Electronic Structure

Questions and Answers

University of Cambridge Part II Natural Sciences Tripos

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Preface

These answers are not endorsed by the lecturers/supervisors so they are in no sense official — in particular, they are far from perfect and all errors are almost surely mine. Also, only the first part of the course is included since the second part is now removed from the syllabus.

1. Give the names of a small, medium and large gaussian basis set and the corresponding number of basis functions for a calculation on H_2O and C_3H_8. Why do nearly all quantum chemistry packages use Gaussian orbitals?

An example might be:

		H	Li – Ne	H_2O	C_3H_8
small:	STO-3G	1 (s)	5 (2s,1p)	7	23
medium:	6-31G*	2 (2s)	15 (3s,2p,1d)	19	61
large:	cc-pVTZ	14 (3s,2p,1d)	30 (4s,3p,2d,1f)	58	202

Theoretically using STOs would be the best, but the integral of product of STOs are impossible to evaluate analytically, while integrating numerically takes a lot of time & mat be inaccurate. Gaussian orbitals are good because the product of Gaussian functions is still a Gaussian function (Gaussian product theorem), and the integral of Gaussian functions have simple analytic formula in closed forms. The shape of Gaussian function also resembles STOs to some extent, so only a few Gaussian functions are needed to mimic an STO closely.

2. (i) Show that all Coulomb integrals, $(ii|jj)$, are positive.
   (ii) Show that all exchange integrals, $(ij|ij)$, are positive.

(i)

$$
\begin{aligned}
(ii|jj) &= \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\frac{\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)}{\|\mathbf{r}_1-\mathbf{r}_2\|} \\
&= \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\frac{|\phi_i(\mathbf{r}_1)|^2\,|\phi_j(\mathbf{r}_2)|^2}{\|\mathbf{r}_1-\mathbf{r}_2\|} \geq 0\,,
\end{aligned}
$$

where the equality holds if and only if either ϕ_i or ϕ_j is identically zero — this is obviously not true, so the Coulomb integral is positive.

(ii)

$$
\begin{aligned}
(ij|ij) &= \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\frac{\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{\|\mathbf{r}_1-\mathbf{r}_2\|} \\
&= \int \mathrm{d}^3\mathbf{r}_1\,\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\int \mathrm{d}^3\mathbf{r}_2\,\frac{\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{\|\mathbf{r}_1-\mathbf{r}_2\|} \\
&= \int \mathrm{d}^3\mathbf{r}_1\,\chi_{ij}(\mathbf{r}_1)\int \mathrm{d}^3\mathbf{r}_2\,\frac{\chi_{ij}^*(\mathbf{r}_2)}{\|\mathbf{r}_1-\mathbf{r}_2\|}\,,
\end{aligned}
$$

where $\chi_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$.[1] The *Green's function*[2] for the 3D Laplacian operator is

$$
G(\mathbf{x}_1,\mathbf{x}_2) = -\frac{1}{4\pi}\frac{1}{\|\mathbf{x}_1-\mathbf{x}_2\|}\,,
$$

i.e. $\forall f:\Omega\to\mathbb{R}$ sufficiently smooth, where $\Omega\subset\mathbb{R}^3$ a compact subset of $\mathbb{R}^3$, equation

$$
\begin{cases}
\nabla^2\varphi(\mathbf{x}) = f(\mathbf{x}) & \mathbf{x}\in\Omega \\
\varphi(\mathbf{x}) = g(\mathbf{x}) & \mathbf{x}\in\partial\Omega, \text{the boundary of } \Omega
\end{cases}
$$

has solution

$$
\varphi(\mathbf{x}_1) = \int_\Omega \mathrm{d}^3\mathbf{x}_2\,f(\mathbf{x}_2)G(\mathbf{x}_1;\mathbf{x}_2) + \int_{\partial\Omega}\mathrm{d}S_2\,g(\mathbf{x}_2)\frac{\partial G(\mathbf{x}_1;\mathbf{x}_2)}{\partial n}\,.
$$

We can generalise this to $\Omega=\mathbb{R}^3$ by taking $\Omega=\lim_{R\to\infty}B(\mathbf{0},R)$, i.e. a ball centred at $\mathbf{0}$ with radius $R\to\infty$. Then its boundary $\partial\Omega=\lim_{R\to\infty}\partial B(\mathbf{0},R)$ is a 2-sphere centred at $\mathbf{0}$ with radius $R\to\infty$. Then for both integral to converge for all $\mathbf{x}_1$, we have to impose the boundary conditions

$$
\begin{cases}
\varphi(\mathbf{x})\to 0 & \text{as } \|\mathbf{x}\|\to\infty \\
\|\boldsymbol{\nabla}\varphi(\mathbf{x})\| = o(1/\|x\|^2) & \text{as } \|\mathbf{x}\|\to\infty
\end{cases}\,, \tag{†}
$$

since then the surface integral vanishes:

$$
\left|\int_{\partial B(\mathbf{0},R)}\mathrm{d}S_2\,g(\mathbf{x}_2)\frac{\partial G(\mathbf{x}_1;\mathbf{x}_2)}{\partial n}\right| \leq \pi R^2 o\left(\frac{1}{R^2}\right)\to 0 \text{ as } R\to\infty\,,
$$

and the first integral over $\mathbb{R}^3$ is finite. Then the equation $\nabla^2\varphi = f(\mathbf{x})$ for $\mathbf{x}\in\mathbb{R}^3$ has solution

$$
\varphi(\mathbf{x}_2) = \int \mathrm{d}^3\mathbf{x}_2\,f(\mathbf{x}_2)G(\mathbf{x}_1;\mathbf{x}_2) = -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{x}_2\,\frac{f(\mathbf{x}_2)}{\|\mathbf{x}_1-\mathbf{x}_2\|}\,.
$$

[1] If you are lazy and make these functions real, as in the hint in the official question sheet, then this problem would be much simpler — a lot of term will vanish.

[2] See my course notes on Part IB Mathematical Methods.

