Programming Project 5 Exercises

1. Derive $\langle\Phi|\,\mathcal{H}\,|\Phi\rangle = \sum_i^n h_{ii} + \sum_{i<j}^n \langle ij|\,|ij\rangle$.

1 Notation

$\mathcal{H} = \sum_i^n \hat{h}(i) + \sum_{i<j}^n \hat{g}(i,j)$

$\Phi = \frac{1}{\sqrt{n!}} \sum_{i=1}^{n!} (-1)^{p_i}\, \mathcal{P}_i\,(\psi_1(1)...\psi_n(n))$

$\mathcal{P}_i$ is a permutation operator that runs over all the n! permutations of electrons 1 ... n.

p_i is the number of transpositions required to restore a given permutation to its natural order 1 ... n.

2 One-electron contribution

2.1 Useful lemma

For a one-electron operator $\hat{h}$, $\langle\Phi_P|\sum_{k=1}^n \hat{h}(k)\,|\Phi_Q\rangle = n\,\langle\Phi_P|\,\hat{h}(1)\,|\Phi_q\rangle\ \forall\, p, q$.

Proof:

Since dummy variables are interchangeable in integration,

$$\begin{aligned}
\int \mathrm{d}(1...k...n)\,\Phi_P^*(1...k...n)\,\hat{h}(k)\,\Phi_Q(1...k...n) &= \int \mathrm{d}(k...1...n)\,\Phi_P^*(k...1...n)\,\hat{h}(1)\,\Phi_Q(k...1...n)\\
&= \int \mathrm{d}(1...k...n)\,\Phi_P^*(k...1...n)\,\hat{h}(1)\,\Phi_Q(k...1...n)\\
&= (-1)\int \mathrm{d}(1...k...n)\,\Phi_P^*(1...k...n)\,\hat{h}(1)\,\Phi_Q(k...1...n)\\
&= (-1)^2\int \mathrm{d}(1...k...n)\,\Phi_P^*(1...k...n)\,\hat{h}(1)\,\Phi_Q(1...k...n)
\end{aligned}$$

where we have used the antisymmetry property of determinants. We exchange electrons 1 and k in each determinant, returning the negative value of that determinant.

Rewriting in Dirac notation, what we have shown is that

$$\langle\Phi_p|\,\hat{h}(k)\,|\Phi_Q\rangle = \langle\Phi_P|\,\hat{h}(k)\,|\Phi_q\rangle\,.$$

We can easily apply this result to the sum over all electrons in the system:

$$\begin{aligned}
\langle\Phi_P|\sum_{k=1}^n \hat{h}(k)\,|\Phi_Q\rangle &= \sum_{k=1}^n \langle\Phi_P|\,\hat{h}(k)\,|\Phi_Q\rangle\\
&= \sum_{k=1}^n \langle\Phi_P|\,\hat{h}(1)\,|\Phi_Q\rangle\\
&= n\,\langle\Phi_P|\,\hat{h}(1)\,|\Phi_Q\rangle\,.
\end{aligned}$$

2.2 Derivation

Expanding the determinants Φ in terms of the perturbation operator,

$$\begin{aligned}\langle\Phi|\sum_{i=1}^{n}\hat{h}\,|\Phi\rangle &= \frac{1}{n!}\left\langle\sum_{i=1}^{n!}(-1)^{p_i}\,\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\middle|\sum_{k=1}^{n}\hat{h}(k)\middle|\sum_{j=1}^{n!}(-1)^{p_j}\,\mathcal{P}_j\left(\psi_1(1)...\psi_n(n)\right)\right\rangle\\ &= \frac{1}{n!}\sum_{i,j}^{n!}(-1)^{p_i+p_j}\left\langle\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\right|\sum_{k=1}^{n}\hat{h}(k)\left|\mathcal{P}_j\left(\psi_1(1)...\psi_n(n)\right)\right\rangle\end{aligned}$$

