

# Coupled-Cluster-Based Methods for Open-Shell

## Electronic States, The Fock Space Approach

Arik Landau

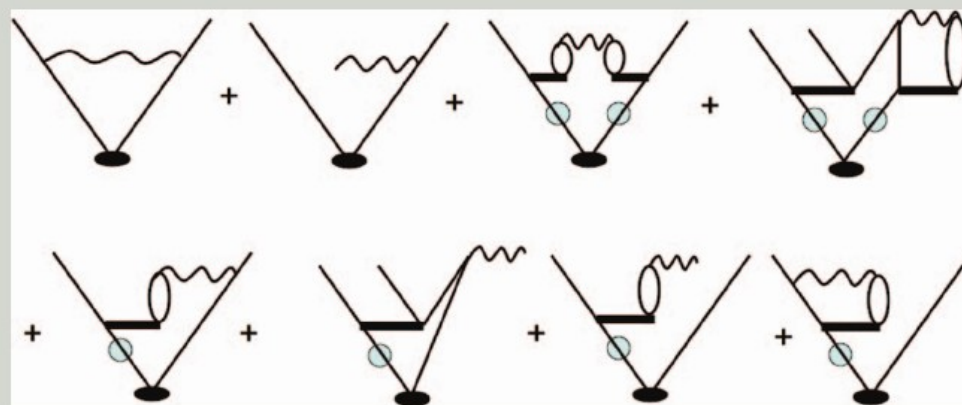


FIG. 9. STEOM-CCSD: the  $\sigma = \mathbf{GR}$  terms.

## The Coupled-Cluster Equations

equation for the cluster operator  $S$  is obtained

from the linked-diagram formula

$$[\Omega, H_0] = (QV\Omega)_{\text{linked}}$$

by considering the *connected* parts of both sides

FOR CLOSED SHELL SYSTEMS

$$[S, H_0] = (QV\Omega)_{\text{conn}}$$

separated into one-, two-, ... body equations

$$[S_n, H_0] = (QV\Omega)_{n,\text{conn}}$$

$$\Omega = \{\exp(S)\}$$

# The Coupled-Cluster Equations

$$|\Psi_0\rangle = e^T |\Phi\rangle$$

$$T^{(\text{CCSD})} = T_1 + T_2$$

$$\langle \Phi_{i_1}^{a_1} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0,$$

$$\langle \Phi_{i_1 i_2}^{a_1 a_2} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad i_1 < i_2, \quad a_1 < a_2,$$

where

$$\bar{H}^{(\text{CCSD})} = e^{-(T_1+T_2)} H e^{T_1+T_2} = (H e^{T_1+T_2})_C$$

$$T_1 = \sum_{i,a} t_i^a \{a^\dagger i\} = \begin{array}{c} i \quad a \\ \searrow \quad \swarrow \\ \text{---} \end{array}$$

$$T_2 = \sum_{i>j, a>b} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} = \begin{array}{c} i \quad a \quad j \quad b \\ \searrow \quad \swarrow \quad \swarrow \quad \searrow \\ \text{---} \end{array}$$

$$E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

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$$\bar{H} = e^{-T} H e^T = (H e^T)_C$$

$$E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

$$T_1 = \sum_{i,a} t_i^a \{a^\dagger i\} = \begin{array}{c} i \quad a \\ \searrow \quad \nearrow \\ \text{---} \end{array}$$

$$T_2 = \sum_{i>j, a>b} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} = \begin{array}{c} i \quad a \quad j \quad b \\ \searrow \quad \nearrow \quad \searrow \quad \nearrow \\ \text{---} \end{array}$$

# Moving from the Hilbert Space into the Fock Space

Coupled Cluster based methods for open-shell electronic states

- **Fock-Space Coupled Cluster**
- **Equation-of-Motion Coupled Cluster**
- **Similarity-Transformed Equation-of-Motion Coupled Cluster**

## Multireference approach

$$H|\Psi_j\rangle = E_j|\Psi_j\rangle$$

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$$H = H_0 + V.$$

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$H_0$  – SCF like HF, DF or DFB

$H_0$  satisfying the eigenvalue equation:

$$H_0|\Phi_i\rangle = E_i|\Phi_i\rangle$$

Where  $\Phi_i = A|\alpha\beta\gamma\delta\dots\nu\rangle$  is an anti-symmetric Slater determinant, constructed of DF orbitals.



## The determinant space

The  $\Phi'_i$ 's span the determinant or function space, which is used to expand the real eigenstates  $|\Psi_j\rangle$

The determinant space is partitioned into a model sub-space ( $P$ -space) and a complementary sub-space ( $Q$ -space).

## The Model space

The model space is characterized by a projection operator:

$$P = \sum_{i \in \mathcal{P}} |\Phi_i\rangle\langle\Phi_i|$$

Projection only to functions that are confined to the model space.

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$$P = \sum_{i \in P} |\Phi_i\rangle\langle\Phi_i|$$

Projection only to functions that are confined to the model space.

$P$ -space functions strongly interact among themselves.

By including them all in  $P$ , we take into account the functions complete contributions to the state of interest:

*Non-dynamic correlation.*

# Illustration, the ground configuration $1s^2 2s^2 2p^2$ of the neutral carbon atom.



All roles ▼ All ▼

2ZaPa-NR  
2ZaPa-NR-CV  
3-21G  
3ZaPa-NR  
3ZaPa-NR-CV  
4-31G  
4ZaPa-NR  
4ZaPa-NR-CV  
5ZaPa-NR  
5ZaPa-NR-CV  
6-21G  
6-31++G  
6-31++G\*  
6-31++G\*\*  
6-31++G\*\*  
6-31+G  
6-31+G\*  
6-31+G\*-J

Total found: 447 basis sets

Select All

Reset Selection

1																2																													
H																He																													
3		4														5		6		7		8		9		10																			
Li		Be														B		C		N		O		F		Ne																			
11		12														13		14		15		16		17		18																			
Na		Mg														Al		Si		P		S		Cl		Ar																			
19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36											
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr											
37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54											
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe											
55		56														57		58		59		60		61		62		63		64		65		66		67		68		69		70		71	
Cs		Ba														La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
87		88														89		90		91		92		93		94		95		96		97		98		99		100		101		102		103	
Fr		Ra														Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	

As we have mentioned, we need a new classification of the single-particle states (orbitals) for open-shell systems. As an illustration we consider **the ground configuration  $1s^2 2s^2 2p^2$  of the neutral carbon atom.** This configuration contains  $\binom{6}{2} = 15$  determinants, some of which are indicated in Table 13.1.

**Table 13.1.** Determinants in the ground configuration of the carbon atom

$1s0^+$	$1s0^-$	$2s0^+$	$2s0^-$	$2p1^+$	$2p0^+$	$2p-1^+$	$2p1^-$	$2p0^-$	$2p-1^-$	$3s0^+$	$3s0^-$	$4s0^+$	...
×	×	×	×	×	×								
×	×	×	×	×		×							
×	×	×	×	×			×						
×	×	×	×	×				×					
×	×	×	×	×					×				
×	×	×	×		×	×							
×	×	×	×		×		×						
—	—	—	—	—	—								

Core states,  
occupied in all  
determinants of the  
model space

Valence states,  
occupied in some  
determinants of the  
model space

Virtual states,  
unoccupied in all  
determinants of the  
model space

## The complementary space

The rest of the  $\{\Phi_i\}_{i \rightarrow Q}$  are confined to the orthogonal  $Q$ -space.  $Q$ -states weakly interact with model space functions.

Contributions from  $Q$ -space are known as:

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$Q$ -space contributions are approximated, depending on the truncation of the scheme.

## The function space

The whole function space is the sum:  $P + Q = 1$ .

## The main idea in multireference scheme:

Resulting "dressed" effective Hamiltonian diagonalized in  $P$ , eigenvalues approximate those of physical Hamiltonian.

$$H = \left( \begin{array}{c|c} PHP & PHQ \\ \hline QHP & QHQ \end{array} \right) ; H_{\text{eff}} = (PH_{\text{eff}}P)$$

Matrix elements of the effective  $H$  are more complicated than for  $H$ , include effects of  $Q$  space.



## Coupled Cluster (CC)

In multireference, open shell we have the Zero-order wave function (ZOWF)

$$\left| \Psi_0^j \right\rangle = \sum_{i \in P} c_i \Phi_i = P \left| \Psi_j \right\rangle \quad .$$

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We assume there is some operator that transforms the ZOWF to the Schrödinger or Dirac eigenstate.

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The exponential ansatz

$$\Omega = \exp(S) = 1 + S + \frac{1}{2} S^2 + \dots \quad S - \text{the cluster operator}$$

The exponential form of the CC wave function guarantees\*:

- *size extensivity*
- *separability condition*

\*Lindgren I. and Mukherjee D. *Phys. Rep.* **125**, 207 (1987)

- Hermitian CC: Lindgren, *J. Phys. B: At. Mol. Opt. Phys.* **24** 1143 (1991)

## Fock-Space Coupled-Cluster (FSCC)

A multireference approach for open shells.

We assume or postulate a Universal wave operator ( $\Omega$ ),  
the method is also known as '*Valence Universal*'.

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For the  $n$ -valence Hilbert-space problem we are considering also all the lower  $m$ -valence Hilbert spaces, with  $0 \leq m < n$ , it becomes a Fock space.

Our Fock space,  $F$ , will then be composed of several Hilbert spaces,  $H$ .

$$F = \sum_{m=0}^n H^{(m)} .$$

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The cluster operator is partitioned into sectors

$$S = \sum_{m \geq 0} \sum_{n \geq 0} \left( S^{(m,n)} \right).$$

$(m,n)$  denotes sector with  $m$ -electrons removed (valence holes) and  $n$ -electrons added (valence particles) with respect to a reference DF function.

## Fock-Space Coupled-Cluster (FSCC)

The subsystem embedding condition (SEC)

The equation for  $s^{(i,j)}$  involves only  $s^{(k,l)}$  terms with  $k \leq i$  and  $l \leq j$  ; only the  $s^{(i,j)}$  are unknown.

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Therefore, the very large system of nonlinear-coupled equations separates into subsystems, which may be solved hierarchically.

## The FSCC working equations

$$Q[S^{(m,n)}, H_0]P = Q(\overline{V\Omega} - \overline{\Omega V\Omega})^{(m,n)} P,$$

For the effective Hamiltonian we have

$$H_{eff}^{(m,n)} = P\overline{H\Omega}^{(m,n)} P .$$

**Note:** These sector separations involve no approximation, but reduce computational effort significantly.

## Summary of the FSCC scheme:

- Iterate the  $s^{(0,0)}$  equation to convergence.
- Solve for  $s^{(0,1)}$  and/or  $s^{(1,0)}$ .
- Continue as needed.

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→ Mg<sup>+</sup>, CC (0,1) sector;

→ Mg, CC (0,2) sector.

