Equation-of-Motion Coupled-Cluster Methods for Open-Shell and Electronically Excited Species

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Outline:

1. CI and truncated CI: overview.
2. Size-extensive alternative: Coupled-cluster ansatz.
3. Extension to electronically excited and open-shell states: EOM-CC formalism.
4. EOM-CC advantages and limitations.
5. Examples.
Exact solution of the Schrödinger equation and configuration interaction (CI) approach

1. Chose one-electron basis set ($M$ orbitals), construct reference determinant ($N$ orbitals) $\Phi_0$

2. Linear ansatz for the wave-function: $\Psi = (1+C_1+C_2+ \ldots C_N)\Phi_0$, where $C_i = \sum c_i a_i^+$
   Thus, operators $C_1..C_N$ will generate all possible distributions of $N$ electrons over $M$ orbitals

3. Energy functional: $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$
   Amplitude equations: Variational Principle $\rightarrow$
   CI eigen-problem for the ground and excited states: $HC = CE$

Exact solution (FCI). Approximations: truncated CI

Hierarchy of approximations: HF $\rightarrow$ CISD $\rightarrow$ CISDT $\rightarrow$ $\ldots$ $\rightarrow$ FCI

Problems with truncated CI: violation of size extensivity

For non-interacting systems ($H_{AB} = H_A + H_B$): $E_{AB} = E_A + E_B$ and $\Psi_{AB} = \Psi_A \times \Psi_B$

But: $\Psi_A^{\text{CISD}} \times \Psi_B^{\text{CISD}}$ is not equal $\Psi_{AB}^{\text{CISD}}$
Solution: Coupled-cluster ansatz:

\[ \Psi = e^T \Phi_0 = (1 + T + \frac{1}{2} T^2 + \frac{1}{6} T^3 + \ldots) \Phi_0, \quad T_1 = \sum t_i a_i a^+_i \]

If \( T = T_1 + T_2 \):
- higher-order excitations are present, e.g., \( (T_1)^2 \), \( (T_2)^2 \), \( (T_2)^2 T_1 \), etc
- size-extensivity is satisfied:
  \[ e^{T_1} e^{TB} = e^{T_1+TB} \] (provided that \( T \) is strictly an excitation operator wrt the reference vacuum);
- but exponential expansion does not terminate in energy functional \( E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \) for variational principle.

Equations (projection principle):

\[ E = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle \]
\[ \langle \Phi_\mu | e^{-T} H e^T - E | \Phi_0 \rangle = 0 \]

Can be recast in a more general variational form and extended to excited states.
Hierarchy of approximations to the exact wave function: Single-reference models for the ground state

SCF: \( \Psi = \Phi_0 = |\varphi_1...\varphi_n> \)

MP2: SCF + \( T_2 \) by PT

CCSD: \( \Psi = \exp(T_1 + T_2) \Phi_0 \)

CCSD(T): CCSD + \( T_3 \) by PT

CCSDT: \( \Psi = \exp(T_1 + T_2 + T_3) \Phi_0 \)

FCI: \( \Psi = (1 + T_1 + T_2 + ... + T_n) \Phi_0 \) - exact!

\[ T_1 = \sum_{ia} t_{i}^{a} \ a^{+} \ j \]

\[ T_2 = 0.25 \sum_{ijab} t_{ij}^{ab} \ a^{+}b^{+} \ ji \]
Why open shells and electronically excited states are difficult?

Electronic degeneracy $\rightarrow$ multi-configurational wavefunctions

The CC hierarchy of approximations breaks down.
Equation-of-motion theory and specific models:

Rowe, Rev. Mod. Phys. 40, 153 (1968)
Simons, Smith, JCP 58, 4899 (1973)
McWeeny, “Methods of Molecular Quantum Mechanics”
Sekino, Bartlett, IJQCS 18 255 (1984)
Stanton, Bartlett, JCP 98, 7029 (1993)
Stanton, Gauss, JCP 101, 8938 (1994)
Nooijen, Bartlett, JCP 102, 3629 (1995)

Also works of Mukherjee, Pal, Piecuch, Emrich, McKoy, Kutzelnigg, Kaldor, Werner, Hirata.
Related: linear response works of Koch, Jorgen, Jensen, Jorgensen, Head-Gordon, Lee, Korona, etc.
SAC-CI by Nakatsuji.
Recent developments: Crawford, Piecuch, Kowalsky.

AND MUCH MORE!!!

