MOLECULAR SYSTEMS FROM THE EQUATION-OF-MOTION COUPLED-CLUSTER THEORY

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Office of Science
U.S. DEPARTMENT OF ENERGY

Office of Basic Energy Sciences
Chemical Sciences, Geosciences
& Biosciences Division

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Workshop of the *Espace de Structure et de Réactions Nucléaires Théorique* on “Near-Degenerate Systems in Nuclear Structure and Quantum Chemistry from *Ab Initio* Many-Body Methods”, March 30 – April 2, 2015, CEA Saclay, Gif-sur-Yvette, France

MANY THANKS TO PROFESSORS CARLO BARBIERI, RODNEY BARTLETT, THOMAS DUGUET, AND GUSTAVO SCUSERIA FOR THE INVITATION

UNDERSTANDING ELECTRONIC EXCITATION, MULTI-PHOTON IONIZATION, AND PHOTO-ELECTRON SPECTRA WITH THE EQUATION-OF-MOTION COUPLED-CLUSTER THEORY

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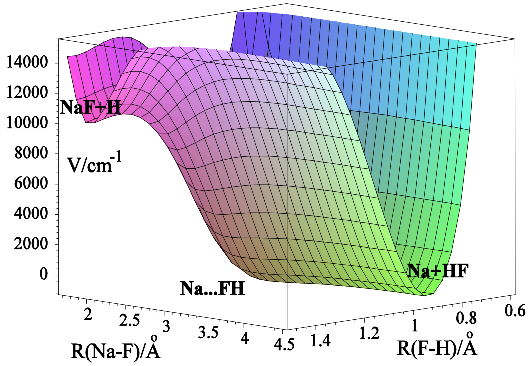
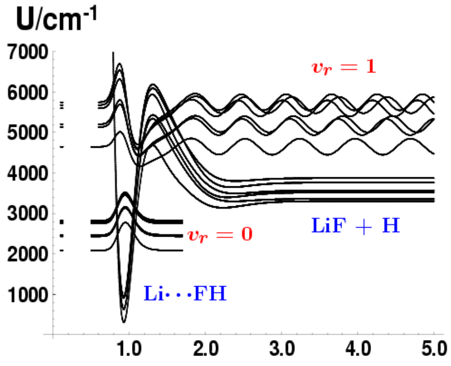
THE ELECTRONIC SCHRÖDINGER EQUATION

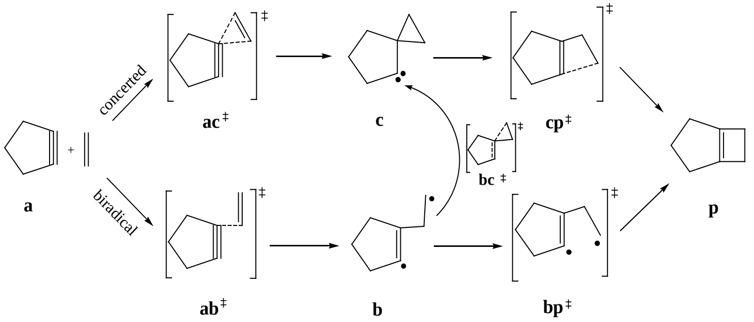
$$\boxed{H_e \Psi_K(\mathbf{X};\mathbf{R}) = E_K(\mathbf{R})\Psi_K(\mathbf{X};\mathbf{R})}$$

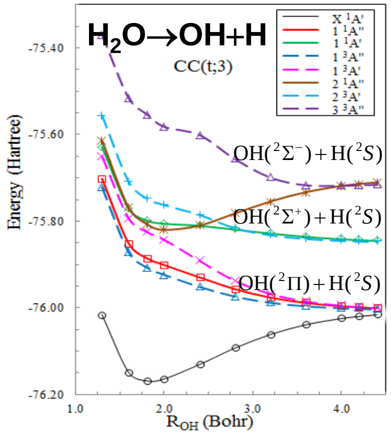
$$H_e = Z + V = \sum_{i=1}^{N} z(\mathbf{x}_i) + \sum_{i>j=1}^{N} v(\mathbf{x}_i, \mathbf{x}_j)$$

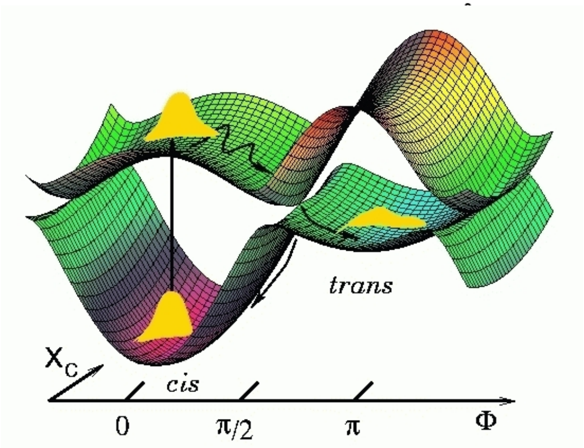
$$z(\mathbf{x}_i) = -\tfrac{1}{2}\Delta_i + \sum^{M} \frac{Z_A}{R_{Ai}}, \qquad v(\mathbf{x}_i, \mathbf{x}_j) = \frac{1}{r_{ij}}$$

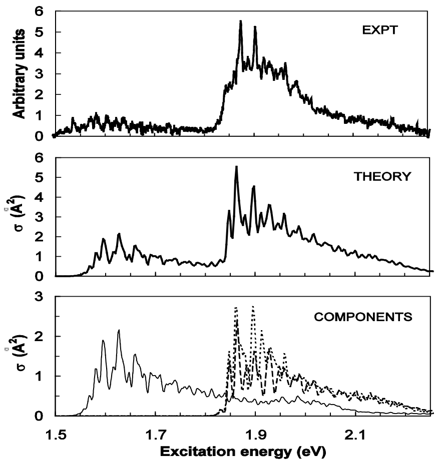










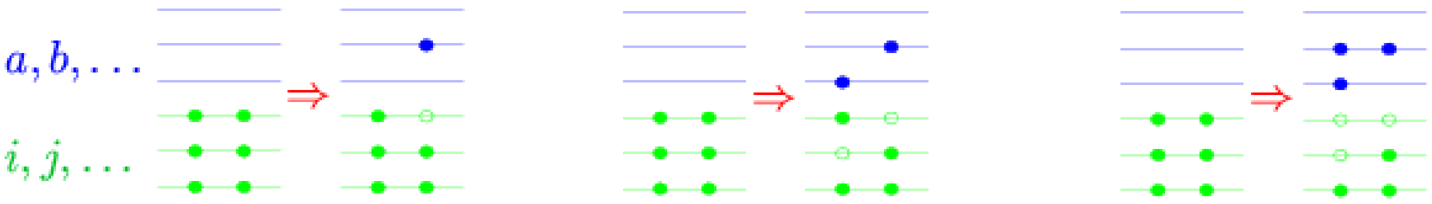


SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

(F. Coester, 1958; F. Coester and H. Kümmel, 1960; J. Čížek, 1966,1969; J. Čížek and J. Paldus, 1971)

$$|\Psi\rangle = e^{T^{(A)}}|\Phi\rangle, \quad T^{(A)} = \sum_{k=1}^{m_A} T_k$$

$$T_1|\Phi\rangle = \sum_{\substack{i\\a}} t_a^i|\Phi_i^a\rangle, \quad T_2\Phi = \sum_{\substack{i>j\\a>b}} t_{ab}^{ij}|\Phi_{ij}^{ab}\rangle, \quad T_3\Phi = \sum_{\substack{i>j>k\\a>b>c}} t_{abc}^{ijk}|\Phi_{ijk}^{abc}\rangle, \quad \text{etc.}$$



1p-1h, singles (S) 2p-2h, doubles (D) 3p-3h, triples (T)

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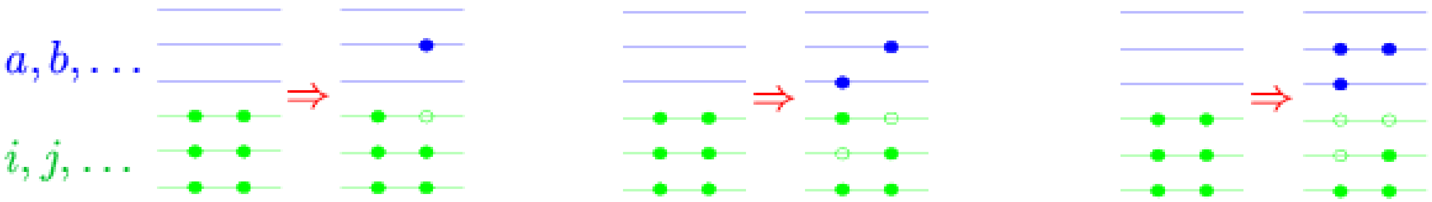

1p-1h, singles (S) **2p-2h, doubles (D)** **3p-3h, triples (T)**

$m_A = N \Rightarrow$ exact theory (full CI), $m_A < N \Rightarrow$ approximations

				CPU time scaling with the system size
$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 \ (n_o^2 n_u^2)$	← **iterative N^6**
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 \ (n_o^3 n_u^3)$	← **iterative N^8**
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 \ (n_o^4 n_u^4)$	← **iterative N^{10}**

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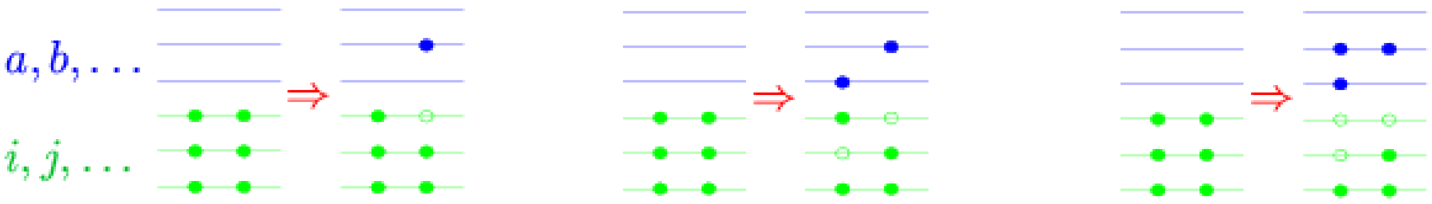

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$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 \; (n_o^4 n_u^4)$	← **iterative N^{10}**

$$\langle \Phi_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k} | \left(H_N e^{T^{(A)}} \right)_C |\Phi\rangle = 0, \quad k = 1 \ldots, m_A$$

$$E_0 = \langle\Phi|H|\Phi\rangle + \langle\Phi| \left(H_N e^{T^{(A)}} \right)_C |\Phi\rangle = \langle\Phi|H|\Phi\rangle + \langle\Phi| \left[H_N (T_1 + T_2 + \tfrac{1}{2} T_1^2) \right]_C |\Phi\rangle$$

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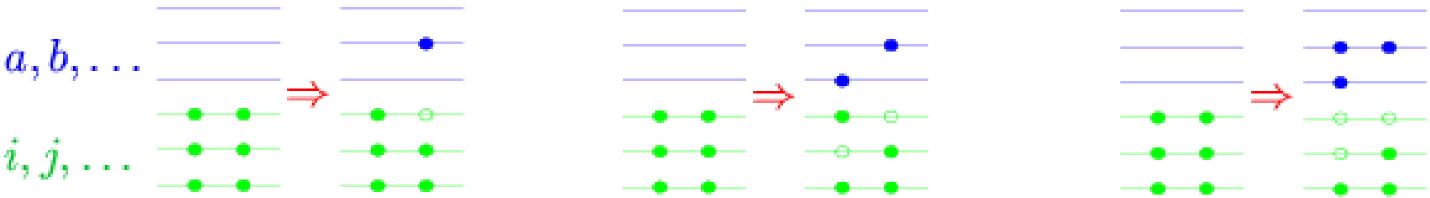

1p-1h, singles (S) **2p-2h, doubles (D)** **3p-3h, triples (T)**

$m_A = N \Rightarrow$ exact theory (full CI), $m_A < N \Rightarrow$ approximations

				CPU time scaling with the system size
$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 \ (n_o^2 n_u^2)$	← iterative N^6
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 \ (n_o^3 n_u^3)$	← iterative N^8
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 \ (n_o^4 n_u^4)$	← iterative N^{10}

To reduce large computer costs of CCSDT, CCSDTQ, etc., one usually approximates T$_3$, T$_4$, etc. This can be done via noniterative corrections to CCSD energies, as in the CCSD(T), CCSD(TQ), and similar approaches, or by reduced scaling iterative CCSDT-*n*, CCSDTQ-*n*, etc. approximations.