This is also valid for complex $\varphi, f : \mathbb{R}^3 \to \mathbb{C}$ as we may separate the real and imaginary parts

$$\begin{aligned}
\nabla_1^2 \varphi(\mathbf{x}_1) &= \nabla_1^2 \operatorname{Re}[\varphi(\mathbf{x}_1)] + i\nabla_1^2 \operatorname{Im}[\varphi(\mathbf{x}_1)] \\
&= -\frac{1}{4\pi}\left[\nabla_1^2 \int \mathrm{d}^3\mathbf{x}_2 \, \frac{\operatorname{Re}[f(\mathbf{x}_2)]}{\|\mathbf{x}_1 - \mathbf{x}_2\|} + i\nabla_1^2 \int \mathrm{d}^3\mathbf{x}_2 \, \frac{\operatorname{Im}[f(\mathbf{x}_2)]}{\|\mathbf{x}_1 - \mathbf{x}_2\|}\right] \\
&= \operatorname{Re}[f(\mathbf{x}_2)] + i \operatorname{Im}[f(\mathbf{x}_2)] \\
&= f(\mathbf{x}_2) \, .
\end{aligned}$$

Therefore, denote

$$\psi_{ij}(\mathbf{r}_1) = \int \mathrm{d}^3\mathbf{r}_2 \, \frac{\chi_{ij}^2(\mathbf{x}_2)}{\|\mathbf{x}_1 - \mathbf{x}_2\|} \, ,$$

we have

$$\nabla^2 \left(-\frac{1}{4\pi}\psi_{ij}\right) = \chi_{ij}^* \, ,$$

where ψ_{ij} satisfies the boundary conditions (†). Then

$$\begin{aligned}
(ij|ij) &= \int \mathrm{d}^3\mathbf{r} \, \chi_{ij}(\mathbf{r})\psi_{ij}(\mathbf{r}) \\
&= -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r} \, \psi_{ij}(\mathbf{r})\nabla^2\psi_{ij}^*(\mathbf{r}) \, .
\end{aligned}$$

Denote $\operatorname{Re}[\psi_{ij}(\mathbf{r})] = \Psi_{ij}(\mathbf{r})$, $\operatorname{Im}[\psi_{ij}(\mathbf{r})] = \Phi_{ij}(\mathbf{r})$. Then

$$\begin{aligned}
(ij|ij) &= -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r} \, (\Psi_{ij} + i\Phi_{ij})\nabla^2(\Psi_{ij} - i\Phi_{ij}) \\
&= -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r} \, \Psi_{ij}\nabla^2\Psi_{ij} + \Phi_{ij}\nabla^2\Phi_{ij} + i(\Phi_{ij}\nabla^2\Psi_{ij} - \Psi_{ij}\nabla^2\Phi_{ij}) \, .
\end{aligned}$$

We need a vector calculus identity.

Lemma. For real $\Psi, \Phi : \mathbb{R}^3 \to \mathbb{R}$ sufficiently smooth,

$$\Psi\nabla^2\Phi = \boldsymbol{\nabla} \cdot (\Psi\boldsymbol{\nabla}\Phi) - \boldsymbol{\nabla}\Psi \boldsymbol{\cdot} \boldsymbol{\nabla}\Phi \, ,$$

and specifically for $\Phi = \Psi$,

$$\Psi\nabla^2\Psi = \boldsymbol{\nabla} \cdot (\Psi\boldsymbol{\nabla}\Psi) - \|\boldsymbol{\nabla}\Psi\|^2 \, .$$

Proof.

$$\begin{aligned}
\boldsymbol{\nabla} \cdot (\Psi\boldsymbol{\nabla}\Phi) &= \frac{\partial}{\partial x_i}(\Psi\boldsymbol{\nabla}\Phi)_i \\
&= \frac{\partial}{\partial x_i}\left(\Psi\frac{\partial}{\partial x_i}\Phi\right) \\
&= \frac{\partial\Psi}{\partial x_i}\frac{\partial\Phi}{\partial x_i} + \Psi\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}\Phi \\
&= \boldsymbol{\nabla}\Psi \boldsymbol{\cdot} \boldsymbol{\nabla}\Phi + \Psi\nabla^2\Phi \, .
\end{aligned}$$

□

Therefore,

$$\begin{aligned}
(ij|ij) = -\frac{1}{4\pi}\int \mathrm{d}^3\mathbf{r} \, &\boldsymbol{\nabla} \cdot (\Psi_{ij}\boldsymbol{\nabla}\Psi_{ij}) - \|\Psi_{ij}\|^2 + \boldsymbol{\nabla} \cdot (\Phi_{ij}\boldsymbol{\nabla}\Phi_{ij}) - \|\boldsymbol{\nabla}\Phi_{ij}\|^2 \\
&+ i[\boldsymbol{\nabla} \cdot (\Phi_{ij}\boldsymbol{\nabla}\Psi_{ij}) - \cancel{\boldsymbol{\nabla}\Phi_{ij} \boldsymbol{\cdot} \boldsymbol{\nabla}\Psi_{ij}} - \boldsymbol{\nabla} \cdot (\Psi_{ij}\boldsymbol{\nabla}\Phi_{ij}) + \cancel{\boldsymbol{\nabla}\Psi_{ij} \boldsymbol{\cdot} \boldsymbol{\nabla}\Phi_{ij}}] \, .
\end{aligned}$$

This integral is over $\mathbb{R}^3$, where we can again thick of it as $\lim_{R\to\infty} B(\mathbf{0}, R)$. By divergence theorem,

$$\begin{aligned}
(ij|ij) &= \frac{1}{4\pi}\left[\int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}\ \|\boldsymbol{\nabla}\Psi_{ij}\|^2 + \|\boldsymbol{\nabla}\Phi_{ij}\|^2\right. \\
&\qquad \left. - \lim_{R\to\infty}\int_{B(\mathbf{0},R)} \mathrm{d}^3\mathbf{r}\,\boldsymbol{\nabla}\cdot\left(\Psi_{ij}\boldsymbol{\nabla}\Psi_{ij} + \Phi_{ij}\boldsymbol{\nabla}\Phi_{ij} + i\Phi_{ij}\boldsymbol{\nabla}\Psi_{ij} - i\Psi_{ij}\boldsymbol{\nabla}\Phi_{ij}\right)\right] \\
&= \frac{1}{4\pi}\left[\int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}\ \|\boldsymbol{\nabla}\Psi_{ij}\|^2 + \|\boldsymbol{\nabla}\Phi_{ij}\|^2\right. \\
&\qquad \left. - \lim_{R\to\infty}\int_{\partial B(\mathbf{0},R)} \mathrm{d}S\,\hat{\mathbf{n}}\boldsymbol{\cdot}\left(\Psi_{ij}\boldsymbol{\nabla}\Psi_{ij} + \Phi_{ij}\boldsymbol{\nabla}\Phi_{ij} + i\Phi_{ij}\boldsymbol{\nabla}\Psi_{ij} - i\Psi_{ij}\boldsymbol{\nabla}\Phi_{ij}\right)\right].
\end{aligned}$$