## Features of the FSCC method:

- Diagonalization of the effective Hamiltonian directly gives energies with respect to closed-shell reference. Energies may be ionization potentials, excitation energies, or electron affinities.
- All transition energies calculated simultaneously (all or nothing).
- Symmetry adaptation (*LS* or *J*) is automatic.

$$H_{eff}^{(m,n)} = P \overline{H\Omega}^{(m,n)} P$$

## Equation-of-motion coupled-cluster (EOM-CC)

In the EOM-CC method the wave function for the  $k$ th excited state is given by

$$|\Psi_k\rangle = R|\Psi_g\rangle, \quad (4)$$

The ground state wave function within the coupled-cluster formalism is expressed as

$$\Psi_g = e^T|\Phi_o\rangle, \quad (1)$$

"Multireference **Fock-space** coupled-cluster and **equation-of-motion** coupled-cluster theories: The detailed **interconnections**."

Musial and Bartlett, *J. Chem. Phys.*, **129**, 134105 (2008)

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and  $R$  is a linear (CI-like) excitation operator, defined as

$$R = R_0 + R_1 + R_2 + R_3, \quad (5)$$

+



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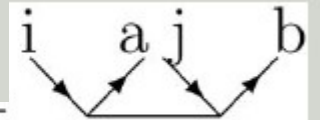
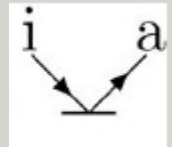
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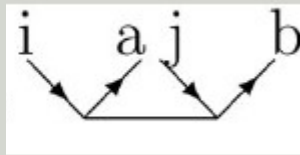
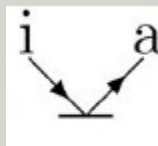
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$$R = R_0 + R_1 + R_2 + R_3, \quad (5)$$

with  $R_n$  defined analogously as  $T_n$ , i.e.,  $R_n = (n!)^{-1} \sum r_{ij}^{ab\dots} \{a^\dagger b^\dagger \dots ji\}$ .

Inserting the  $|\Psi_k\rangle$  wave function, Eq. (4), into the Schrödinger equation we obtain



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$$e^{-T} \rightarrow H R e^T|\Phi_o\rangle = E R e^T|\Phi_o\rangle, \quad (6)$$



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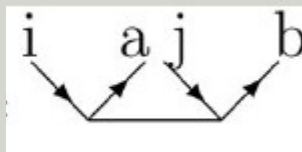
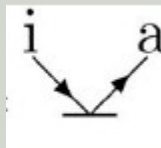
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$$H R e^T|\Phi_o\rangle = E R e^T|\Phi_o\rangle, \quad (6)$$

or, since the  $R$  and  $T$  operators commute,

$$\bar{H} R|\Phi_o\rangle = E R|\Phi_o\rangle, \quad \bar{H} = e^{-T} H e^T = (H e^T)_C \quad (7)$$



Equation-of-motion  
coupled-cluster (EOM-CC)

$$|\Psi_{EOM}\rangle = R e^T |\Phi_0\rangle$$

$$\bar{H} R_k |\Phi_0\rangle = E_k R_k |\Phi_0\rangle$$

$$\bar{\mathbf{H}} \mathbf{R}_k = \mathbf{E}_k \mathbf{R}_k$$

$$\bar{\mathbf{H}} = e^{-T} H e^T =$$

	$ \Phi_0\rangle$	$\{ \Phi_I\rangle\}$
$\langle\Phi_0 $	$E_{CC}$	$\langle\Phi_0 \bar{H} \Phi_I\rangle$
$\{\langle\Phi_J \}$	0	$\langle\Phi_J \bar{H} \Phi_I\rangle$

# Truncated Configuration Interaction

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{ijab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

$$= \sum_I^{all} C_I |\Phi_0\rangle = \sum_I^{all} c_I |\Phi_I\rangle$$

$$C_I = C_0 + C_1 + C_2 + C_3 \dots$$

# Configuration Interaction (CI)

$$HC_k|\Phi_0\rangle = E_k C_k|\Phi_0\rangle$$

$$\mathbf{H}\mathbf{C}_k = \mathbf{E}_k\mathbf{C}_k$$

$$\mathbf{H} = \begin{array}{c|cc} & |\Phi_0\rangle & \{|\Phi_I\rangle\} \\ \hline \langle\Phi_0| & \langle\Phi_0|H|\Phi_0\rangle & \langle\Phi_0|H|\Phi_I\rangle \\ \{\langle\Phi_J|\} & \langle\Phi_J|H|\Phi_0\rangle & \langle\Phi_J|H|\Phi_I\rangle \end{array}$$

## EOM-CC

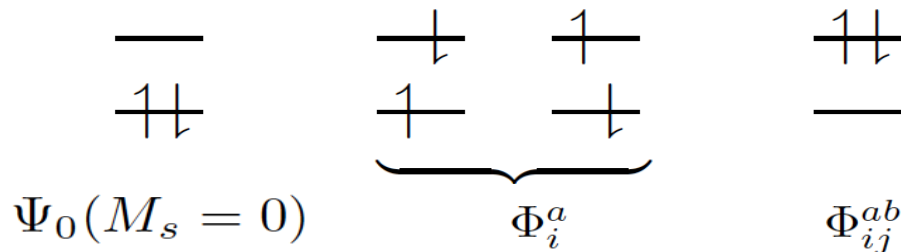
$$\overline{\mathbf{H}} = e^{-T} H e^T = \begin{array}{c|cc} & |\Phi_0\rangle & \{|\Phi_I\rangle\} \\ \hline \langle\Phi_0| & E_{CC} & \langle\Phi_0|\overline{H}|\Phi_I\rangle \\ \{\langle\Phi_J|\} & 0 & \langle\Phi_J|\overline{H}|\Phi_I\rangle \end{array}$$

Equation-of-motion  
coupled-cluster (EOM-CC)

$$\bar{\mathbf{H}}\mathbf{R}_k = \mathbf{E}_k\mathbf{R}_k$$

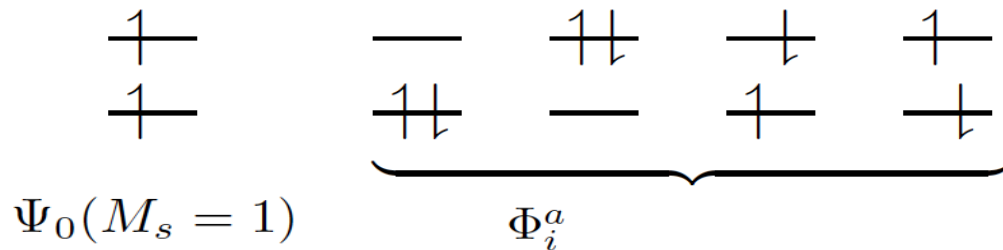
Within EOMCC we calculate the CC ground state, and (unlike in FSCC) move directly into the EE space.

**EOM-EE**     $\Psi(M_s = 0) = R(M_s = 0)\Psi_0(M_s = 0)$



The ground state represent the FS (0,0) sector and EE is the (1,1) sector, within FSCC we also consider the (1,0) and (0,1) sector before the (1,1).

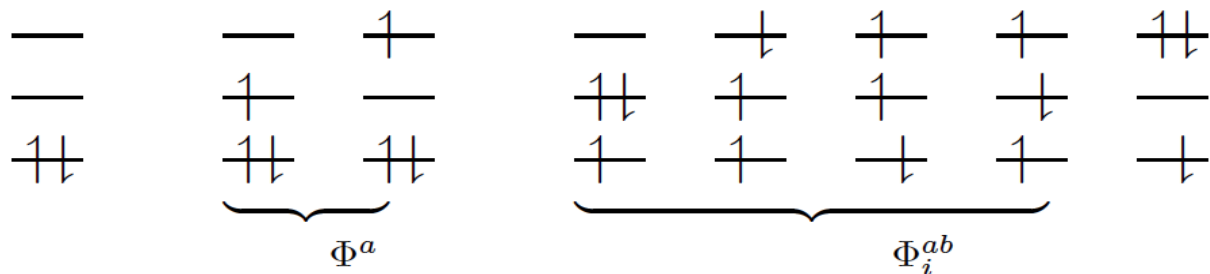
**EOM-SF**     $\Psi(M_s = 0) = R(M_s = -1)\Psi_0(M_s = 1)$



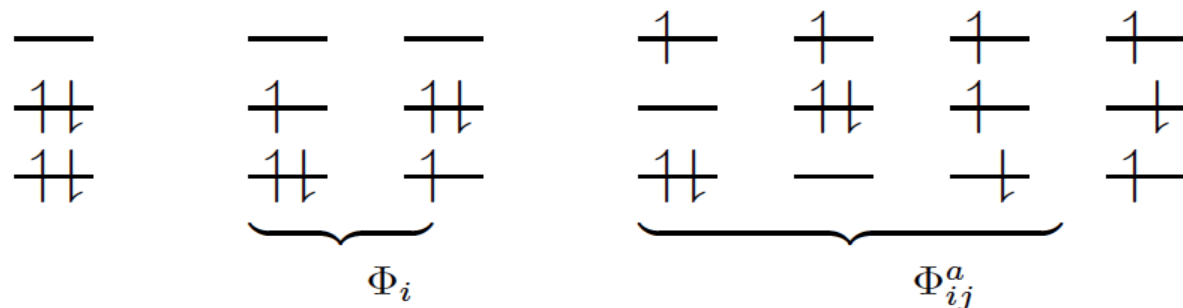
Equation-of-motion  
coupled-cluster (EOM-CC)

$$\bar{\mathbf{H}}\mathbf{R}_k = \mathbf{E}_k\mathbf{R}_k$$

**EOM-EA**  $\Psi(N) = R(+1)\Psi_0(N-1)$



**EOM-IP**  $\Psi(N) = R(-1)\Psi_0(N+1)$



The EA/IP EOMCC schemes  
are equivalent to the  
FSCC (1,0) and (0,1) sectors.

