Molecular properties for the CC and EOM-CC methods

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Coupled cluster (CC) method

CC method

Wave function:

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

$$T = T_1 + T_2 + T_3 ... + T_N$$

where

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

- amplitude equation:

$$\langle\Phi_{ij...}^{ab...}|e^{-T}He^{T}|\Phi_o\rangle = 0$$

- energy expression:

$$E = \langle\Phi_o|e^{-T}He^{T}|\Phi_o\rangle$$

CC method

Important quantity in the CC theory

$\bar{H}$ - similarity transformed Hamiltonian

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

Equation-Of-Motion Coupled Cluster method (EOM-CC)

EOM-CC method

Schrödinger equation:

$$H|\Psi_k\rangle = E_k\,|\Psi_k\rangle \quad k = 1, 2, \cdots$$

Wave function for excited states:

$$|\Psi_k\rangle \;=\; R(k)\,|\Psi_0\rangle$$

Excitation operator:

$$R(k) = r_0(k) + R_1(k) + R_2(k) + R_3(k) + \cdots + R_N(k)$$

$$R(k) \;= r_o(k) + \;\frac{1}{2}\sum_{i,a} r_i^a(k)a^\dagger i + \frac{1}{4}\sum_{abij} r_{ij}^{ab}(k)a^\dagger b^\dagger ji + \ldots$$

EOM-CC method

Eigenvalue equation:

$$\mathbf{\bar{H}R(k)} = \omega_{\mathbf{k}}\mathbf{R(k)}$$

where: ω_k – excitation energies

EOM-CC method

Similarity transformed Hamiltonian, $\bar{H}$, is
a non-Hermitian matrix

- two eigenvectors:

  right-hand $(R(k))$ and left-hand $(L(k))$

$$|\Psi\rangle = e^{T} R(k) |\Phi_o\rangle$$

$$\langle\widetilde{\Psi}| = \langle\Phi_o| L(k) e^{-T}$$

Thus, each root of $\bar{H}$ is asociated with two eigenvectors that correspond to distinct bra and ket states.

EOM-CC method

- General form of L (deexcitation operator):

$$L(k) = l_0(k) + L_1(k) + L_2(k) + L_3(k) + \cdots$$

$$L(k) \;=\; l_0(k) + \sum_{ia} l_a^i i^\dagger a + \frac{1}{4}\sum_{abij} l_{ab}^{ij} i^\dagger j^\dagger b a + \ldots$$

Metoda EOM-CC

- The distinction beetwen bra and ket states is not important if we are only interested in evaluating the excitation energies since both corresponding to the same eigenvalue but both are needed to obtain density matrices.

Molecular properties

The Hellmann-Feynman theorem sates that the derivative of the total energy with respect to a parameter (perturbation) is equivalent to the expectation value of the derivative of the Hamiltonian with respect to that same parameter (perturbation), that is:

$$\frac{dE(0)}{d\lambda} = \langle\Psi|\frac{dH}{d\lambda}|\Psi\rangle$$

This expression is valid only for variational wavefunctions.

Molecular properties

For non-variational methods first order properties can be determined as:

- derivatives of the energy with respect to a certain perturbation
- or expectation value with approximate wave function

Derivatives of the energy can be obtained within quantum-chemical methods via numerical or analytical differentiation.

Molecular properties

Analytical first derivatives of the energy with respect to the arbitrary perturbation within the CC and EOM-CC approximation

Molecular properties

First derivative of the energy with respect to a perturbation
Ground state

Starting point:

$$\Delta E(\lambda) = \langle \Phi_o | \, e^{-T(\lambda)} H_N(\lambda) e^{T(\lambda)} \, | \Phi_o \rangle$$

We assue that the Hamiltonian is expressed as:

$$H(\lambda) = H + \lambda O$$

where:

- H - unperturbed Hamiltonian
- λ - parameter characterizing strenght of a perturbation represented by the O operator

Molecular properties

Straightforward differentiation of the above equation with respect to the arbitrary perturbation symbolized by λ after simple algebra gives:

$$\Delta E^{\lambda} = \langle \Phi_o | (1 + \Lambda) \bar{O}_N | \Phi_o \rangle$$

i.e., the analytical derivative of the energy where Λ is a deexcitation operator:

$$\begin{aligned} \Lambda &= \Lambda_1 + \Lambda_2 + \cdots + \Lambda_N = \\ &= \sum_{ia} \lambda_a^i i^\dagger a + \frac{1}{4} \sum_{ijab} \lambda_{ab}^{ij} i^\dagger j^\dagger b a + \cdots + \\ &+ \frac{1}{(n!)^2} \sum_{i,j,l \cdots a,b,c \cdots} \lambda_{abc \cdots}^{ijl \cdots} i^\dagger j^\dagger l^\dagger \cdots cba \end{aligned}$$