← iterative N^6 plus noniterative N^7 or N^9, or iterative N^7 or N^9

EXCITED STATES: EQUATION-OF-MOTION CC (EOMCC) THEORY, SYMMETRY-ADAPTED-CLUSTER CONFIGURATION INTERACTION APPROACH (SAC-CI), AND RESPONSE CC METHODS

(H. Monkhorst, 1977; D. Mukherjee and P.K. Mukherjee, 1979; H. Nakatsuji and K. Hirao, 1978; K. Emrich, 1981; M. Takahashi and J. Paldus; 1986; J. Geertsen, M. Rittby, and R.J. Bartlett, 1989)

$$|\Psi_K\rangle = R_K|\Psi_0\rangle, \qquad |\Psi_0\rangle = e^T|\Phi\rangle$$

$$T = T_1 + T_2 + \cdots, \quad R_K = R_{K,0} + R_{K,\text{open}}, \quad R_{K,\text{open}} = R_{K,1} + R_{K,2} + \cdots$$

$$T_n = \sum_{\substack{i_1 < \,\ldots\, < i_n \\ a_1 < \,\ldots\, < a_n}} t^{i_1 \ldots i_n}_{a_1 \ldots a_n} a^{a_1} \ldots a^{a_n} a_{i_n} \ldots a_{i_1}, \quad R_{K,n} = \sum_{\substack{i_1 < \,\ldots\, < i_n \\ a_1 < \,\ldots\, < a_n}} r^{i_1 \ldots i_n}_{K,a_1 \ldots a_n} a^{a_1} \ldots a^{a_n} a_{i_n} \ldots a_{i_1}$$

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EOMCC

(K. Emrich, 1981; J. Geertsen, M. Rittby, and R.J. Bartlett, 1989; J.F. Stanton and R.J. Bartlett, 1993)

In the exact theory,

$$(\bar{H}_{N,\text{open}} R_{K,\text{open}})_C|\Phi\rangle = \omega_K R_K|\Phi\rangle \text{ or } [\bar{H}_{N,\text{open}}, R_{K,\text{open}}]|\Phi\rangle = \omega_K R_K$$

$$\bar{H}_N = e^{-T} H_N e^T = (H_N e^T)_C, \quad \omega_K = E_K - E_0, \quad R_{K,\text{open}} = R_K - R_{K,0}.$$

In approximate methods,

$$T \simeq T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad R_K \simeq R_K^{(A)} = \sum_{n=0}^{m_A} R_{K,n} \quad (m_A < N)$$

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$$T_n = \sum_{\substack{i_1<\,\ldots\,<i_n\\ a_1<\,\ldots\,<a_n}} t^{i_1\ldots i_n}_{a_1\ldots a_n}\, a^{a_1}\ldots a^{a_n} a_{i_n}\ldots a_{i_1}, \quad R_{K,n} = \sum_{\substack{i_1<\,\ldots\,<i_n\\ a_1<\,\ldots\,<a_n}} r^{i_1\ldots i_n}_{K,a_1\ldots a_n}\, a^{a_1}\ldots a^{a_n} a_{i_n}\ldots a_{i_1}$$

EOMCC

(K. Emrich, 1981; J. Geertsen, M. Rittby, and R.J. Bartlett, 1989; J.F. Stanton and R.J. Bartlett, 1993)

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$$\bar{H}_N = e^{-T} H_N e^{T} = (H_N e^{T})_C, \quad \omega_K = E_K - E_0, \quad R_{K,\text{open}} = R_K - R_{K,0}.$$

In approximate methods,

$$T \simeq T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad R_K \simeq R_K^{(A)} = \sum_{n=0}^{m_A} R_{K,n} \quad (m_A < N)$$

Basic approximation: EOMCCSD

(J. Geertsen, M. Rittby, and R.J. Bartlett, 1989; J.F. Stanton and R.J. Bartlett, 1993)

$$m_A = 2 : T = T_1 + T_2$$

$$R_K = R_{K,0} + R_{K,1} + R_{K,2}$$

$$\bar{\mathbf{H}}^{\mathrm{CCSD}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} \end{pmatrix}$$

m_A	T	R_K	method	CPU scaling
2	$T_1 + T_2$	$R_{K,0} + R_{K,1} + R_{K,2}$	EOMCCSD	$n_o^2 n_u^4$
J.F. Stanton & R.J. Bartlett, J. Chem. Phys., 1993				
3	$T_1 + T_2 + T_3$	$R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3}$	EOMCCSDT	$n_o^3 n_u^5$
K. Kowalski & P. Piecuch, J. Chem. Phys., 2001, Chem. Phys. Lett., 2001; S.A. Kucharski et al., J. Chem. Phys., 2001				
4	$T_1 + T_2 + T_3 + T_4$	$R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3} + R_{K,4}$	EOMCCSDTQ	$n_o^4 n_u^6$
S. Hirata, J. Chem. Phys., 2004; M. Kallay and J. Gauss, J. Chem. Phys., 2004				

Basic approximation: EOMCCSD

(J. Geertsen, M. Rittby, and R.J. Bartlett, 1989; J.F. Stanton and R.J. Bartlett, 1993)

$$m_A = 2 : T = T_1 + T_2$$

$$R_K = R_{K,0} + R_{K,1} + R_{K,2}$$

$$\bar{\mathbf{H}}^{\mathrm{CCSD}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} \end{pmatrix}$$

m_A	T	R_K	method	CPU scaling
2	$T_1 + T_2$	$R_{K,0} + R_{K,1} + R_{K,2}$	EOMCCSD	$n_o^2 n_u^4$
J.F. Stanton & R.J. Bartlett, J. Chem. Phys., 1993				
3	$T_1 + T_2 + T_3$	$R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3}$	EOMCCSDT	$n_o^3 n_u^5$
K. Kowalski & P. Piecuch, J. Chem. Phys., 2001, Chem. Phys. Lett., 2001; S.A. Kucharski et al., J. Chem. Phys., 2001				
4	$T_1 + T_2 + T_3 + T_4$	$R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3} + R_{K,4}$	EOMCCSDTQ	$n_o^4 n_u^6$
S. Hirata, J. Chem. Phys., 2004; M. Kallay and J. Gauss, J. Chem. Phys., 2004				

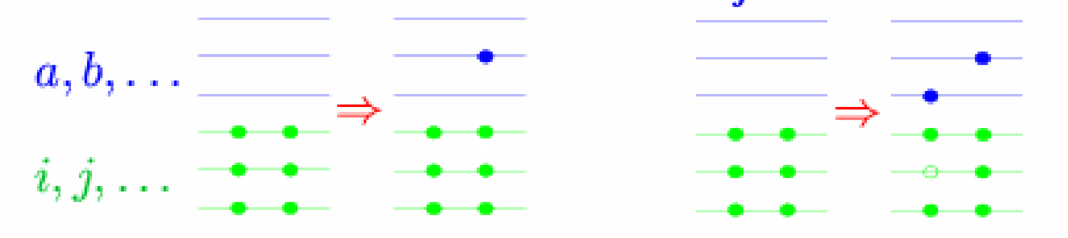
Again, large costs of EOMCCSDT, EOMCCSDTQ, etc. computations can be reduced by designing noniterative corrections to EOMCCSD energies, as in the EOMCCSD(T) and similar approaches, or by reduced scaling iterative EOMCCSDT-*n* etc. approximations, pioneered by Watts and Bartlett in 1995/1996 (cf., also, CC3 and CCSDR3 approximations to linear response CCSDT developed by Jørgensen et al.).

Electron-Attached (EA) and Ionized (IP) EOMCC Methods

$$|\Psi_\mu^{(N\pm1)}\rangle = R_\mu^{(N\pm1)}|\Psi_0\rangle, \quad R_\mu^{(N+1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)p-nh}, \quad R_\mu^{(N-1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)h-np}$$

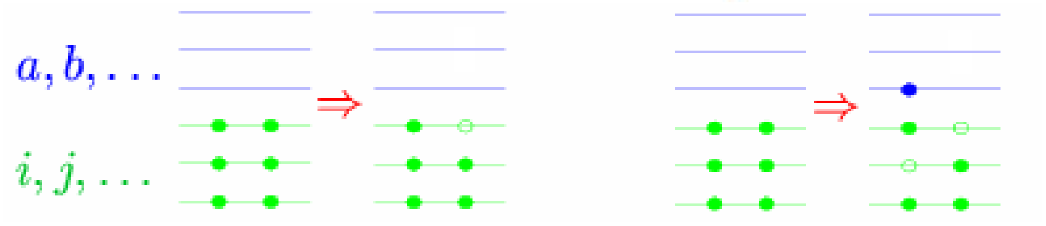
EA

$$R_{\mu,1p} = \sum_{a} r_a|\Phi^a\rangle, \quad R_{\mu,2p\text{-}1h} = \sum_{\substack{a<b\\ j}} r_{ab}^{\ \ j}|\Phi^{ab}_{\ \ j}\rangle, \quad etc.$$



IP

$$R_{\mu,1h} = \sum_{i} r^i|\Phi_i\rangle, \quad R_{\mu,2h\text{-}1p} = \sum_{\substack{i<j\\ b}} r^{ij}_{\ \ b}|\Phi_{ij}^{\ \ b}\rangle, \quad etc.$$



Solve the Eigenvalue Problem

$$(\bar{H}_{N,\text{open}}\, R_\mu^{(N\pm1)})_C|\Phi\rangle = \omega_\mu^{(N\pm1)} R_\mu^{(N\pm1)}|\Phi\rangle,$$

$$\omega_\mu^{(N+1)} = E_\mu^{(N+1)} - E_0^{(N)}, \quad \omega_\mu^{(N-1)} = E_\mu^{(N-1)} - E_0^{(N)}$$

M. Nooijen and R.J. Bartlett, 1995; R.J. Bartlett and J.F. Stanton, 1994; M. Nooijen and J.G. Snijders, 1992-1993; J.F. Stanton and J. Gauss, 1994; …, Musiał et al., 2003 -; Piecuch et al., 2005 -; …

Properties (including density matrices)

$$|\Psi_K\rangle = R_K e^T|\Phi\rangle$$

$$T = T_1 + T_2 + \cdots, \quad R_K = R_{K,0} + R_{K,\text{open}}, \quad R_{K,\text{open}} = R_{K,1} + R_{K,2} + \cdots$$

$$(\bar{H}_{N,\text{open}}\, R_{K,\text{open}})_C|\Phi\rangle = \omega_K R_K|\Phi\rangle \text{ or } [\bar{H}_{N,\text{open}}, R_{K,\text{open}}]|\Phi\rangle = \omega_K R_K$$

$$\bar{H}_N = e^{-T} H_N e^T = (H_N e^T)_C, \quad \omega_K = E_K - E_0, \quad R_{K,\text{open}} = R_K - R_{K,0}.$$

$$\langle\Psi_K| = \langle\Phi|L_K e^{-T}$$

$$\langle\Phi|L_K\, R_{K'}|\Phi\rangle = \delta_{K,K'}$$

$$L_K = \delta_{K,0} + L_{K,\text{open}}, \quad L_{K,\text{open}} = L_{K,1} + L_{K,2} + \cdots$$

$$\langle\Phi|L_K \bar{H}_{N,\text{open}} = \omega_K \langle\Phi|L_K$$

For the ground $(K = 0)$ state, $|\Psi_0\rangle = e^T|\Phi\rangle$, $\langle\Psi_0| = \langle\Phi|(1 + \Lambda)e^{-T}$

$$\bar{H}_N|\Phi\rangle = \Delta E_0|\Phi\rangle, \quad \langle\Phi|(1 + \Lambda)\,\bar{H}_N = \Delta E_0\langle\Phi|(1 + \Lambda)$$

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$$\boxed{(\bar{H}_{N,\text{open}}\, R_{K,\text{open}})_C |\Phi\rangle = \omega_K R_K |\Phi\rangle} \text{ or } [\bar{H}_{N,\text{open}}, R_{K,\text{open}}]|\Phi\rangle = \omega_K R_K$$

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$$\langle\Phi| L_K\, R_{K'} |\Phi\rangle = \delta_{K,K'}$$

$$L_K = \delta_{K,0} + L_{K,\text{open}}, \quad L_{K,\text{open}} = L_{K,1} + L_{K,2} + \cdots$$

$$\langle\Phi| L_K \bar{H}_{N,\text{open}} = \omega_K \langle\Phi| L_K$$

For the ground ($K = 0$) state, $|\Psi_0\rangle = e^T|\Phi\rangle$, $\langle\Psi_0| = \langle\Phi|(1+\Lambda)e^{-T}$

$$\bar{H}_N|\Phi\rangle = \Delta E_0|\Phi\rangle, \quad \langle\Phi|(1+\Lambda)\,\bar{H}_N = \Delta E_0\langle\Phi|(1+\Lambda)$$

Properties (including density matrices)

$$|\Psi_K\rangle = R_K e^{T}|\Phi\rangle$$

$$T = T_1 + T_2 + \cdots, \quad R_K = R_{K,0} + R_{K,\text{open}}, \quad R_{K,\text{open}} = R_{K,1} + R_{K,2} + \cdots$$

$$\boxed{(\bar{H}_{N,\text{open}}\, R_{K,\text{open}})_C|\Phi\rangle = \omega_K R_K|\Phi\rangle} \text{ or } [\bar{H}_{N,\text{open}}, R_{K,\text{open}}]|\Phi\rangle = \omega_K R_K$$

$$\bar{H}_N = e^{-T} H_N e^{T} = (H_N e^{T})_C, \quad \omega_K = E_K - E_0, \quad R_{K,\text{open}} = R_K - R_{K,0}.$$

$$\langle\Psi_K| = \langle\Phi|L_K e^{-T}$$

$$\langle\Phi|L_K\, R_{K'}|\Phi\rangle = \delta_{K,K'}$$

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$$\bar{H}_N|\Phi\rangle = \Delta E_0|\Phi\rangle, \quad \langle\Phi|(1+\Lambda)\,\bar{H}_N = \Delta E_0\langle\Phi|(1+\Lambda)$$

Expectation values, transition matrix elements

$$\langle \Psi_K | \Theta | \Psi_{K'} \rangle = \langle \Phi | L_K \bar{\Theta} R_{K'} | \Phi \rangle,$$

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

1-RDMs

$$\gamma^p_q(K, K') \equiv \langle \Psi_K | a^p a_q | \Psi_{K'} \rangle = \langle \Phi | L_K \overline{a^p a_q} R_{K'} | \Phi \rangle,$$

$$\overline{a^p a_q} = e^{-T} a^p a_q \, e^{T}$$

2-RDMs

$$\gamma^{pq}_{rs}(K, K') \equiv \langle \Psi_K | a^p a^q a_s a_r | \Psi_{K'} \rangle = \langle \Phi | L_K \overline{a^p a^q a_s a_r} R_{K'} | \Phi \rangle,$$

$$\overline{a^p a^q a_s a_r} = e^{-T} (a^p a^q a_s a_r) \, e^{T}$$

For example,

$$\langle \Psi_K | \Theta | \Psi_{K'} \rangle = \theta^q_p \, \gamma^p_q(K, K'), \quad \Theta = \theta^q_p a^p a_q$$

$$\gamma_K(\mathbf{x} | \mathbf{x}') = \sum_{p,q} \gamma^q_p(K, K) [\psi_p(\mathbf{x})]^* \psi_q(\mathbf{x}')$$

SOME OF THE KEY CHALLENGES IN EOMCC

- Potential energy surfaces along bond breaking coordinates, radical and biradical electronic spectra, energy gaps in magnetic systems, electronic excitations dominated by two-electron transitions, … (generally, multi-reference problems, systems with strong non-dynamical correlations).
- Steep increase of computer costs with the system size (CPU steps and memory requirements of the leading approximations scale as N^6-N^7 and N^4, respectively, with the system size N).