## ST-EOM-CC

In STEOM-CCSD the Hamiltonian expressed in the language of second quantization is transformed twice to yield

$$\hat{G} = \{e^{\hat{S}}\}^{-1} e^{-\hat{T}} \hat{H} e^{\hat{T}} \{e^{\hat{S}}\}$$

## EOM-CC

- Transformed Hamiltonian

$$\begin{aligned}\hat{\bar{H}} &= e^{-\hat{T}}\hat{H}e^{\hat{T}} = \bar{h}_0 + \sum_{p,q} \bar{h}_{p;q} \{\hat{p}^\dagger \hat{q}\} \\ &\quad + \frac{1}{4} \sum_{p,q,r,s} \bar{h}_{pq;rs} \{\hat{p}^\dagger \hat{r} \hat{q}^\dagger \hat{s}\} + \dots\end{aligned}$$

- CC equations:

$$\bar{h}_{ai} = \langle \Phi_i^a | \hat{\bar{H}} | \Phi_0 \rangle = \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0,$$

$$\bar{h}_{abij} = \langle \Phi_{ij}^{ab} | \hat{\bar{H}} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0.$$



## STEOM-CC

- Second similarity transformation

$$\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{H} \{e^{\hat{S}}\}$$

$$= g_0 + \sum_{p,q} g_{p;q} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{p,q,r,s} g_{pq;rs} \{\hat{p}^\dagger r \hat{q}^\dagger \hat{s}\} + \dots$$

- Equation for the  $S$  amplitudes

$$g_{mi'} = \langle \Phi_{i'} | \hat{G} | \Phi_m \rangle = 0,$$

$$g_{mbij} = \langle \Phi_{ji}^b | \hat{G} | \Phi_m \rangle = 0,$$

$$g_{a'e} = \langle \Phi^{a'} | \hat{G} | \Phi^e \rangle = 0,$$

$$g_{abej} = \langle \Phi_j^{ba} | \hat{G} | \Phi^e \rangle = 0,$$

Occ: $i, j \dots$ active: $m, n \dots$
Virts: $a, b \dots$ active: $e, f \dots$

$$g_{ai} = \bar{g}_{abij} = 0$$

$$g_0 = \bar{h}_0 = E_{CC}$$

# The coupled-cluster operators

- where  $T$  is:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \{\hat{a}^\dagger \hat{i}\} + \frac{1}{4} \sum_{i,a} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}$$

Occ:  $i, j \dots$   
active:  $m, n \dots$

- where  $S$  is:

$$\text{EA: } \hat{S}^+ = \hat{S}_1^+ + \hat{S}_2^+ = \sum_{a',e} s_e^{a'} \{\hat{a}'^\dagger \hat{e}\} + \frac{1}{2} \sum_{a,b,e,i} s_{ie}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{e}\}$$

$$\text{IP: } \hat{S}^- = \hat{S}_1^- + \hat{S}_2^- = \sum_{i',m} s_{i'}^m \{\hat{m}^\dagger \hat{i}'\} + \frac{1}{2} \sum_{i,j,a,m} s_{ij}^{am} \{\hat{a}^\dagger \hat{i} \hat{m}^\dagger \hat{j}\}$$

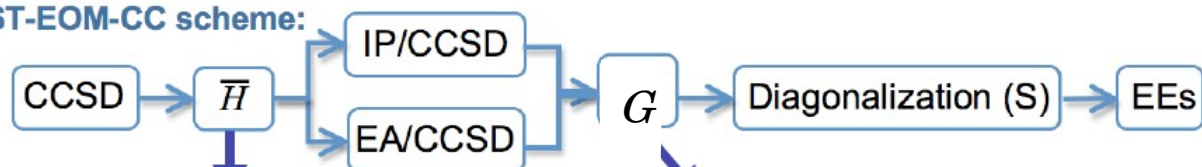
Virts:  $a, b \dots$   
active:  $e, f \dots$

## STEOM-CCSD vs. EOM-CCSD

EOM-CC scheme:



ST-EOM-CC scheme:

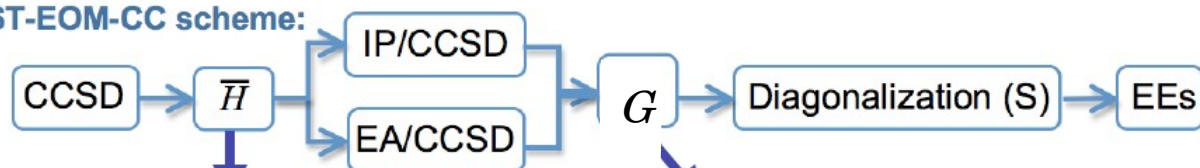


# STEOM-CCSD vs. EOM-CCSD

EOM-CC scheme:



ST-EOM-CC scheme:



$$\begin{matrix}
 0 \\
 S \\
 D \\
 T
 \end{matrix}
 \begin{pmatrix}
 0 & S & D & T \\
 \mathbf{X} & \mathbf{X} & \mathbf{X} & 0 \\
 0 & \mathbf{X} & \mathbf{X} & \mathbf{X} \\
 0 & \mathbf{X} & \mathbf{X} & \mathbf{X} \\
 \sim & \sim & \mathbf{X} & \mathbf{X}
 \end{pmatrix}$$

**EOM-CC:** Stanton and Bartlett  
*J Chem Phys* 98, 7029(1993)

$$\begin{matrix}
 0 \\
 S \\
 D \\
 T
 \end{matrix}
 \begin{pmatrix}
 0 & S & D & T \\
 \mathbf{X} & \mathbf{X} & \mathbf{X} & 0 \\
 0 & \mathbf{X} & \mathbf{X} & \mathbf{X} \\
 0 & \sim & \mathbf{X} & \mathbf{X} \\
 \sim & \sim & \sim & \mathbf{X}
 \end{pmatrix}$$

**STEOM-CC:** Nooijen and Bartlett  
*J Chem Phys* 107, 6812 (1997)

CI

$\hat{H}$	$ \Phi_0\rangle$	$ \Phi_i^a\rangle$	$ \Phi_{ij}^{ab}\rangle$	$ \Phi_{ijk}^{abc}\rangle$	$ \Phi_{ijkl}^{abcd}\rangle$
$\langle\Phi_0 $	$h_0$	<b>X</b>	<b>X</b>	<b>0</b>	<b>0</b>
$\langle\Phi_i^a $	$f_i^a\{\hat{a}^\dagger\hat{i}\}$	<b>X</b>	<b>X</b>	<b>X</b>	<b>0</b>
$\langle\Phi_{ij}^{ab} $	$V_{ij}^{ab}\{\hat{a}^\dagger\hat{i}\hat{b}^\dagger\hat{j}\}$	$f_i^a\{\hat{a}^\dagger\hat{i}\}, V_{ij}^{kb}\{\hat{k}^\dagger\hat{i}\hat{b}^\dagger\hat{j}\}, V_{cj}^{ab}\{\hat{a}^\dagger\hat{c}\hat{b}^\dagger\hat{j}\}$	<b>X</b>	<b>X</b>	<b>X</b>
$\langle\Phi_{ijk}^{abc} $	<b>0</b>	$V_{ij}^{ab}\{\hat{a}^\dagger\hat{i}\hat{b}^\dagger\hat{j}\}$	<b>X</b>	<b>X</b>	<b>X</b>
$\langle\Phi_{ijkl}^{abcd} $	<b>0</b>	<b>0</b>	<b>X</b>	<b>X</b>	<b>X</b>

EOMCCSD

$\hat{H}$	$ \Phi_0\rangle$	$ \Phi_i^a\rangle$	$ \Phi_{ij}^{ab}\rangle$	$ \Phi_{ijk}^{abc}\rangle$	$ \Phi_{ijkl}^{abcd}\rangle$
$\langle\Phi_0 $	$\bar{h}_0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	<b>0</b>	<b>0</b>
$\langle\Phi_i^a $	$\bar{h}_i^a \equiv 0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	<b>0</b>
$\langle\Phi_{ij}^{ab} $	$\bar{h}_{ij}^{ab} \equiv 0$	$\bar{h}_i^a \equiv 0, \bar{h}_{ij}^{kb}\{\hat{k}^\dagger\hat{i}\hat{b}^\dagger\hat{j}\}, \bar{h}_{cj}^{ab}\{\hat{a}^\dagger\hat{c}\hat{b}^\dagger\hat{j}\}, \sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijk}^{abc} $	$\sim$	$\bar{h}_{ij}^{ab} \equiv 0, \sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijkl}^{abcd} $	$\sim$	$\sim$	$\sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$

ST-EOM-  
CCSD

$\hat{G}$	$ \Phi_0\rangle$	$ \Phi_i^a\rangle$	$ \Phi_{ij}^{ab}\rangle$	$ \Phi_{ijk}^{abc}\rangle$	$ \Phi_{ijkl}^{abcd}\rangle$
$\langle\Phi_0 $	$g_0 = \bar{h}_0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\mathbf{0}$	$\mathbf{0}$
$\langle\Phi_i^a $	$g_i^a \equiv 0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\mathbf{0}$
$\langle\Phi_{ij}^{ab} $	$g_{ij}^{ab} \equiv 0$	$g_i^a \equiv 0, g_{ij}^{mb} \equiv 0, g_{ej}^{ab} \equiv 0, \approx$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijk}^{abc} $	$\approx$	$g_{ij}^{ab} \equiv 0, \approx$	$\approx$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijkl}^{abcd} $	$\approx$	$\approx$	$\approx$	$\approx$	$\bar{\mathbf{X}}$

EOMCCSD

$\hat{H}$	$ \Phi_0\rangle$	$ \Phi_i^a\rangle$	$ \Phi_{ij}^{ab}\rangle$	$ \Phi_{ijk}^{abc}\rangle$	$ \Phi_{ijkl}^{abcd}\rangle$
$\langle\Phi_0 $	$\bar{h}_0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\mathbf{0}$	$\mathbf{0}$
$\langle\Phi_i^a $	$\bar{h}_i^a \equiv 0$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\mathbf{0}$
$\langle\Phi_{ij}^{ab} $	$\bar{h}_{ij}^{ab} \equiv 0$	$\bar{h}_i^a \equiv 0, \bar{h}_{ij}^{kb} \{k^\dagger \hat{i} b^\dagger j\}, \bar{h}_{cj}^{ab} \{\hat{a}^\dagger \hat{c} b^\dagger j\}, \sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijk}^{abc} $	$\sim$	$\bar{h}_{ij}^{ab} \equiv 0, \sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$
$\langle\Phi_{ijkl}^{abcd} $	$\sim$	$\sim$	$\sim$	$\bar{\mathbf{X}}$	$\bar{\mathbf{X}}$

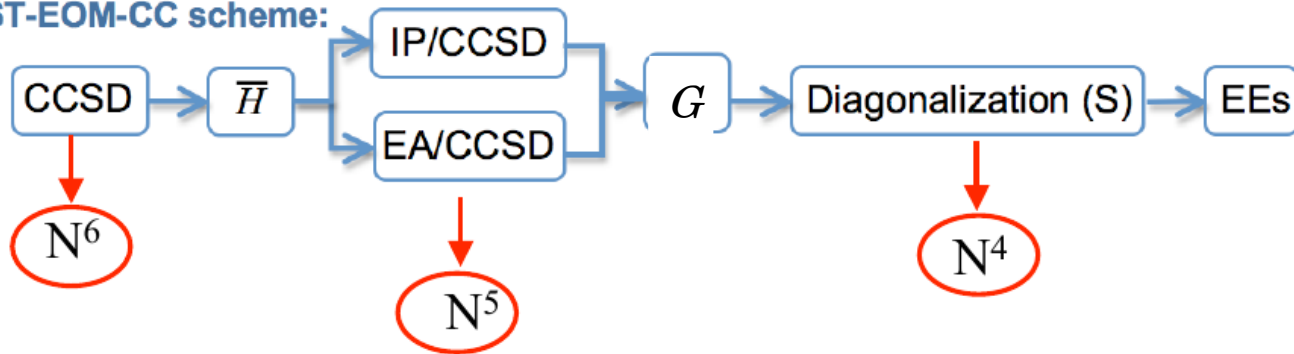
# STEOM-CCSD vs. EOM-CCSD

EOM-CC scheme:



$N^6$

ST-EOM-CC scheme:



$N^6$

$N^5$

$N^4$

STEOM-CC

vs.

