1 Derivation of the spin-restricted MP2 equations

Given a basis of Hartree-Fock (HF) spin-orbitals $\{\psi_p\}$, the MP2 correlation energy has the following form:

$$E^{(2)} = \frac{1}{4}\sum_{ijab}^{N} \frac{\left|\langle\psi_i\psi_j||\psi_a\psi_b\rangle\right|^2}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} \tag{1.1}$$

For a closed-shell system these spin-MOS's come in (α,β) pairs

$$\psi_{2P-1}(\mathbf{r},s)=\phi_P(\mathbf{r})\alpha(s) \qquad\qquad \psi_{2P}(\mathbf{r},s)=\phi_P(\mathbf{r})\beta(s)$$

where the index P runs over the $\frac{N}{2}$ spatial MOs $\{\phi_P\}$. We can expand equation 1.1 in this basis with a little algebra.

$$\begin{aligned}
\langle\psi_i\psi_j|\,|\psi_a\psi_b\rangle &= \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\phi_i^*(\mathbf{r}_1)\,\omega_i^*(s_1)\,\phi_j^*(\mathbf{r}_2)\,\omega_j^*(s_2)\,[1-\hat{P}_{12}]\,\phi_a(\mathbf{r}_1)\,\omega_a(s_1)\,\phi_b(\mathbf{r}_2)\omega_b(s_2)\\
&= \langle\phi_i\phi_j|\phi_a\,\phi_b\rangle\,\langle\omega_i\omega_j|\omega_a\,\omega_b\rangle - \langle\phi_i\phi_j|\phi_b\,\phi_a\rangle\,\langle\omega_i\omega_j|\omega_b\,\omega_a\rangle\\
&= 2\left(\langle\phi_i\phi_j|\phi_a\,\phi_b\rangle\,\langle\omega_i\omega_j|\omega_a\,\omega_b\rangle - \langle\phi_i\phi_j|\phi_b\,\phi_a\rangle\,\langle\omega_i\omega_j|\omega_b\,\omega_a\rangle\right)\\
&= \langle\phi_i\phi_j||\phi_a\phi_b\rangle\left(\int \mathrm{d}s_1\,\mathrm{d}s_2\,\omega_i^*(s_1)\,\omega_j^*(s_2)\,\omega_a(s_1)\,\omega_b(s_2) + \int \mathrm{d}s_1\,\mathrm{d}s_2\,\omega_i^*(s_1)\,\omega_j^*(s_2)\,\omega_b(s_1)\,\omega_a(s_2)\right)\\
\sum_{ijab}\left|\langle\psi_i\psi_j|\,|\psi_a\psi_b\rangle\right|^2 &= \left|\langle\phi_i\phi_j|\,|\phi_a\phi_b\rangle\left(\int \mathrm{d}s_1\,\mathrm{d}s_2\,\omega_i^*(s_1)\,\omega_j^*(s_2)\,\omega_a(s_1)\,\omega_b(s_2) + \int \mathrm{d}s_1\,\mathrm{d}s_2\,\omega_i^*(s_1)\,\omega_j^*(s_2)\,\omega_b(s_1)\,\omega_a(s_2)\right)\right|^2\\
&= 2\left|\langle\phi_i\phi_j|\,|\phi_a\phi_b\rangle\left(\int \mathrm{d}s_1\,\mathrm{d}s_2\,\alpha_i^*(s_1)\,\omega_j^*(s_2)\,\omega_a(s_1)\,\omega_b(s_2) + \int \mathrm{d}s_1\,\mathrm{d}s_2\,\alpha_i^*(s_1)\,\omega_j^*(s_2)\,\omega_b(s_1)\,\omega_a(s_2)\right)\right|^2\\
&= \langle\phi_i\phi_j|\phi_a\phi_b\rangle\int \mathrm{d}s_1\,\mathrm{d}s_2\,\alpha_i^*(s_1)\,\alpha_j^*(s_2)\,\alpha_a(s_1)\,\alpha_b(s_2)\\
&- \langle\phi_i\phi_j|\phi_b\phi_a\rangle\int \mathrm{d}s_1\,\mathrm{d}s_2\,\alpha_i^*(s_1)\,\alpha_j^*(s_2)\,\alpha_b(s_1)\,\alpha_a(s_2)
\end{aligned}$$