

# Programming Project 4: RMP2

## *Second-order Møller-Plesset perturbation theory (closed-shell)*

Let  $\{\phi_P\}$  be RHF spatial orbitals with orbital energies  $\{\epsilon_P\}$  and basis expansion coefficients  $C_{\mu P}$ .

$$\langle \phi_P \phi_Q | \phi_R \phi_S \rangle = \sum_{\mu\nu\rho\sigma} \langle \chi_\mu \chi_\nu | \chi_\rho \chi_\sigma \rangle C_{\mu P}^* C_{\nu Q}^* C_{\rho R} C_{\sigma S} \quad (1)$$

$$E^{(2)} = \sum_{IJAB} \frac{\langle \phi_I \phi_J | \phi_A \phi_B \rangle (2 \cdot \langle \phi_I \phi_J | \phi_A \phi_B \rangle - \langle \phi_I \phi_J | \phi_B \phi_A \rangle)}{\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B} \quad (2)$$

### Procedure

1. Run RHF code to obtain MO coefficients  $\{C_{\mu P}\}$  and orbital energies  $\{\epsilon_P\}$ .
2. Transform two-electron integrals from the AO basis  $\{\chi_\mu\}$  to the MO basis  $\{\phi_P\}$  (equation 1)
3. Evaluate MP2 energy expression (equation 2)