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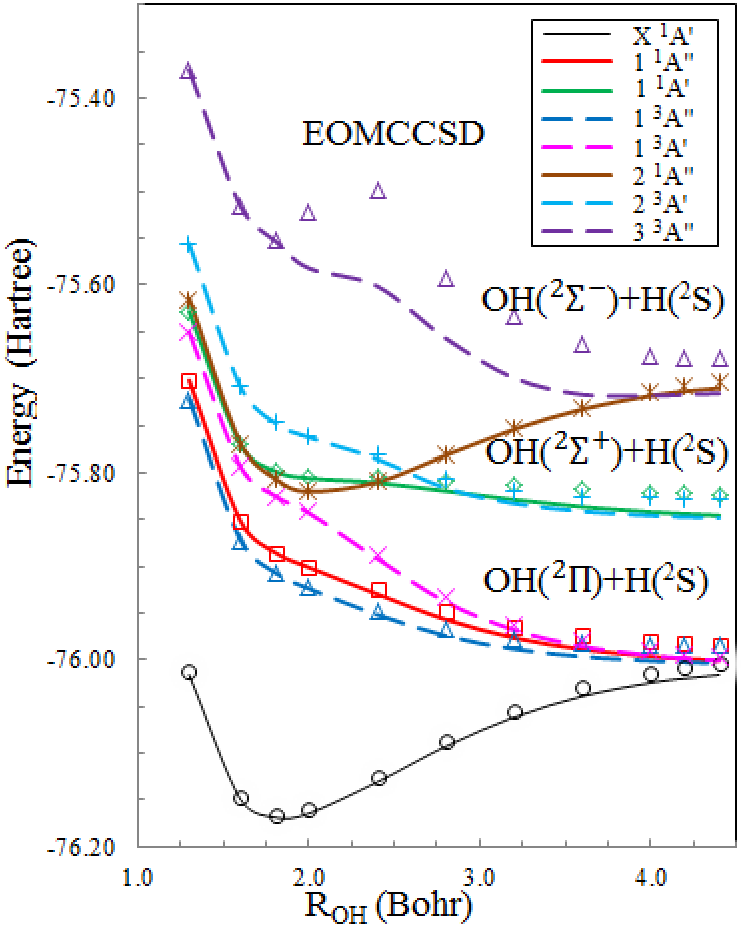
PROBLEMS WITH THE STANDARD CC/EOMCC APPROXIMATIONS

$$\left(T^{(A)} = \sum_{n=1}^{m_A} T_n,\ R^{(A)} = \sum_{n=0}^{m_A} R_{K,n},\ m_A < N\right)$$



$H_2O \rightarrow OH + H$

[J.J. Lutz and P. Piecuch, 2014]

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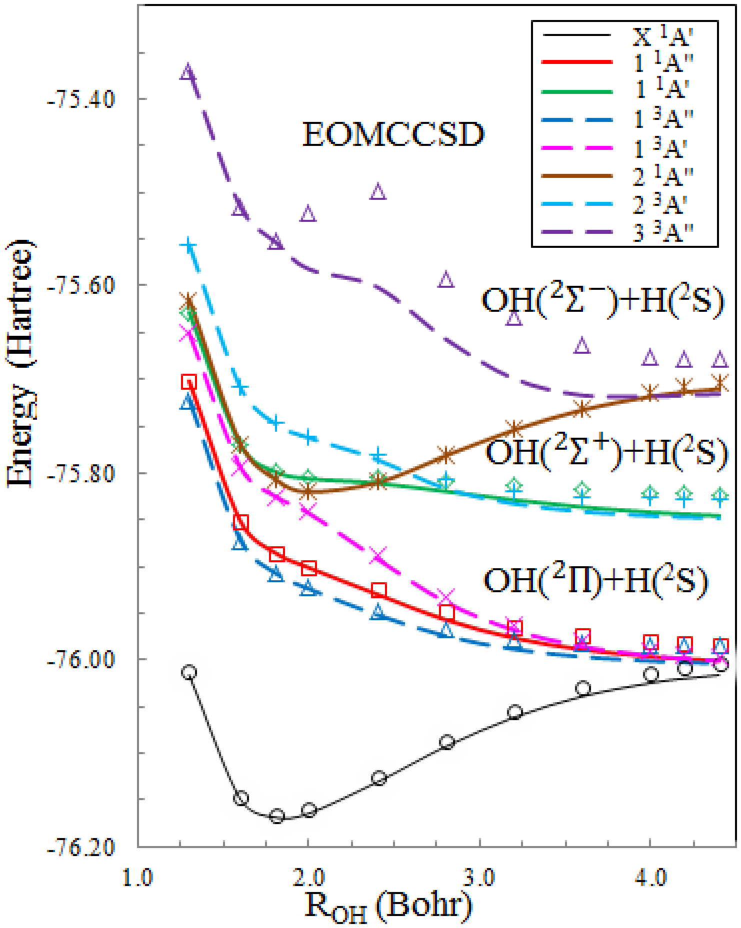

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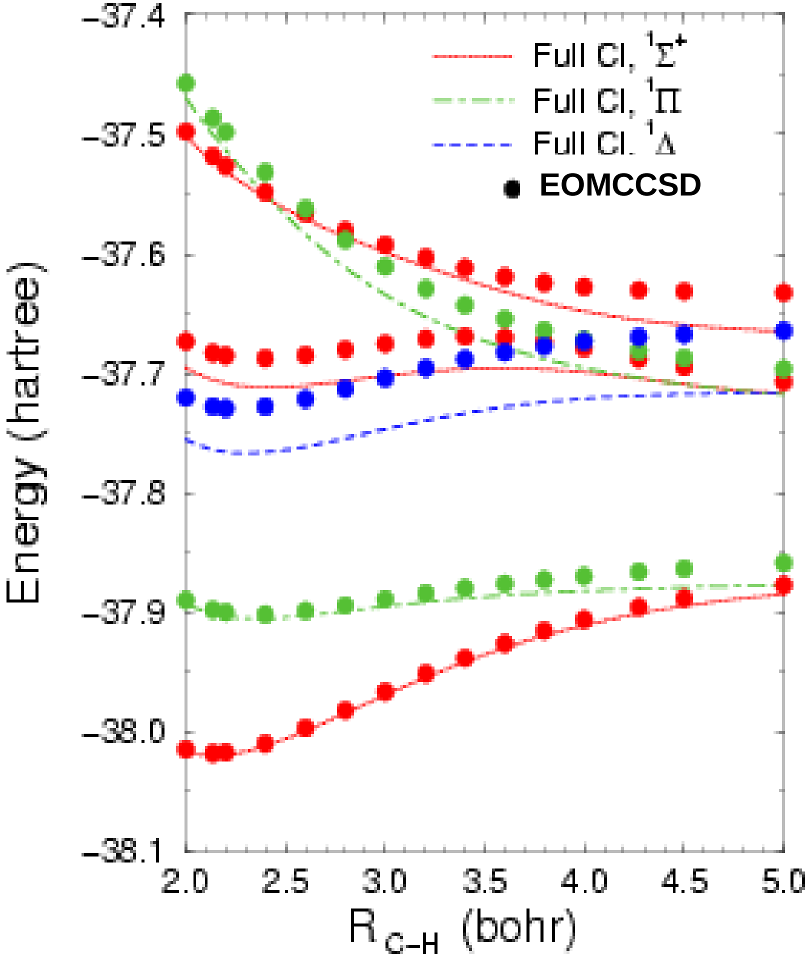

$CH^+ \rightarrow C+H^+$

[K. Kowalski and P. Piecuch, 2001]

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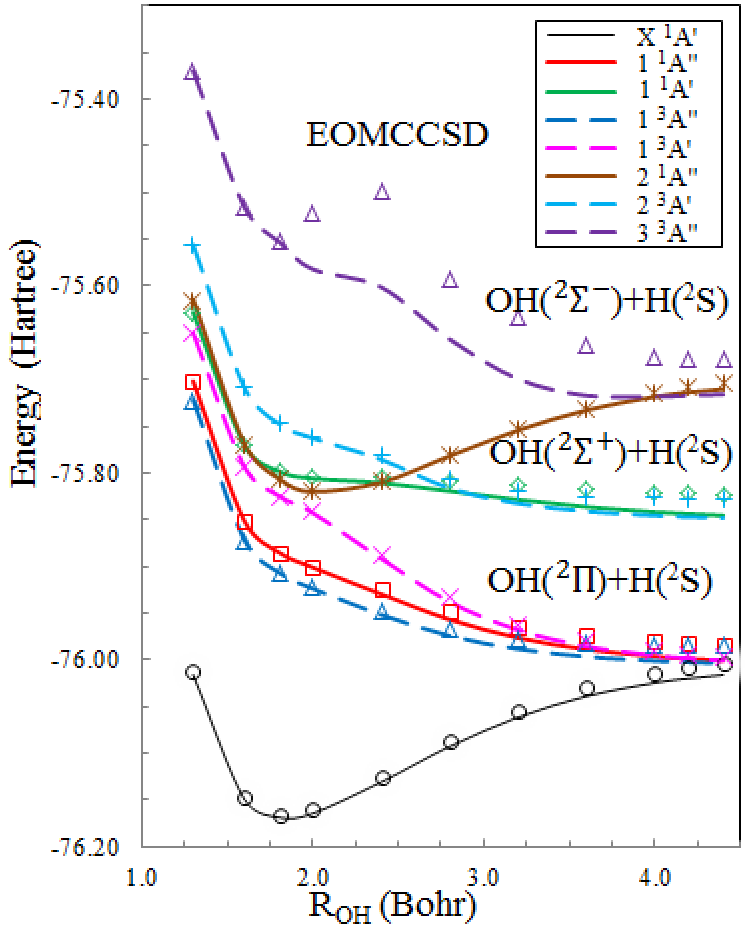

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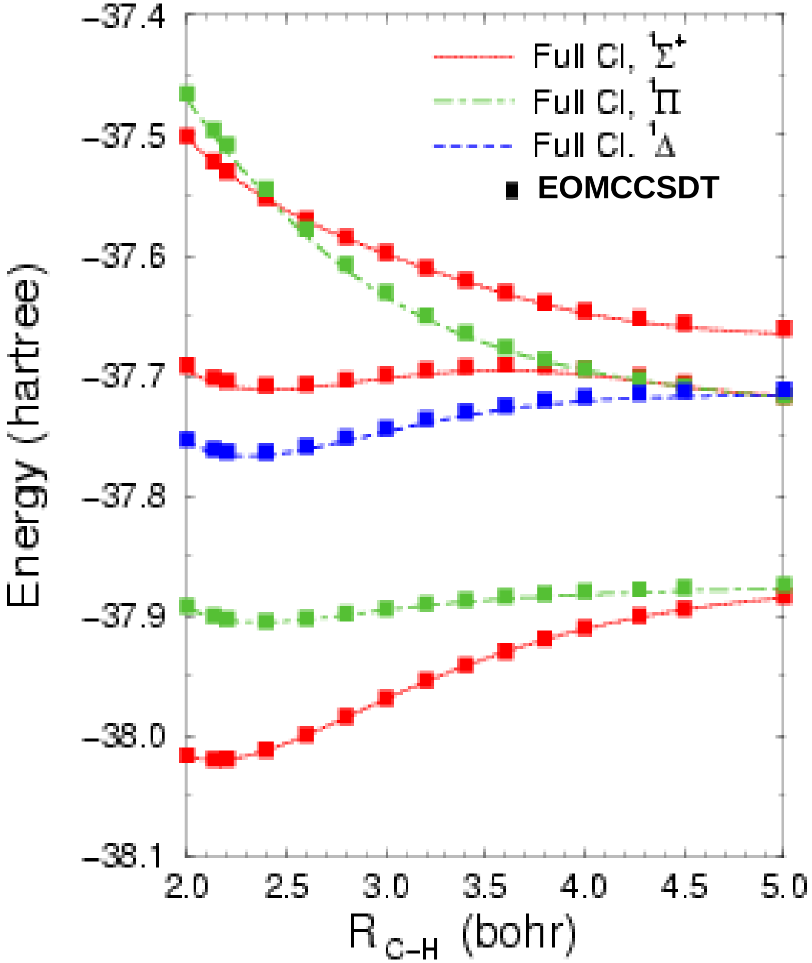

