Introduction to coupled-cluster and equation-of-motion methods in Q-Chem

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Coupled-cluster theory for the ground state
Transition state theory

Definition

*Transition state* complex is the activated complex corresponding to a maximum on an energy path along the coordinate of an elementary reaction.

The transition state corresponds to a saddle point on the potential energy surface. Hence, one negative eigenvalue of the Hessian, a matrix of partial second derivatives.

Temperature dependence of the reaction rate is given by the Arrhenius equation:

\[
k(T) = Ae^{-E_a/RT}\]
Study of a chemical reaction

$$C_2H_4 + \cdot CH_3 \rightarrow \cdot CH_2CH_2CH_3$$

Reactants
react_c2h4_ch3.xyz

Transition state
react_c3h7_ts.xyz

Product
react_c3h7.xyz

$rem$
method = ccsd
basis = cc-pvdz
gui = 2
$end$
Study of a chemical reaction

\[ \text{C}_2\text{H}_4 + \bullet\text{CH}_3 \rightarrow \bullet\text{CH}_2\text{CH}_2\text{CH}_3 \]

Reactants
- Reactant 1: reac_c2h4_ch3.xyz
- Reactant 2: reac_c3h7_ts.xyz

Transition state
- Transition state: reac_c3h7_ts.xyz

Product
- Product: reac_c3h7.xyz

**Results:**

<table>
<thead>
<tr>
<th>Method</th>
<th>Reactants Energy</th>
<th>Transition State Energy</th>
<th>Product Energy</th>
<th>Energy Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP 6-31G*</td>
<td>-118.422822</td>
<td>-118.419142</td>
<td>-118.470852</td>
<td>-2.3 kcal/mol</td>
</tr>
<tr>
<td>CCSD cc-pVDZ</td>
<td>-118.055116</td>
<td>-118.044096</td>
<td>-118.100818</td>
<td>-6.9 kcal/mol</td>
</tr>
<tr>
<td>CCSD(T) cc-pVDZ</td>
<td>-118.067803</td>
<td>-118.057938</td>
<td>-118.112890</td>
<td>-6.2 kcal/mol</td>
</tr>
</tbody>
</table>

1 a.u. = 627.51 kcal/mol
Equation-of-motion theory for excited states
Equation-of-motion method (EOM)

Based on the couple-cluster wave function for the ground state

\[ |\Psi_{EOM}^m\rangle = R_m |\Psi^{CC}\rangle = R_m e^T |\Phi_0\rangle \]

\[ T = T_1 + T_2 + \cdots \]
\[ T_1 = \sum_{ia} t_i^a a_i^\dagger \]
\[ T_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_i^\dagger b_j^\dagger \]

\[ R_m = r_{m,0} + R_{m,1} + R_{m,2} + \cdots \]

Electronic correlation is folded into a similarity transformed Hamiltonian

\[ \bar{H} = e^{-T} H e^T \]

Wave functions satisfy the following equations

\[ \langle \Phi_\mu | \bar{H} - E^{CC} | \Phi_0 \rangle = 0 \]
\[ \langle \Phi_\mu | \bar{H} - E_{EOM}^m | R_m \Phi_0 \rangle = 0 \]

Excited state eigenfunctions are found by diagonalizing the similarity transformed Hamiltonian in the Fock space.
Equation-of-motion method (EOM)

Variations of the EOM methods depend on the character of operator $R$. Here is some of them:

- **EOM-EE (Excitation energy)**
  - $\psi_0$
  - $\psi_i^a$
  - $\psi_{ij}^{ab}$

- **EOM-SF (Spin-flip)**
  - $\psi_0$
  - $\psi_i^a$

- **EOM-IP (Ionization energy)**
  - $\psi_0$
  - $\psi_i$
  - $\psi_{ij}^a$

- **EOM-EA (Electron affinity)**
  - $\psi_0$
  - $\psi_i^a$
  - $\psi_{ij}^{ab}$
Equation-of-motion method (EOM)

Benefits of EOM methods:
- Black box approach: no need to manually select active molecular orbitals.
- Target states of different character (local, Rydberg, charge transfer) are found in a single calculation.
- Reference state can be chosen based on convenience, not relevance to the target states.

Q-Chem capabilities:
- Analytic gradients for geometry optimization.
- Excited state and transition properties.
- Minimization of potential surface crossings.

Important note:
- EOM solutions are not orthogonal, but biorthogonal because the similarity transformed Hamiltonian is not Hermitian.

\[
\langle \Psi^{CC} L_I | R_J \Psi^{CC} \rangle = \delta_{IJ}
\]
Problems

1. Charge transfer state in Cs + triazine.

2. Character of excited state in diazirine (CH$_2$N$_2$).
Cs + triazine

Q-Chem input file triazine.in:

$rem
jobtype = sp
method = eom-ccsd
basis = 3-21g*

scf_algorithm = diis
scf_guess = core
max_scf_cycles = 200
n_frozen_core = fc

ee_singlets = [8,8]
$end
Diazirine

In a two-step process $S_1$ state is excited first, then $S_2$. Both transitions must be allowed, and $S_1$ state must have some lifetime.

The energy of photons in a REMPI(2+1) experiment is 3.9 eV. The problem is to find which states are accessible in the experiment and describe their character.

How to solve this problem?

- Compute the vertical excitation energies of the lowest states. Which ones agree with the photon energy in the experiment?
- Calculate the properties of the respective electronic transitions and verify that the transitions are allowed (i.e. have non-zero oscillator strength).
Diazirine

Q-Chem input file
diazirine.in:

$rem
jobtype = sp
method = eom-ccsd
basis = 6-31g*
ee_singlets = [2,2,2,2]
!cc_state_to_opt = [4,1]
cc_trans_prop = true
$end