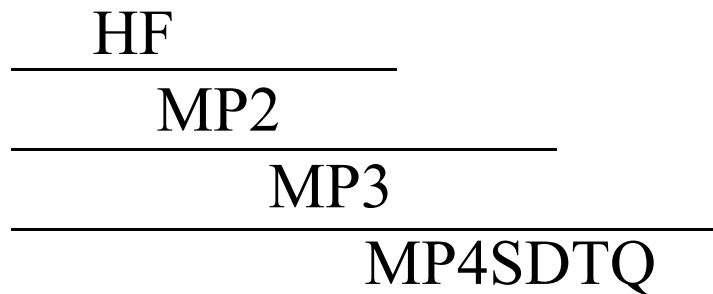
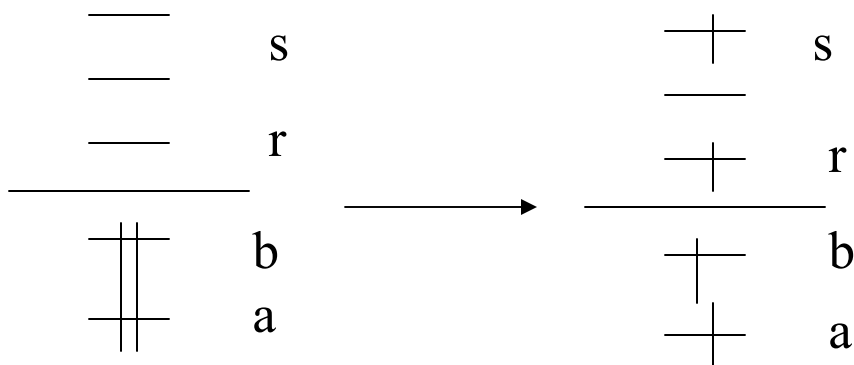


Electron Correlation - PT

$$E = \underline{E^{(0)}} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} + \dots$$



$$E^{(2)} = \sum_{\substack{a,b \\ r,s}} \frac{\langle 0 | V | de \rangle \langle de | V | 0 \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$



$\langle 0 | V | se \rangle = 0$, Brillouin's theorem

$$\Psi^{(1)} = |0\rangle + \sum |de\rangle \langle de | v | 0 \rangle$$

$$= |0\rangle + \sum_{\substack{a,b \\ r,s}} \frac{\begin{array}{|c} \widetilde{rs} \\ \widetilde{ab} \end{array} \begin{array}{|c} \widetilde{rs} \\ \widetilde{ab} \end{array} | V | 0 \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Negative, ~90-110% correlation energy

$$|de\rangle = \begin{array}{|c} \widetilde{rs} \\ \widetilde{ab} \end{array}$$

$$\langle 0 | V | \begin{array}{|c} \widetilde{rs} \\ \widetilde{ab} \end{array} \rangle =$$

$$\langle ab | V | rs \rangle - \langle ab | V | sr \rangle$$

MP2 recovers leading dispersion contributions

Consider 2 He atoms

$$E^{disp} = \sum \frac{\left| \langle 1s_A \bar{1}s_A 1s_B \bar{1}s_B | \hat{V} | 1s_A \bar{2}p_A 1s_B \bar{2}p_B \rangle \right|^2}{2\varepsilon_{1s} - 2\varepsilon_{2p}}$$

(have to allow for excitation of α and β spins and for p_x, p_y, p_z)

The key is the dipole-allowed excitation on each atom.

MO picture

$$\Psi^{HF} = |1\sigma_g \bar{1}\sigma_g 1\sigma_u \bar{1}\sigma_u|$$

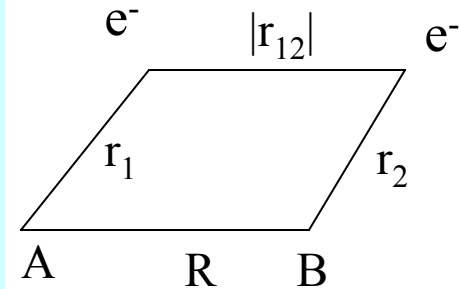
$$1\sigma_g \sim 1s_A + 1s_B$$

$$1\sigma_u \sim 1s_A - 1s_B$$

So the key transitions are

$$\text{involve } 1\sigma_g \rightarrow 2\sigma_u, 1\pi_u$$

$$1\sigma_u \rightarrow 1\sigma_g, 1\pi_g$$



Develop $\frac{1}{r_{12}}$

as Taylor series to see that dispersion goes as

$$\frac{1}{R^6}$$

Perturbation theory

- non-variational
- size extensive (scales properly with number of particles)