Molecular properties

The above equation can be obtained starting with the following expression:

$$\begin{aligned}\mathcal{E}(\Lambda, T) &= \langle \Phi_o | (1 + \Lambda) e^{-T} H_N e^{T} | \Phi_o \rangle \\ &= \langle \Phi_o | (1 + \Lambda) \bar{H}_N | \Phi_o \rangle\end{aligned}$$

Molecular properties

The analytical first derivative of the energy with respect to the arbitrary perturbation for excited states within EOM-CC method

Staring point:

$$\varepsilon(L,T,R) = \langle\Phi_o|\, Le^{-T} H_N e^{T} R \,|\Phi_o\rangle$$

L, R, T, H_N depending upon a parameter λ.
Differentiation of the above equation with respect to the arbitrary perturbation (λ) gives the analytical derivative of the energy:

$$\varepsilon^{\lambda} = \langle\Phi_o|\, Le^{-T} \frac{\partial H_N}{\partial\lambda} e^{T} R \,|\Phi_o\rangle + \langle\Phi_o|\, Z e^{-T} \frac{\partial H_N}{\partial\lambda} e^{T} \,|\Phi_o\rangle \qquad (*)$$

Molecular properties

First term of equation (*) - expression for the expectation value $\frac{\partial H_N}{\partial \lambda}$

$$\mathcal{E}^{\lambda} = \langle \tilde{\Psi} | \frac{\partial H_N}{\partial \lambda} | \Psi \rangle$$

Remembering that $\tilde{\Psi}$ and Ψ are defined as:

$$\begin{aligned} \langle \tilde{\Psi} | &= \langle \Phi_o | L e^{-T} \\ | \Psi \rangle &= e^{T} R | \Phi_o \rangle \end{aligned}$$

Second term of equation (*) consists of Z operator (same role as Λ operator in CC, i.e. for ground state).

Molecular properties

Z operator within the CCSD model is defined as:

$$Z = Z_1 + Z_2 = \sum_{ia} z_a^i i^\dagger a + \frac{1}{4} \sum_{ijab} z_{ab}^{ij} i^\dagger j^\dagger b a$$

Molecular properties

Expression for the one-particle density matrix assuming that:

$$H(\lambda) = H + \lambda O$$

where λ – parameter characterizing strenght of a perturbation represented by the O operator.

$$\varepsilon^{\lambda} = \langle\Phi_o|\, L e^{-T} O e^{T} R \,|\Phi_o\rangle + \langle\Phi_o|\, Z e^{-T} O e^{T} \,|\Phi_o\rangle$$

$$\underline{\gamma_{pq} = \langle\Phi_o|\, L \left(p^{\dagger} q e^{T}\right)_c R \,|\Phi_o\rangle + \langle\Phi_o|\, Z \left(p^{\dagger} q e^{T}\right)_c \,|\Phi_o\rangle}$$

where $p, q, ...$ - generic indices

The generalized expectation value prescription

For the ground state the approach is equivalent to differentiating the CC energy in the presence of the field but using the zero-field orbitals in all calculations (applied by Salter, Sekino and Bartlett - approximation - no orbital response on electrical properties (in order to include it we have to solve coupled perturbed Hartree-Fock (CPHF) equations)).

For the excited states the approach, the expectation value procedure, corresponds to the energy derivatives with a frozen reference state (the zero-field orbitals and T amplitudes must be used - Stanton, Bartlett).

The generalized expectation value prescription

The perturbation induced relaxation of the reference state does not make a significant contribution to the excited state properties. Thus the generalized expectation value method provides a useful means for studying properties of excited states.

The generalized expectation value prescription

It should be empasized that this apparoach for calculating properties is not equivalent to the response property (i.e., by differentiating the energy), as it does not include the contribution of reference state relaxation (the change in the molecular orbital and T amplitudes due to interaction with the perturbation).

Analytical determination of properties

The analytical first derivative of the energy with respect to the arbitrary perturbation within the CC and EOM-CC methods.

Analytically - **response theory**

Ground state (via CC method):
Λ vector $\longrightarrow$ density matrix $\longrightarrow$ molecular properties

Excited states (via EOM-CC method):
Determination of molecular properties $\longrightarrow$ bra and ket states $\longrightarrow$ density matrix

Response properties by numerically differentiating energies calculated in the presence of an applied electric field

finite field method

$$\frac{E(\alpha) - E(-\alpha)}{2\alpha}$$

where α – field strenght

Relaxed orbitals (i.e., coupled Hartree-Fock (CHF) equation is solved).

