

Exercises on Post Hartree-Fock method

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Exercise 1

In the following, the general equation for calculating the second-order correction of the ground state energy according to the Møller-Plesset Perturbation Theory, and a simplified equation for computing the same quantity in the case of working with a restricted closed-shell system, are presented.

$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (1)$$

$$E_0^{(2)} = \sum_{a,b=1}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab|rs\rangle - (2\langle rs|ab\rangle - \langle rs|ba\rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (2)$$

Knowing that the first equation is written in term of spin-orbitals while the second in terms of orbitals, that a and b indicate occupied while r and s indicate virtual spin-orbitals, that N is the number of electrons in the system and K the number of orbitals, try to derive the second equation from the first one.

Solution:

The notation $\langle ab||rs\rangle$ represents the antisymmetrized two-electron integral:

$$\langle ab||rs\rangle = \langle ab|rs\rangle - \langle ab|sr\rangle$$

Thus,

$$\begin{aligned} \sum_{abrs} |\langle ab||rs\rangle|^2 &= \sum_{abrs} |\langle ab|rs\rangle - \langle ab|sr\rangle|^2 \\ &= \sum_{abrs} \left(\underbrace{\langle ab|rs\rangle \langle rs|ab\rangle}_{I_1} + \underbrace{\langle ab|sr\rangle \langle sr|ab\rangle}_{I_2} - \underbrace{\langle ab|rs\rangle \langle sr|ab\rangle}_{I_3} - \underbrace{\langle ab|sr\rangle \langle rs|ab\rangle}_{I_4} \right) \end{aligned}$$

We let I_1, I_2, I_3, I_4 be equal to each part.

$$I_1 = \sum_{abrs} \langle ab|rs\rangle \langle rs|ab\rangle$$

Expanding explicitly in terms of spin-orbital configurations, we include all possible spin combinations for the orbitals:

$$\begin{aligned} &= \sum_{a=1}^N \sum_{b=1}^N \sum_{r=N+1}^{2K} \sum_{s=N+1}^{2K} \left(\langle ab|rs\rangle \langle rs|ab\rangle + \langle \bar{a}\bar{b}|rs\rangle \langle rs|\bar{a}\bar{b}\rangle + \langle a\bar{b}|rs\rangle \langle rs|\bar{a}\bar{b}\rangle \right. \\ &\quad + \langle ab|\bar{r}s\rangle \langle \bar{r}s|ab\rangle + \langle ab|r\bar{s}\rangle \langle r\bar{s}|ab\rangle + \langle \bar{a}\bar{b}|rs\rangle \langle rs|\bar{a}\bar{b}\rangle \\ &\quad \left. + \langle \bar{a}\bar{b}|\bar{r}s\rangle \langle \bar{r}s|\bar{a}\bar{b}\rangle + \langle \bar{a}\bar{b}|r\bar{s}\rangle \langle r\bar{s}|\bar{a}\bar{b}\rangle + \langle a\bar{b}|\bar{r}s\rangle \langle \bar{r}s|ab\rangle \right) \end{aligned}$$

$$\begin{aligned}
& + \langle a\bar{b}|r\bar{s}\rangle \langle r\bar{s}|a\bar{b}\rangle + \langle ab|\bar{r}\bar{s}\rangle \langle \bar{r}\bar{s}|ab\rangle + \langle \bar{a}\bar{b}|\bar{r}s\rangle \langle \bar{r}s|\bar{a}\bar{b}\rangle \\
& + \langle \bar{a}\bar{b}|r\bar{s}\rangle \langle r\bar{s}|\bar{a}\bar{b}\rangle + \langle \bar{a}b|\bar{r}s\rangle \langle \bar{r}s|ab\rangle + \langle a\bar{b}|\bar{r}\bar{s}\rangle \langle \bar{r}\bar{s}|ab\rangle \\
& + \langle \bar{a}\bar{b}|\bar{r}\bar{s}\rangle \langle \bar{r}\bar{s}|\bar{a}\bar{b}\rangle
\end{aligned}$$

Given that the spin functions (commonly denoted and) are orthonormal,

$$\langle \alpha | \alpha \rangle = 1, \quad \langle \beta | \beta \rangle = 1, \quad \langle \alpha | \beta \rangle = 0, \quad \langle \beta | \alpha \rangle = 0.$$

any term where the bra and ket spin configurations differ vanishes. This means that in the expansion, only the terms where the spin states match in both the bra and ket contribute to the final expression.

