Comparative analysis of the Fock space and equation-of-motion coupled cluster approach

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The excited states are described within the coupled cluster (CC) theory via equation-of-motion (EOM) approach or with the multireference (MR) formalism. The EOM formalism is straightforward and relies on the diagonalization of the CI-like matrix corresponding to the similarity transformed Hamiltonian. The price we pay for the straightforwardness of the method is the lack of the size-extensivity property which reveals itself in the incorrect separability of the charge transfer (CT) excited states. On the other hand the multireference CC approach offers more complex formalism which can be realized via several formulations, most of them exploiting the notion of the effective Hamiltonian. The advantage of the majority of the MR formulations is a rigorous size-extensivity property while the weak point of the MR-CC approaches based on the effective Hamiltonian scheme are frequent convergence problems due to the intruder states.

The MR method studied in this work is known as a Fock space (FS) (or valence universal) approach which – in addition to being fully size-extensive – can be easily formulated within the intermediate Hamiltonian (IH) framework, i.e. with avoidance of the construction of the effective Hamiltonian. The IH realization of the Fock space approach is based on the diagonalization of the $\bar{H}$ matrix the elements of which are modified by adding some new (connected and disconnected) diagrammatic terms (so called *dressing*). It turns out that, e.g., the IH matrix constructed for the FS-MR-CCSDT model is very close to the matrix obtained within the equation-of-motion scheme at the CCSD level.

In the current approach we study various modifications to the EOM method by adding some new terms to the EOM matrix and then making CT separability tests. Several models obtained by adding, e.g. disconnected terms to the $\bar{H}$ matrix show proper asymptotic behavior [1]. This can be considered as a possibility of constructing a new computational scheme with the full size-extensivity property.

1. L. Meissner, R. J. Bartlett, *J. Chem. Phys.*, **102**, 7490 (1995).

COUPLED CLUSTER METHOD

$$\mathbf{H_N|\Psi_o\rangle = \Delta E_o|\Psi_o\rangle}$$

$$\mathbf{|\Psi_o\rangle = e^T|\Phi_o\rangle}$$

$$\mathbf{T = T_1 + T_2 + T_3 + ... + T_n}$$

where

$$\mathbf{T_n = (n!)^{-2}\Sigma_{ab...}\Sigma_{ij...}t_{ij...}^{ab...}a^\dagger b^\dagger ...ji}$$

$$\mathbf{\langle\Phi_{ij...}^{ab...}|(H_N e^T)_c|\Phi_o\rangle = \langle\Phi_{ij...}^{ab...}|\bar{H}_N|\Phi_o\rangle = 0}$$

$$\mathbf{\Delta E_o = \langle\Phi_o|(H_N e^T)_c|\Phi_o\rangle}$$

EOM-CC METHOD

The kth excited, ionized or electron-attached state wave function is expressed as

$$\mathbf{|\Psi_k^{XX}\rangle = R^{XX}(k)|\Psi_o\rangle} \qquad (1)$$

$$\mathbf{R^{XX}(k) = r_o^{XX}(k) + R_1^{XX}(k) + R_2^{XX}(k) + R_3^{XX}(k) + ...}$$

where $\mathbf{XX} \equiv$ **EE, IP** or **EA**

and r_o is a constant for EE and zero for IP and EA

Inserting (1) into the Schrödinger equation we obtain EOM:

$$\mathbf{\bar{H}_N R^{XX}(k) = \omega_k^{XX} R^{XX}(k)}$$

where

$$\mathbf{\bar{H}_N = e^{-T} H_N e^T = (H_N e^T)_c}$$

and ω_k^{XX} is **the energy of the studied process (excitation, ionization or electron-attachment)**

