Equation-of-motion coupled cluster theory for describing arbitrary conical intersections

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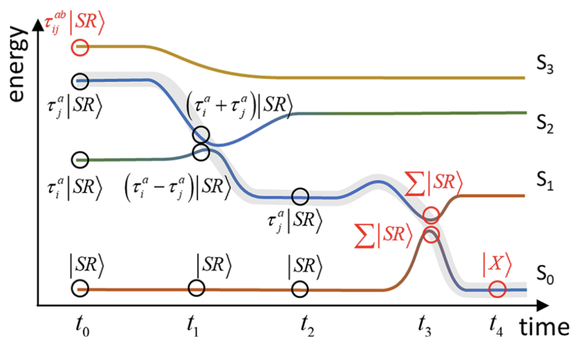
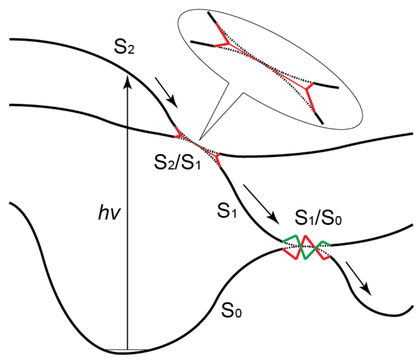


Schematic time evolution of potential energy surfaces during an excited-state dynamics [1]. Strong correlation (multiconfigurational character) is required for the ground state to simulate the dynamics passing a S_1/S_0 conical intersection (CoIn).



Conical intersections between excited states described by non-unitary truncated EOM-CC/CCLR have topological defect.

Introduction

- Balanced description of strong and weak correlations is still challenging.
- This time, we report that a modified version of the coupled cluster (CC) theory named CCSD0, which was rediscovered by Scuseria Group [2], is outstanding among the theories proposed for describing strong correlation. Weak correlation is supplemented to CCSD0 in the F12 scheme [3].
- With adoption of the conventional equation-of-motion scheme, the theory called "EOM-CCSD0-F12" can describe S_1/S_0 conical intersections (CoIns) as well.
- We are developing an algorithm to correct the topology of CoIns between excited states. Once the algorithm has been adopted to EOM-CCSD0-F12, the theory can describe arbitrary CoIns without introducing active space.

Similarity between CCSD0 [2] and PHF by Hirao and Nakatsuji [4]

CCSD0

Doubles excitation of the coupled-cluster singles and doubles (CCSD) is de-coupled to the spin-singlet and triplet pairs. The triplet-pair doubles excitation is dropped.

$$|\mathrm{CCSD0}\rangle = \exp\left(\hat{T}_1 + \hat{T}_2^{[0]}\right)|\mathrm{HF}\rangle$$

$$\hat{T}_2^{[0]} = \frac{1}{2}\sum_{ijab}\sigma_{ij}^{ab}\hat{P}_{ab}^{\dagger}\hat{P}_{ij}$$

$$\hat{P}_{ij} = \frac{1}{\sqrt{2}}\left(\hat{C}_{j\alpha}\hat{C}_{i\beta} + \hat{C}_{i\alpha}\hat{C}_{j\beta}\right)$$

$$|\mathrm{PHF2}\rangle = N\hat{\wp}_{\mathrm{R}}\exp\left(\sum_{ia} w_{i,0}^{a}\hat{S}_{i,0}^{a\dagger}\right)|\Phi_0\rangle, w_{i,z}^{a} \in \mathbb{C}$$

$$\sim|\bar{\Phi}_0\rangle + \sum_{ia} c_{ii}^{aa}|\bar{\Phi}_{ii}^{aa}\rangle + \sum_{ijab} c_{ij}^{ab}|\bar{\Phi}_{ij}^{ab}(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)/2\rangle + \cdots$$

Projected Hartree-Fock (PHF) theory

In the cluster expansion expressed by the Thouless theorem or unitary transformation, which are equivalent, the single-excitation operator is spin-adopted, utilizing the Pauli matrices.

$$\hat{T}_1 = \sum_{ia}\left(w_{i,0}^{a}\hat{S}_{i,0}^{a\dagger} + \sum_{\tau=x,y,z} w_{i,\tau}^{a}\hat{S}_{i,\tau}^{a\dagger}\right), w_{i,\gamma}^{a} \in \mathbb{C}$$

$$\hat{S}_{i,\gamma}^{a\dagger} = \frac{1}{\sqrt{2}}\hat{\boldsymbol{C}}_{\boldsymbol{a}}^{\dagger}\sigma_{\gamma}\hat{\boldsymbol{C}}_{\boldsymbol{i}} \quad (\gamma = 0{,}1(x), 2(y), 3(z))$$

$$\hat{\boldsymbol{C}}_{\boldsymbol{a}}^{\dagger} = \begin{pmatrix}\hat{C}_{a\alpha}^{\dagger} & \hat{C}_{a\beta}^{\dagger}\end{pmatrix}, \hat{\boldsymbol{C}}_{\boldsymbol{i}} = \begin{pmatrix}\hat{C}_{i\alpha} \\ \hat{C}_{i\beta}\end{pmatrix}$$

The ansatz optimized in a symmetry-projected variational space overcomes the restricted Hartree-Fock (RHF) stability dilemma while solving the symmetry dilemma. One of the possible PHF theories gives an ansatz which shares the leading configurations with CCD!

EOM-CCSD0-F12

Since CCSD0 is approximately equivalent to one of the PHF theories, CCSD0 barely describes weak correlation. Weak correlation is supplemented to CCSD0 in the F12 scheme [3].