Next, we use the orthogonality condition of the spin orbitals. Suppose that in permutations $\mathcal{P}_i$, $\mathcal{P}_j$ electron k is in orbitals ψ_i,ψ_j respectively. Then $\langle\psi_i(k)\,|\,\psi_j(k)\rangle = \delta_{ij}$ by orthogonality, so the integral will vanish unless $i = j\ \ \forall\ \ i, j$. So we let $\mathcal{P}_i = \mathcal{P}_j$.

$$\langle\Phi|\sum_{i=1}^{n}\hat{h}\,|\Phi\rangle = \frac{1}{n!}\sum_{i=1}^{n!}(-1)^{2p_i}\left\langle\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\right|\sum_{k=1}^{n}\hat{h}(k)\left|\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\right\rangle$$

Now by lemma 2.1,

$$\begin{aligned}\langle\Phi|\sum_{i=1}^{n}\hat{h}\,|\Phi\rangle &= n\,\frac{1}{n!}\sum_{i=1}^{n!}\left\langle\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\right|\hat{h}(1)\left|\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)\right\rangle\\ &= \frac{1}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}(1)\,|\psi_k(1)\rangle\sum_{i=1}^{(n-1)!}\left\langle\mathcal{P}_i\left(\psi_1(1)...\cancel{\psi_k(k)}...\psi_n(n)\right)\middle|\,\mathcal{P}_i\left(\psi_1(1)...\cancel{\psi_k(k)}...\psi_n(n)\right)\right\rangle\\ &= \frac{1}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}(1)\,|\psi_k(1)\rangle\sum_{i=1}^{(n-1)!}(1)\quad\text{by orthogonality.}\\ &= \frac{(n-1)!}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}(1)\,|\psi_k(1)\rangle\\ &= \sum_{k=1}^{n}\langle\psi_k|\,\hat{h}\,|\psi_k\rangle\quad\blacksquare.\end{aligned}$$

3 Two-electron contribution

3.1 Useful lemma

For a two-electron operator $\hat{g}$, $\langle\Phi_P|\ \sum\limits_{i<j}^{n} \hat{g}(1,2)\ |\Phi_Q\rangle = \frac{n(n-1)}{2}\ \langle\Phi_P|\ \hat{g}(j,k)\ |\Phi_Q\rangle$.

Proof (same logic as 1.1.1):

$$
\begin{aligned}
&\int \mathrm{d}(1,2...j,k...n)\, \Phi_P^*(1,2...j,k...n)\, \hat{g}(j,k)\, \Phi_Q(1,2...j,k...n) = \\
&\qquad = \int \mathrm{d}(j,k...1,2...n)\, \Phi_P^*(j,k...1,2...n)\, \hat{g}(1,2)\, \Phi_Q(j,k...1,2...n) \\
&\qquad = \int \mathrm{d}(1,2...j,k...n) \Phi_P^*(j,k...1,2...n)\, \hat{g}(1,2)\, \Phi_Q(j,k...1,2...n) \\
&\qquad = -\int \mathrm{d}(1,2...j,k...n) \Phi_P^*(1,2...j,k...n)\, \hat{g}(1,2)\, \Phi_Q(j,k...1,2...n) \\
&\qquad = \int \mathrm{d}(1,2...j,k...n) \Phi_P^*(1,2...j,k...n)\, \hat{g}(1,2)\, \Phi_Q(1,2...j,k...n)
\end{aligned}
$$

where we have again used interchangeability of dummy variables and antisymmetry of determinants.

Rewriting in Dirac notation, what we have shown is that

$$\langle\Phi_p|\, \hat{g}(j,k)\, |\Phi_Q\rangle = \langle\Phi_P|\, \hat{g}(1,2)\, |\Phi_q\rangle\,.$$

We can easily apply this result to the sum over all distinct pairs of electrons in the system:

$$
\begin{aligned}
\langle\Phi_P| \sum_{i<j}^{n} \hat{g}(j,k)\, |\Phi_Q\rangle &= \sum_{j<k}^{n} \langle\Phi_P|\, \hat{g}(j,k)\, |\Phi_Q\rangle \\
&= \sum_{j<k}^{n} \langle\Phi_P|\, \hat{g}(1,2)\, |\Phi_Q\rangle \\
&= \frac{n(n-1)}{2}\, \langle\Phi_P|\, \hat{g}(1,2)\, |\Phi_Q\rangle\,.
\end{aligned}
$$