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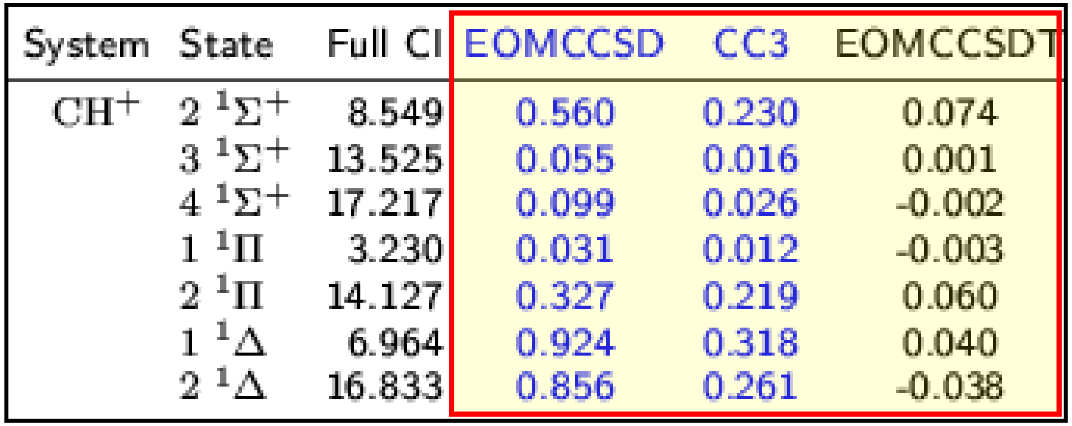
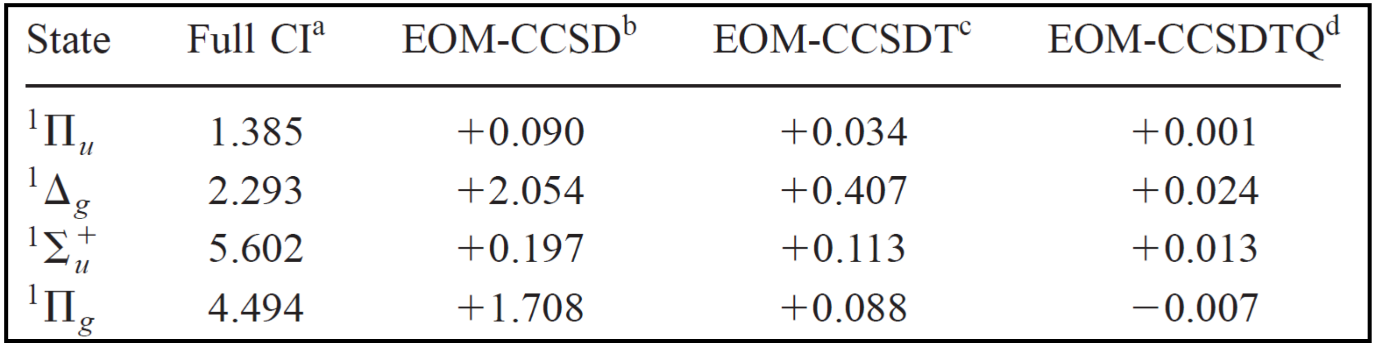
Vertical excitation energies of CH^+ (in eV) [K. Kowalski and P. Piecuch, 2001]



System	State	Full CI	EOMCCSD	CC3	EOMCCSDT
CH^+	$2\ ^1\Sigma^+$	8.549	0.560	0.230	0.074
	$3\ ^1\Sigma^+$	13.525	0.055	0.016	0.001
	$4\ ^1\Sigma^+$	17.217	0.099	0.026	-0.002
	$1\ ^1\Pi$	3.230	0.031	0.012	-0.003
	$2\ ^1\Pi$	14.127	0.327	0.219	0.060
	$1\ ^1\Delta$	6.964	0.924	0.318	0.040
	$2\ ^1\Delta$	16.833	0.856	0.261	-0.038

errors relative to full CI (eV)

Vertical excitation energies of C_2 (in eV) [K. Kowalski and P. Piecuch, 2002; S. Hirata, 2004]



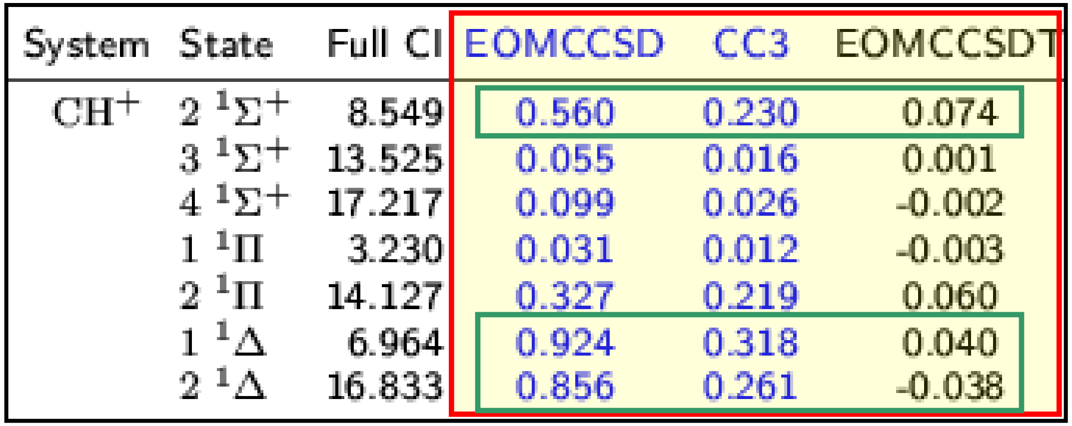
State	Full CI[a]	EOM-CCSD[b]	EOM-CCSDT[c]	EOM-CCSDTQ[d]
$^1\Pi_u$	1.385	+0.090	+0.034	+0.001
$^1\Delta_g$	2.293	+2.054	+0.407	+0.024
$^1\Sigma_u^+$	5.602	+0.197	+0.113	+0.013
$^1\Pi_g$	4.494	+1.708	+0.088	−0.007

errors relative to full CI (eV)

Adiabatic excitation energies of the CH radical (in eV) [S. Hirata, 2004]

State	EOMCCSD	EOMCCSDT	EOMCCSDTQ	Experiment
a $^4\Sigma^-$	**0.95**	**0.66**	**0.65**	**0.74**
A $^2\Delta$	**3.33**	**3.02**	**3.00**	**2.88**
B $^2\Sigma^-$	**4.41**	**3.27**	**3.27**	**3.23**
C $^2\Sigma^+$	**5.29**	**4.07**	**4.04**	**3.94**

Vertical excitation energies of CH^+ (in eV) [K. Kowalski and P. Piecuch, 2001]



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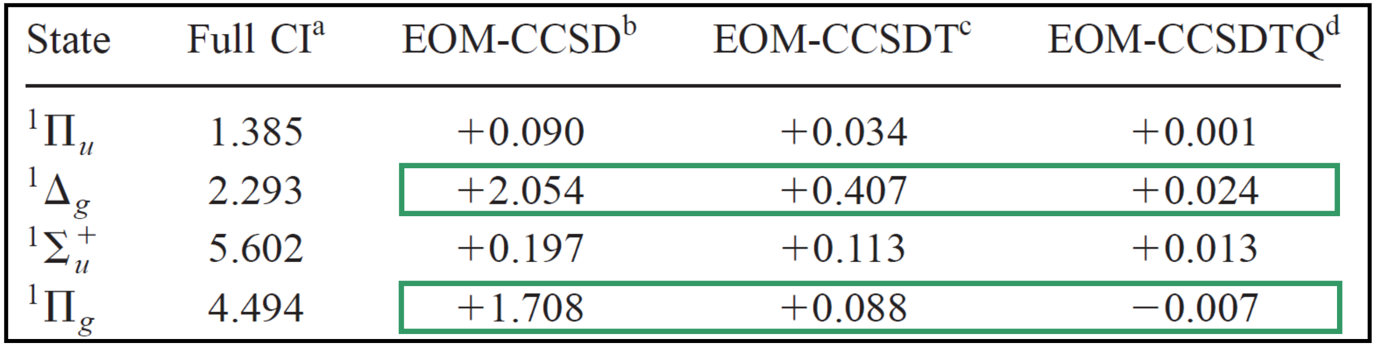

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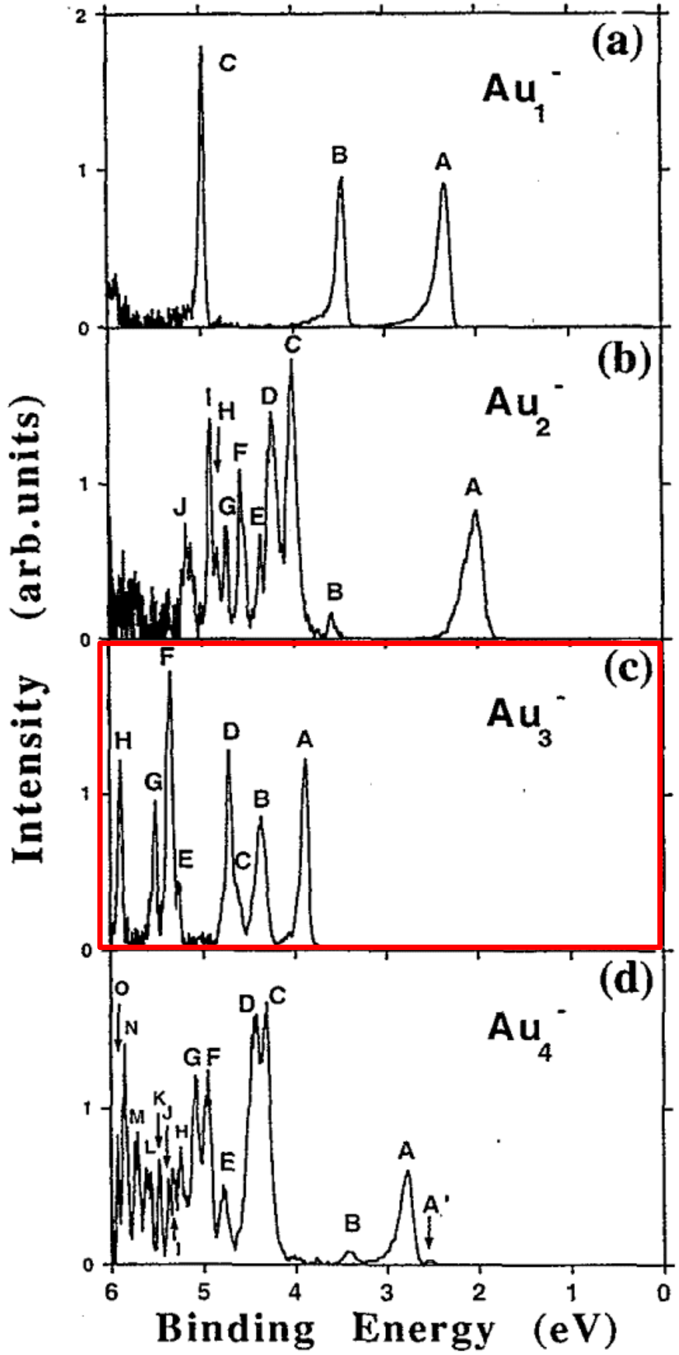
> 1 eV errors