EOM-CC

$$|\Psi\rangle = e^{\hat{T}} \{e^{\hat{S}}\} \hat{C} |\Phi_0\rangle$$

$$|\Psi\rangle = e^{\hat{T}} \hat{R} |\Phi_0\rangle$$

In the exact case:  $\{e^{\hat{S}}\} \hat{C} |\Phi_0\rangle = \hat{R} |\Phi_0\rangle$

$$\hat{C}_1 = \hat{R}_1$$

$$[\hat{S} = \hat{S}_2]$$

$$\hat{S} \hat{C}_1 + \hat{C}_2 = \hat{R}_2$$

$$C = C_1$$

$$R = R_1 + R_2$$

$$\frac{1}{2} \{\hat{S}^2\} \hat{C}_1 + \hat{S} \hat{C}_2 + \hat{C}_3 = \hat{R}_3$$

$$\frac{1}{2} \{\hat{S}^2\} \hat{C}_2 + \hat{S} \hat{C}_3 + \hat{C}_4 = \hat{R}_4$$



## Davidson's Diagonalization

$$\bar{H}R_k = E_k R_k$$

- A generalized Davidson iterative diagonalization procedure, which requires calculation of the **products of the transformed Hamiltonian acting on trial vectors**

for EOMCC

$$\sigma = \bar{H}R$$

or for ST-EOMCC

$$\sigma = G\tilde{R}$$

- The original (full) matrix is projected onto a search sub-space of an increasing dimension and diagonalized within this subspace, yielding approximate eigenpairs of the full matrix
- Davidson iterative diagonalization procedure for the Hermitian matrices is appropriately modified for the case of non-Hermitian matrices (Hirao and Nakatsuji 1982).

# Davidson's diagonalization requires the $\sigma$ terms

(products of the transformed Hamiltonian with trial vectors).

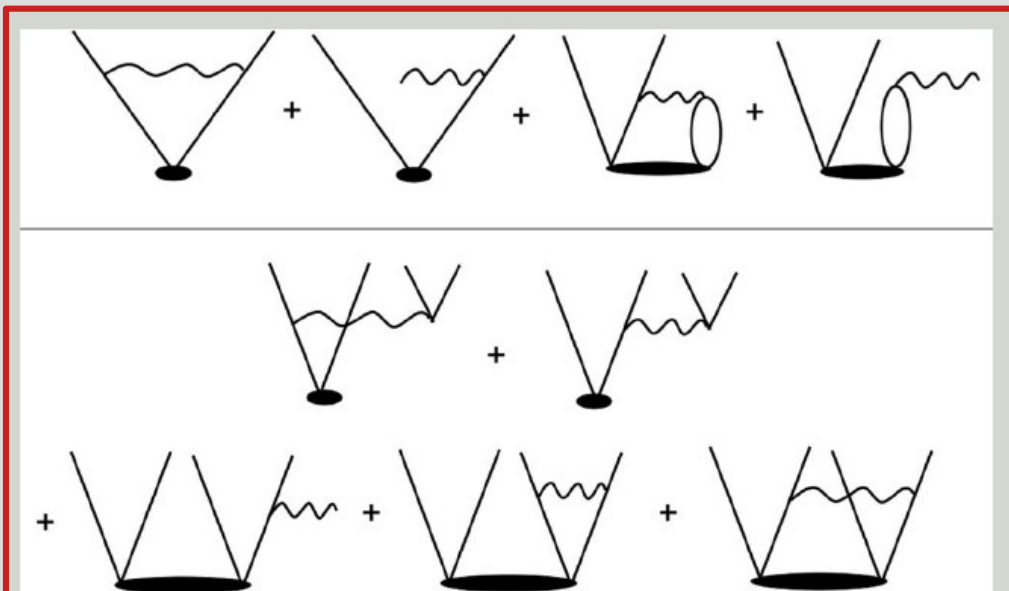


FIG. 10. EOM-CCSD: the  $\sigma = \bar{H}R$  singles (top) and doubles (bottom) terms.  $R_2$  vector is represented by the two-electron oval interaction.

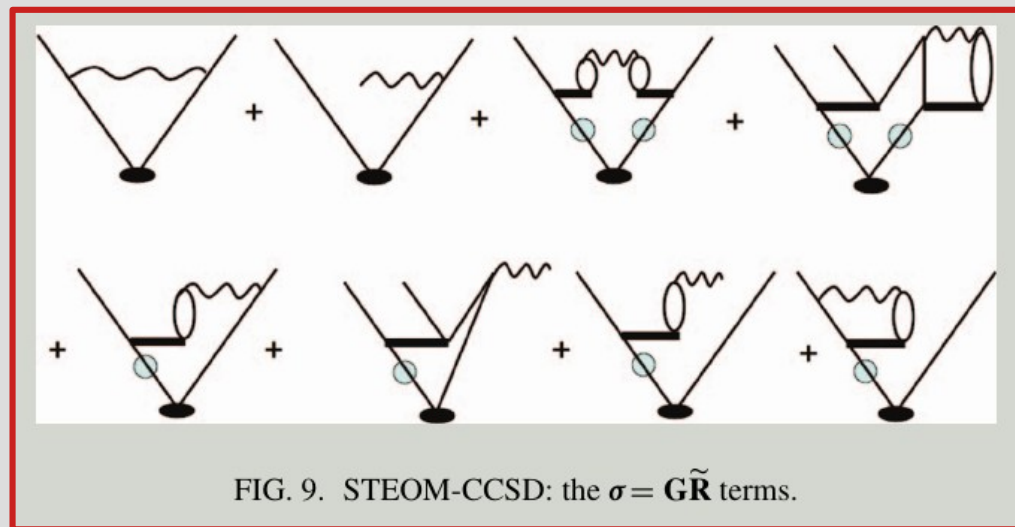


FIG. 9. STEOM-CCSD: the  $\sigma = \tilde{\mathbf{G}}\tilde{\mathbf{R}}$  terms.

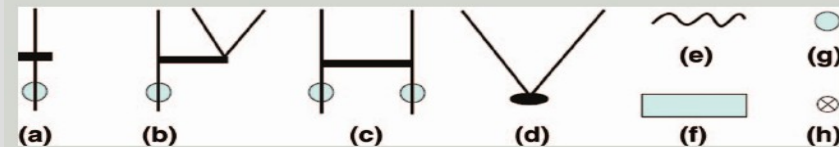


FIG. 2. Definitions of the diagrammatic symbols; anti-symmetrized skeleton diagrams are used, where the direction of the arrows is omitted: (a) and (b) one- and two-body IP/EA FSCC operators:  $S^1 = S^{IP} + S^{EA}$ . (c) FSCC excitation operators:  $S^{EE}$  or  $S_Q$ . (d) Single-excitations:  $\tilde{R}$ . (e) The transformed-Hamiltonian interaction:  $\bar{H}$ . (f) The effective-Hamiltonian interaction:  $H_{eff}$ . (g) Restriction to active orbitals. (h) Orbitals can be active and inactive (unlike in  $S^1$ ).

# Davidson's diagonalization requires the $\sigma$ terms

(products of the transformed Hamiltonian with trial vectors).

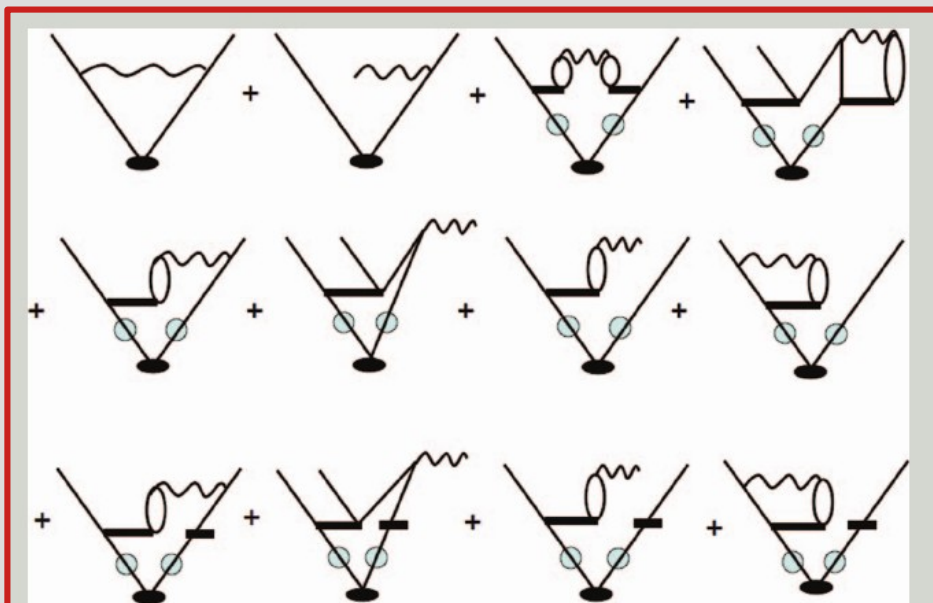


FIG. 8. The FS-CCSD  $\sigma$  terms obtained by the product of the transformed Hamiltonian [ $\bar{H}$ , Figs. 6 and 7] with a single-excitation eigenvector  $\tilde{R}$ .

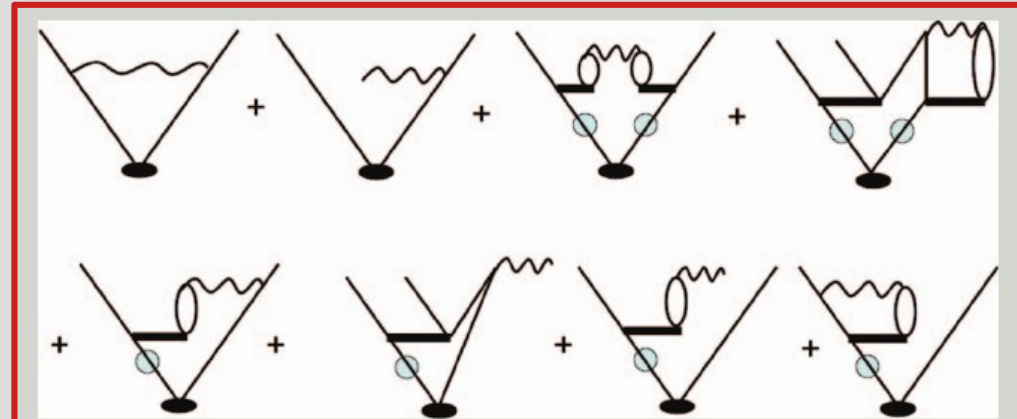


FIG. 9. STEOM-CCSD: the  $\sigma = \tilde{G}\tilde{R}$  terms.