Because ψ_{ij} satisfies the boundary conditions (†), its real and imaginary parts also satisfies $\Phi_{ij}(\mathbf{r}), \Psi_{ij}(\mathbf{r}) \to 0$ as $r\to\infty$, and $\|\boldsymbol{\nabla}\Psi_{ij}(\mathbf{r})\|, \|\boldsymbol{\nabla}\Psi_{ij}(\mathbf{r})\| = o(r^{-2})$ as $r\to\infty$. Thus the latter surface integral is bounded above by $\|\partial B(\mathbf{0},R)\|\cdot 0\cdot o(r^{-2}) \sim 0\cdot r^2\cdot o(r^{-2}) = 0$ as $R\to\infty$. Therefore,

$$(ij|ij) = \frac{1}{4\pi}\int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}\ \|\boldsymbol{\nabla}\Psi_{ij}\|^2 + \|\boldsymbol{\nabla}\Phi_{ij}\|^2 > 0$$

as Φ_{ij}, Ψ_{ij} are not identically zero.

3. Show that the triplet state He(1s2s) as a single Slater determinant will have a lower energy than the $M_S = 0$ Slater determinants for this configuration, in the SCF approximation, if

   (i) the same spatial orbitals are used to represent both states.

   (ii) the best spatial orbitals are used to represent both states.

   Does this still apply to the true multi-determinantal $S = 0$, $M_S = 0$ state for this configuration?

(i) $\Psi_{\text{trip}} = \frac{1}{\sqrt{2}}(\phi_1^\alpha \phi_2^\alpha)$.

$$\left\langle \Psi_{\text{trip}} \middle| \hat{H} \middle| \Psi_{\text{trip}} \right\rangle = \sum_{i=1}^{2} h_{ii} + \sum_{i>j} [(ii|jj) - (ij|ij)]$$
$$= h_{11} h_{22} + (22|11) \langle \alpha|\alpha \rangle_1 \langle \alpha|\alpha \rangle_2 - (21|21) \langle \alpha|\alpha \rangle_1 \langle \alpha|\alpha \rangle_2$$
$$= h_{11} + h_{22} + (22|11) - (21|21) \ .$$

$\Psi_{M_S=0} = \frac{1}{\sqrt{2}}(\phi_1^\alpha \phi_2^\beta)$.

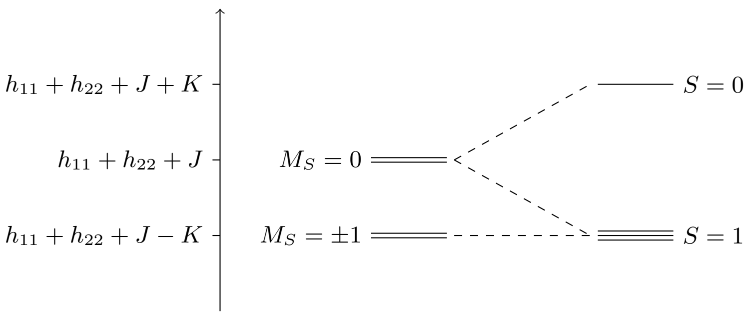
$$\left\langle \Psi_{M_S=0} \middle| \hat{H} \middle| \Psi_{M_S=0} \right\rangle = h_{11} h_{22} + (22|11) \langle \alpha|\beta \rangle_1 \langle \alpha|\beta \rangle_2 - (21|21) \langle \alpha|\beta \rangle_1 \langle \alpha|\beta \rangle_2$$
$$= h_{11} + h_{22} + (22|11) \ .$$

$(21|21) > 0$, so

$$\left\langle \Psi_{M_S=0} \middle| \hat{H} \middle| \Psi_{M_S=0} \right\rangle > \left\langle \Psi_{\text{trip}} \middle| \hat{H} \middle| \Psi_{\text{trip}} \right\rangle \ .$$

(ii) Let ϕ_1, ϕ_2 be the best spatial orbitals for the triplet state and let ψ_1, ψ_2 be the best orbitals for the $M_S = 0$ state.

$$E_{\text{trip}}^{\min} = \left\langle \hat{\mathcal{A}}\, \phi_1^\alpha \phi_2^\alpha \middle| \hat{H} \middle| \hat{\mathcal{A}}\, \phi_1^\alpha \phi_2^\alpha \right\rangle$$
$$\leq \left\langle \hat{\mathcal{A}}\, \psi_1^\alpha \psi_2^\alpha \middle| \hat{H} \middle| \hat{\mathcal{A}}\, \psi_1^\alpha \psi_2^\alpha \right\rangle$$
$$< \left\langle \hat{\mathcal{A}}\, \psi_1^\alpha \psi_2^\beta \middle| \hat{H} \middle| \hat{\mathcal{A}}\, \psi_1^\alpha \psi_2^\beta \right\rangle$$
$$= E_{M_S=0}^{\min} \ .$$



This still applies to the multi-determinantal $S = 0$, $M_S = 0$ state. The linear combination of the two single-determinantal $M_S = 0$ states gives the $S = 1$, $M_S = 0$ state and the $S = 0$, $M_S = 0$ state. The singlet state $(S = 0, M_S = 0)$ has even higher energy.

$$E_{\text{trip}}^{\min} < E_{M_S=0}^{\min} < E_{S=0, M_S=0}^{\min}$$

4. Evaluate the matrix elements
   (i) $\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle$
   (ii) $\left\langle \Psi_i^a \middle| \sum_k \hat{h}(k) \middle| \Psi_i^a \right\rangle$
   (iii) $\left\langle \Psi_i^a \middle| \sum_{k>l} \frac{1}{r_{k,l}} \middle| \Psi_j^b \right\rangle$ for $i \neq j$ and $a \neq b$.