MULTIREFERENCE FORMALISM

Model space: M P **Orthogonal space:** $M_\perp$ Q

$$\mathbf{\Psi_k^o = P\Psi_k} \qquad \mathbf{\Psi_k = \Omega\Psi_k^o}$$

BLOCH EQUATION **EFFECTIVE HAMILTONIAN**

$$\mathbf{H\Omega P = \Omega P H\Omega P} \qquad \mathbf{H_{eff} = PH\Omega P}$$

$$\mathbf{H_{eff}\Psi_k^o = E_k\Psi_k^o}$$

FOCK SPACE FORMALISM

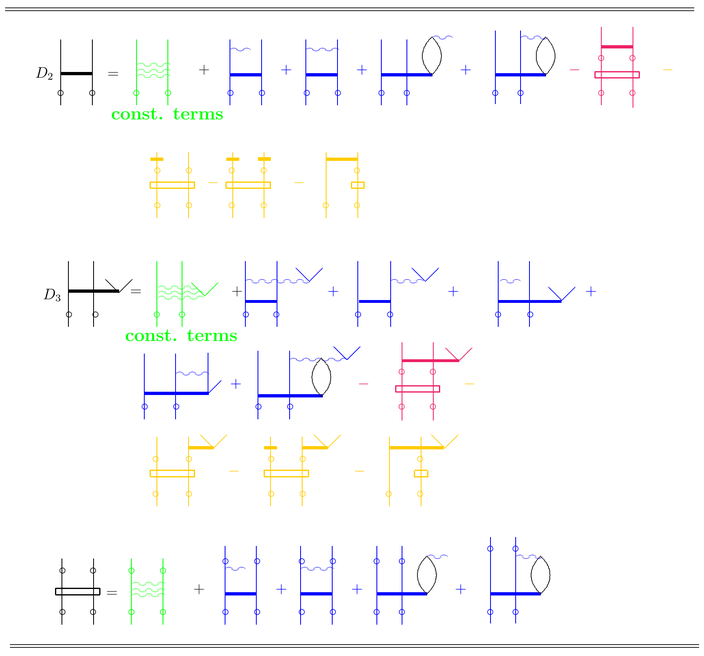
$\mathbf{\Omega = \{e^{\tilde{S}^{(k,l)}}\}P}$ **k** – number of valence particles **l** – number of valence holes

$$\mathbf{\tilde{S}^{(k,l)} = \tilde{S}_1^{(k,l)} + \tilde{S}_2^{(k,l)} + \tilde{S}_3^{(k,l)} + \cdots + \tilde{S}_n^{(k,l)}} \qquad \mathbf{\tilde{S}^{(k,l)} \sum_{i=0}^{k}\sum_{j=0}^{l} S^{(i,j)}}$$

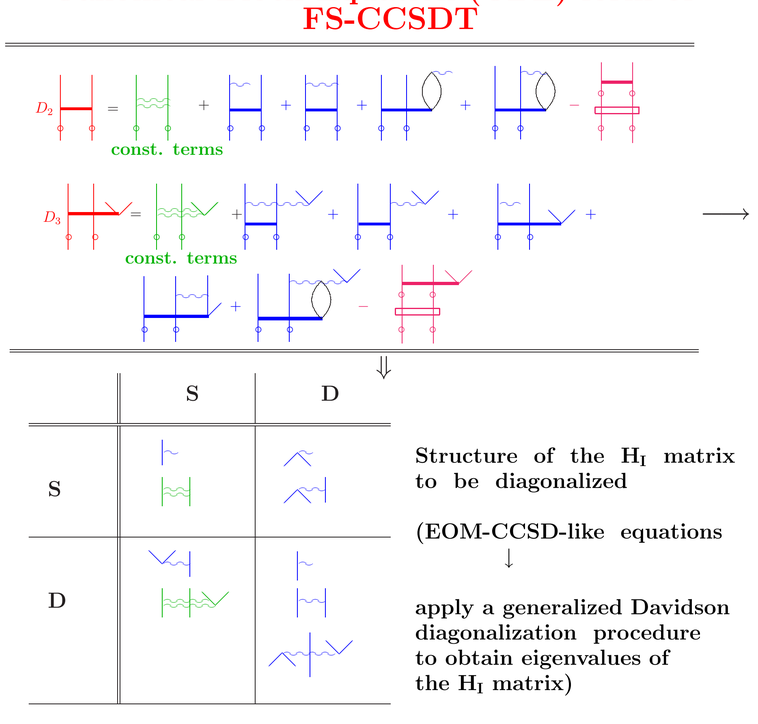
$$\mathbf{\tilde{S}_n^{(k,l)} = \frac{1}{(n!)^2}\Sigma'_{\bar{a}\bar{b}...\bar{i}\bar{j}...}s_{\bar{i}\bar{j}...}^{\bar{a}\bar{b}...}\{\bar{a}^\dagger\bar{b}^\dagger\cdots\bar{j}\bar{i}\}}$$