Equation-of-Motion Coupled-Cluster Methods

1. $\bar{H} = \exp(-T)H \exp(T)$ regardless of $T$, has same spectrum as $H$

2. $\Psi = \Phi_0 + R_1 \Phi_0 + R_2 \Phi_0 + \ldots$, where $R_n$ is some general excitation operator, e.g., $R_1 = \Sigma r_i a^+ i$ (or $R_1 = \Sigma r^a a^+$ or $R_1 = \Sigma r_i i$, etc)

3. Apply bi-Variational Principle: EOM eigen-problem

$$\bar{H} R \Phi_0 = E R \Phi_0$$

4. Specific EOM model:
   choice of excitation operators $T$, $R$, and the reference $\Phi_0$
EOM models: Choice of T

1. Excitation level, e.g., $T = T_1 + T_2$
2. Amplitude equations.

If $T$ satisfies CC equations, $\langle \Phi_{ex} | \overline{H} | \Phi_0 \rangle = 0$

- size extensivity
- compact wf-s, e.g., $\Psi_{exact} = \Phi_0$
- correlation effects are "wrapped in": same scaling but higher accuracy
EOM MODELS: CHOICE OF R and Φ₀

EOM-EE:  \( \Psi(M_s=0) = R(M_s=0) \Psi₀(M_s=0) \)

EOM-IP:  \( \Psi(N) = R(-1) \Psi₀(N+1) \)

EOM-EA:  \( \Psi(N) = R(+1) \Psi₀(N-1) \)

EOM-SF:  \( \Psi(M_s=0) = R(M_s=-1) \Psi₀(M_s=1) \)
Size-extensivity: Be example

Be /6-31G*

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<tr>
<th>State</th>
<th>FCI</th>
<th>CISD</th>
<th>SF-CISD</th>
<th>EOM-CCSD</th>
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<td>0.0</td>
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<tr>
<td>$^3P(1s^22s2p)$</td>
<td>2.86</td>
<td>2.88</td>
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<tr>
<td>$^1P(1s^22s2p)$</td>
<td>6.58</td>
<td>6.60</td>
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Be @ USC & Ne @ Berkeley

<table>
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<tr>
<th>State</th>
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<th>SF-CISD</th>
<th>EOM-CCSD</th>
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<td>9.39</td>
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</table>

Krylov, CPL 350, 522 (2001); Sears, Sherrill, Krylov, JCP, 118, 9084 (2003)
Equation-of-Motion Coupled-Cluster Theory

Truncated EOM model, e.g., EOM-CCSD: diagonalize $H$-bar in the basis of singly and doubly excited determinants (amplitudes $T$ from CCSD equations).

Same cost as CISD ($N^6$) but:
- size-intensive
- has higher accuracy (correlation is “wrapped in” through the similarity transformation).

Multistate method, describes degeneracies and near-degeneracies, as well as interacting states of different nature (just because it is diagonalization problem). Bi-variational formulation facilitates properties calculations (Hellmann-Feynman theorem).
Limitations of CCSD and EOM-CCSD:

1. Scaling is $N^6$.
2. Need triples corrections for “chemical accuracy”, e.g. CCSD(T) (scales $N^7$).
3. Not always possible to find a well-behaved reference from which target states of interest can be accessed via single excitations -> cannot describe global potential energy surfaces.
4. Non-hermitian nature sometimes causes problems (e.g., wrong dimensionality of conical intersections).
Excited states of sym-triazine

- All low-lying excited states of Tz involve transitions from/to degenerate MOs.
- Some are Jahn-Teller distorted and some exhibit glancing-like intersections.
- EOM-EE describes accurately these manifolds, interactions, and degeneracies.

Schuurman and Yarkony, JCP 126, 044104 (2007)
Excited singlet states of sym-triazine

Neutral geometry

\[ \begin{align*}
8.43 \, ^1E' & \quad \pi\pi^* \\
8.29 \, ^1A_1' & \quad \pi\pi^* \\
8.25 \, ^1E'' & \quad \text{n\pi}^* \\
8.24 \, ^1A_2' & \quad \pi\pi^* \\
7.54 \, ^1A_1' & \quad \pi\pi^* \\
7.41 \, ^1E' & \quad \text{n\pi} \\
6.01 \, ^1A_2' & \quad \pi\pi^* \\
5.06 \, ^1E'' & \\
5.04 \, ^1A_2'' & \quad \text{n\pi}^* \\
4.99 \, ^1A_1'' & \\
\end{align*} \]