(i)

$$\Psi = \hat{\mathcal{A}}(\phi_1 \dots \phi_n) = \frac{1}{\sqrt{n!}} \sum_u \sigma_u \hat{P}_u \Phi$$

$$\hat{H} = \underbrace{\sum_{A>B} \frac{Z_A Z_B}{r_{AB}}}_{C} + \sum_{k=1}^{n} \hat{h}(k) + \sum_{k>l}^{n} \frac{1}{r_{kl}} \, .$$

We will evaluate

$$\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_u \sigma_u \left\langle \Phi \middle| C + \sum_{k=1}^{n} \hat{h}(k) + \sum_{k>l}^{n} \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi \right\rangle$$

term by term.

(1) C:

$$\begin{aligned} &\sum_u \sigma_u \left\langle \Phi \middle| C \middle| \hat{P}_u \Phi \right\rangle \\ &= \sum_u C \sigma_u \underbrace{\prod_{i=1}^{n} \left\langle \phi_i \middle| \phi_{\hat{P}_u(i)} \right\rangle_i}_{=0 \text{ if } \hat{P}_u \text{ is non-trivial}} \\ &= C \end{aligned}$$

(2) $\sum_{k=1}^{n} \hat{h}(k)$:

$$\begin{aligned} &\sum_u \sigma_u \left\langle \Phi \middle| \hat{h}(k) \middle| \hat{P}_u \Phi \right\rangle \\ &= \sum_u \sigma_u \underbrace{\left[\prod_{i \neq k}^{n} \left\langle \phi_i \middle| \phi_{\hat{P}_u(i)} \right\rangle_i \right]}_{\hat{P}_u \text{ can't permute any } i \neq k} \left\langle \phi_k \middle| \hat{h} \middle| \phi_{\hat{P}_u(k)} \right\rangle_k \\ &= h_{kk} \, . \end{aligned}$$

$$\left\langle \Psi \middle| \sum_{k=1}^{n} \hat{h}(k) \middle| \Psi \right\rangle = \sum_{k=1}^{n} h_{kk} \, .$$

(3) $\sum_{k>l}^{n} \frac{1}{r_{kl}}$:

$$\begin{aligned} &\sum_u \sigma_u \left\langle \Phi \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi \right\rangle \\ &= \sum_u \sigma_u \underbrace{\left[\prod_{i \neq k,l}^{n} \left\langle \phi_i \middle| \phi_{\hat{P}_u(i)} \right\rangle_i \right]}_{\hat{P}_u \text{ can permute only } k,l} \left\langle \phi_k(k) \phi_l(l) \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \phi_k(k) \phi_l(l) \right\rangle_{k,l} \\ &= (kk|ll) - (kl|kl) \, . \end{aligned}$$

$$\left\langle \Psi \middle| \sum_{k>l}^{n} \frac{1}{r_{kl}} \middle| \Psi \right\rangle = \sum_{k>l}^{n} [(kk|ll) - (kl|kl)] \,.$$

Therefore,

$$\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_{A>B}^{N} \frac{Z_A Z_B}{r_{AB}} + \sum_{k=1}^{n} \hat{h}_{kk} + \sum_{k>l}^{n} [(kk|ll) - (kl|kl)] \,.$$

(ii)

$$\left\langle \Psi_i^a \middle| \hat{h}(k) \middle| \Psi_i^a \right\rangle = \sum_u \sigma_u \left\langle \Phi_i^a \middle| \hat{h}(k) \middle| \hat{P}_u \Phi_i^a \right\rangle$$

If $\hat{P}_u$ permutes anything other than i, k, say j, then $\left\langle \phi_j \middle| \phi_{\hat{P}_u(j)} \right\rangle_j = 0$. If $\hat{P}_u$ permutes i, then $\left\langle \phi_a \middle| \phi_{\hat{P}_u(i)} \right\rangle_i = 0$. Hence only $\hat{P}_u = \hat{E}$ contributes.

$$\left\langle \Psi_i^a \middle| \hat{h}(k) \middle| \Psi_i^a \right\rangle = \left\langle \Phi_i^a \middle| \hat{h}(k) \middle| \Phi_i^a \right\rangle = \begin{cases} h_{kk} & \text{if } i \neq k \\ h_{aa} & \text{if } i = k \,. \end{cases}$$

Therefore,

$$\left\langle \Psi_i^a \middle| \sum_{k=1}^{n} \hat{h}(k) \middle| \Psi_i^a \right\rangle = \sum_{k \neq i}^{n} h_{kk} + h_{aa} \,.$$

(iii)

$$\left\langle \Psi_i^a \middle| \frac{1}{r_{kl}} \middle| \Psi_j^b \right\rangle = \sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_j^b \right\rangle$$

- $\hat{P}_u$ can't permute anything other than i, j, k, l or there will be vanishing overlap integral.
- If $i \neq k$ or l, then there will be $\langle \phi_a | \phi_{i \text{ or } b \text{ or } k \text{ or } l} \rangle = 0$.[3]
- If $j \neq k$ or l, then there will be $\langle \phi_j | \phi_{i \text{ or } b \text{ or } k \text{ or } l} \rangle = 0$.

