

# 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,

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

Where the first term is often noted as the opposite-spin (OS) term while the second, the same-spin (SS) term. Its worth thinking about why these are labeled in this way, and why the same-spin term has an exchange-like component to it. There is also a variant of MP2 which attempts to correct for the MP2 errors by scaling the spin term separately, this is denoted as spin-component scaled MP2 (SCS-MP2)<sup>1</sup>. The following parameters are often used,

$$E_{\text{SCS-MP2}} = \frac{1}{3}E_{\text{MP2-SS}} + \frac{6}{5}E_{\text{MP2-OS}} \quad (2)$$

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

$$(ia|jb) = C_{\mu i}C_{\nu a}(\mu\nu|\lambda\sigma)C_{\lambda j}C_{\sigma b} \quad (3)$$

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,

$$\begin{aligned} (i\nu|\lambda\sigma) &\leftarrow C_{\mu i}(\mu\nu|\lambda\sigma) \\ (i\nu|j\sigma) &\leftarrow C_{\lambda j}(i\nu|\lambda\sigma) \\ (ia|j\sigma) &\leftarrow C_{\nu a}(i\nu|j\sigma) \\ (ia|jb) &\leftarrow C_{\sigma b}(ia|j\sigma) \end{aligned} \quad (4)$$

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

The density-fitted discussion in the JK algorithm notes recall,

$$g_{\mu\nu\lambda\sigma} \approx (\mu\nu|P)(P|\lambda\sigma) \quad (5)$$

At this point it would be trivial to reform the  $(ia|jb)$  tensor; while this would be slightly cheaper than the direct transformation of the 4-index integral above we would still create a large matrix in memory which is best avoided.

A better approach would be to build small blocks of the  $(ia|jb)$  tensor at a time. Consider the following pseudocode,

```
for i in range(ndocc):  
    for j in range(i, ndocc):  
        I_ab <- iaQ j bQ
```

In the above we only build a single block of virtual by virtual integrals which can then be contracted into the energy. This is one of the primary benefits of density-fitted MP2 builds.

Unlike the JK example previous you want to use a different fitting basis, in this case the RIFIT which has been optimized to recover MP2-like energies rather than the JK like properties used previously.

```
# Build the complementary RIFIT basis for the aug-cc-pVDZ basis (for example)  
psi4.core.BasisSet.build(mol, fitrole="RIFIT", other="aug-cc-pVDZ")
```

## REFERENCES

<sup>1</sup>S. Grimme, J. Chem. Phys. **118**, 9095 (2003).