EOM-CCSD/6-311++G**

Cation geometry

\[ \begin{align*}
8.61 \, ^1A_1 & \quad \pi\pi^* \\
8.60 \, ^1B_2 & \quad \text{n\pi}^* \\
7.90 \, ^1B_2 & \quad \text{n\pi} \\
7.84 \, ^1A_1 & \quad \pi\pi^* \\
7.71 \, ^1B_2 & \quad \text{n\pi} \\
7.03 \, ^1A_1 & \quad \pi\pi^* \\
6.49 \, ^1B_2 & \quad \pi\pi^* \\
5.53 \, ^1A_2 & \quad \text{n\pi}^* \\
5.30 \, ^1B_1 & \quad \text{n\pi}^* \\
4.78 \, ^1B_1 & \quad \text{n\pi}^* \\
4.53 \, ^1A_2 & \quad \text{n\pi}^* \\
\end{align*} \]
EOM for the $[\text{Cs}..\text{Tz}]^+$ complex

$\text{Cs} \cdot \cdot \text{Tz}^+ \rightarrow \text{Cs}^+ \cdot \cdot \text{Tz}^*$

**Initial charge transfer state**

$\begin{align*}
\text{Initial CT state} & : & \pi & \uparrow & \uparrow & + \\
& & n & \uparrow & \uparrow & \text{Cs}
\end{align*}$

$[\text{Cs}..\text{Tz}^+(\sigma)]$

**Final charge transfer states**

**Single excitations of initial CT state**

$\begin{align*}
\text{Single excitations} & : & \pi^* & \uparrow \\
& & R & \leftarrow \\
& & \pi & \uparrow & \uparrow \\
& & n & \uparrow & \uparrow \\
\end{align*}$

$[\text{Cs}^-.\text{Tz}(n\pi^*)]$  
$[\text{Cs}^+.\text{Tz}(nR)]$

**EOM reference:** $[\text{Cs}^+..\text{Tz}]$

$\begin{align*}
\pi & \uparrow & \uparrow & - \\
n & \uparrow & \uparrow & \text{Cs}^+ \\
\text{Tz} & & & [\text{Cs}^+..\text{Tz}]
\end{align*}$
Equation-of-motion formalism

Consider the Hamiltonian $H$ (non-hermitian), and its exact eigenstates $|0\rangle$ & $|f\rangle$:

$$H|0\rangle = E_0 |0\rangle \quad \& \quad H|f\rangle = E_f |f\rangle$$

Consider excitation operator $R(f)$: $R(f)|0\rangle = |f\rangle$

Define $R(f)$ as: $R(f) = |f\rangle\langle 0 |$

For any $|0\rangle$ ($\langle 0 | 0 \rangle$ non-zero): $R(f)|0\rangle = |f\rangle \langle 0 | 0 \rangle \Rightarrow [H, R(f)]|0\rangle = \omega_{of} \ R(f)|0\rangle$ (*)

- no knowledge of exact initial and final states is necessary to determine exact $\omega_{of}$

- (*) is an operator equation, valid not only in a subspace.

Define de-excitation operator $L(f)$: $L(f) = |0\rangle\langle f |$

EOM functionals:

$$\omega_{of} = \langle 0 | L(f) [H, R(f)] | 0 \rangle / \langle 0 | L(f) R(f) | 0 \rangle$$

$$\omega_{of} = \langle 0 | [L(f), [H, R(f)]] | 0 \rangle / \langle 0 | [L(f), R(f)] | 0 \rangle$$

$$\omega_{of} = \langle 0 | [L(f), [H, R(f)]]_+ | 0 \rangle / \langle 0 | [L(f), R(f)]_+ | 0 \rangle$$

ALL three functionals:

- exact result when $R$, $L$ is expanded over the complete basis set
- identical equations when the killer condition is satisfied:

  $L(f) \ | 0 \rangle = 0$ (reference is “true” vacuum)
  
or

  $L(f) \ | 0 \rangle = | 0 \rangle \langle f | 0 \rangle = 0$ (reference is orthogonal to final states)
1. Expand $R$, $L$ over a finite operator basis set:

$$R(f) = \sum_k r_k \rho_k$$
$$L(f) = \sum_k l_k \lambda_k$$

2. Use bivariational principle with any of the three functionals, arrive to the matrix equations:

$$(H-E_0)R = R\Omega$$
$$L(H-E_0) = \Omega L$$
$$E_0 = \langle 0|H|0 \rangle$$