3.2 Derivation

$$\langle\Phi| \sum_{i<j}^{n} \hat{g}(i,j) \; |\Phi\rangle = \frac{1}{n!} \left\langle \sum_{k=1}^{n!} (-1)^{p_k} \mathcal{P}_k(\psi_1(1)...\psi_n(n)) \right| \sum_{i<j}^{n} \hat{g}(i,j) \; \left| \sum_{l=1}^{n!} (-1)^{p_l} \mathcal{P}_l(\psi_1(1)...\psi_n(n)) \right\rangle$$

$$= \frac{1}{n!} \sum_{k=1}^{n!} \sum_{l=1}^{n!} (-1)^{p_k+p_l} \; \langle \mathcal{P}_k(\psi_1(1)...\psi_n(n))| \sum_{i<j}^{n} \hat{g}(i,j) \; |\mathcal{P}_l(\psi_1(1)...\psi_n(n))\rangle$$

By lemma 3.1,

$$= \frac{n(n-1)}{2n!} \sum_{k=1}^{n!} \sum_{l=1}^{n!} (-1)^{p_k+p_l} \; \langle \mathcal{P}_k(\psi_1(1)...\psi_n(n))| \; \hat{g}(1,2) \; |\mathcal{P}_l(\psi_1(1)...\psi_n(n))\rangle$$

Since $\hat{g}$ only acts on electrons 1 and 2, we can separate this integral into two separate products, where the first factor is the sum over all possible orbital occupations of electrons 1 and 2, and the second is the sum over all permutations of electrons 3...n in the remaining orbitals:

$$\langle\Phi| \sum_{i<j}^{n} \hat{g}(i,j) \; |\Phi\rangle = \frac{1}{2(n-2)!} \sum_{i,j}^{n} \left[\langle \psi_i(1)\psi_j(2)| \, \hat{g}(1,2) \, |\psi_i(1)\psi_j(2)\rangle - \langle \psi_i(1)\psi_j(2)| \, \hat{g}(1,2) \, |\psi_i(2)\psi_j(1)\rangle \right]$$

$$\times \sum_{k=1}^{(n-2)!} \sum_{l=1}^{(n-2)!} (-1)^{p_k+p_l} \; \left\langle \mathcal{P}_k(\psi_1(1)...\cancel{\psi_i(i)}...\cancel{\psi_j(j)}...\psi_n(n)) \, \middle| \, \mathcal{P}_l(\psi_1(1)......\cancel{\psi_i(i)}...\cancel{\psi_j(j)}...\psi_n(n)) \right\rangle$$

Because the basis set is orthonormal, each term will integrate to 0 unless the permutations $\mathcal{P}_k$ and $\mathcal{P}_l$ are identical, so $k = l$.

$$= \frac{1}{2(n-2)!} \sum_{i<j}^{n} 2 \, \langle \psi_i(1)\psi_j(2)| \, |\psi_i(1)\psi_j(2)\rangle \sum_{k=1}^{(n-2)!} \sum_{l=1}^{(n-2)!} (-1)^{p_k+p_l} \delta_{kl}$$

$$= \frac{1}{(n-2)!} \sum_{i<j}^{n} \langle ij| \, |ij\rangle \sum_{k=1}^{(n-2)!} (-1)^{2p_k} \delta_{kk}$$

$$= \frac{1}{(n-2)!} \sum_{i<j}^{n} \langle ij| \, |ij\rangle \sum_{k=1}^{(n-2)!} (1)$$

$$= \frac{(n-2)!}{(n-2)!} \sum_{i<j}^{n} \langle ij| \, |ij\rangle$$

$$= \sum_{i<j}^{n} \langle ij| \, |ij\rangle \quad \blacksquare.$$

2. Write the one-electron integrals S, T, and V (spin AO basis) in terms of $\bar{\mathbf{S}}$, $\bar{\mathbf{T}}$, and $\bar{\mathbf{V}}$ (spatial AO basis).