$$\text{MP3} \sim \langle 0 | v | de \rangle \langle de | V | de' \rangle \langle de' | V | 0 \rangle / \text{denom.}$$

$$\text{MP4} \sim \langle 0 | V | de \rangle \langle de | V | X \rangle \langle X | V | de'' \rangle \langle de'' | V | 0 \rangle / \text{denom.}$$

$$|X\rangle = |se\rangle, |de'\rangle, |te\rangle, |qe\rangle$$

MP2 is widely used, but MP3 and MP4 are rarely used anymore

Series not well convergent, may actually diverge.

MP2 works best when HF provides a reasonably good description.

Coupled cluster theory (includes contributions to all orders)

$$\Psi = e^A |0\rangle = (1 + A + \frac{1}{2}A^2 + \dots) |0\rangle$$

$$A = T_2 \quad \text{CCD}$$

$$A = T_1 + T_2 \quad \text{CCSD}$$

CCSD(T) - adds triples perturbatively

Much faster than CCSDT, with a T_3 term also in A

Gives nearly quantitative energies (unless near degeneracy)

Nonvariational

Size extensive

With a large basis set, the limit would be about 15 atoms

HF $\sim O(N^4)$

MP2 $\sim O(N^5)$

MP4 $\sim O(N^7)$

CCSD(T) $\sim O(N^7)$

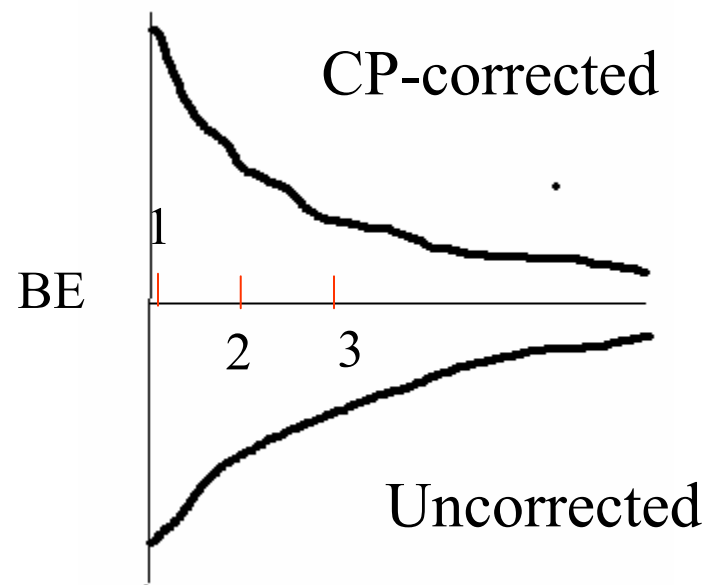
Actually, the excitation part of MP2 is $O(N^4)$; the $O(N^5)$ comes from the AO \rightarrow MO transformation.

Other considerations

Correlated methods require larger basis set to converge than HF calculations.

BSSE larger in correlated calculations than in HF

Extrapolation to complete basis set limit



1 = cc-pVDZ, 2 = cc-pVTZ, 3 = cc-pVQZ

Nuts and bolts

- MP2, MP4, CCSD(T) can use lots of disk space

G03 provides some control over disk (especially for MP2)

```
mp2(maxdisk=200000000)
```

will use maximum of 1.6 GBytes (for rwfile)

If the job needs more disk than specified by maxdisk breaks calculation into pieces (takes more CPU time)

- There is a "resource" file on your computer that sets maximum memory and disk that maxdisk and %mem can't override.

On your own computer, you can change these

- Careful – you need to know how big the scratch area is on your system and if the operating system has a file size limit.
- Gaussian allows you to "piece files together" (only an issue on 32 bit computers, where the maximum file size might be 2 GBytes)
- Opt. and freq. jobs are more demanding in terms of disk than single-point calculations