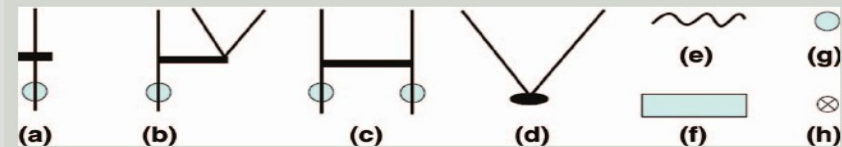


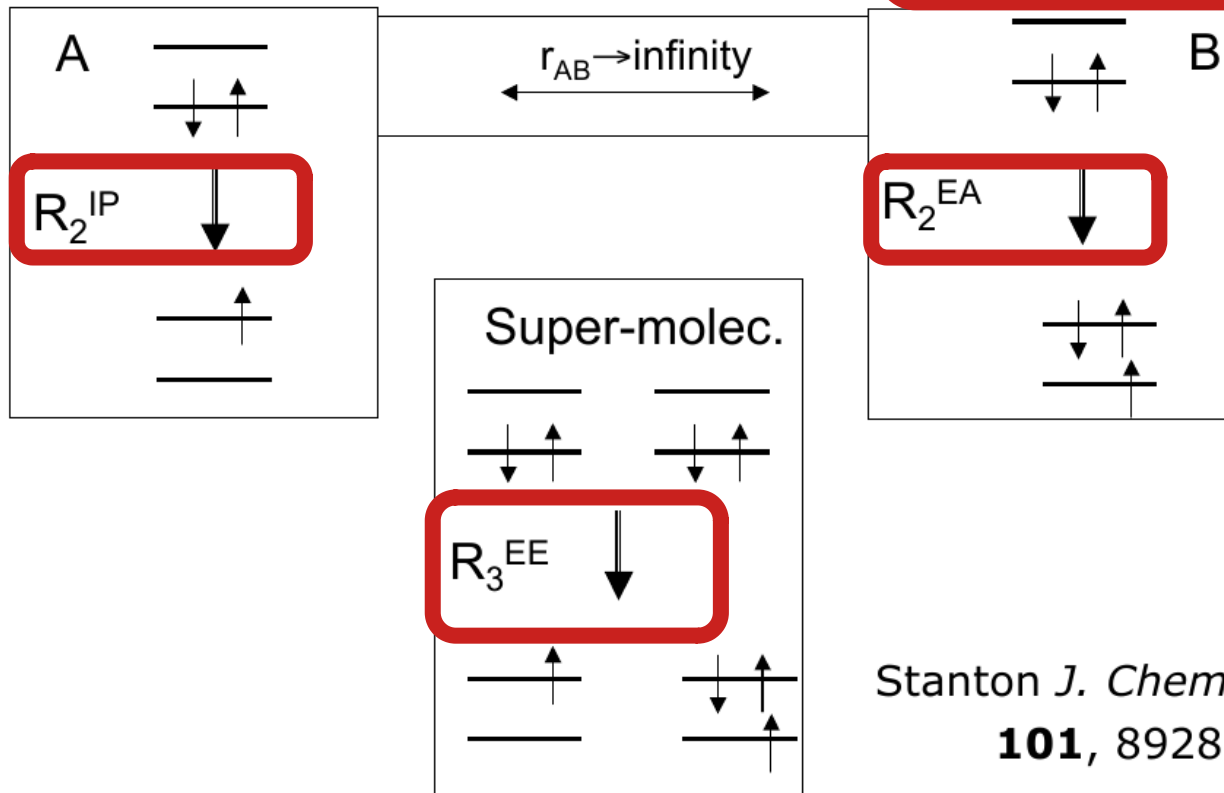
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# Coupled Cluster based methods for open-shell electronic states

- FSCC, ST-EOM-CC, EOM-CC and CI methods can be presented in a very similar way both conceptually and technically.
- The computational cost of the diagonalization step is approximately the same for the CI and EOM-CC models truncated at the same level of excitation.
- The computational cost of the diagonalization step is lower for FSCC and ST-EOM-CC, compared to EOM-CC and CI.
- The truncated EOM-CC model is superior to the CI truncated at the same level because effects of higher excitations are “folded in” through the similarity transformation into  $\bar{H}$ . The role of the similarity transformation is to achieve more compact representation of the right and left vectors R,L.
- Similarly, FSCC and ST-EOM-CC “fold” additional terms into the effective Hamiltonian relative to EOM-CC, however the procedure becomes somewhat cumbersome.

# EOM-CC and size extensivity

# Charge transfer determinants

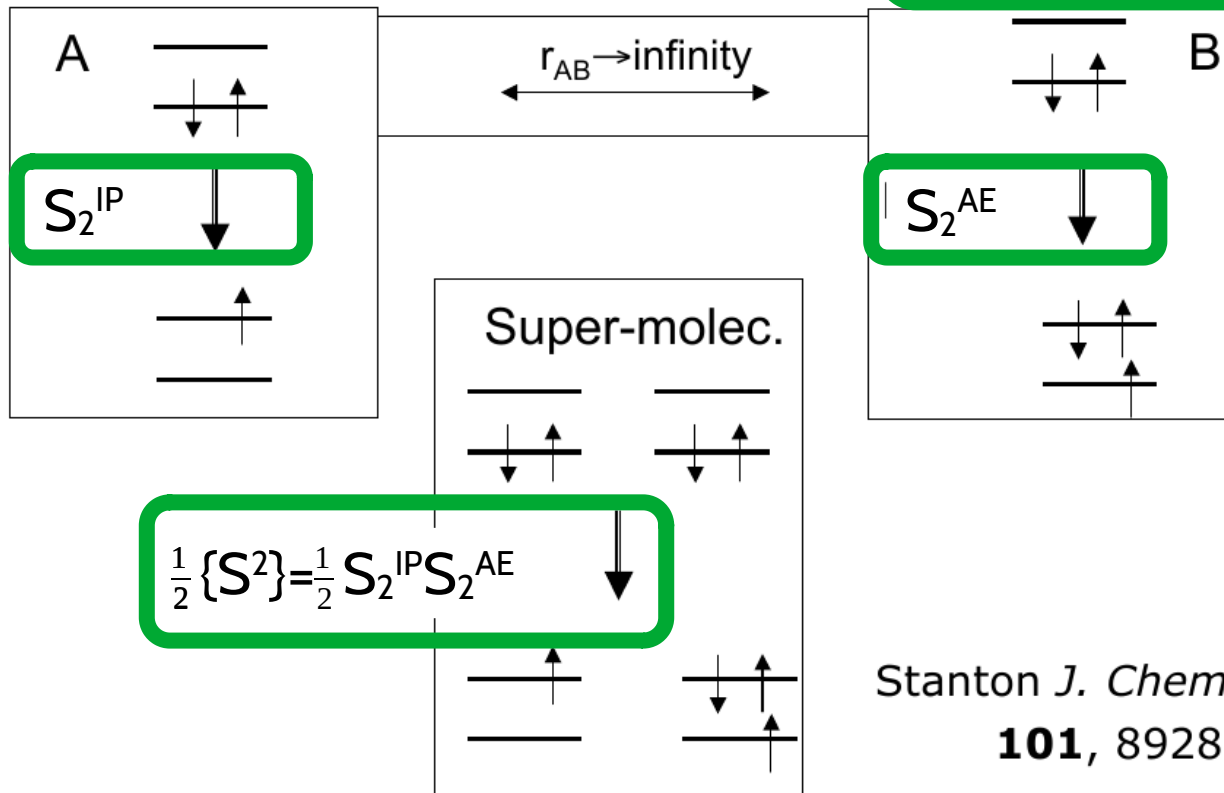


Stanton *J. Chem. Phys.*  
**101**, 8928 (1994)

FSCC

and size extensivity

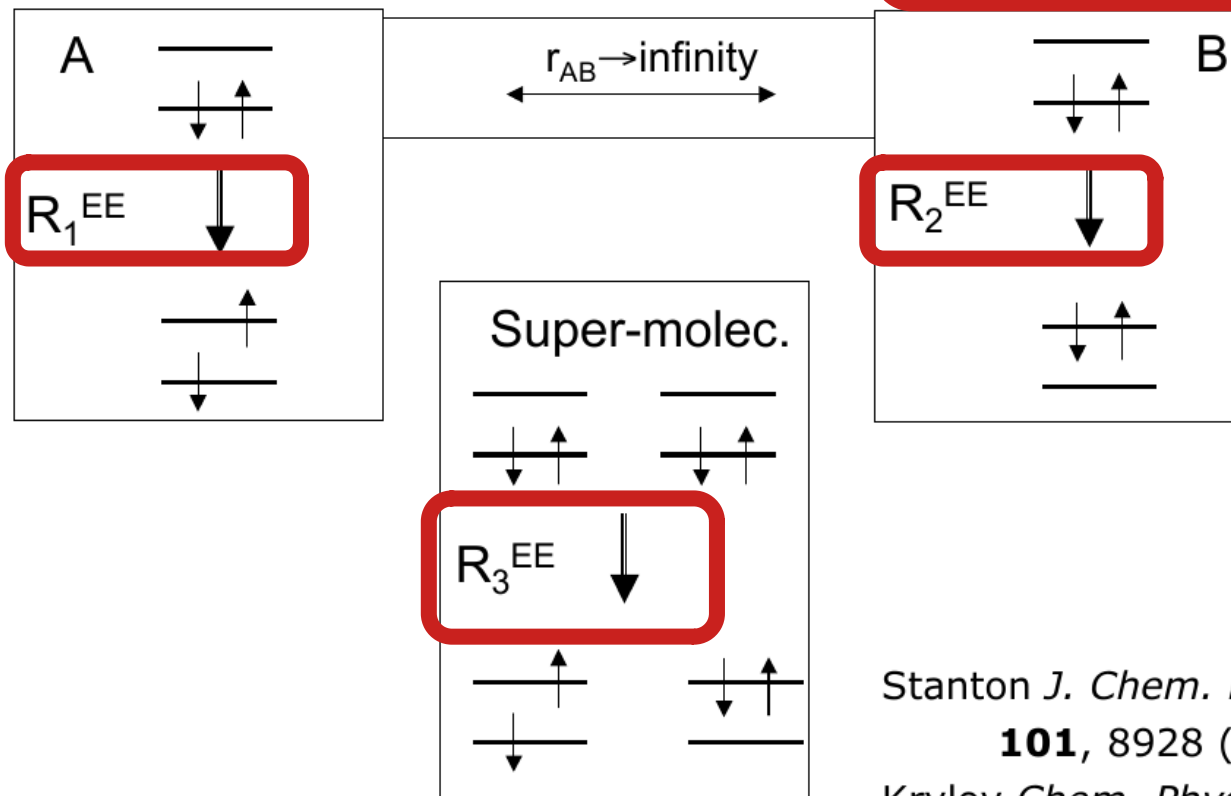
Charge transfer  
determinants



Stanton *J. Chem. Phys.*  
**101**, 8928 (1994)