Therefore, $i = k, k = l$ or $i = l, j = k$, and $\hat{P}_u = \hat{E}$ or $\hat{P}_{ij}$. This corresponds to a single term in $\sum_{k>l}$, depending on whether i or j is larger. Therefore,

$$\begin{aligned} \left\langle \Psi_i^a \middle| \frac{1}{r_{kl}} \middle| \Psi_j^b \right\rangle &= \left\langle \Phi_i^a \middle| \frac{1}{r_{ij}} \middle| (\hat{E} + \hat{P}_{ij}) \Phi_j^b \right\rangle \\ &= \left(\phi_a(i)\phi_j(j) \middle| \frac{1}{r_{ij}} \right) \phi_i(i)\phi_b(j) - \left(\phi_a(i)\phi_j(j) \middle| \frac{1}{r_{ij}} \right) \phi_b(i)\phi_i(j) \\ &= (ai|jb) - (ab|ji) \ . \end{aligned}$$

[3]If $a = b$, this condition will be loosen. See the next question.

5. (i) Evaluate the matrix element $\left\langle\Psi_i^a\middle|\hat{H}-E_{\mathrm{HF}}\middle|\Psi_j^b\right\rangle$ for the general case where i might equal to j and/or a might equal to b.
   (ii) Show that this can be simplified in terms of the Fock matrix elements and some two electron integrals.
   (iii) Give the form when canonical Hartree–Fock orbitals are used.

(i) $\left\langle\Psi_i^a\middle|\hat{H}-E_{\mathrm{HF}}\middle|\Psi_j^b\right\rangle = \sum_u \sigma_u \left\langle\Phi_i^a\middle|\sum_{A>B}\frac{Z_A Z_B}{r_{AB}} + \sum_{k=1}^n \hat{h}(k) + \sum_{k>l}^n \frac{1}{r_{kl}} - E_{\mathrm{HF}}\middle|\hat{P}_u\Phi_j^b\right\rangle$.

(1) Constant terms $C = \sum_{A>B}\frac{Z_A Z_B}{r_{AB}} - E_{\mathrm{HF}}$:

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|C\middle|\hat{P}_u\Phi_j^b\right\rangle$$

- Can't have $\hat{P}_u$ permuting anything other than i, j
- Since $\langle\phi_a(i)|$ in the bra, $|\phi_a(i)\rangle$ must be in the ket, so

$$a = b \text{ and } \begin{cases} i = j, \hat{P}_u = \hat{E}\,, \text{ or} \\ i \neq j, \hat{P}_u = \hat{P}_{ij}\,. \end{cases}$$

- If $\hat{P}_u = \hat{P}_{ij}$, then $|\phi_i(j)\rangle$ in ket, but no $|\phi_i\rangle$ in bra, so $\hat{P}_u \neq \hat{P}_{ij}$.

Therefore, only $a = b, i = j, \hat{P}_u = \hat{E}$ contributes, so

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|C\middle|\hat{P}_u\Phi_j^b\right\rangle = C\delta_{ab}\delta_{ij}\,.$$

(2) $\sum_u \sigma_u \left\langle\Phi_i^a\middle|\sum_{k=1}^n \hat{h}(k)\middle|\hat{P}_u\Phi_j^b\right\rangle$:

- $i = j = k$:

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(i)\middle|\hat{P}_u\Phi_i^b\right\rangle = h_{ab}\,.$$

- $i = j \neq k$:

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(k)\middle|\hat{P}_u\Phi_i^b\right\rangle = \delta_{ab}h_{kk}\,.$$

- $i \neq j = k$:

$$\begin{aligned} &\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(j)\middle|\hat{P}_u\Phi_j^b\right\rangle && \text{contribute if } \hat{P}_u = \hat{P}_{ij} \\ &= -\langle\phi_a|\phi_b\rangle_i \left\langle\phi_j\middle|\hat{h}\middle|\phi_i\right\rangle_j && \text{contribute if } a = b \\ &= -\delta_{ab}h_{ji}\,. \end{aligned}$$

- $k = i \neq j$:

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(i)\middle|\hat{P}_u\Phi_j^b\right\rangle$$

  - $\hat{P}_u$ can't permute anything other than i, j.
  - $\hat{P}_u = \hat{E}$: $\langle\phi_j|\phi_b\rangle_j = 0$.
  - $\hat{P}_u = \hat{P}_{ij}$: $\langle\phi_j|\phi_i\rangle_j = 0$.

  Nothing contributes,

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(i)\middle|\hat{P}_u\Phi_j^b\right\rangle = 0\,.$$

- $k \neq i \neq j \neq k$:

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(k)\middle|\hat{P}_u\Phi_j^b\right\rangle$$

– $\hat{P}_u$ can't permute anything other than i, j, k.
– $\langle\phi_a(i)|$ in the bra, must have $|\phi_a(i)\rangle$ in the ket, so $a = b$ and $\hat{P}_u(i) = j$.

Therefore we can either have $\hat{P}_u = (i\ j)$ or $(i\ j\ k)$.

– If $\hat{P}_u = (i\ j)$:

$$\langle\phi_a|\phi_a\rangle_i \cancelto{0}{\langle\phi_j|\phi_i\rangle_j} \left\langle\phi_k\middle|\hat{h}\middle|\phi_k\right\rangle_k = 0\,.$$

– If $\hat{P}_u = (i\ j\ k)$:

$$\langle\phi_a|\phi_a\rangle_i \cancelto{0}{\langle\phi_j|\phi_k\rangle_j} \left\langle\phi_k\middle|\hat{h}\middle|\phi_i\right\rangle_k = 0\,.$$

Therefore,

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\hat{h}(k)\middle|\hat{P}_u\Phi_j^b\right\rangle = 0\,.$$

This gives us the total result

$$\begin{aligned}\sum_u \sigma_u \left\langle\Phi_i^a\middle|\sum_{k=1}^n \hat{h}(k)\middle|\hat{P}_u\Phi_j^b\right\rangle &= \begin{cases}\sum_{k\neq i}^n h_{kk} + h_{aa} & i=j, a=b\\ h_{ab} & i=j, a\neq b\\ -h_{ij} & i\neq j, a=b\\ 0 & i\neq j, a\neq b\end{cases}\\ &= \delta_{ij}\delta_{ab}\sum_{k=1}^n h_{kk} - \delta_{ab}h_{ij} + \delta_{ij}h_{ab}\,.\end{aligned}$$

(3) $\sum_u \sigma_u \left\langle\Phi_i^a\middle|\sum_{k>l}\frac{1}{r_{kl}}\middle|\hat{P}_u\Phi_j^b\right\rangle$.