Thus, the surviving terms are:

$$= \sum_{a=1}^N \sum_{b=1}^N \sum_{r=N+1}^{2K} \sum_{s=N+1}^{2K} \left(\langle ab|rs\rangle \langle rs|ab\rangle + \langle \bar{a}\bar{b}|\bar{r}s\rangle \langle \bar{r}s|\bar{a}\bar{b}\rangle + \langle a\bar{b}|r\bar{s}\rangle \langle r\bar{s}|a\bar{b}\rangle + \langle \bar{a}\bar{b}|\bar{r}\bar{s}\rangle \langle \bar{r}\bar{s}|\bar{a}\bar{b}\rangle \right)$$

Since each term appears in identical form for both spin components, the final result simplifies to:

$$I_1 = 4 \sum_{a=1}^N \sum_{b=1}^N \sum_{r=N+1}^{2K} \sum_{s=N+1}^{2K} \langle ab|rs\rangle \langle rs|ab\rangle$$

Similarly, we obtain the second term after canceling the zero terms from the summation:

$$I_2 = 4 \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} \sum_{r=N/2+1}^K \sum_{s=N/2+1}^K \langle ab|sr\rangle \langle sr|ab\rangle$$

By interchanging the spatial orbitals s, r , we find that I_1 and I_2 are equal:

$$I_1 = I_2$$

In the expression for I_3 , we analyze the two-electron integrals appearing in the summation:

$$I_3 = \sum_{abrs} \langle ab|rs\rangle \langle sr|ab\rangle$$

In the first term $\langle ab|rs\rangle$ a and r correspond to electron 1 and b and s correspond to electron 2.

In the second term $\langle sr|ab\rangle$, the orbital assignments change, a and s now refer to electron 1 and b and r correspond to electron 2.

Therefore the only terms that survive after expanding in terms of spin-orbital configurations are:

$$\begin{aligned}
I_3 &= \sum_{a=1}^N \sum_{b=1}^N \sum_{r=N+1}^{2K} \sum_{s=N+1}^{2K} (\langle ab|rs\rangle \langle sr|ab\rangle + \langle \bar{a}\bar{b}|\bar{r}\bar{s}\rangle \langle \bar{r}\bar{s}|\bar{a}\bar{b}\rangle) \\
I_3 &= 2 \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} \sum_{r=N/2+1}^K \sum_{s=N/2+1}^K \langle ab|rs\rangle \langle sr|ab\rangle
\end{aligned}$$

And I_4 is the same:

$$\begin{aligned}
I_4 &= \sum_{abrs} \langle ab|sr\rangle \langle rs|ab\rangle \\
I_4 &= \sum_{a=1}^N \sum_{b=1}^N \sum_{r=N+1}^{2K} \sum_{s=N+1}^{2K} (\langle ab|sr\rangle \langle rs|ab\rangle + \langle \bar{a}\bar{b}|\bar{s}\bar{r}\rangle \langle \bar{s}\bar{r}|\bar{a}\bar{b}\rangle) \\
I_4 &= 2 \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} \sum_{r=N/2+1}^K \sum_{s=N/2+1}^K \langle ab|sr\rangle \langle rs|ab\rangle
\end{aligned}$$

Substituting into equation 1:

$$E_0^{(2)} = \frac{1}{4} \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} \sum_{r=N/2+1}^K \sum_{s=N/2+1}^K \frac{8\langle ab|rs\rangle \langle rs|ab\rangle - 4\langle ab|rs\rangle \langle sr|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Taking $\langle ab|rs\rangle$ as a common factor and simplifying:

$$E_0^{(2)} = \sum_{a,b=1}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab|rs\rangle - (2\langle rs|ab\rangle - \langle rs|ba\rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Exercise 2.

Without considering any spatial- or spin-symmetry constraints, of how many determinants will be reduced the CI expansion of the wave-function passing from a CASSCF(4,8) wave-function to a RASSCF(0,0|4,4|2,4) wave-function?

A CASSCF(4,8) wavefunction places 4 electrons in 8 spatial orbitals (i.e. 16 spin orbitals). Without symmetry constraints, the number of Slater determinants is given by:

$$N_{CAS} = \binom{16}{4} = \frac{16!}{4! 12!} = 1820$$

We partition the 8 orbitals into three groups (RAS1, RAS2 and RAS3):

- RAS1: (0 orbitals), so it does not enter the counting.
- RAS2: 4 orbitals (8 spin orbitals) with *no upper limit* on occupancy,

- RAS3: 4 orbitals (8 spin orbitals) with a maximum of 2 electrons,

We have 4 electrons total. Let $i = 0, 1, 2$ be the number of electrons in RAS3. Then:

$$\underbrace{\binom{8}{i}}_{\text{electrons in RAS3}} \times \underbrace{\binom{8}{4-i}}_{\text{electrons in RAS2}}.$$

Hence, the total determinant count is

$$N_{\text{RAS}} = \sum_{i=0}^2 \binom{8}{i} \binom{8}{4-i}.$$

Explicitly,

$$\begin{aligned} i = 0 : \quad & \binom{8}{0} \binom{8}{4} = 1 \times 70 = 70, \\ i = 1 : \quad & \binom{8}{1} \binom{8}{3} = 8 \times 56 = 448, \\ i = 2 : \quad & \binom{8}{2} \binom{8}{2} = 28 \times 28 = 784. \end{aligned}$$

Summing these,

$$N_{\text{RAS}} = 70 + 448 + 784 = 1302$$

The reduction in the number of determinants when going from CASSCF(4,8) to RASSCF (0,0 | 4,4 | 2,4) is:

$$1820 - 1302 = 518.$$