_1} \hat{a}^+_{r,\sigma_2} \hat{a}_{s,\tau_2} \hat{a}_{q,\tau_1}$

$$= \sum_{pq} h_{pq} \underbrace{\left(\sum_{\sigma} \hat{a}^+_{p,\sigma} \hat{a}_{q,\sigma} \right)}_{\hat{E}_{pq}} + \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle \sum_{\sigma_1\sigma_2} \underbrace{\hat{a}^+_{p,\sigma_1} \hat{a}^+_{r,\sigma_2} \hat{a}_{s,\sigma_2} \hat{a}_{q,\sigma_1}}_{-\hat{a}^+_{p,\sigma_1} \hat{a}^+_{r,\sigma_2} \hat{a}_{q,\sigma_1} \hat{a}_{s,\sigma_2}}$$

$$\underbrace{\hat{a}^+_{r,\sigma_2} \hat{a}_{q,\sigma_1}}_{\delta_{\sigma_1\sigma_2}\delta_{rq} - \hat{a}_{q,\sigma_1}\hat{a}^+_{r,\sigma_2}}$$

$$\rightarrow \boxed{\hat{H} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle \left(\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \right)}$$

EX p 18/19

(1) • $D_{pq} = \langle \Psi | \hat{E}_{pq} | \Psi \rangle \Rightarrow D_{qp} = \langle \Psi | \hat{E}_{qp} | \Psi \rangle \underset{\text{real algebra}}{=} \langle \Psi | \hat{E}_{qp} | \Psi \rangle^* = \langle \hat{E}_{qp} \Psi | \Psi \rangle = \langle \Psi | \underbrace{\hat{E}^+_{qp}}_{\hat{E}_{pq}} | \Psi \rangle$

$= D_{pq}$.

• $n_p = \langle \Psi | \hat{E}_{pp} | \Psi \rangle = \sum_{\sigma} \underbrace{\langle \Psi | \hat{n}_{p\sigma} | \Psi \rangle}$

$0 \leq \quad \leq 1$ according to question (5) in EX p 11.

therefore $\boxed{0 \leq n_p \leq 2}$

• $\sum_p D_{pp} = \sum_p \sum_\sigma \langle \Psi | \hat{a}^+_{p,\sigma} \hat{a}_{p,\sigma} | \Psi \rangle = \langle \Psi | \underset{\text{Counting operator}}{\hat{N}} | \Psi \rangle = N \underbrace{\langle \Psi | \Psi \rangle}_{1} = N$.

(2) $\langle\Psi|\hat{H}|\Psi\rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2}\sum_{pqrs} \langle pr|qs\rangle D_{pqrs}$

Since $\sum_r D_{pqrr} = \sum_r \langle\Psi|\hat{E}_{pq}\hat{E}_{rr} - \delta_{qr}\hat{E}_{pr}|\Psi\rangle = \langle\Psi|\hat{E}_{pq}\underbrace{\sum_r \hat{E}_{rr}}_{\hat{N}}|\Psi\rangle - \sum_r \delta_{qr}\langle\Psi|\hat{E}_{pr}|\Psi\rangle$

$= N\underbrace{\langle\Psi|\hat{E}_{pq}|\Psi\rangle}_{D_{pq}} - \underbrace{\langle\Psi|\hat{E}_{pq}|\Psi\rangle}_{D_{pq}}$

$$\boxed{\sum_r D_{pqrr} = (N-1) D_{pq}}$$

it comes $\boxed{\langle\Psi|\hat{H}|\Psi\rangle = \sum_{pq}\sum_r \frac{h_{pq}}{(N-1)} D_{pqrr} + \frac{1}{2}\sum_{pqrs}\langle pr|qs\rangle D_{pqrs}}$

(3) • $D_{pq} = \langle\Phi|\hat{E}_{pq}|\Phi\rangle$ with $|\Phi\rangle = \prod_{i=1}^{N/2}\prod_{\sigma=\alpha,\beta} \hat{a}^{+}_{i,\sigma}|vac\rangle$

let us denote $a, b, \ldots$ the orbitals that are not occupied in $|\Phi\rangle$.

$D_{ab} = \langle\Phi|\sum_\sigma \hat{a}^{+}_{a,\sigma}\underbrace{\hat{a}_{b,\sigma}|\Phi\rangle}_{0} = 0 = D_{ba}$

$D_{ia} = \langle\Phi|\sum_\sigma \hat{a}^{+}_{i,\sigma}\underbrace{\hat{a}_{a,\sigma}|\Phi\rangle}_{0} = 0 = D_{ai}$

• $D_{ij} = \langle\Phi|\sum_\sigma \hat{a}^{+}_{i,\sigma}\hat{a}_{j,\sigma}|\Phi\rangle$ where i and j are occupied in $|\Phi\rangle$.