- $i \neq j, a \neq b$. We have done this in Q4 (iii).

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\sum_{k>l}\frac{1}{r_{kl}}\middle|\hat{P}_u\Phi_j^b\right\rangle = (ai|jb) - (ab|ji)\ .$$

- $i \neq j, a = b$.
As we discussed in Q4 (iii), if $j \neq k$ or l, then there will be

$$\langle\phi_j|\phi_{i \text{ or } b \text{ or } k \text{ or } l}\rangle = 0\,.$$

We have a few other cases to consider
– $j = k$, $i \neq l$.

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\frac{1}{r_{jl}}\middle|\hat{P}_u\Phi_j^a\right\rangle = \sum_u \sigma_u \left\langle\phi_a(i)\phi_j(j)\phi_l(l)\middle|\frac{1}{r_{jl}}\middle|\hat{P}_u\phi_i(i)\phi_a(j)\phi_l(l)\right\rangle\ .$$

This is non-zero if $\hat{P}_u$ permutes j to i, so $\hat{P}_u = (j\ i)$ or $(j\ i\ l)$. These give

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\frac{1}{r_{jl}}\middle|\hat{P}_u\Phi_j^a\right\rangle = -(ji|ll) + (jl|li)\ .$$

– $j = l$, $i \neq k$.

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\frac{1}{r_{kj}}\middle|\hat{P}_u\Phi_j^a\right\rangle = -(ji|kk) + (jk|ki)\ .$$

– $\{i, j\} = \{k, l\}$.

$$\sum_u \sigma_u \left\langle\Phi_i^a\middle|\frac{1}{r_{kj}}\middle|\hat{P}_u\Phi_j^a\right\rangle = (ai|ja) - (aa|ji)\ .$$

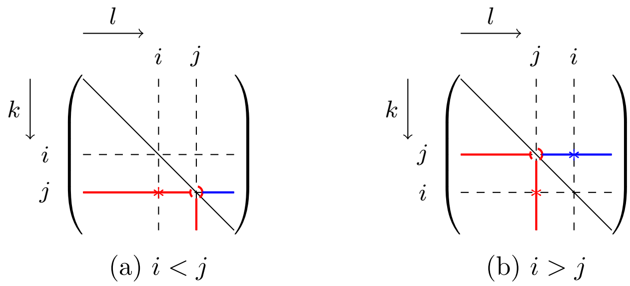


Figure 1: The condition of the sum $k > l$ corresponds to the lower triangular block of the matrix, and those with non-zero contributions are the ones on the red lines. We can reflect segment to the blue segment as the matrix is Hermitian.

We need to sum these contributions up for all $k > l$. The diagram may help you get your head around it.
Therefore,

$$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_j^a \right\rangle = \sum_{l \neq i,j} (jl|li) - (ji|ll) + (ai|ja) - (aa|ji) \ .$$

- $i = j, a \neq b$.

$$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_i^b \right\rangle \ .$$

  i must be k or l, and $\hat{P}_u$ can only be $\hat{E}$ or $\hat{P}_{kl}$.
  - $i = k$:

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{il}} \middle| \hat{P}_u \Phi_i^b \right\rangle = (ab|ll) - (al|lb) \ .$$

  - $i = l$:

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{ki}} \middle| \hat{P}_u \Phi_i^b \right\rangle = (ab|kk) - (ak|kb) \ .$$

  Summing these up

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \sum_{k>l} \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_i^b \right\rangle = \sum_{k \neq i}^{n} [(ab|kk) - (ak|kb)] \, .$$

- $i = j$, $a = b$.

$$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_i^a \right\rangle \ .$$

  Contributes if $\hat{P}_u = \hat{E}$ or $\hat{P}_{kl}$.
  - $i \neq k, l$:

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_i^a \right\rangle = (kk|ll) - (kl|kl) \ .$$

  - $i = k \neq l$:

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{il}} \middle| \hat{P}_u \Phi_i^a \right\rangle = (aa|ll) - (al|al) \ .$$

  - $i = l \neq k$:

  $$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \frac{1}{r_{ki}} \middle| \hat{P}_u \Phi_i^a \right\rangle = (kk|aa) - (ka|ka) \ .$$

Summing these up

$$\sum_u \sigma_u \left\langle \Phi_i^a \middle| \sum_{k>l} \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_i^a \right\rangle = \sum_{l\neq i}^n \sum_{k>l,k\neq i}^n [(kk|ll) - (kl|kl)] + \sum_{k\neq i}^n [(aa|kk) - (ak|ak)]\,.$$

This gives us the total result

$$\begin{aligned}
&\sum_u \sigma_u \left\langle \Phi_i^a \middle| \sum_{k>l} \frac{1}{r_{kl}} \middle| \hat{P}_u \Phi_j^b \right\rangle \\
&= \begin{cases}
\sum_{k\neq i}^n [(aa|kk) - (ak|ak)] + \sum_{l\neq i}^n \sum_{k>l,k\neq i}^n [(kk|ll) - (kl|kl)] & i=j, a=b \\
\sum_{k\neq i}^n [(ab|kk) - (ak|bk)] & i=j, a\neq b \\
\sum_{l\neq i,j} [(jl|il) - (ji|ll)] + (ai|aj) - (aa|ij) & i\neq j, a\neq b \\
(ai|bj) - (ab|ij) & i\neq j, a\neq b
\end{cases} \\
&= \delta_{ij}\delta_{ab} \sum_{k>l}^n [(kk|ll) - (kl|kl)] + \delta_{ij} \sum_{k=1}^n [(ab|kk) - (ak|bk)] \\
&\quad - \delta_{ab} \sum_{l=1}^n [(ji|ll) - (jl|il)] - [(ab|ij) - (ai|bj)]\,.
\end{aligned}$$

