Second-order Møller-Plesset Perturbation Theory (MP2)

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I. CANONICAL MP2

For a canonical RHF reference the MP2 equations are rather straightforwardly,

$$E_{\mathrm{MP2}} = 2\frac{(ia|jb)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \frac{(ia|jb)(ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{1}$$

The rate-limiting step of MP2 is the four-index transformation of the ERI tensor from atomic to molecular orbitals,

$$(ia|jb) = C_{\mu i} C_{\nu a} (\mu\nu|\lambda\sigma) C_{\lambda j} C_{\sigma b} \tag{2}$$

If this is performed in a single step this cost is $\mathcal{O}\mathrm{N}^8$! However, factoring this However, factoring this transformation leads to rather straightforward intermediates and the overall contraction scales as $\mathcal{O}\mathrm{N}^5$ as seen below,

$$\begin{aligned}
(i\nu|\lambda\sigma) &\leftarrow C_{\mu i}(\mu\nu|\lambda\sigma) \\
(i\nu|j\sigma) &\leftarrow C_{\lambda j}(i\nu|\lambda\sigma) \\
(ia|j\sigma) &\leftarrow C_{\nu a}(i\nu|j\sigma) \\
(ia|jb) &\leftarrow C_{\sigma b}(ia|j\sigma)
\end{aligned} \tag{3}$$

Notice the order of occupied indices and then virtual indices, as the virtual index is generally much larger than the occupied one this ordering is quite important for performance.

II. DENSITY-FITTED MP2

Recall

$$g_{\mu\nu\lambda\sigma} \approx (\mu\nu|P)(P|\lambda\sigma) \tag{4}$$