# EOM-CC and size extensivity

## Doubly excited determinants



Stanton *J. Chem. Phys.*

**101**, 8928 (1994)

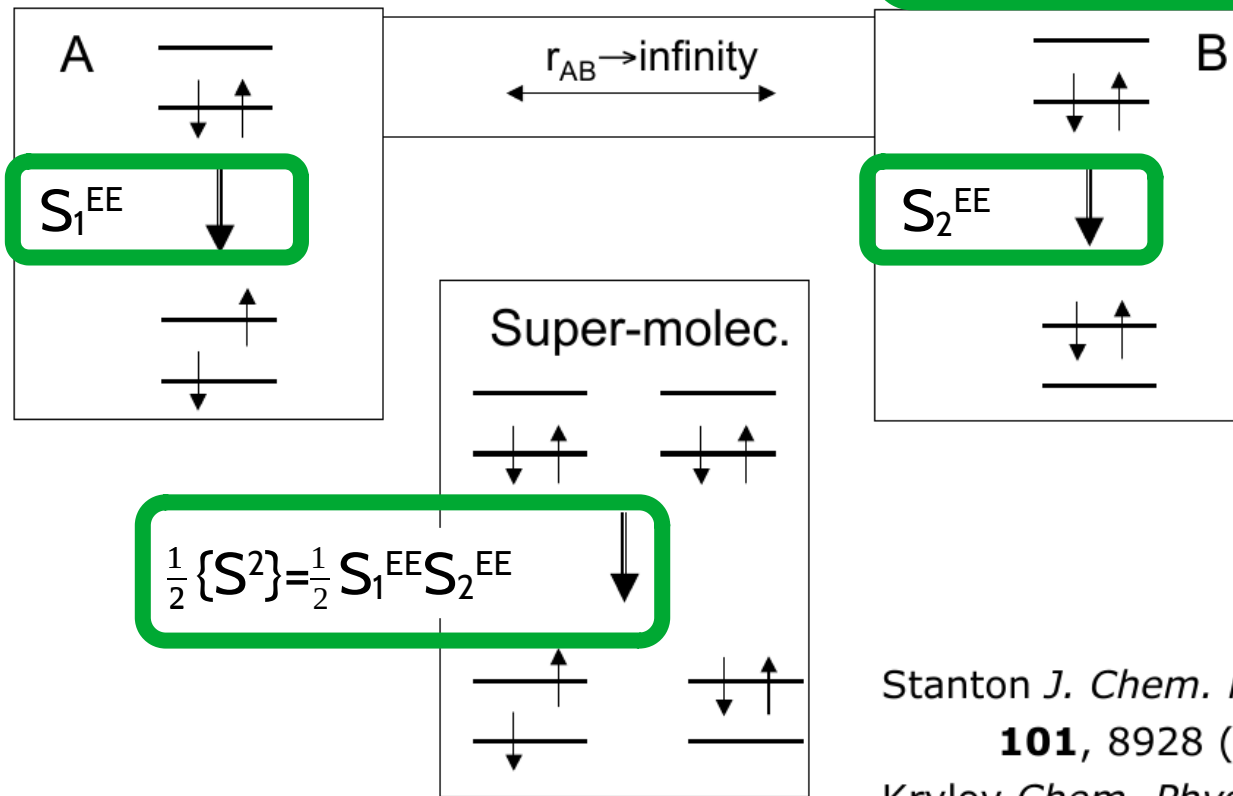
Krylov *Chem. Phys. Lett.*

**350**, 522 (2001)

FSCC

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Doubly excited  
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Stanton *J. Chem. Phys.*

**101**, 8928 (1994)

Krylov *Chem. Phys. Lett.*

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## EOM-CC and size intensive

Excitaton energy is size-intensive when *only one* subsystem is excited.

It is additively separable into *one open-shell* fragment and one (or many) closed-shell fragments

Mukerjee and co-authors *Theor. Chim. Acta.* **80**, 441 (1991)

Nooijen, Shamasundar and Mukerjee *Molec. Phys.* **103**, 2277 (2005)

$$E \rightarrow E_A + E_B$$

$$\{E\} \rightarrow \{E_A + E_B, E_A + E_B^S, E_A^S + E_B, E_A^- + E_B^+, E_A^+ + E_B^-\}$$

Missner and Bartlett *J. Chem. Phys.* **102**, 7490 (1995)

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This theoretical shortcoming is not as ominous as one might fear, however, since excitation energies obtained in monomer calculations persist in the supermolecule.

Stanton *J. Chem. Phys.* **101**, 8928 (1994)

## Summary

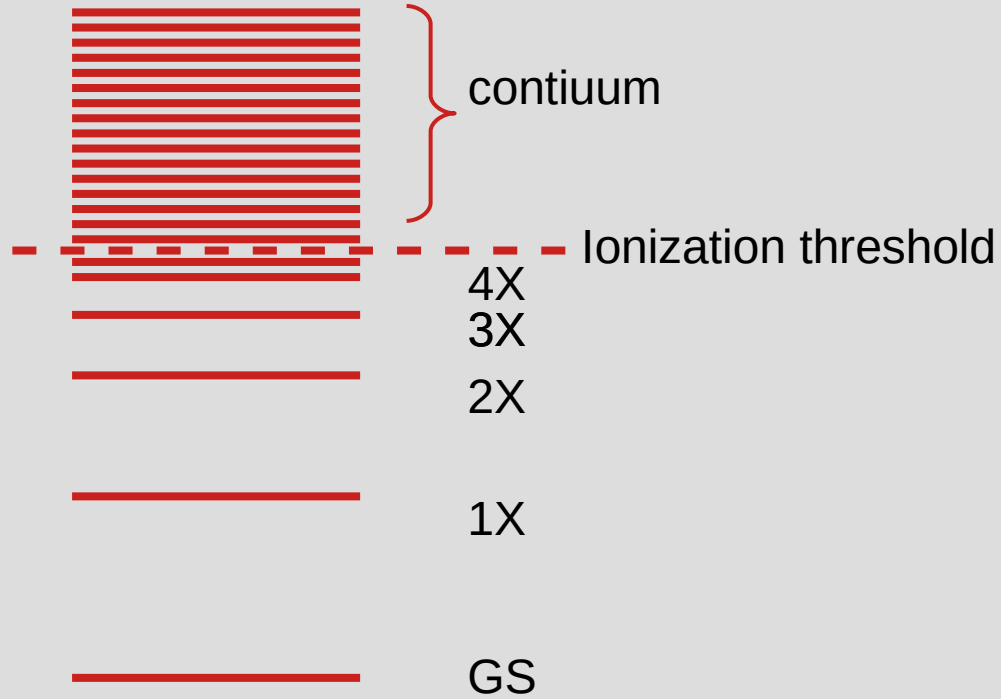
- Coupled-cluster (CC) based methods that work within Fock Space, i.e., FSCC, EOMCC and STEOM-CC, are **robust, reliable and accurate tools for calculating transition energies,**

Energies may be ionization potentials, excitation energies, or electron affinities.

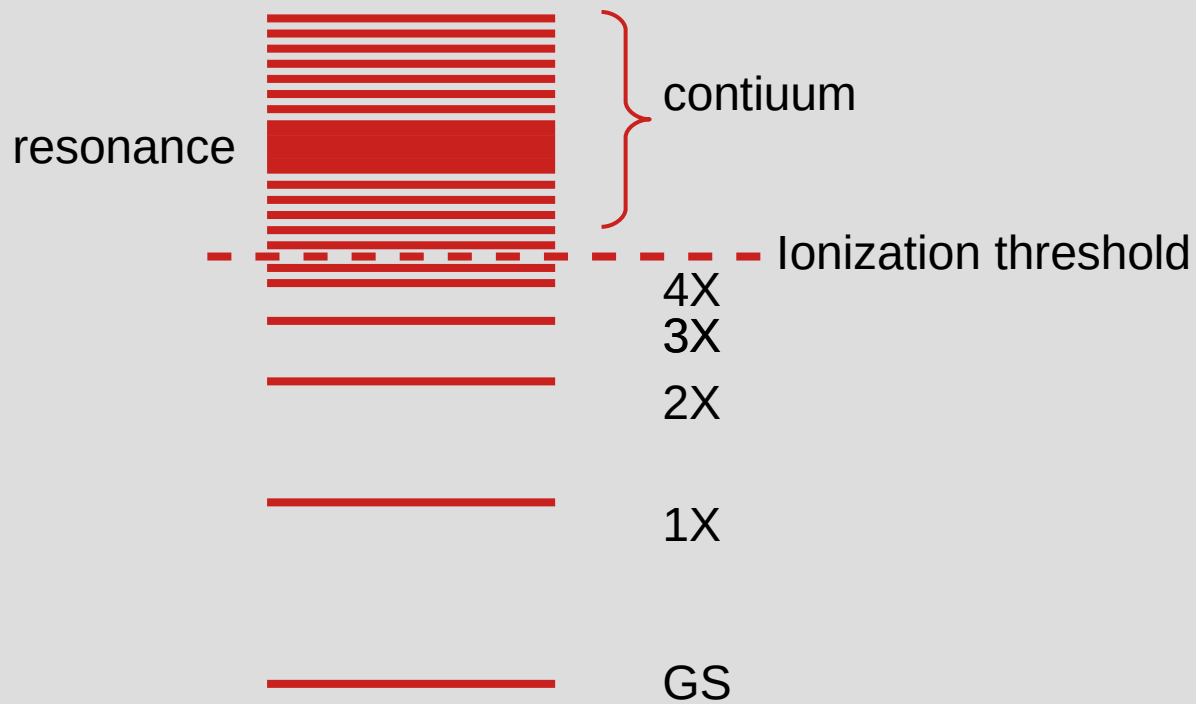
- All transition energies calculated simultaneously (~~all or nothing~~).
- Symmetry adaptation (*LS* or *J*) is automatic.

- Lets me say few words on my current research...