Finally, combine the three terms, we get the total expression

$$\begin{aligned}
&\left\langle \Psi_i^a \middle| \sum_{A>B} \frac{Z_A Z_B}{r_{AB}} + \sum_{k=1}^n \hat{h}(k) + \sum_{k>l}^n \frac{1}{r_{kl}} - E_{\mathrm{HF}} \middle| \Psi_j^b \right\rangle \\
&= \delta_{ij}\delta_{ab} \left\{ \sum_{A>B} \frac{Z_A Z_B}{r_{AB}} - E_{\mathrm{HF}} + \sum_{k=1}^n h_{kk} + \sum_{k>l}^n [(kk|ll) - (kl|kl)] \right\} \\
&\quad + \delta_{ij} \left\{ h_{ab} + \sum_{k=1}^n [(ab|kk) - (ak|bk)] \right\} - \delta_{ab} \left\{ h_{ij} + \sum_{l=1}^n [(ji|ll) - (jl|il)] \right\} \\
&\quad - [(ab|ij) - (ai|bj)]\,.
\end{aligned}$$

This looks horrible at first glance, but the terms in $\delta_{ij}\delta_{ab}$, except E_{HF} itself, is exactly the Hartree–Fock energy!

$$E_{\mathrm{HF}} = \sum_{A>B} \frac{Z_A Z_B}{r_{AB}} + \sum_{k=1}^n \hat{h}(k) + \sum_{k>l}^n \frac{1}{r_{kl}}$$

Therefore, we are left with

$$\begin{aligned}
\left\langle \Psi_i^a \middle| \hat{H} - E_{\mathrm{HF}} \middle| \Psi_j^b \right\rangle = \delta_{ij} &\left\{ h_{ab} + \sum_{k=1}^n [(ab|kk) - (ak|bk)] \right\} \\
&- \delta_{ab} \left\{ h_{ij} + \sum_{l=1}^n [(ji|ll) - (jl|il)] \right\} - [(ab|ij) - (ai|bj)]\,.
\end{aligned}$$

(ii) What makes it even nicer is that the terms in δ_{ij} and δ_{ab} are exactly the Fock matrix elements

$$F_{pq} = h_{pq} + \sum_r [(pq|rr) - (pr|qr)]\,.$$

This simplifies our expression to

$$\left\langle \Psi_i^a \middle| \hat{H} - E_{\mathrm{HF}} \middle| \Psi_j^b \right\rangle = \delta_{ij} F_{ab} - \delta_{ab} F_{ij} - [(ab|ij) - (ai|bj)]\,.$$

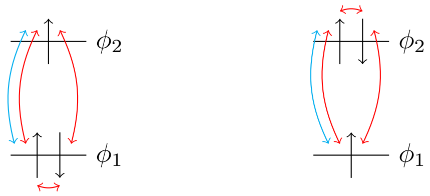
(iii) Recall that the canonical Hartree–Fock orbitals diagonalises the Fock matrix

$$F_{pq} = \epsilon_p \delta_{pq}\,.$$

Therefore

$$\left\langle \Psi_i^a \middle| \hat{H} - E_{\mathrm{HF}} \middle| \Psi_j^b \right\rangle = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ai|bj) - (ab|ij)\,.$$

6. Consider the wavefunctions of the lithium atom, $\Psi_1 = \hat{\mathcal{A}}(\phi_1^\alpha \phi_2^\alpha \phi_1^\beta)$ and $\Psi_2 = \hat{\mathcal{A}}(\phi_1^\alpha \phi_2^\alpha \phi_2^\beta)$. Work out the matrix elements of the FCI secular matrix $\left\langle \Psi_i \middle| \hat{H} \middle| \Psi_j \right\rangle$.



$$H_{11} = \left\langle \Psi_1 \middle| \hat{H} \middle| \Psi_1 \right\rangle = 2h_{11} + h_{22} + (11|11) + 2\,(11|22) - (12|12)$$
$$H_{22} = \left\langle \Psi_2 \middle| \hat{H} \middle| \Psi_2 \right\rangle = h_{11} + 2h_{22} + (22|22) + 2\,(11|22) - (12|12)$$

$$\begin{aligned}
H_{12} = H_{21} &= \left\langle \Psi_1 \middle| \hat{H} \middle| (\Psi_1)_{1\beta}^{2\beta} \right\rangle \\
&= h_{12} + \sum_i [(2\beta\ 1\beta|ii) - (2\beta\ i|1\beta\ i)] \\
&= h_{12} + (2\beta\ 1\beta|1\alpha\ 1\alpha) - \cancel{(2\beta\ 1\alpha|1\beta\ 1\alpha)} \\
&\qquad + \cancel{(2\beta\ 1\beta|1\beta\ 1\beta)} - \cancel{(2\beta\ 1\beta|1\beta\ 1\beta)} \\
&\qquad + (2\beta\ 1\beta|2\alpha\ 2\alpha) - \cancel{(2\beta\ 2\alpha|1\beta\ 2\alpha)} \\
&= h_{12} + (21|11) + (21|22)\ .
\end{aligned}$$

7. If $\Psi = \hat{\mathcal{A}}(\phi_1\phi_2\ldots\phi_r\ldots\phi_n)$, $\Psi' = \hat{\mathcal{A}}(\phi_1\phi_2\ldots\phi_r'\ldots\phi_n)$, where all orbitals are orthonormal, show that $\left\langle\Psi\middle|\sum_{ij}\frac{1}{r_{ij}}\middle|\Psi'\right\rangle = 2\sum_i[(ii|rr') - (ir|ir')]$.[4] Prove Brillouin's theorem for a one determinant SCF wavefunction, that $\left\langle\Psi_i^a\middle|\hat{H}\middle|\Psi\right\rangle = 0$.