Photoelectron Spectrum of Au_3^-



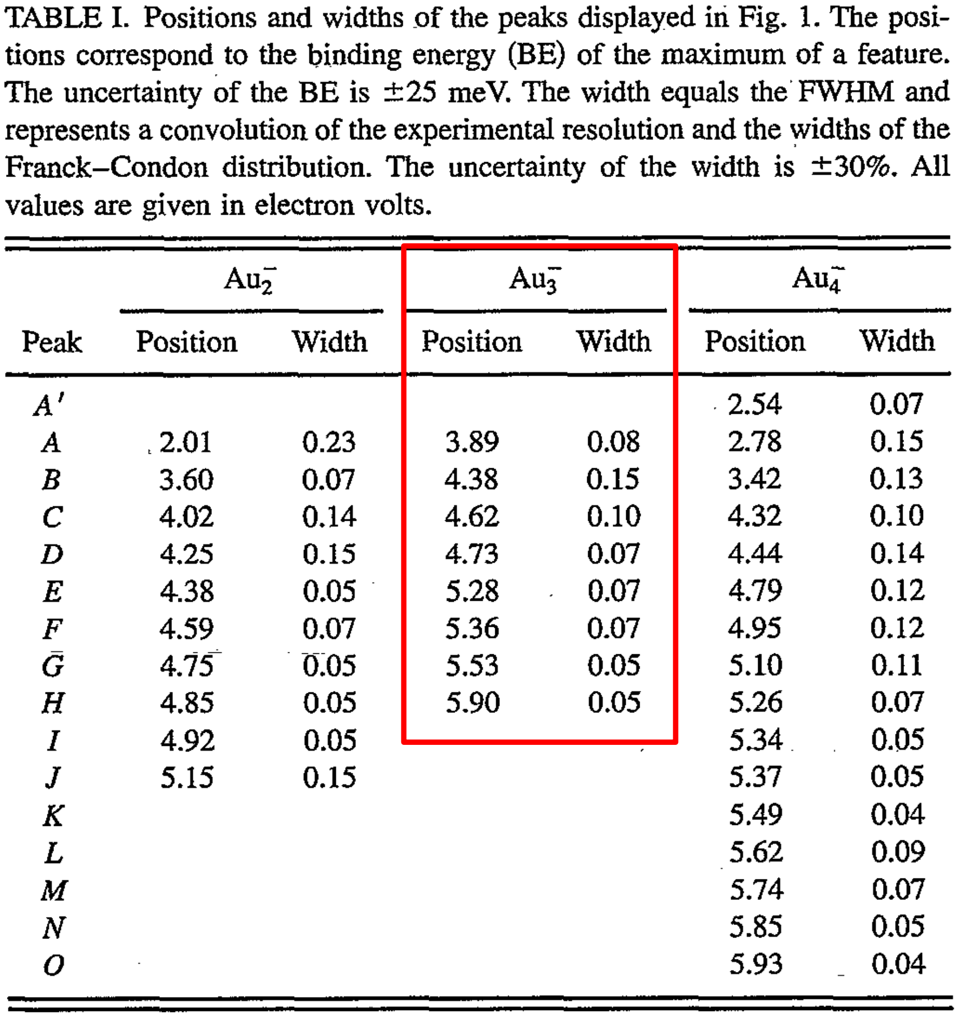
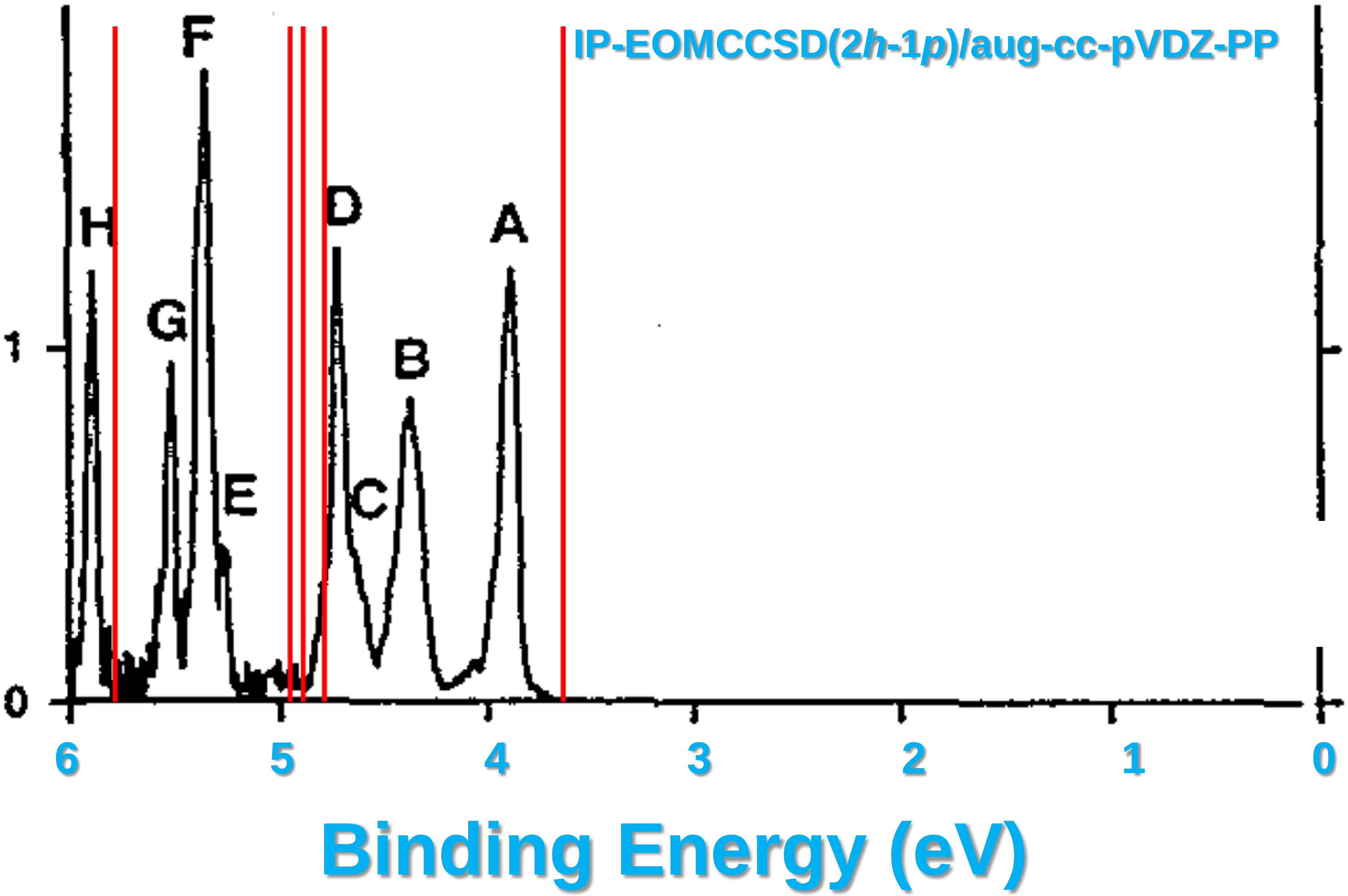


TABLE I. Positions and widths of the peaks displayed in Fig. 1. The positions correspond to the binding energy (BE) of the maximum of a feature. The uncertainty of the BE is ±25 meV. The width equals the FWHM and represents a convolution of the experimental resolution and the widths of the Franck–Condon distribution. The uncertainty of the width is ±30%. All values are given in electron volts.

	Au_2^-		Au_3^-		Au_4^-	
Peak	Position	Width	Position	Width	Position	Width
A'					2.54	0.07
A	2.01	0.23	3.89	0.08	2.78	0.15
B	3.60	0.07	4.38	0.15	3.42	0.13
C	4.02	0.14	4.62	0.10	4.32	0.10
D	4.25	0.15	4.73	0.07	4.44	0.14
E	4.38	0.05	5.28	0.07	4.79	0.12
F	4.59	0.07	5.36	0.07	4.95	0.12
G	4.75	0.05	5.53	0.05	5.10	0.11
H	4.85	0.05	5.90	0.05	5.26	0.07
I	4.92	0.05			5.34	0.05
J	5.15	0.15			5.37	0.05
K					5.49	0.04
L					5.62	0.09
M					5.74	0.07
N					5.85	0.05
O					5.93	0.04

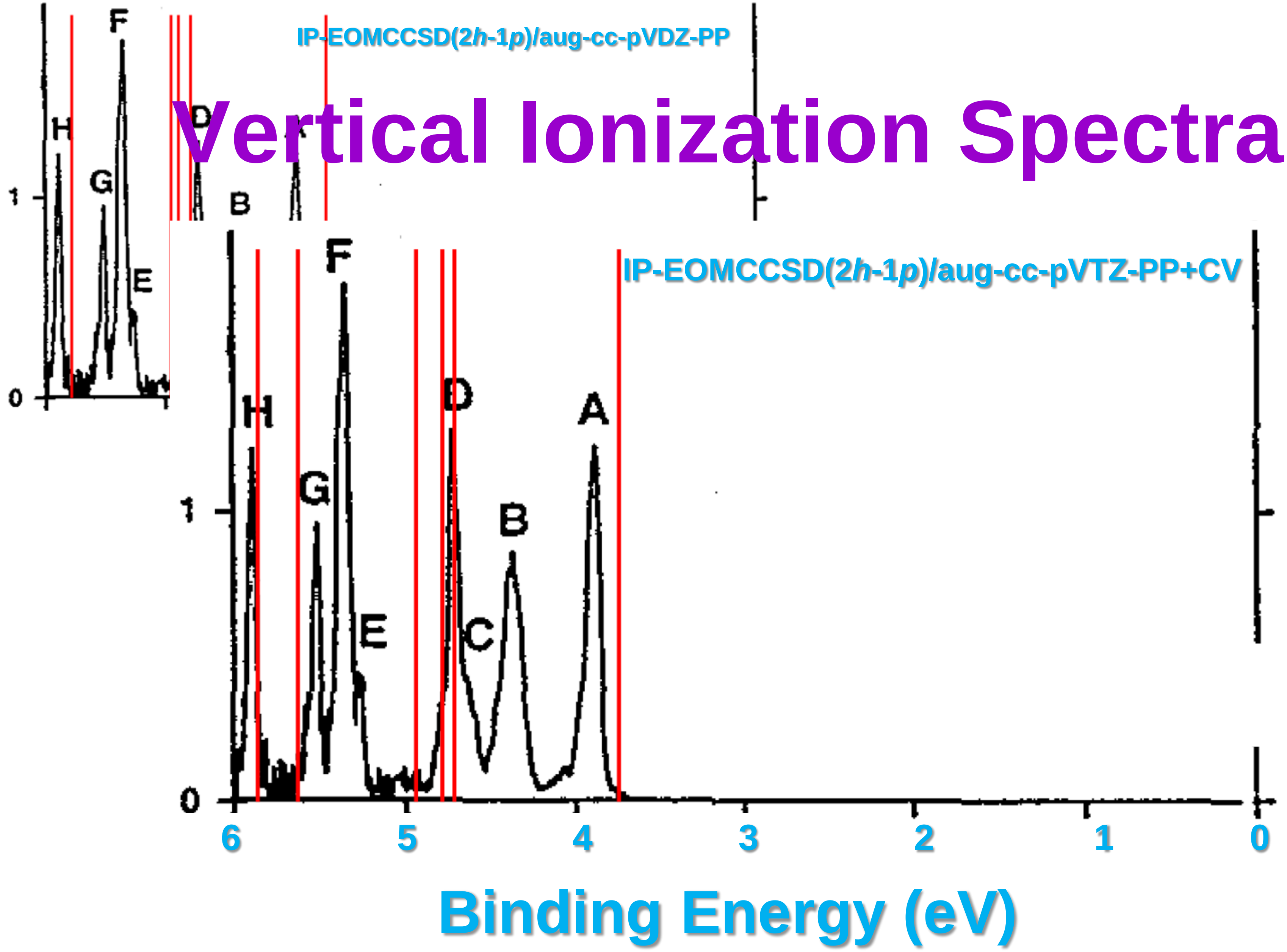
H. Handschuh, et al., *J. Chem. Phys.* **100**, 7093 (1994)

Vertical Ionization Spectra



N.P. Bauman, J.A. Hansen, M. Ehara, and P. Piecuch,
J. Chem. Phys. **141**, 101102 (2014)

Vertical Ionization Spectra



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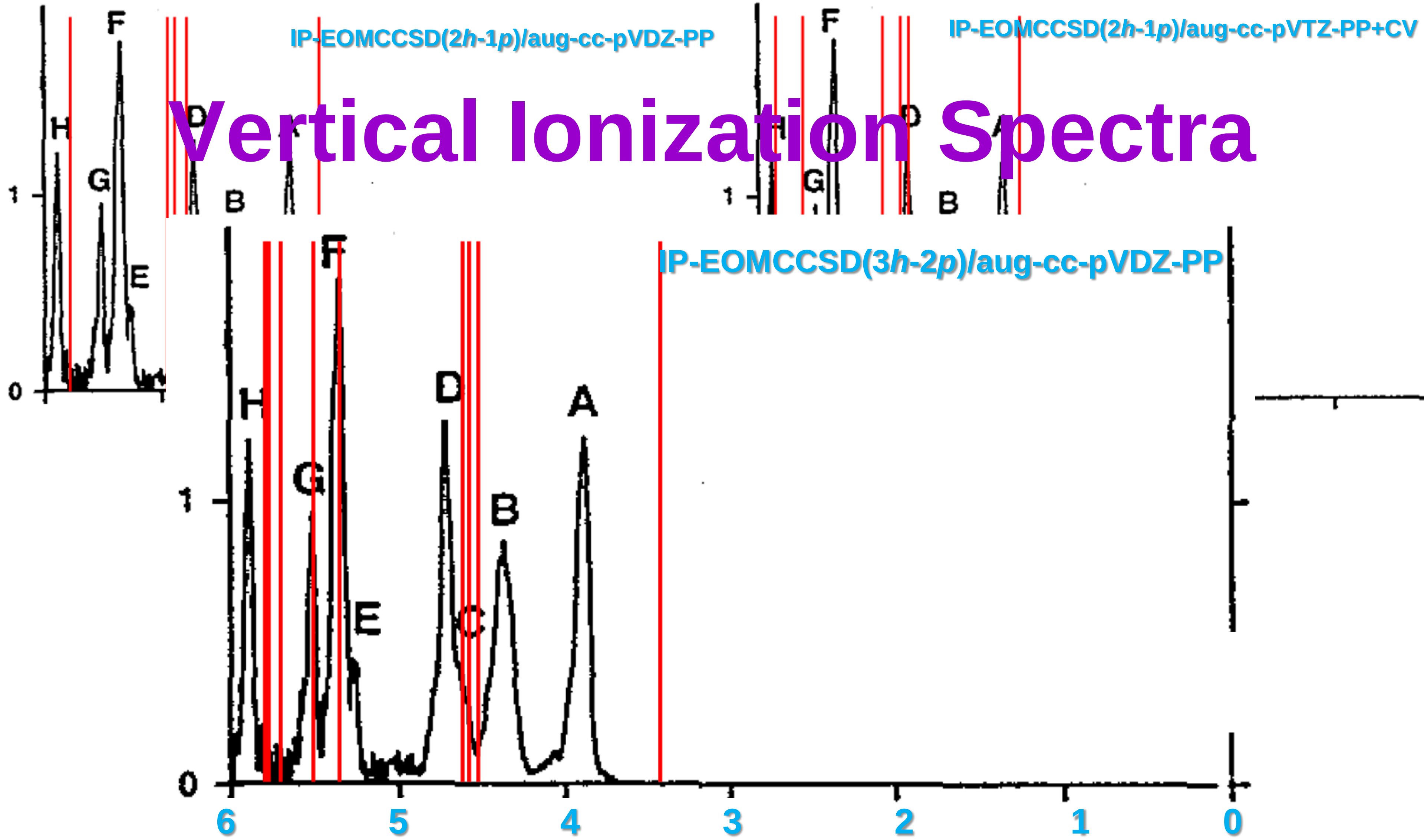
IP-EOMCCSD(2*h*-1*p*)/aug-cc-pVDZ-PP

