

# 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,

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

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

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

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

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

## II. DENSITY-FITTED MP2

Recall

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