First of all,

$$\left\langle\Psi\middle|\sum_{i,j}\frac{1}{r_{ij}}\middle|\Psi_r^{r'}\right\rangle = \sum_{i,j}\sum_u\sigma_u\left\langle\Phi\middle|\frac{1}{r_{ij}}\middle|\hat{P}_u\Phi_r^{r'}\right\rangle$$

as always. If $\hat{P}_u$ permute anything other than i,j, this term will vanish. Also, r must equal to i or j, otherwise will have $\langle\phi_r|\phi_r'\rangle_r = 0$. Then

$$\begin{aligned}\left\langle\Psi\middle|\sum_{i,j}\frac{1}{r_{ij}}\middle|\Psi_r^{r'}\right\rangle &= \sum_{j=1}^n\left\langle\Phi\middle|\frac{1}{r_{rj}}\middle|(\hat{E}-\hat{P}_{rj})\Phi_r^{r'}\right\rangle + \sum_{i=1}^n\left\langle\Phi\middle|\frac{1}{r_{ir}}\middle|(\hat{E}-\hat{P}_{ir})\Phi_r^{r'}\right\rangle \\ &= \sum_{j=1}^n[\langle rj|r'j\rangle - \langle rj|jr'\rangle] + \sum_{i=1}^n[\langle ir|ir'\rangle - \langle ir|r'i\rangle] \\ &= 2\sum_{i=1}^n[(ii|rr') - (ir|ir')]\,.\end{aligned}$$

The second half of this question is bookwork. Have

$$\left\langle\Psi_i^a\middle|\hat{H}\middle|\Psi\right\rangle = \sum_u\sigma_u\left\langle\Phi_i^a\middle|\sum_{A>B}\frac{Z_AZ_B}{r_{AB}} + \sum_{k=1}^n\hat{h}(k) + \sum_{k>l}^n\frac{1}{r_{kl}}\middle|\hat{P}_u\Phi\right\rangle\,.$$

- The first term: contain vanishing overlap integral $\implies 0$.
- The second term: non-zero when $k=i$ and $\hat{P}_u = \hat{E} \implies h_{ii}$.
- The third term: $\sum_{k=1}^n[(kk|ia) - (ki|ka)]$.

$$\implies \left\langle\Psi_i^a\middle|\hat{H}\middle|\Psi\right\rangle = h_{ai} + \sum_{k=1}^n[(kk|ia) - (ki|ka)]\,.$$

This is exactly the Fock matrix element, which is set to zero in SCF. To show this, we set the first-order variation of energy when $\phi_i \to \phi_i + \epsilon\phi_a$ to zero, The SCF energy is

$$\left\langle\Psi\middle|\hat{H}\middle|\Psi\right\rangle = \sum_k h_{kk} + \sum_{k>l}[(kk|ll) - (kl|kl)]\,.$$

The energy variation is

$$\begin{aligned}&\left\langle\phi_i+\epsilon\phi_a\middle|\hat{h}\middle|\phi_i+\epsilon\phi_a\right\rangle + \sum_{k\neq i}[(kk|i+\epsilon a\ i+\epsilon a) - (k\ i+\epsilon a|k\ i+\epsilon a)] - h_{ii} - \sum_{k\neq i}[(kk|ii) - (ki|ki)] \\ &= (h_{ii} + 2\epsilon h_{ai} - h_{ii}) + \sum_{k\neq i}[(kk|ii) + 2\epsilon\,(kk|ia) - (ki|ki) - 2\epsilon\,(ki|ka) - (kk|ii) + (ki|ki)] + O(\epsilon^2) \\ &= 2\epsilon\underbrace{\left[h_{ai} + \sum_{k\neq i}(kk|ia) - (ki|ka)\right]}_{=F_{ai}=\left\langle\Psi_i^a\middle|\hat{H}\middle|\Psi\right\rangle} + O(\epsilon^2) = 0 + O(\epsilon^2)\,.\end{aligned}$$

[4]The official exercises sheet uses the unconventional notation Φ to denote the Slater determinant. We change it to Ψ here. Also, a factor of 2 is missing in the original question — or perhaps the question meant to take the sum over $i>j$ instead of all i,j.

8. Rewrite the closed shell energy expression $E = 2\sum_i h_{ii} + \sum_{ij} 2\,(ii|jj) - (ij|ij)$ in terms of the density matrix $D_{\mu\nu} = \sum_i C_{\mu i} C^*_{\nu i}$ and the basis function integrals $h_{\mu\nu}$ and $(\mu\nu|\sigma\tau)$.

We will use summation convention throughout.

$$
\begin{aligned}
h_{ii} &= \left\langle \phi_i \middle| \hat{h} \middle| \phi_i \right\rangle \\
&= \left\langle \eta_\mu C_{\mu i} \middle| \hat{h} \middle| \eta_\nu C_{\nu i} \right\rangle \\
&= C^*_{\mu i} C_{\nu i} \left\langle \eta_\mu \middle| \hat{h} \middle| \eta_\nu \right\rangle \\
&= D_{\nu\mu} h_{\mu\nu}\,.
\end{aligned}
$$

$$
\begin{aligned}
2\,(ii|jj) - (ij|ij) &= 2\,\langle \phi_i \phi_j | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \phi_j \phi_i \rangle \\
&= 2\,\langle \eta_\mu C_{\mu i} \eta_\sigma C_{\sigma j} | \eta_\nu C_{\nu i} \eta_\tau C_{\tau j} \rangle - \langle \eta_\mu C_{\mu i} \eta_\sigma C_{\sigma j} | \eta_\tau C_{\tau i} \eta_\nu C_{\nu j} \rangle \\
&= 2 C^*_{\mu i} C_{\nu i} C^*_{\sigma j} C_{\tau j}\,\langle \eta_\mu \eta_\sigma | \eta_\nu \eta_\tau \rangle - C^*_{\mu i} C_{\nu i} C^*_{\sigma j} C_{\tau j}\,\langle \eta_\mu \eta_\sigma | \eta_\tau \eta_\nu \rangle \\
&= D_{\nu\mu} D_{\tau\sigma} [2\,(\mu\nu|\sigma\tau) - (\mu\tau|\nu\sigma)]\,.
\end{aligned}
$$

Therefore

$$
\begin{aligned}
E &= 2 D_{\nu\mu} h_{\mu\nu} + D_{\nu\mu} D_{\tau\sigma} [2\,(\mu\nu|\sigma\tau) - (\mu\tau|\nu\sigma)] \\
&= 2 \sum_{\mu\nu} D_{\nu\mu} h_{\mu\nu} + \sum_{\mu\nu\sigma\tau} D_{\nu\mu} D_{\tau\sigma} [2\,(\mu\nu|\sigma\tau) - (\mu\tau|\nu\sigma)]\,.
\end{aligned}
$$