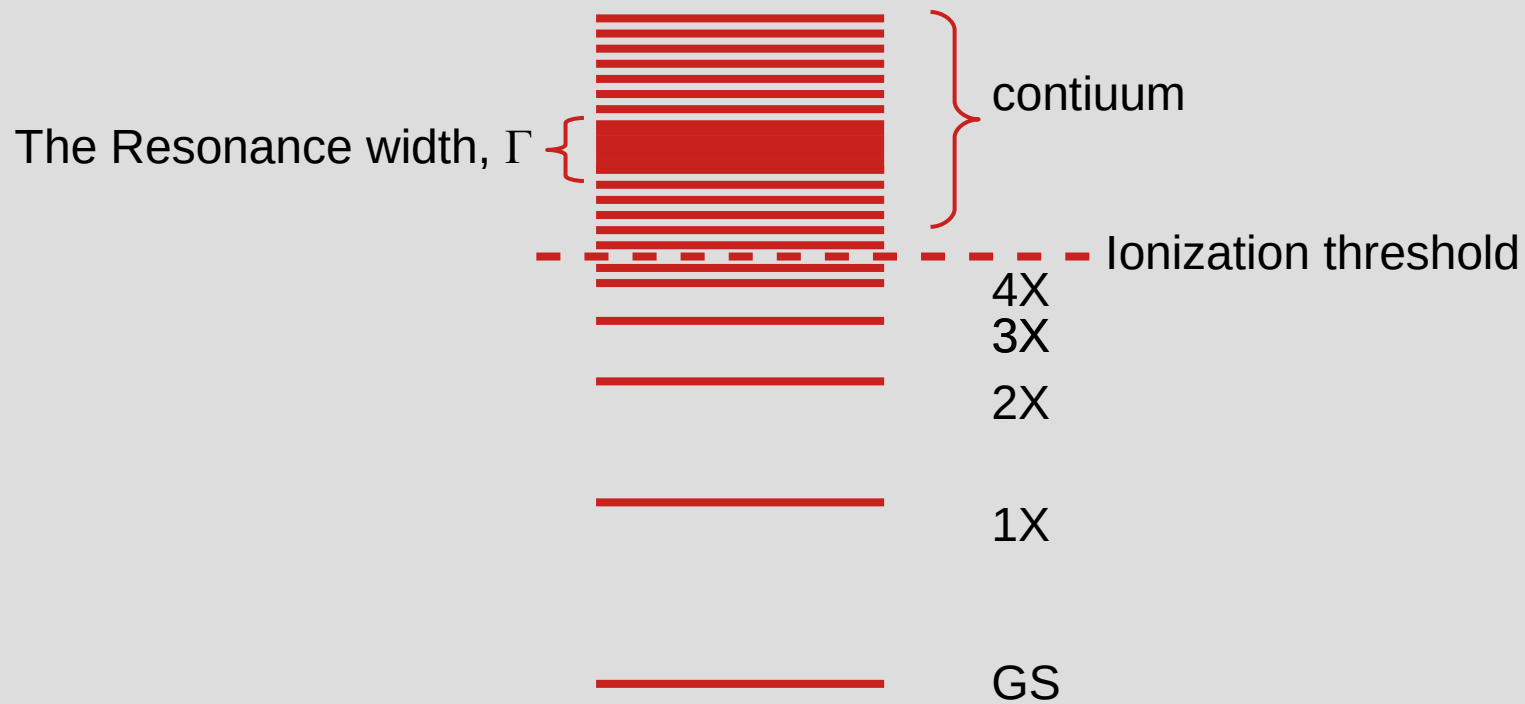
# atomic/molecular spectrum



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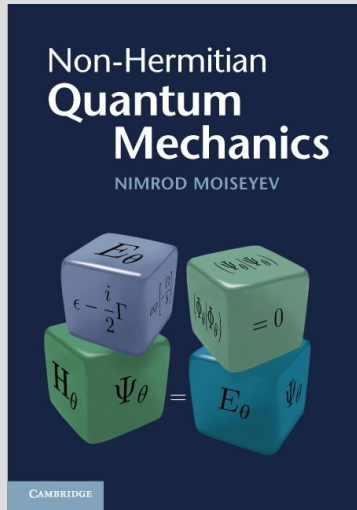
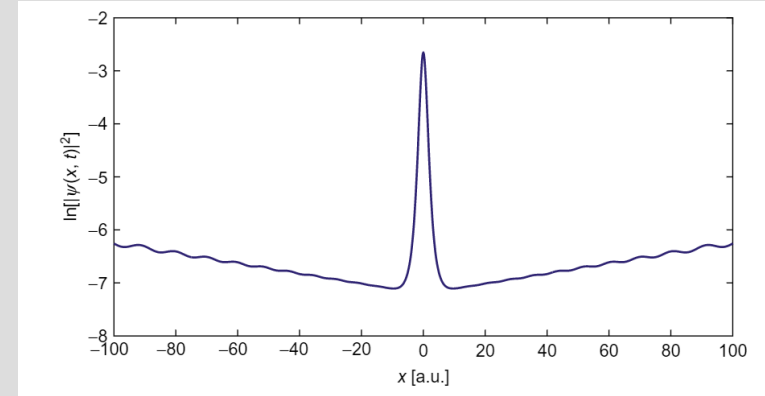
# Electronic and Nuclear resonances by ab-initio calculations

Resonances are *complex poles* of Scattering matrix,  $S(E)=A_{out}(E)/A_{in}(E)$ .

$$E_{res} = \text{Energy} - \frac{i}{2}\Gamma \quad (\text{width} = \text{INVERSE LIFETIME}) \quad S(E_{res}) = \infty$$

Direct calculations of Resonances  
by solving the TISE equation

$$\widehat{H} \Psi_{res} = E_{res} \Psi_{res}$$



$$\Psi_{res}(r) \xrightarrow{\text{out-going}; A_{in}(E_{res})=0} e^{+i \text{Re}[k]r} e^{-\text{Im}[k]r} \xrightarrow{\frac{k^2}{2}=E_{res}} \infty$$

$$\Psi_{res}(F(r)) \xrightarrow{F(r) \xrightarrow{r \rightarrow \infty} r e^{i\theta}} 0$$

**ONLY NOW BASIS SET CAN BE USED**

# Introduction – Resonances via Padé – Methodology



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- We want to calculate electronic **complex** PES, which are required for **molecular dynamics** of **resonance states**.

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- Resonances via **Padé** (RVP) yields resonance energies from **standard-quantum-chemistry** packages.
- It is based on **stabilization graphs**.
- Move into the complex plane by analytical continuation (**Padé**).

# The Stabilizations Technique – Basis Set Scaling

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- The scaled BFs are the most diffuse functions.
- It is a series of calculations in which  $\alpha$  is continually varied.
- For  $\alpha < 1$  the spatial distribution of the basis set compresses..... while for  $\alpha > 1$  it expands.

## The Stabilizations Graph – He( $2s^2$ )

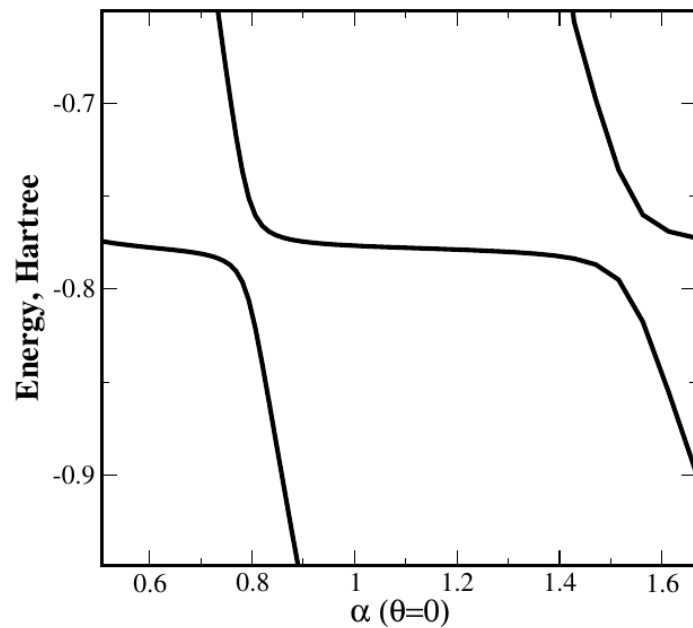
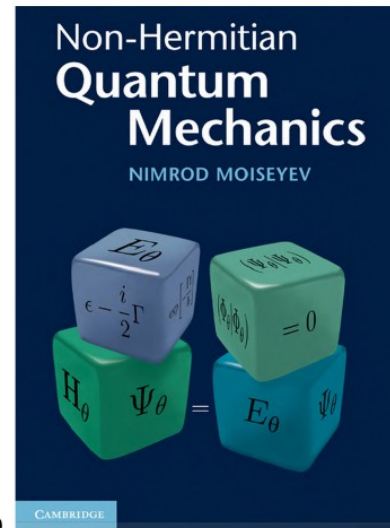
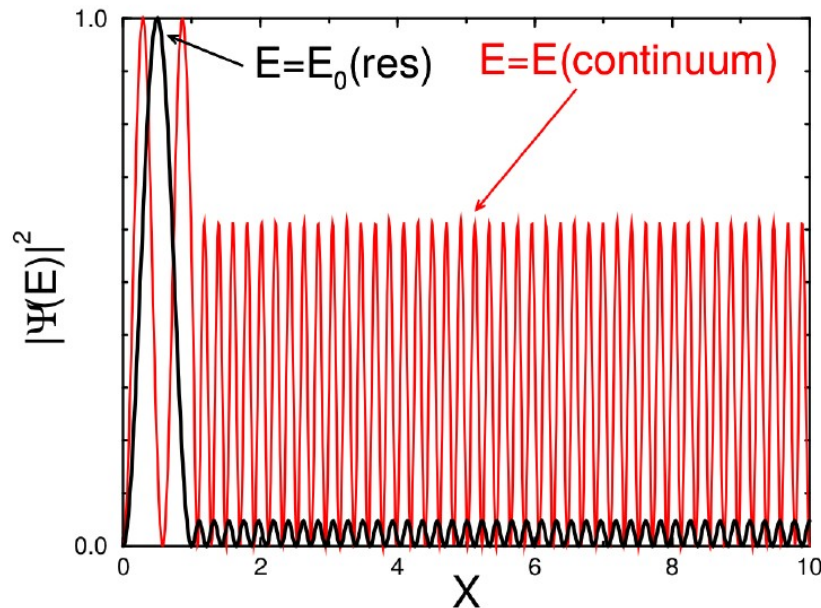


