Coupled Cluster TheorIES

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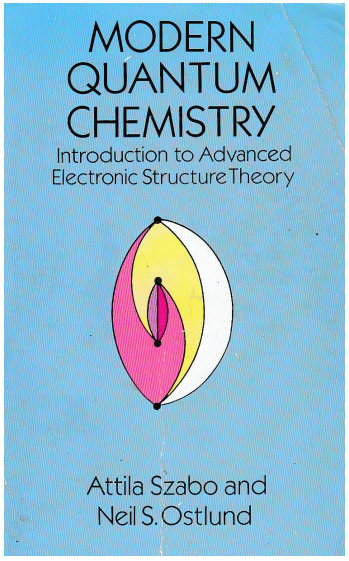

UdS - UMR 7177 Laboratoire de Chimie Quantique

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1. Correlation Energy
   - Hamiltonian Partitioning
   - Correlation Energy Partitionning
2. Independent Electron Pair Approximation (IEPA)
3. Coupled Cluster from Perturbation Theory
4. Conclusions and References

Correlation Energy

Hamiltonian partitioning

One wants to solve :

$$\hat{\mathcal{H}}|\Psi^\alpha\rangle = E^\alpha|\Psi^\alpha\rangle$$

writing

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}$$

$$\hat{\mathcal{H}}_0|\alpha\rangle = E_0^\alpha|\alpha\rangle \quad \text{with} \quad \langle\alpha|\beta\rangle = \delta_{\alpha\beta}$$

$\hat{\mathcal{V}}$ as a perturbation

In practice, the starting point is Hartree-Fock :

$$\hat{\mathcal{H}}_0 = \sum_{i=1}^{N} \hat{\mathcal{F}}(i) = \sum_{i=1}^{N} \left(\hat{h}(i) + \hat{v}_{HF}(i) \right)$$

Correlation Energy Partitioning

Using the intermediate normalization :

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{a,r} c_a^r |\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \cdots$$

The Schrödinger equation $\hat{\mathcal{H}}|\Psi\rangle = E\Psi\rangle$ can be projected on the successive class of excitations reference, singles, doubles...:

$$\langle\Psi_0|\hat{\mathcal{H}}|\Psi\rangle = E\langle\Psi_0|\Psi\rangle$$

Using Brillouin's theorem $\langle\Psi_0|\hat{\mathcal{H}}|\Psi_a^r\rangle = 0$ and Slater's rule $\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{abc}^{rst}\rangle = 0$

$$E_0 + \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle = E$$

leading to the correlation energy (see previous lectures)

$$E_{corr} = \frac{1}{4}\sum_{ab,rs} c_{ab}^{rs}\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle = \sum_{a<b,r<s} c_{ab}^{rs}\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle$$

Independent Electron Pair Approximation

$$E_{corr} = \sum_{a<b,r<s} c_{ab}^{rs} \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle$$

$$E_{corr} = \sum_{a<b} e_{ab} \quad \text{with} \quad e_{ab} = \sum_{r<s} c_{ab}^{rs} \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle$$

Important : c_{ab}^{rs} are functions of all CI coefficients !

Definition : e_{ab} is the *correlation energy* of the pair ab.

This is the **Independent Electron Pair Approximation**

$\rightarrow$ how do we calculate the $\frac{N(N-1)}{2}$ e_{ab} correlation energies ?

Pair Functions Construction

Let us write for simplicity the pair functions as :

$$|\Psi_{ab}\rangle = |\Psi_0\rangle + \sum_{r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle$$

The energy of this wavefunction simply read as :

$$E_{ab} = E_0 + e_{ab}$$

The simultaneous projections onto $\langle\Psi_0|$ and $\langle\Psi_{ab}^{rs}|$ lead to :

$$\sum_{t<u} c_{ab}^{tu} \langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{tu}\rangle = e_{ab}$$

$$\langle\Psi_{ab}^{rs}|\hat{\mathcal{H}}|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu} \langle\Psi_{ab}^{rs}|\hat{\mathcal{H}} - E_0|\Psi_{ab}^{tu}\rangle = e_{ab} c_{ab}^{rs}$$

$\rightarrow$ e_{ab} can be calculated and $E_{corr}(IEPA) = \sum_{a<b} e_{ab}$

Pair Functions Energy

Similarities/differences with DCI (Doubles CI) :

- similar equations, much smaller
- *IEPA* is variational for e_{ab} but not for E_{corr} !
- no coupling between pairs *ab* and *cd*
  "pair at a time"
- *IEPA* is not invariant under MOs rotation

The leading contributions correspond to $r = s$ and $t = u$

$$e_{ab} = -\sum_{r<s} \frac{\left|\langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle\right|^2}{\langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} - E_0 | \Psi_{ab}^{rs} \rangle - e_{ab}} \approx -\sum_{r<s} \frac{\left|\langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle\right|^2}{\langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} - E_0 | \Psi_{ab}^{rs} \rangle}$$

Finally if the excitation energies are approximated by $\Delta\epsilon$:

$$E_{corr}(IEPA) = \sum_{a<b,r<s} \frac{\left|\langle \Psi_0 | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle\right|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad \leftarrow \text{MP2 !}$$

Coupled Cluster Theory
back to CI and perturbation

What do we have in the CISD ?