$'$ – excitations within model space excluded

Standard formulation of the FS-CCSDT approach



Canonical Bloch Equation (CBE) form of FS-CCSDT



Structure of the H_I matrix to be diagonalized

(EOM-CCSD-like equations

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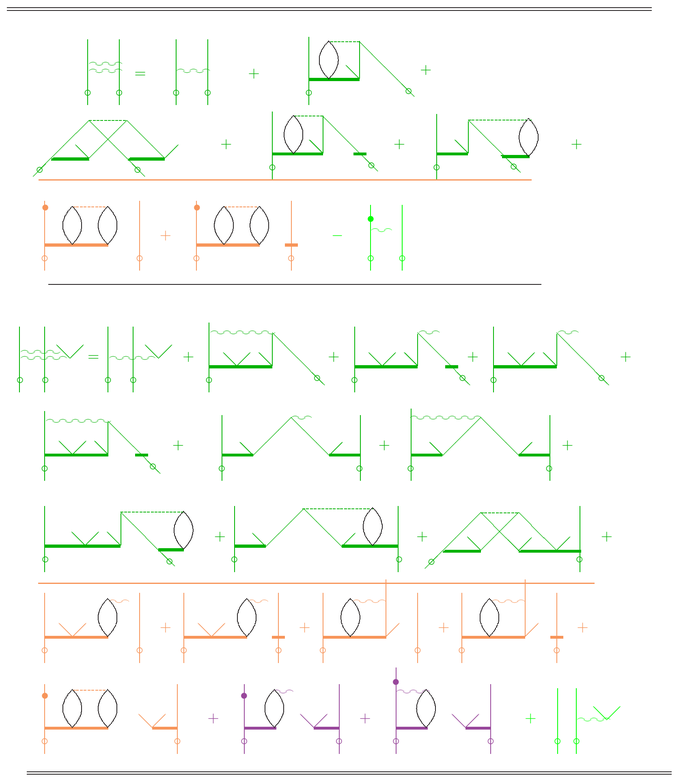
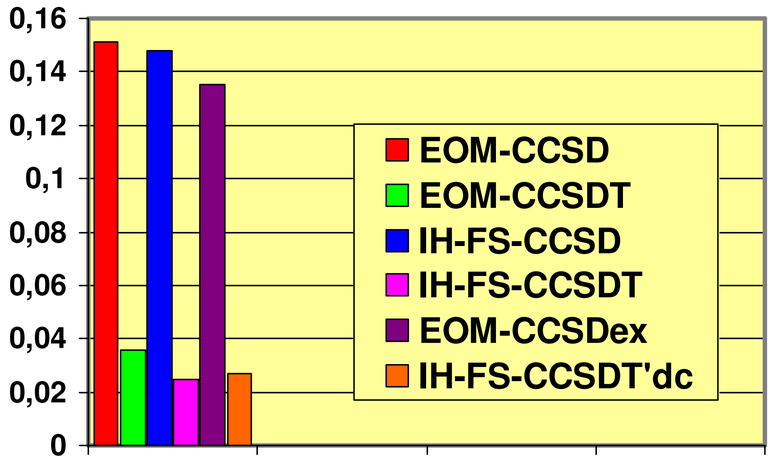
apply a generalized Davidson diagonalization procedure to obtain eigenvalues of the H_I matrix)



Behavior of charge transfer excitation in a Be···C_2 complex

R (Å)	$-\frac{e^2}{R}$ (eV)	$EE-(IP+EA)$ (in eV)					
		EOM-CC			IH-FS-CC		
		SD	SDT	SDex	SD	SDT	SDT′dc
5	-2.880	-2.937 (-0.057)	-2.872 (0.008)	-3.012 (-0.132)	-2.929 (-0.049)	-3.027 (-0.147)	-3.037 (-0.157)
10	-1.440	-1.375 (0.065)	-1.437 (0.003)	-1.440 (0.000)	-1.438 (0.002)	-1.440 (0.000)	-1.439 (0.001)
100	-0.1440	-0.0799 (0.064)	-0.1411 (0.003)	-0.1440 (0.000)	-0.1440 (0.000)	-0.1440 (0.000)	-0.1440 (0.000)
1000	-0.0144	0.0496 (0.064)	-0.0115 (0.003)	-0.0144 (0.000)	-0.0144 (0.000)	-0.0144 (0.000)	-0.0144 (0.000)

Mean absolute deviation (eV) from the FCI values for excitation energies (Ne, HF, N_2, C_2, H_2O)



CONCLUSIONS

- EOM-CC and FS-CC methods provide results of comparable quality, e.g. CCSD m.a.e.: ∼0.15 eV; CCSDT m.a.e.: ∼ 0.02-0.04 eV.
- FS- CC approach shows correct separability for the CT excitations.
- The correct CT separability can be achieved also for the EOM-CC approach by adding "dressing" (composed of disconnected diagrams).
- "Dressing" improves the EE values also for the local excitations.

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