Let $\bar{\mathbf{S}}$, $\bar{\mathbf{T}}$, and $\bar{\mathbf{V}}$ be one-electron integral matrices with respect to the spatial AO basis $\{\chi_i\}$.
Let $\mathbf{S}$, $\mathbf{T}$, and $\mathbf{V}$ be one-electron integral matrices with respect to the spin AO basis $\{\xi_\mu\} = \{\chi_\mu\alpha\} \cup \{\chi_\mu\beta\}$.

5. Show that $\mathbf{f}_{\mu\nu} = \mathbf{h}_{\mu\nu} + \sum\limits_{\rho\sigma} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\sigma \rangle \, \mathbf{D}_{\sigma\rho}$.

First define the density matrix $D_{\mu\nu} = \sum\limits_{i=1}^{n} C_{\mu i} C^*_{\nu i}$,
where $C_{\mu p}$ are the expansion coefficients of ψ_p in the previously defined spin-AO basis $\{\xi_\mu\}$.
Now consider the matrix element

$$\begin{aligned}
f_{\mu\nu} &= \langle \xi_\mu | \, \hat{f} \, | \xi_\nu \rangle \\
&= \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \sum_i \langle \xi_\mu | \, \hat{J}_i \, | \xi_\nu \rangle - \langle \xi_\mu | \, \hat{K} i \, | \xi_\nu \rangle \\
&= \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \sum_i \langle \xi_\mu \psi_i | \, | \xi_\nu \psi_i \rangle \\
&= \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \sum_i \sum_{\rho\sigma} \langle \xi_\mu \xi_\rho C_{\rho i} | \, | \xi_\nu \xi_\sigma C_{\sigma i} \rangle \\
&= \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \sum_i \sum_{\rho\sigma} C_{\sigma i} C^*_{\rho i} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\sigma \rangle \\
&= h_{\mu\nu} + \sum_i \sum_{\rho\sigma} D_{\sigma\rho} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\sigma \rangle \;\; \blacksquare.
\end{aligned}$$

6. Show that $\langle \Phi | \, \mathcal{H} \, | \Phi \rangle = \sum\limits_{\mu\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum\limits_{\mu\nu\rho\sigma} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\sigma \rangle \, D_{\nu\mu} D_{\sigma\rho}$.

As we derived in problem 1,

$$\begin{aligned}
\langle \Phi | \, \mathcal{H} \, | \Phi \rangle &= \sum_i^n \langle \psi_i | \, \hat{h} \, | \psi_i \rangle + \frac{1}{2} \sum_{ij} \langle \psi_i \psi_j | \, | \psi_i \psi_j \rangle \\
&= \sum_i \sum_{\mu\nu} \langle \xi_\mu C_{\mu i} | \, \hat{h} \, | \xi_\nu C_{\nu i} \rangle + \frac{1}{2} \sum_{ij} \sum_{\mu\nu\rho\sigma} \langle \xi_\mu C_{\mu i} \xi_\rho C_{\rho j} | \, | \xi_\nu C_{\nu i} \xi_\rho C_{\sigma j} \rangle \\
&= \sum_i \sum_{\mu\nu} C^*_{\mu i} C_{\nu i} \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \frac{1}{2} \sum_{ij} \sum_{\mu\nu\rho\sigma} C^*_{\mu i} C_{\nu i} C^*_{\rho j} C_{\sigma j} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\rho \rangle \\
&= \sum_{\mu\nu} D_{\nu\mu} \langle \xi_\mu | \, \hat{h} \, | \xi_\nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\nu\mu} D_{\sigma\rho} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\rho \rangle \\
&= \sum_{\mu\nu} D_{\nu\mu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\nu\mu} D_{\sigma\rho} \langle \xi_\mu \xi_\rho | \, | \xi_\nu \xi_\rho \rangle \;\; \blacksquare.
\end{aligned}$$