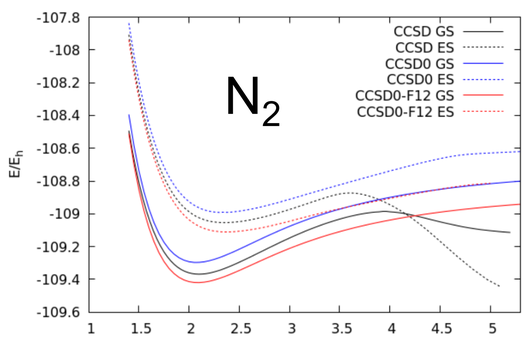
$$|\mathrm{CCSD0{-}F12}\rangle = \exp\left(\hat{T}_1 + \hat{T}_2^{[0]} + \hat{R}_1 + \hat{R}_2\right)|\mathrm{HF}\rangle$$

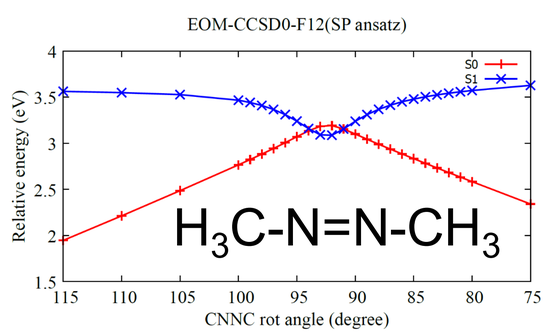
$$\hat{R}_1 = \sum_{ik} c_k^i \sum_{j\alpha}\bar{F}_{\alpha j}^{kj}\tilde{a}_i^{\alpha}$$

$$\hat{R}_2 = \frac{1}{4}\sum_{ijkl} c_{kl}^{ij}\left(\sum_{\alpha\beta}\bar{F}_{\alpha\beta}^{kl}\tilde{a}_{ij}^{\alpha\beta} + \sum_{b\alpha}\bar{F}_{\alpha b}^{kl}\tilde{a}_{ij}^{\alpha b} + \sum_{ab}\bar{F}_{ij}^{ab}\tilde{a}_{ij}^{ab}\right)$$

$$F(r_{12}) = \exp(-\gamma r_{12})$$

Here is preliminary EOM-CCSD0-F12 curves for the nitrogen (N_2) and azomethane (H_3C-N=N-CH_3) molecules. The S_1/S_0 CoIn is expected to be corrected in the coming updated implementation.





EOM-CC under the orthogonality condition derived by Kjønstad [5]

1)Solve normal EOM-CC, $\bar{\boldsymbol{H}}\boldsymbol{r}^{(L)} = \omega_L\boldsymbol{r}^{(J)}$.
2)if ${}^{T}\boldsymbol{r}^{(K)}\boldsymbol{r}^{(L)} = 0$ for every $K \neq L$ then
3) Stop.
4)else
5) Slightly increase $\max\{\mathrm{Re}(\omega_K), \mathrm{Re}(\omega_L)\}$ and decrease $\min\{\mathrm{Re}(\omega_K), \mathrm{Re}(\omega_L)\}$.
6) Optimize ${}^{T}\boldsymbol{r}^{(K)}[\bar{\boldsymbol{H}} - \omega_L\boldsymbol{M}_{KL}]\boldsymbol{r}^{(L)}$ by deviating it along $\nabla\left({}^{T}\boldsymbol{r}^{(K)}[\bar{\boldsymbol{H}} - \omega_L\boldsymbol{M}_{KL}]\boldsymbol{r}^{(L)}\right)$ where $\nabla = {}^{T}\left[\frac{\partial}{\partial\boldsymbol{r}^{(K)}} \quad \frac{\partial}{\partial\boldsymbol{r}^{(L)}}\right]$.
7) If ${}^{T}\boldsymbol{r}^{(K)}[\bar{\boldsymbol{H}} - \omega_L\boldsymbol{M}_{KL}]\boldsymbol{r}^{(L)} = 0$ is achieved at a point where $\nabla\left({}^{T}\boldsymbol{r}^{(K)}[\bar{\boldsymbol{H}} - \omega_L\boldsymbol{M}_{KL}]\boldsymbol{r}^{(L)}\right)=0$ then
8) Stop.
9) else
10) Go to 5.
11) end if
12) end if

$$\bar{H} \equiv \exp(-\hat{T})\hat{H}_N\exp(\hat{T}) \qquad \hat{H}_N = \hat{H} - \langle\mathrm{HF}|\hat{H}|\mathrm{HF}\rangle$$

$$(\bar{\boldsymbol{H}})_{\mu\nu} = \langle\Phi_\mu|\bar{H}|\Phi_\nu\rangle \qquad \Omega_{\sigma\nu} = \langle\Phi_\sigma|\exp(\hat{T})|\Phi_\nu\rangle$$

$$\boldsymbol{M}_{KL} \equiv {}^{T}\boldsymbol{\Omega}\wp_{KL}\boldsymbol{\Omega} \qquad \wp_{KL} = [\boldsymbol{r}^{(K)} \quad \boldsymbol{r}^{(L)}]\boldsymbol{G}_{KL}^{-1}\begin{bmatrix}{}^{T}\boldsymbol{r}^{(K)} \\ {}^{T}\boldsymbol{r}^{(L)}\end{bmatrix} \qquad \boldsymbol{G}_{KL} = \begin{bmatrix}{}^{T}\boldsymbol{r}^{(K)} \\ {}^{T}\boldsymbol{r}^{(L)}\end{bmatrix}[\boldsymbol{r}^{(K)} \quad \boldsymbol{r}^{(L)}]$$

References

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