MP2 for singlet state of He

Lesson 4 gives second order Møller–Plesset expression for the correlation energy as:

$$\boxed{E^{(2)} = \sum_{\substack{\cancel{abrs} \\ a<b \\ r<s}} \frac{|[ar\|bs]|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}}$$

where $[ar\|bs]_x = [ar|bs]_x - [as|br]_x$ and

$$[ij|kl]_x = \int d^4x \int d^4x' \, \frac{\varphi_i^*(\vec{x})\varphi_j(\vec{x})\varphi_k^*(\vec{x}')\varphi_l(\vec{x}')}{|\vec{r}-\vec{r}'|}$$

- Our goal is to simplify $E^{(2)}$ and eliminate spins.

1.) First $E^{(2)} = \frac{1}{4}\sum_{abrs} \frac{|[ar\|bs]_x|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$ because $[a\cancel{r\|b}s]$ $E^{(2)}$ vanishes for $a=b$ or $r=s$ (reindexing)

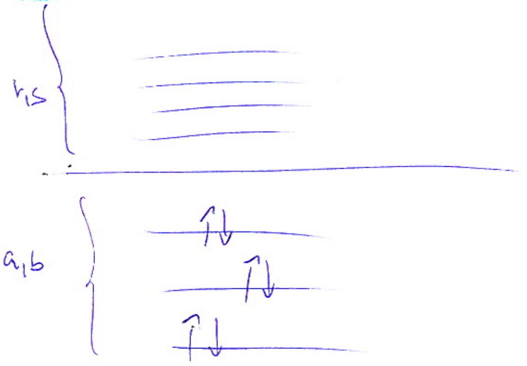
2.) Second

$$E^{(2)} = \frac{1}{4}\left\{ \sum_{abrs} \frac{[ar|bs]_x[ra|sb]_x}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} + \sum_{abrs} \overset{s \longleftrightarrow r}{\frac{[as|br]_x[sa|rb]_x}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}} \right.$$

$$\left. - \sum_{abrs} \frac{[ar|bs]_x[sa|rb]_x}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \sum_{abrs} \overset{s \longleftrightarrow r}{\frac{[ra|sb]_x[as|br]_x}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}} \right\}$$

$$\boxed{= \frac{1}{2}\sum_{abrs} \left([ar|bs]_x[ra|sb]_x - [ar|bs]_x[sa|rb]_x \right)}$$

3.) Elimination of spins



- sums a,b,r,s go over spinorbitals
- we want them to go over spatial orbitals only

first term $\quad \frac{1}{2}\sum_{abrs} [a\overset{\circ}{r}|b\overset{\times}{s}]_{\times}[\overset{\circ}{r}a|\overset{\times}{s}b]_{\times} = 2\sum_{abrs}[ar|bs][ra|sb]$

∘ "r" must go over the same spins as "a"

× "s" must go over the same spins as "b"

only "a" and "b" double the sum

second term $\quad -\frac{1}{2}\sum_{abrs}[a\overset{\circ}{r}|b\overset{\times}{s}]_{\times}[\overset{+}{s}a|rb]_{\times} = -\sum_{abrs}[ar|bs][sa|rb]$

∘ "r" must go over the same spins as "a"

× "s" must go over the same spins as "b"

\+ "s" also must go over the same spins as "a"

} all 4 spinorbitals must have the same spin in the sum ⇒ only "a" doubles the sum

Finally:

$$\boxed{E^{(2)} = \sum_{abrs} \frac{[ar|bs]\overbrace{\left(2[ra|sb]-[sa|rb]\right)}^{(2[ar|bs]^{*}-[as|br]^{*})}}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}}$$

LMAX	$E^{(2)}$ (mH)
0	~~-13~~ -13.5
1	-32.4
2	-35.6

Transformation of integrals from AO basis to MO basis

$$[ar|bs] = \sum_{\alpha\beta\gamma\delta}[\alpha\beta|\gamma\delta]\, C^{*}_{\alpha a}\, C_{\beta r}\, C^{*}_{\gamma b}\, C_{\delta s}$$

Scaling: $N^2K^6 \quad \sim K^6$ in case of He atom since $N=2$

1.) Implementation with the naive 6-loop transformation

2.) Explain the stepwise index transformation