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{a,r} c_a^r |\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \cdots$$

Using perturbation theory :

- couplings with the di-excitations :

  $$c_{ab}^{rs} \leftarrow \langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} | \Psi_0 \rangle = \langle ab||rs\rangle$$
  $$= (ar, bs) - (as, br)\,\delta_S$$

  $\rightarrow$ order 2 to the energy : $c_{ab}^{rs}\langle ab||rs\rangle$

- couplings between the di-excitations :

  $$\langle \Psi_{ab}^{rs} | \hat{\mathcal{H}} | \Psi_{ab}^{tu} \rangle = \langle rs||tu\rangle$$

  $\rightarrow$ *part* of order 3 to the energy :

  $$c_{ab}^{rs}\langle rs||tu\rangle c_{ab}^{tu}$$

Factorization
hierarchy

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{a,rb} c_a^r |\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + + \cdots$$

As usual, the Schrödinger equation is projected :

- $\langle \Psi_0 |$

$$H_{00} - E + \sum_{a<b,r<s} c_{ab}^{rs} \langle ab||rs\rangle = 0$$

- $\langle \Psi_I | = \langle \Psi_{ab}^{rs} |$

$$H_{I0} + (H_{II} - E)\, c_I + \sum_{J \neq I} H_{IJ} c_J + \sum_{\alpha} H_{I\alpha} c_\alpha = 0$$

where $\{|\alpha\rangle\}$ belongs to singles $\{|S\rangle\}$, triples $\{|T\rangle\}$, quadruples $\{|Q\rangle\}$ excitations spaces

and so on !

$\rightarrow$ decoupling of this *generation* scheme ?

Factorization : Generation Scheme

Let us focus on the $\{|Q\rangle\}$ space participation :

$$c_\alpha = \sum_{T_J^\dagger T_I^\dagger |0\rangle = |\alpha\rangle} c_I c_J \quad ?$$

How do we "reach" $|\alpha\rangle = \Psi^{rstu}_{abcd}$ from $|\Psi_0\rangle$?

- $|\Psi_0\rangle \rightarrow |\Psi^{rs}_{ab}\rangle \rightarrow |\Psi^{rstu}_{abcd}\rangle$
- $|\Psi_0\rangle \rightarrow |\Psi^{tu}_{cd}\rangle \rightarrow |\Psi^{rstu}_{abcd}\rangle$ and other routes !

Let us write $\Delta E_\alpha = E_0 - E_\alpha$. From perturbation theory :

$$\begin{aligned} c_\alpha &= \frac{\langle ab||rs\rangle}{\Delta E_1} \times \frac{\langle cd||tu\rangle}{\Delta E_\alpha} + \frac{\langle cd||tu\rangle}{\Delta E_2} \times \frac{\langle ab||rs\rangle}{\Delta E_\alpha} \\ &= \frac{\langle ab||rs\rangle\langle cd||tu\rangle}{\Delta E_\alpha} \left[\frac{1}{\Delta E_1} + \frac{1}{\Delta E_2}\right] \end{aligned}$$

If $\Delta E_\alpha = \Delta E_1 + \Delta E_2$ then $\boxed{c_\alpha = c_1 \times c_2}$

$\rightarrow$ *factorization* and *separability :* $\Psi = \Psi_A \Psi_B$ for $A \cdots\cdots B$

Analysis of the EigenEquations

Let us reconsider the projection onto $|\Psi_I\rangle = |\Psi^{rs}_{ab}\rangle$:

$$\cdots + (H_{II} - E)\, c_I + \cdots + \sum_{\alpha} H_{I\alpha}\, c_\alpha = 0$$

$$E = E_0 + \sum_{K} c_K H_{0K}$$

Using $c_\alpha = c_I c_J$ and $H_{I\alpha} = H_{0J}$, the contribution $(H_{0J} c_J)\, c_I$ is cancelled

Conclusion : there is a systematic suppression of some of the di-excitations contributions

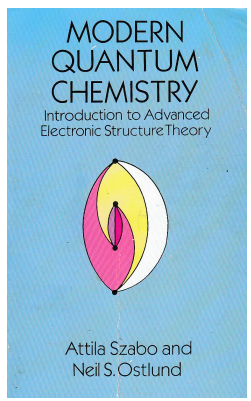
$\rightarrow$ *unlinked diagrams* are suppressed

Note : an efficient/compact formulation lies in the *diagrams* tool

Not a variational method !

Conclusion and References

- benchmak calculations for methods
- size consistence and size extensivity
- though demanding calculations



see Emmanuel Fromager's lecture