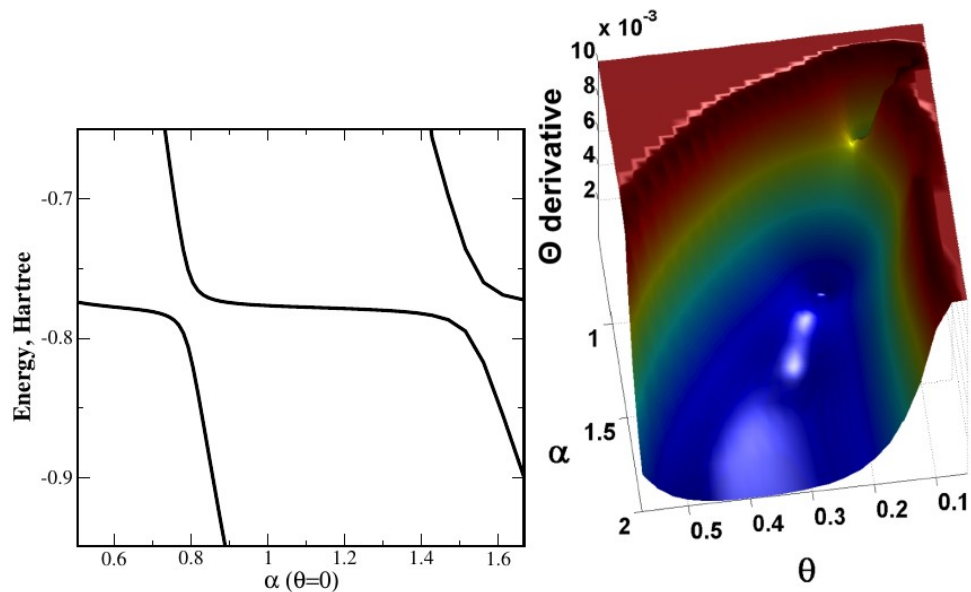
Figure: FCI/19s15p10d8f –  $\alpha$  is a *real* scaling parameter

# The Stabilizations Technique

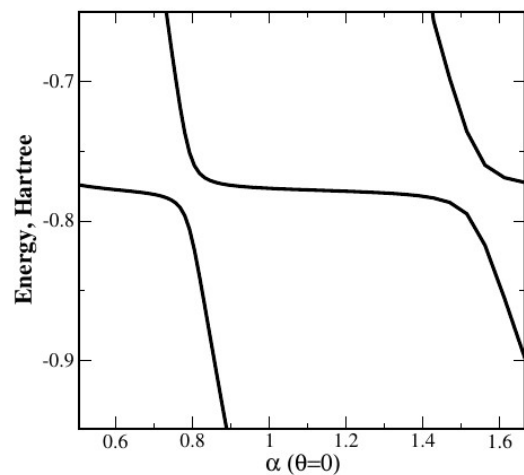


**Figure: Solutions** to the time-independent Schrödinger equation for a simple **analytically solvable one-dimensional repulsive potential**

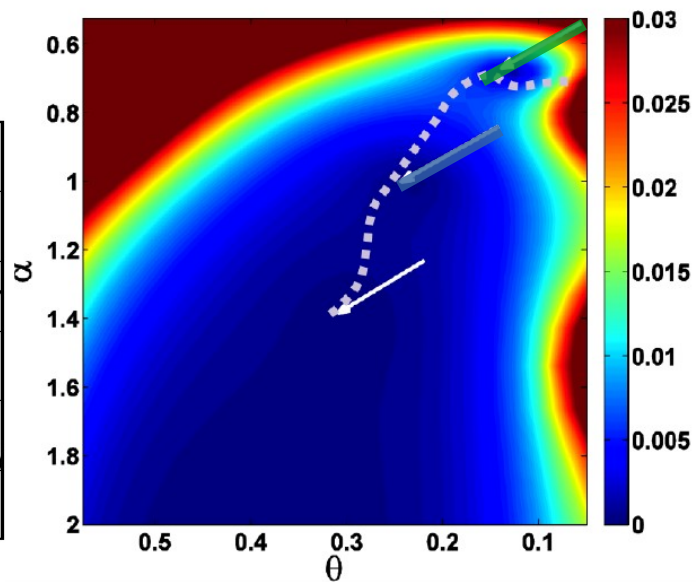
# First Derivative of the Eigenvalues w.r.t. Scaling Parameters — for the He( $2s^2$ ) resonance — UCS/FCI/19s15p10d8f



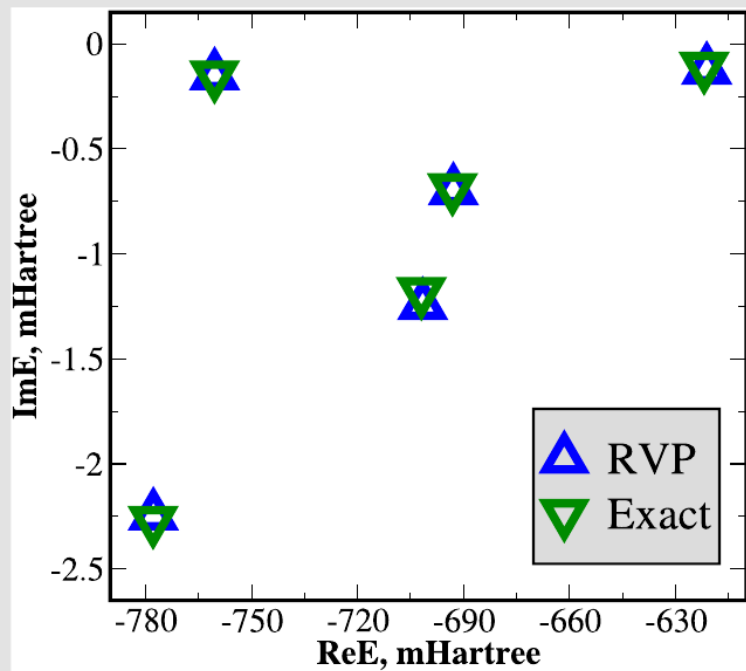
# First Derivative of the Eigenvalues w.r.t. Scaling Parameters — for the He( $2s^2$ ) resonance — UCS/FCI/19s15p10d8f



## $\Theta$ derivative



# Case Study – The Doubly Excited He\* Atom



Complex energies of the doubly excited Feshbach He\*  
RVP vs. Exact, in mhartree.

## Multiple He\* Feshbach Complex Energies

state	Re $E$ , mhartree		Im $E$ , mhartree	
	RVP	exact	RVP	exact
$1A_g^2$	-777.7858	-777.8676 <sup>64</sup>	-2.246	-2.271 <sup>64</sup>
$3A_g B_{xu}$	-760.4625	-760.4906 <sup>74</sup>	-0.151	-0.1495 <sup>74</sup>
$1B_{xu} B_{xu}$	-701.5648	-701.946 <sup>72</sup>	-1.244	-1.181 <sup>72</sup>
$1A_g B_{xu}$	-692.8821	-693.1349 <sup>73</sup>	-0.698	-0.687 <sup>73</sup>
$2A_g^2$	-621.1877	-621.9273 <sup>64</sup>	-0.120	-0.108 <sup>64</sup>

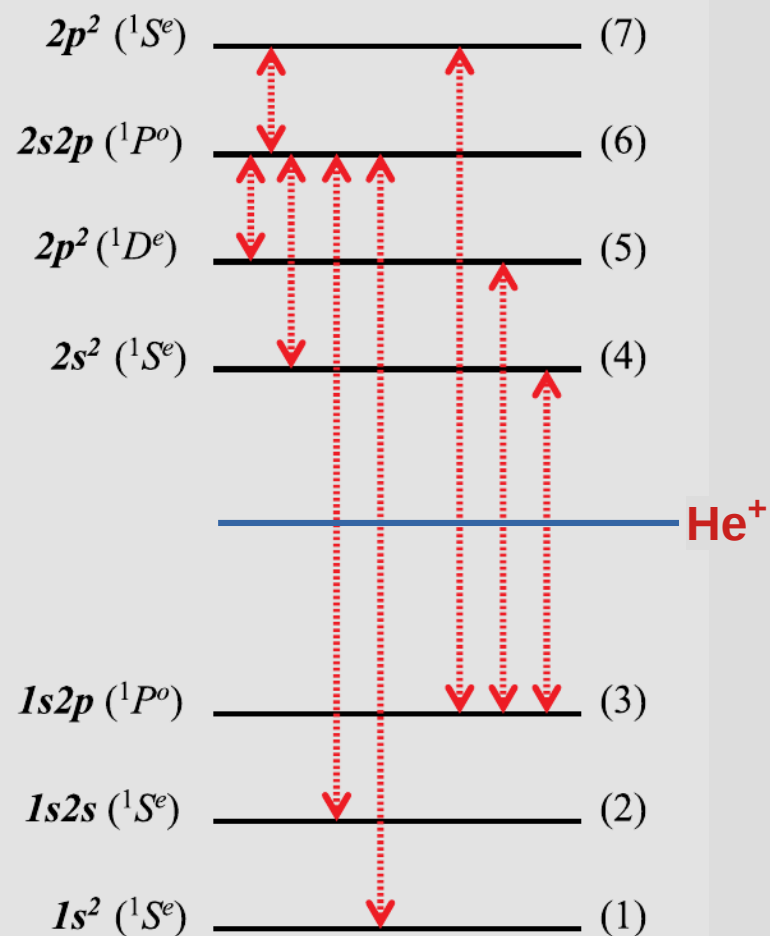
<sup>a</sup>The doubly-excited states are presented using the  $D_{2h}$  point group ( $x$

**RVP is in good agreement with the exact values**

**RVP yields reliable complex energy difference**

# Doubly Excited He\* - Transitions

- Schematic energy levels.
- Three bound (bottom) and four resonance states (top).
- The red arrows represent allowed dipole transitions.
- We have calculated all *eight* complex transition dipoles.





# Doubly Excited He\* - Transition Dipoles

Comparison of Complex Transition Dipoles in m.a.u.<sup>a</sup>

transition	CS\ExTG5G <sup>3,27</sup>		RVP\basis I		RVP\basis II	
	Re $\mu$	Im $\mu$	Re $\mu$	Im $\mu$	Re $\mu$	Im $\mu$
1 $\leftrightarrow$ 6	35.4	+12.11	34.88	+12.44	35.99	+12.99
2 $\leftrightarrow$ 6	313.0	-3.598	313.0	-3.021	313.1	-4.136
3 $\leftrightarrow$ 4	-123.1	-2.554	-122.8	-2.403	-125.5	-2.367
3 $\leftrightarrow$ 5	328.8	+0.193	326.8	+0.140	321.4	+0.119
3 $\leftrightarrow$ 7	-192.5	+0.3475	-192.4	+0.3571	-192.4	+0.2619
4 $\leftrightarrow$ 6	1522.7	-9.73	1528.9	-10.24	1529.3	-10.79
5 $\leftrightarrow$ 6	1705.45	-3.767	1704.42	-4.030	1693.6	-4.499
6 $\leftrightarrow$ 7	-2161.4	-1.007	-2163.4	-1.164	-2167.5	-2.570

<sup>a</sup>ExTG5G is a highly optimized (complete) basis set and represents accurate CS/FCI values for comparison. Basis I and basis II are truncated ExTG5G bases. Basis I is larger than basis II, and they represent the current RVP calculations. The transition indexing is defined in [Figure 1](#).

1s2s  $\leftrightarrow$  2s2p

CS/FCI/ExTG5G :: Kaprálová-Žďánská, Šmydke, and Civiš *JCP* 139, 104314 (2013)

Bhattacharya, Landau, and Moiseyev *J. Phys. Chem. Lett.* **11**, 5601 (2020)