IP-EOMCCSD(2*h*-1*p*)/aug-cc-pVTZ-PP+CV

IP-EOMCCSD(3*h*-2*p*)/aug-cc-pVDZ-PP

Binding Energy (eV)

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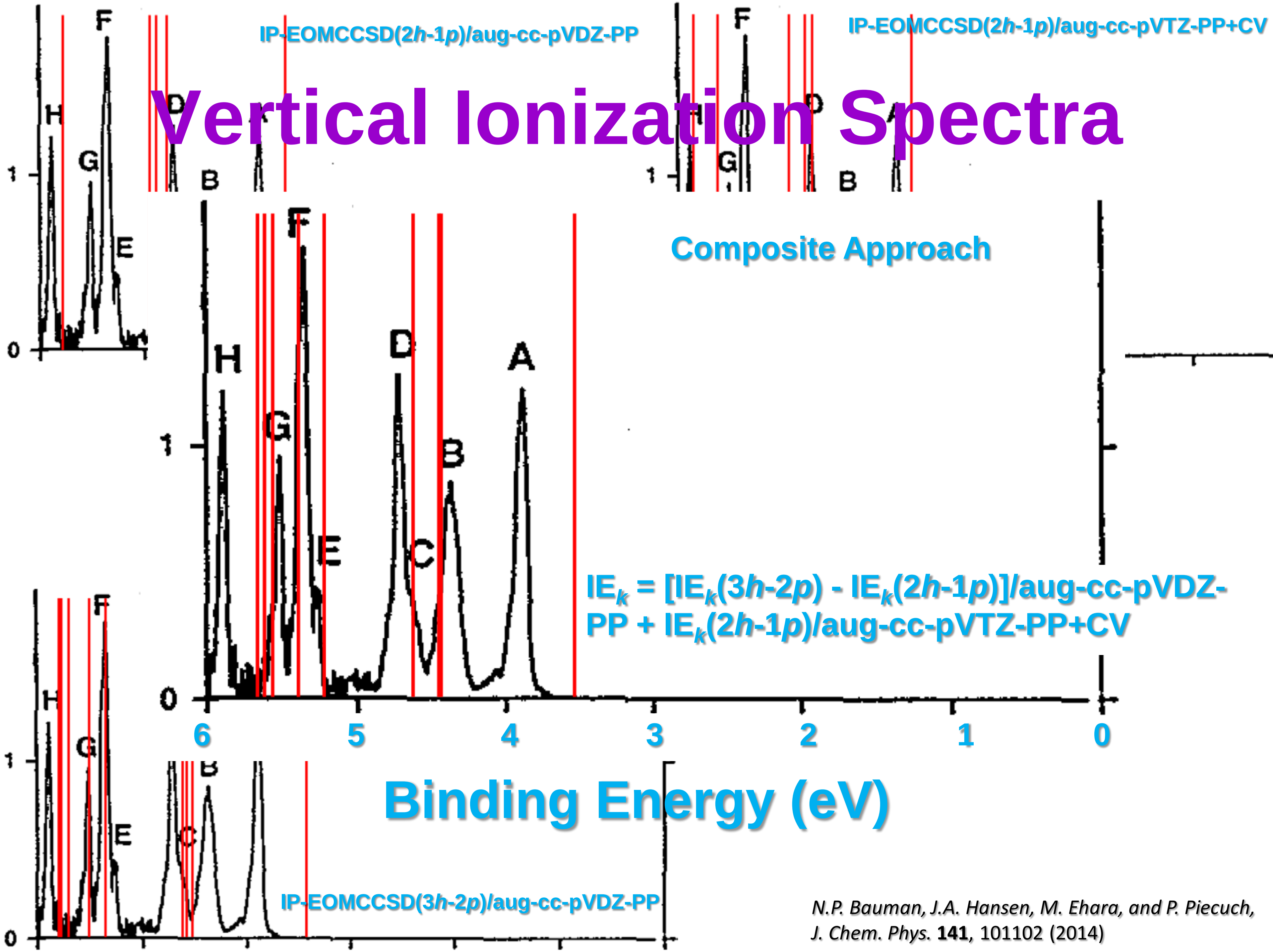
Vertical Ionization Spectra



IP-EOMCCSD(2*h*-1*p*)/aug-cc-pVDZ-PP

IP-EOMCCSD(2*h*-1*p*)/aug-cc-pVTZ-PP+CV

Composite Approach

$IE_k = [IE_k(3h\text{-}2p) - IE_k(2h\text{-}1p)]/\text{aug-cc-pVDZ-PP} + IE_k(2h\text{-}1p)/\text{aug-cc-pVTZ-PP+CV}$

IP-EOMCCSD(3*h*-2*p*)/aug-cc-pVDZ-PP

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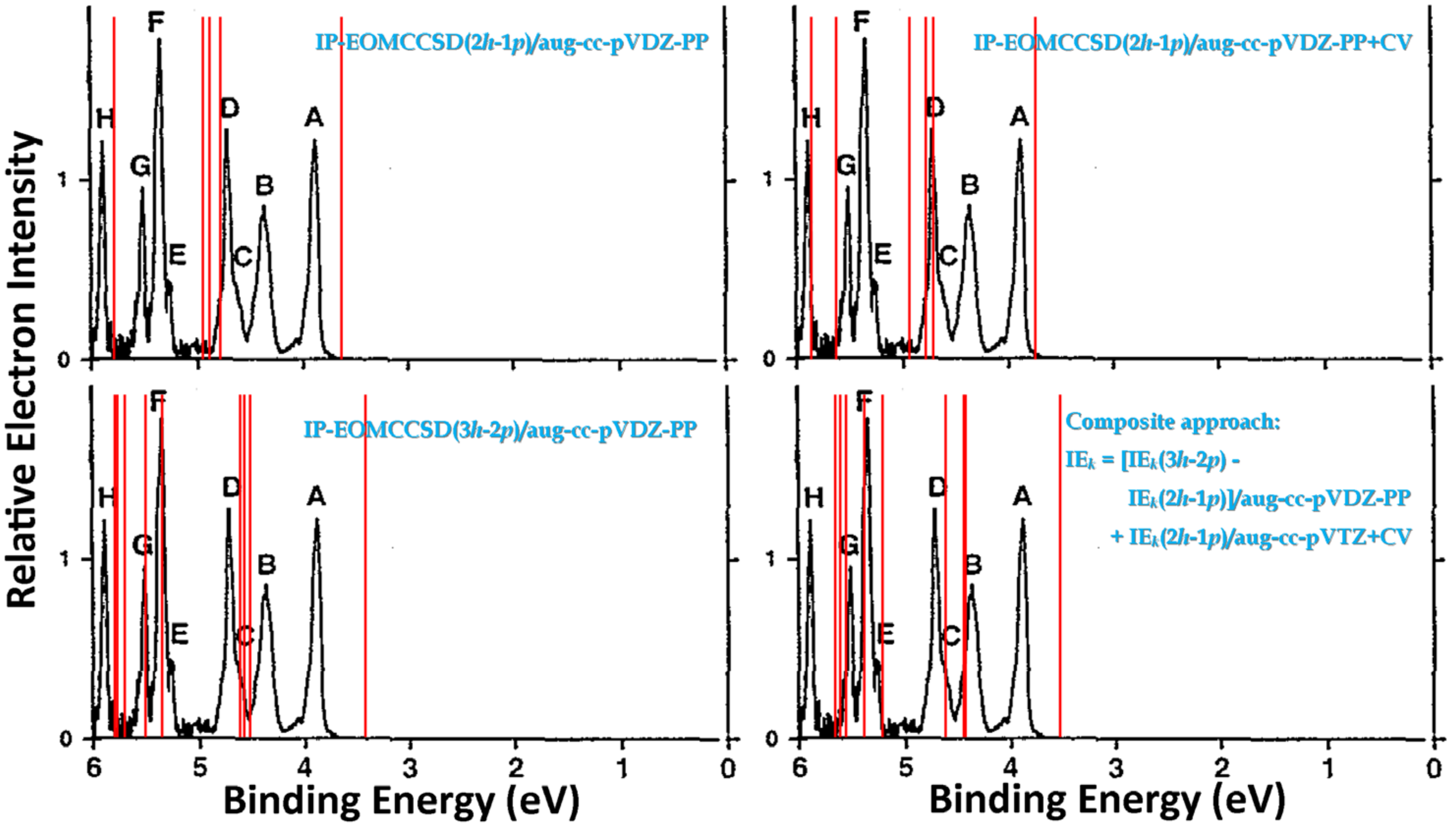

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TABLE I. Vertical[a] (V) and adiabatic[b] (Ad) IEs (in eV) of Au_3^- with respect to its ground state computed using the scalar relativistic IP-EOMCCSD(2h-1p)/aug-cc-pVxZ-PP (x = D,T), IP-EOMCCSD(2h-1p)/aug-cc-pVxZ-PP+CV (x = D,T), and IP-EOMCCSD(3h-2p)/aug-cc-pVDZ-PP approaches.

~0.1-0.2 eV

		Geometry		2h-1p		2h-1p		3h-2p		
Ionization energy	State of Au_3	$r_{Au\text{-}Au}$(Å)	θ(deg)	5d6s[c]	5s5p5d6s[d]	5d6s[c]	5s5p5d6s[d]	5d6s[c]	Extrapolated[e]	Experiment[f]
				x = D		x = T		x = D		
V	$^2\Sigma_u^+(D_{\infty h})$	2.593	180	3.621	3.683	3.670	3.735	3.427	3.541	A:3.89(0.08)
Ad	$X_0\ ^2B_1(C_{2v})$	2.725	67	3.539	3.578	3.571	3.604	3.341	3.406	
Ad	$X_1\ ^2B_1(C_{2v})$	2.575	142	3.562	3.598	3.614	3.645	3.371	3.454	
V	$^2\Sigma_g^+(D_{\infty h})$	2.593	180	4.781	4.546	4.857	4.709	4.520	4.448	B:4.38(0.15)
Ad	$^2\Sigma_g^+(D_{\infty h})$	2.500	180	4.710	4.408	4.781	4.538	4.440	4.268	
V	$^2\Pi_g(D_{\infty h})$	2.593	180	4.949	4.597	5.079	4.787	4.613	4.451	C:4.62(0.10)
Ad	$^2\Pi_g(D_{\infty h})$	2.479	180	4.812	4.413	4.895	4.562	4.509	4.259	
V	$^2\Sigma_g^+(D_{\infty h})$	2.593	180	4.883	4.853	4.982	4.932	4.577	4.626	D:4.73(0.07)
Ad	$^2\Sigma_g^+(D_{\infty h})$	2.582	180	4.878	4.860	4.969	4.938	4.583	4.643	
V	$^2\Delta_g(D_{\infty h})$	2.593	180	5.758	5.409	5.895	5.608	5.373	5.223	E:5.28(0.07)
V	$^2\Delta_u(D_{\infty h})$	2.593	180	6.001	5.658	6.140	5.856	5.551	5.406	F:5.36(0.07)
V	$^2\Pi_u(D_{\infty h})$	2.593	180	6.209	5.889	6.326	6.061	5.696	5.548	
V	$^2\Sigma_u^+(D_{\infty h})$	2.593	180	6.257	5.930	6.365	6.091	5.767	5.601	G:5.53(0.05)
V	$^2\Delta_g(D_{\infty h})$	2.593	180	6.194	5.866	6.329	6.060	5.784	5.650	
V	$^2\Pi_g(D_{\infty h})$	2.593	180	7.114	6.828	7.227	6.995	6.602	6.483	H:5.90(0.05)

[a] Vertical IEs were determined using the Au_3^- geometry, which was optimized at the scalar relativistic CCSD/aug-cc-pVDZ-PP level and resulted in a $D_{\infty h}$ structure where the distance between neighboring gold atoms, $r_{Au\text{-}Au}$, is 2.593 Å.

[b] Adiabatic IEs were calculated as the differences between the ground- and excited-state energies of Au_3 determined using the corresponding geometries that were optimized at the scalar relativistic IP-EOMCCSD(2h-1p)/aug-cc-pVDZ-PP level of theory and the ground-state energy of Au_3^- determined using the geometry optimized at the scalar relativistic CCSD/aug-cc-pVDZ-PP level (see footnote a). Each geometry is defined by the distance between the nearest-neighbor gold atoms, $r_{Au\text{-}Au}$, and the Au–Au–Au bond angle, θ.

[c] The $5d^{10}6s^1$ valence electrons of each gold atom and an additional electron due to the charge were correlated.

[d] The $5s^25p^6$ semi-core and $5d^{10}6s^1$ valence electrons of each gold atom and an additional electron due to the charge were correlated.

[e] Extrapolated using Eq. (1).

[f] The labels, positions, and, in parentheses, widths of the peaks in the photoelectron spectrum of Au_3^- were taken from Ref. 21. Except for C and E, which are shoulders of D and F, respectively, all peak positions correspond to the maxima in the photoelectron spectrum. The width of each peak is the full width at half maximum (see Ref. 21 for further details; the analogous photoelectron spectrum can also be found in Ref. 22).