If $i \neq j$ then $D_{ij} = -\langle\Phi|\sum_\sigma \hat{a}_{j,\sigma}\underbrace{\hat{a}^{+}_{i,\sigma}|\Phi\rangle}_{0} = 0$ (Pauli principle)

if $i=j$ then $D_{ii} = 2$ since $\sum_\sigma \hat{a}^{+}_{i,\sigma}\hat{a}_{i,\sigma}|\Phi\rangle = \sum_\sigma \hat{n}_{i,\sigma}|\Phi\rangle = \sum_\sigma |\Phi\rangle = 2|\Phi\rangle$

$$\boxed{D_{ij} = 2\delta_{ij}}$$

- According to EX p17, $D_{pqrs} = \langle \Phi | \sum_{\sigma\tau} \hat{a}^{+}_{p,\sigma} \hat{a}^{+}_{r,\tau} \hat{a}_{s,\tau} \hat{a}_{q,\sigma} | \Phi \rangle$

$$= \sum_{\sigma\tau} \underbrace{\langle \hat{a}_{r,\tau} \hat{a}_{p,\sigma} \Phi | \hat{a}_{s,\tau} \hat{a}_{q,\sigma} | \Phi \rangle}$$

Therefore: s and q must be occupied.
r and p as well.

$$D_{ijkl} = \langle \Phi | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Phi \rangle = \langle \Phi | \hat{E}_{ij} \hat{E}_{kl} | \Phi \rangle - \delta_{jk} \underbrace{D_{il}}_{2\delta_{il}}$$

l must be equal to k

otherwise $\hat{E}_{kl} | \Phi \rangle = \sum_{\sigma} \hat{a}^{+}_{k,\sigma} \hat{a}_{l,\sigma} | \Phi \rangle$

$$= - \sum_{\sigma} \hat{a}_{l,\sigma} \underbrace{\hat{a}^{+}_{k,\sigma} | \Phi \rangle}_{0}$$

Therefore $D_{ijkl} = \underbrace{\langle \Phi | \hat{E}_{ij} \underbrace{\hat{E}_{kl} | \Phi \rangle \delta_{kl}}_{2\delta_{kl} | \Phi \rangle}}_{2\delta_{kl} D_{ij}} - 2\delta_{il}\delta_{jk}$

Thus leading to $\boxed{D_{ijkl} = 4\delta_{kl}\delta_{ij} - 2\delta_{il}\delta_{jk}}$

- $\langle \Phi | \hat{H} | \Phi \rangle = \sum_{ij} h_{ij} D_{ij} + \frac{1}{2} \sum_{ijkl} \langle ik | jl \rangle D_{ijkl}$

$$= 2 \sum_{i} h_{ii} + \frac{1}{2} \sum_{ijkl} \langle ik | jl \rangle [4\delta_{kl}\delta_{ij} - 2\delta_{il}\delta_{jk}]$$

$$\langle \Phi | \hat{H} | \Phi \rangle = 2 \sum_{i} h_{ii} + \sum_{i,k} 2 \langle ik | ik \rangle - \sum_{i,j} \langle ij | ji \rangle$$

$\Downarrow$

$$\langle \Phi | \hat{H} | \Phi \rangle = 2 \sum_{i} h_{ii} + \sum_{ij} 2 \langle ij | ij \rangle - \langle ij | ji \rangle$$

Coulomb integrals

exchange integrals

(4)

$$| \Phi_i^a \rangle = \frac{1}{\sqrt{2}} \hat{E}_{ai} | \Phi \rangle$$

$$= \frac{1}{\sqrt{2}} \sum_{\sigma} \hat{a}^{+}_{a,\sigma} \underbrace{\hat{a}_{i,\sigma} | \Phi \rangle}$$

ionized state (electron occupying $\varphi_{i\sigma}$ has been removed)

Creating an electron in the spin-orbital $\varphi_{a\sigma}$

All in all, it looks like an electron has been excited from $\varphi_{i\sigma}$ to $\varphi_{a\sigma}$.

$$| \Phi_{ij}^{ab} \rangle = \frac{1}{2} \hat{E}_{ai} \hat{E}_{bj} | \Phi \rangle$$

In this case the product of two single-excitation operators removes two electrons (one in $\varphi_{i\sigma}$ and one in $\varphi_{j\tau}$) and create two electrons (one in $\varphi_{a\sigma'}$ and one in $\varphi_{b\tau'}$). All in all it looks like two electrons have been excited from $\varphi_{i\sigma}$ and $\varphi_{j\tau}$ to $\varphi_{a\sigma'}$ and $\varphi_{b\tau'}$.