A Recipe for Computing the Second-Order Møller-Plesset Perturbation Theory Energy

T. Daniel Crawford, *Virginia Tech*

1. Obtain the list of two-electron repulsion integrals in the (real) atomic-orbital (AO) basis:

$$(\mu\nu|\lambda\sigma) \equiv \int \phi_\mu(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)r_{12}^{-1}\phi_\lambda(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

2. Obtain the molecular orbital (MO) coefficients, C_μ^p.

3. Obtain the MO energies, ε_p.

4. Transform the AO integrals to the MO basis:

$$(pq|rs) = \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma C_\mu^p C_\nu^q (\mu\nu|\lambda\sigma) C_\lambda^r C_\sigma^s$$

   This transformation may be carried out using the above $O(N^8)$ expression or using a series of $O(N^5)$ single-index transforms.[1]

5. Compute the closed-shell MP2 energy:[2,3]

$$E_{\rm MP2} = \sum_{ab}\sum_{rs} \frac{(ar|bs)\left[2(ar|bs) - (as|br)\right]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s},$$

   where a and b refer to occupied MO's and r and s refer to unoccupied MO's.

References

[1] S. Wilson, in *Electron correlation in atoms and molecules*, Vol. 1 of *Methods in Computational Chemistry*, edited by S. Wilson (Plenum Press, New York, 1987), Chap. 3, pp. 251–309.

[2] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[3] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, 1st ed. (McGraw-Hill, New York, 1989).