N.P. Bauman, J.A. Hansen, M. Ehara, and P. Piecuch,
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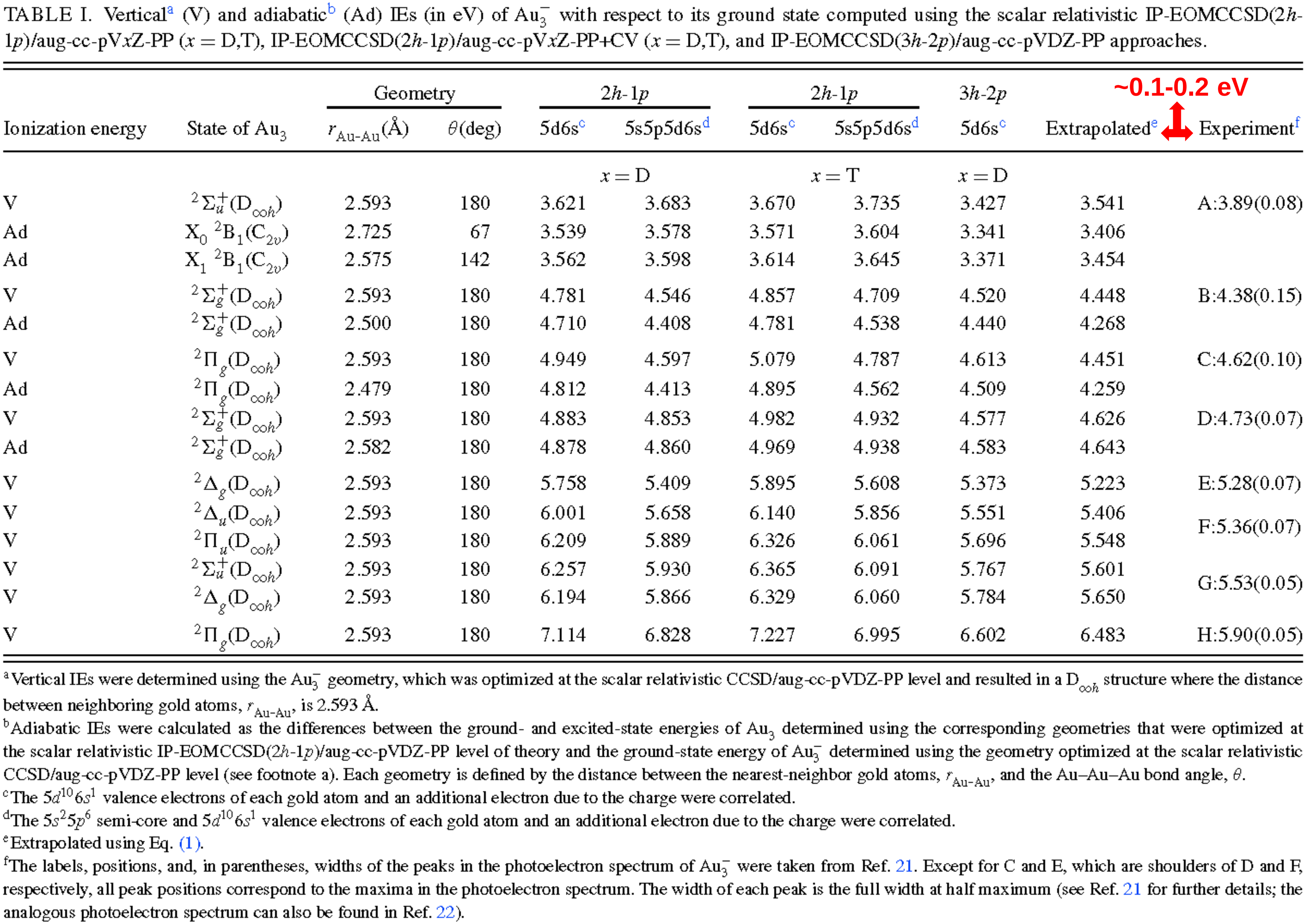

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Ionization energy	State of Au_3	Geometry $r_{Au\text{-}Au}$(Å)	Geometry θ(deg)	2h-1p 5d6s[c]	2h-1p 5s5p5d6s[d]	2h-1p 5d6s[c]	2h-1p 5s5p5d6s[d]	3h-2p 5d6s[c]	Extrapolated[e]	Experiment[f]
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V	$^2\Pi_u(D_{\infty h})$	2.593	180	6.209	5.889	6.326	6.061	5.696	5.548	
V	$^2\Sigma_u^+(D_{\infty h})$	2.593	180	6.257	5.930	6.365	6.091	5.767	5.601	G:5.53(0.05)
V	$^2\Delta_g(D_{\infty h})$	2.593	180	6.194	5.866	6.329	6.060	5.784	5.650	
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[a] Vertical IEs were determined using the Au_3^- geometry, which was optimized at the scalar relativistic CCSD/aug-cc-pVDZ-PP level and resulted in a $D_{\infty h}$ structure where the distance between neighboring gold atoms, $r_{Au\text{-}Au}$, is 2.593 Å.

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~0.1-0.2 eV

Ionization energy	State of Au_3	Geometry		$2h$-$1p$		$2h$-$1p$		$3h$-$2p$	Extrapolated[e]	Experiment[f]
		$r_{\text{Au-Au}}$(Å)	θ(deg)	5d6s[c]	5s5p5d6s[d]	5d6s[c]	5s5p5d6s[d]	5d6s[c]		
				$x = \text{D}$		$x = \text{T}$		$x = \text{D}$		
V	$^2\Sigma_u^+(D_{\infty h})$	2.593	180	3.621	3.683	3.670	3.735	3.427	3.541	A:3.89(0.08)
Ad	$X_0\ ^2B_1(C_{2v})$	2.725	67	3.539	3.578	3.571	3.604	3.341	3.406	
Ad	$X_1\ ^2B_1(C_{2v})$	2.575	142	3.562	3.598	3.614	3.645	3.371	3.454	
V	$^2\Sigma_g^+(D_{\infty h})$	2.593	180	4.781	4.546	4.857	4.709	4.520	4.448	B:4.38(0.15)
Ad	$^2\Sigma_g^+(D_{\infty h})$	2.500	180	4.710	4.408	4.781	4.538	4.440	4.268	
V	$^2\Pi_g(D_{\infty h})$	2.593	180	4.949	4.597	5.079	4.787	4.613	4.451	C:4.62(0.10)
Ad	$^2\Pi_g(D_{\infty h})$	2.479	180	4.812	4.413	4.895	4.562	4.509	4.259	
V	$^2\Sigma_g^+(D_{\infty h})$	2.593	180	4.883	4.853	4.982	4.932	4.577	4.626	D:4.73(0.07)
Ad	$^2\Sigma_g^+(D_{\infty h})$	2.582	180	4.878	4.860	4.969	4.938	4.583	4.643	
V	$^2\Delta_g(D_{\infty h})$	2.593	180	5.758	5.409	5.895	5.608	5.373	5.223	E:5.28(0.07)
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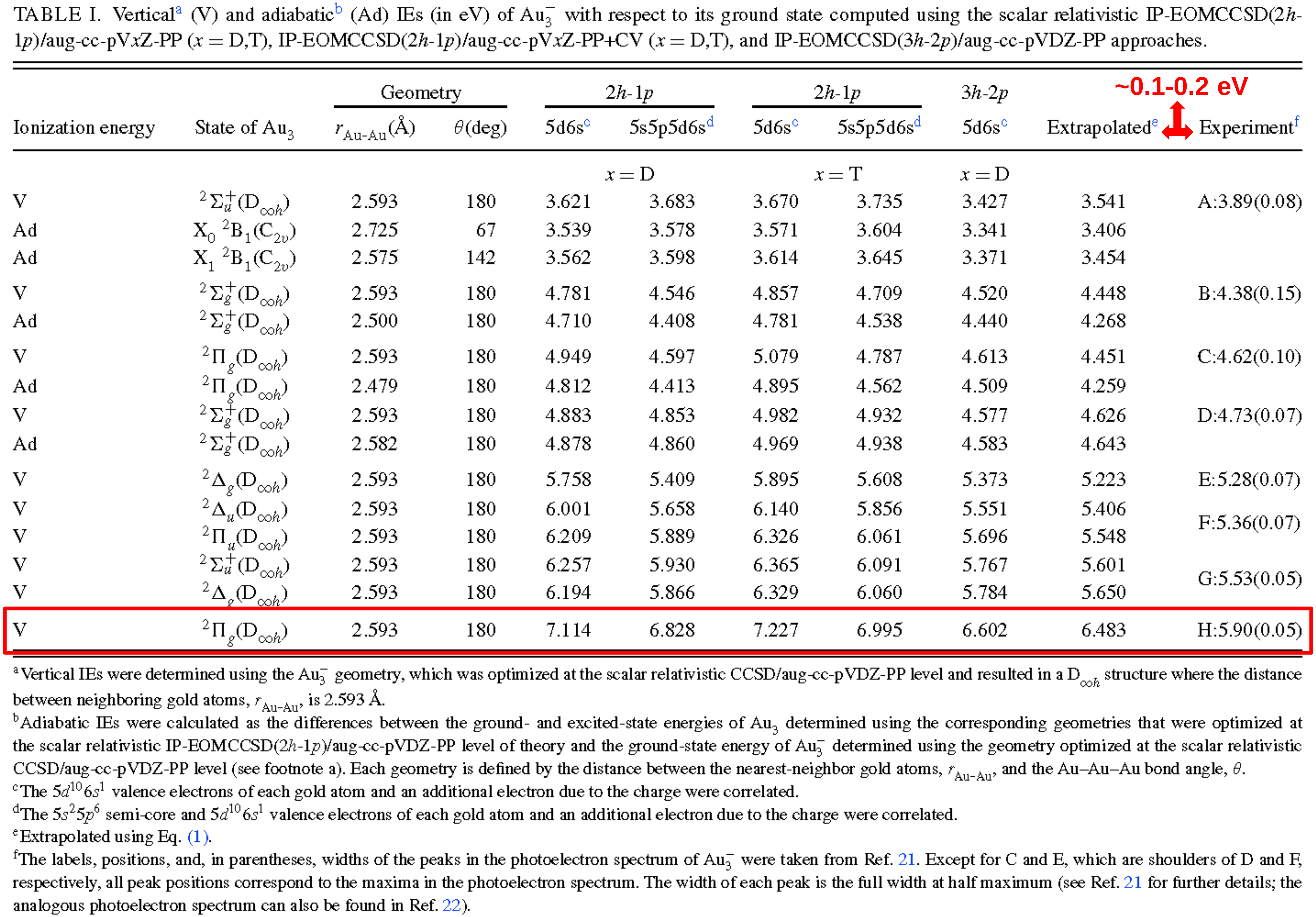

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AMONG THE SOLUTIONS WITHIN EOMCC (EXAMPLES):

Completely renormalized CC/EOMCC approaches (Piecuch et al.)

Objective: Use asymmetric energy formulas and moment expansions to capture the most relevant dynamical and non-dynamical correlations through noniterative corrections to total or excitation energies obtained in lower-order CC/EOMCC calculations , such as CCSD/EOMCCSD (CR-EOMCCSD(T), δ-CR-EOMCCSD(T), CR-EOMCC(2,3), δ-CR-EOMCC(2,3), etc.).

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Objective: Use spin-flipping excitation operators within the EOMCC framework to obtain low-spin states with larger non-dynamical correlations from the weakly correlated high-spin state.

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Objective: Use active orbitals in single-reference CC/EOMCC to incorporate the leading non-dynamical correlations through selection of higher-than-double excitations.

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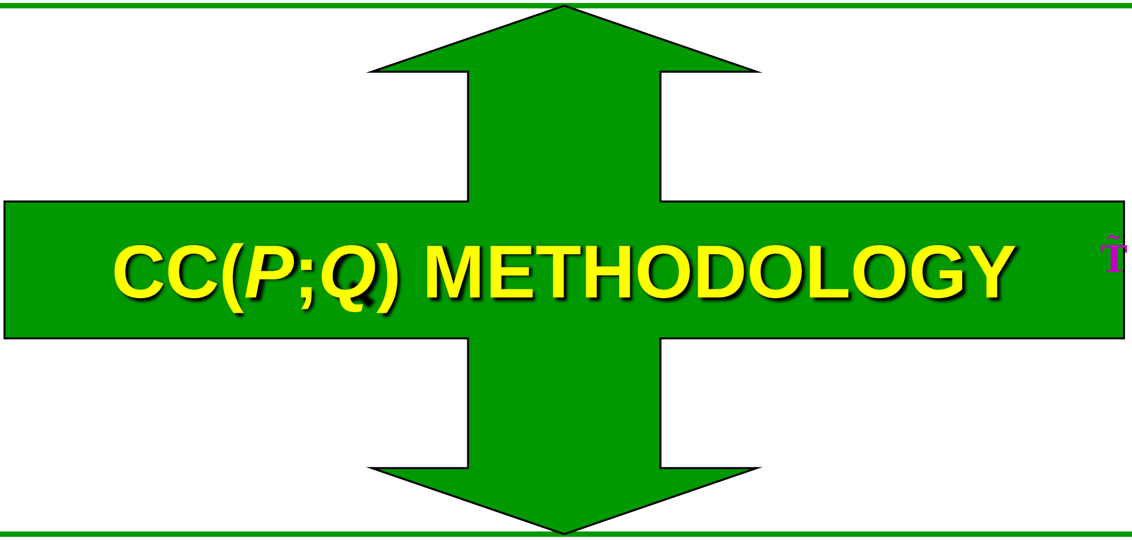