Numerical determination of dipole moment

```
Test run on H2O EOM-CCSD props
O
H 1 R
H 1 R 2 A

R=0.957
A=104.5

*ACES2(BASIS=PBS,CALCLEVEL=CCSD,UNITS=0
MEMORY_SIZE=5GB,SYMMETRY=ON
SCF_MAXCYC=600,SCF_CONV=12,REF=RHF
SPHERICAL=ON,CC_CONV=12,CC_MAXCYC=500
EXCITE=EOMEE,EE_SYM=2-2-2-2,ZFIELD=200)
```

Numerical determination of dipole moment

```
                        Calculations with   ZFIELD=200

------------------------------------------------------------------------------

               CCSD        energy is     -76.289515087068 a.u.

------------------------------------------------------------------------------

  Summary of EOM-CCSD excitation energies

  SYM.  ROOT #     EE(eV)     EE(cm-1)    OSC. STR.     TOTAL ENERGY

---------------------------------------------------------------------------------

   1          1                9.8176       79184.43      -75.92872426
   2          1                7.3942       59637.83      -76.01778515
   3          1               11.5608       93244.08      -75.86466377
   4          1                9.1500       73800.06      -75.95325725

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```

Numerical determination of dipole moment

Calculations without ZFIELD

```
---------------------------------------------------------------------------

               CCSD        energy is     -76.289660900287 a.u.

---------------------------------------------------------------------------

  Summary of EOM-CCSD excitation energies

  SYM.  ROOT #     EE(eV)     EE(cm-1)     OSC. STR.     TOTAL ENERGY

--------------------------------------------------------------------------------

   1           1                     9.8243    79238.03      -75.92862587
   2           1                     7.4016    59697.89      -76.01765731
   3           1                    11.5679    93301.45      -75.86454819
   4           1                     9.1569    73855.17      -75.95315198

--------------------------------------------------------------------------------
```

Analytical determination of dipole moment according to the generalized expectation value prescription

```
Test run on H2O EOM-CCSD props
O
H 1 R
H 1 R 2 A

R=0.957
A=104.5

*ACES2(BASIS=PBS,CALCLEVEL=CCSD,UNITS=0
MEMORY_SIZE=5GB,SYMMETRY=ON
SCF_MAXCYC=600,SCF_CONV=12,REF=RHF
SPHERICAL=ON,CC_CONV=12,CC_MAXCYC=500
ESTATE_PROP=EXPECTATION,EXCITE=EOMEE,EE_SYM=1-0-0-0)
```

Analytical determination of dipole moment according to the generalized expectation value prescription

```
-----------------------------------------------------------------
                Ground state properties
-----------------------------------------------------------------
 Dipole moment  -0.000000000000  -0.000000000000   0.724043731619
 Second moment of charge distribution :
 XX :     5.846697 YY :     7.462874 ZZ :     6.759556
 XY :     0.000000 YZ :     0.000000 YZ :     0.000000
 Spherical average :     6.689709
-----------------------------------------------------------------
                Excited state properties
-----------------------------------------------------------------
 Dipole moment  -0.000000000000  -0.000000000000  -0.523936420278
 Second moment of charge distribution :
 XX :    10.584618 YY :    14.384101 ZZ :    12.303047
 XY :     0.000000 YZ :     0.000000 YZ :     0.000000
 Spherical average :    12.423922
 Solution of   1 roots required   21 iterations.
-----------------------------------------------------------------
```

Dipole moments (a.u.) of HF (aug-cc-pVQZ basis set; R_{exp}=0.9168; $\mu_{exp.}$=0.7090 a.u.)

	Gen. expect. value	Finite field
CCSD	0.7113	0.7153
CCSDT	-	0.7081
CCSD(T)	-	0.7083

Dipole moments (a.u.) of H_2O
(PBS basis set; $R_{exp} = 0.957$, $\angle = 104.5^\circ$)$^{a)}$

Sym.	Gen. expect. value	Finite field
X^1A_1	0.724	0.730
2^1A_1	-0.523	-0.485
3^1A_1	1.096	1.093
1^1B_1	-0.654	-0.632
2^1B_1	2.428	2.414
1^1B_2	-0.603	-0.573
2^1B_2	0.052	0.069
1^1A_2	-0.539	-0.522
2^1A_2	0.513	0.527

$^{a)}$ J. F. Stanton, R. J. Bartlett, **98**, 7029 (1993).