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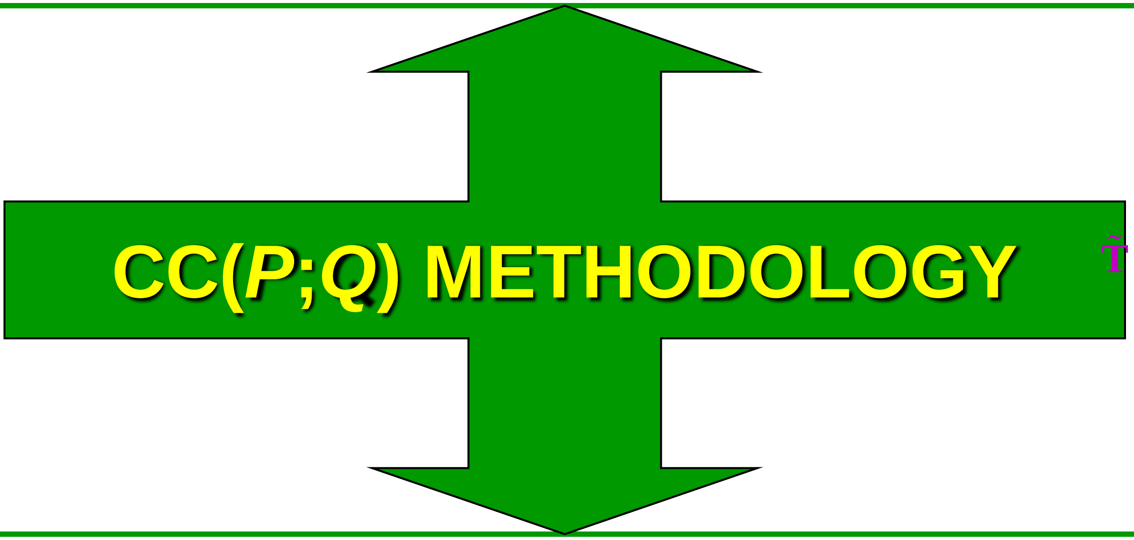

CC(*P*;*Q*) METHODOLOGY

$\tilde{T}$

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IN SEARCH FOR BLACK-BOX METHODS FOR POTENTIAL SURFACES ALONG BOND BREAKING COORDINATES AND MULTI-REFERENCE EXCITED STATES

METHOD OF MOMENTS OF COUPLED-CLUSTER EQUATIONS (MMCC) AND COMPLETELY RENORMALIZED CC/EOMCC APROACHES

Main idea:

$$\boxed{\delta_K^{(A)} = E_K - E_K^{(A)} = \Lambda[\Psi_K; \mathcal{M}_{K,i_1\ldots i_k}^{a_1\ldots a_k}(m_A),\ k > m_A]}$$

$E_K^{(A)}$ – the energy of electronic state K obtained using standard coupled-cluster calculations (e.g., CCSD or EOMCCSD)

E_K – the exact (full CI) energy of state K in a basis set

Ψ_K – the exact (full CI) wave function in a basis set

$\mathcal{M}_{K,i_1\ldots i_k}^{a_1\ldots a_k}(m_A)$ – the *generalized moments of coupled-cluster equations*

$$\boxed{E_K^{\mathrm{MMCC}} = E_K^{(A)} + \delta_K^{\mathrm{MMCC}}}$$

MMCC ENERGY FORMULA: ORIGINAL FORMULATION

(the ground-state problem: P. Piecuch and K. Kowalski, 2000; excited states: K. Kowalski and P. Piecuch, 2001)

Instead of conventional $E_0 = \langle \Phi | H \; e^{T_1 + T_2 + \cdots + T_N} | \Phi \rangle$**, use**

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$$\downarrow$$

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} \; (He^{T^{(A)}})_C | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = E_0^{(A)} + \delta_0^{(A)}$$

MMCC ENERGY FORMULA: ORIGINAL FORMULATION

(the ground-state problem: P. Piecuch and K. Kowalski, 2000; excited states: K. Kowalski and P. Piecuch, 2001)

Instead of conventional $E_0 = \langle \Phi | H \; e^{T_1 + T_2 + \cdots + T_N} | \Phi \rangle$**, use**

$$\Lambda[\Psi] = \frac{\langle \Psi | H \; e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle}$$

MMCC functional

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \cdots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0$$

exact, independent of truncation m_A defining $T^{(A)}$

$$E_0 = \frac{\langle \Psi_0 | \; e^{T^{(A)}} e^{-T^{(A)}} H \; e^{T^{(A)}} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = \frac{\langle \Psi_0 | e^{T^{(A)}} \boxed{(e^{-T^{(A)}} H e^{T^{(A)}})} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

$$\boxed{|\Phi\rangle\langle\Phi| + \sum_{n=1}^{N} \sum_{i_1 < \cdots < i_n, a_1 < \cdots a_n} |\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle\langle\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}|}$$

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} \; (H e^{T^{(A)}})_C | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = E_0^{(A)} + \delta_0^{(A)}$$

$$\langle \Phi_{i_1 \ldots i_k}^{a_1 \ldots a_k} | (H_N e^{T^{(A)}})_C | \Phi \rangle$$

$$= \mathcal{M}_{i_1 \ldots i_k}^{a_1 \ldots a_k}(m_A)$$

(moments of CC equations)

MMCC ENERGY FORMULA: BIORTHOGONAL FORMULATION

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

MMCC ENERGY FORMULA: BIORTHOGONAL FORMULATION

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$$\boxed{|\Phi\rangle\langle\Phi| + \sum_{n=1}^{N} \sum_{i_1<\cdots<i_n, a_1<\cdots<a_n} |\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\rangle\langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}|}$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}} \Big\downarrow (He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

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before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0 e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^{N} L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

MMCC ENERGY FORMULA: BIORTHOGONAL FORMULATION

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$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|H e^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}} \downarrow (He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

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exact, independent of truncation m_A defining $T^{(A)}$

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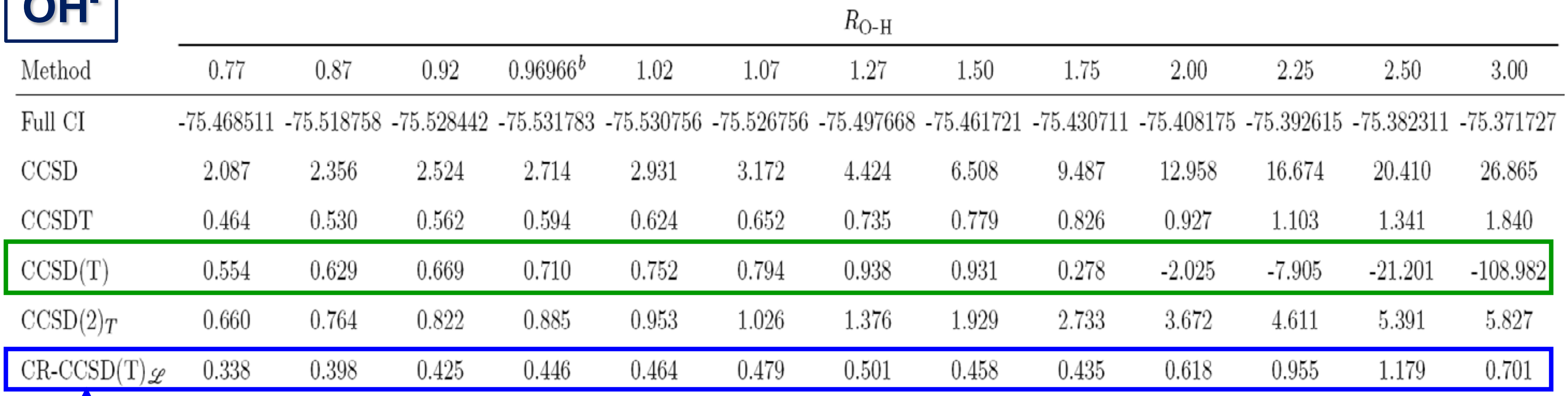
BIORTHOGONAL MMCC EXPANSION

$$\delta_0^{(A)} \equiv E_0 - E_0^{(A)} = \sum_{n=m_A+1}^{N_{0,A}} \langle\Phi|L_{0,n} M_{0,n}(m_A)|\Phi\rangle = \sum_{n=m_A+1}^{N_{0,A}} \sum_{i_1<\cdots<i_n,\, a_1<\cdots<a_n} \ell_{0,a_1\ldots a_n}^{i_1\ldots i_n} M_{0,i_1\ldots i_n}^{a_1\ldots a_n}(m_A)$$

Example: CR-CC(2,3), single-reference noniterative triples correction for bond breaking

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-CCL in GAMESS

OH^-



	$R_{\text{O-H}}$												
Method	0.77	0.87	0.92	0.96966^b	1.02	1.07	1.27	1.50	1.75	2.00	2.25	2.50	3.00
Full CI	-75.468511	-75.518758	-75.528442	-75.531783	-75.530756	-75.526756	-75.497668	-75.461721	-75.430711	-75.408175	-75.392615	-75.382311	-75.371727
CCSD	2.087	2.356	2.524	2.714	2.931	3.172	4.424	6.508	9.487	12.958	16.674	20.410	26.865
CCSDT	0.464	0.530	0.562	0.594	0.624	0.652	0.735	0.779	0.826	0.927	1.103	1.341	1.840
CCSD(T)	0.554	0.629	0.669	0.710	0.752	0.794	0.938	0.931	0.278	-2.025	-7.905	-21.201	-108.982
CCSD(2)$_T$	0.660	0.764	0.822	0.885	0.953	1.026	1.376	1.929	2.733	3.672	4.611	5.391	5.827
CR-CCSD(T)$_{\mathscr{L}}$	0.338	0.398	0.425	0.446	0.464	0.479	0.501	0.458	0.435	0.618	0.955	1.179	0.701

CR-CC(2,3)

Example: CR-CC(2,3), single-reference noniterative triples correction for bond breaking

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-CCL in GAMESS

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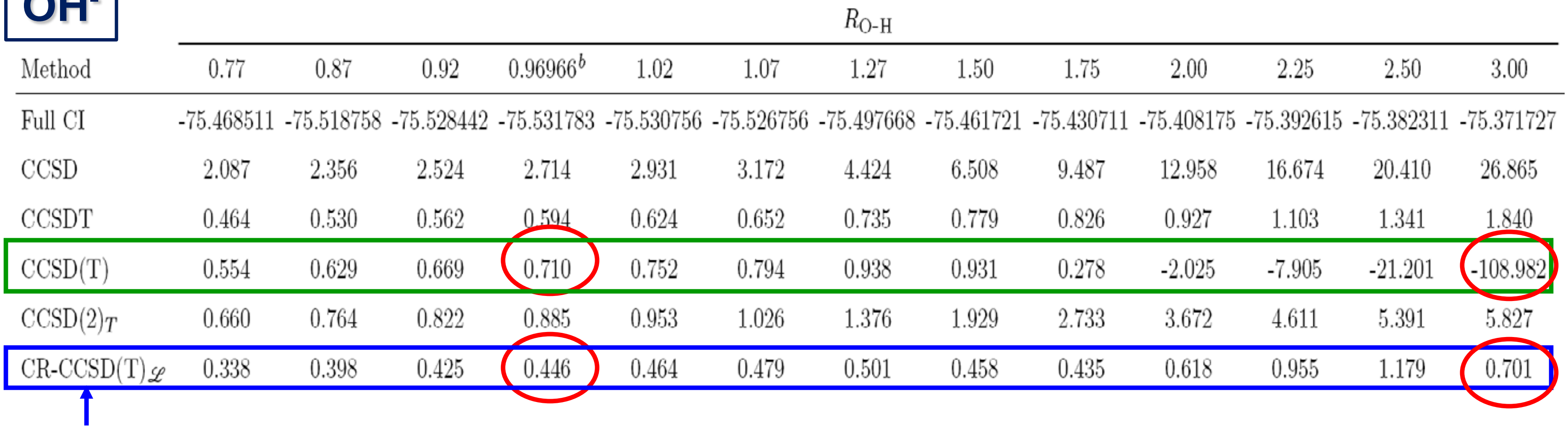

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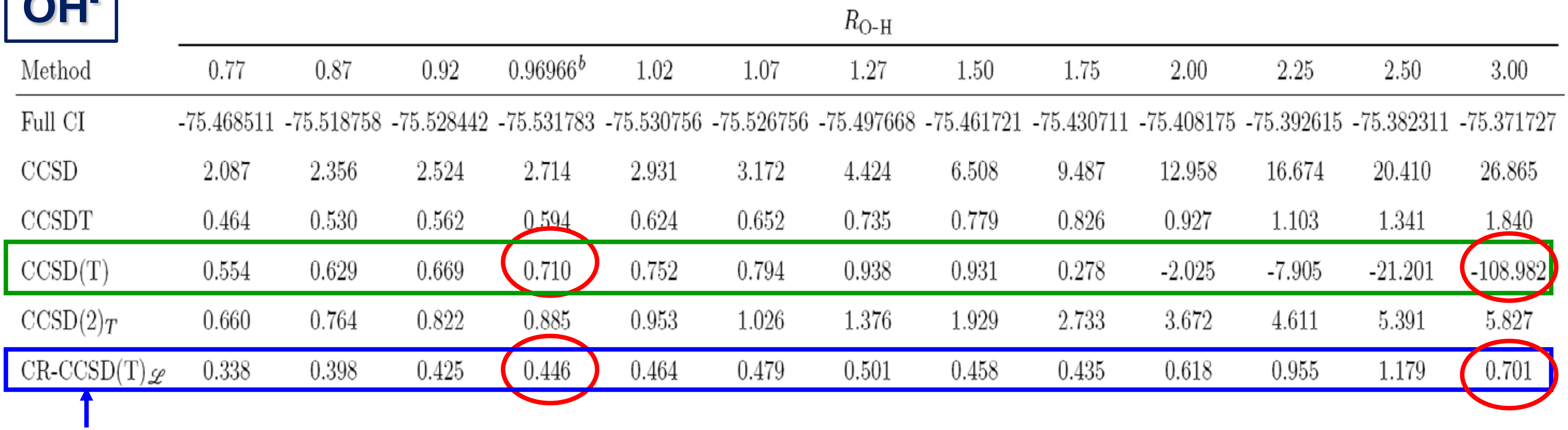

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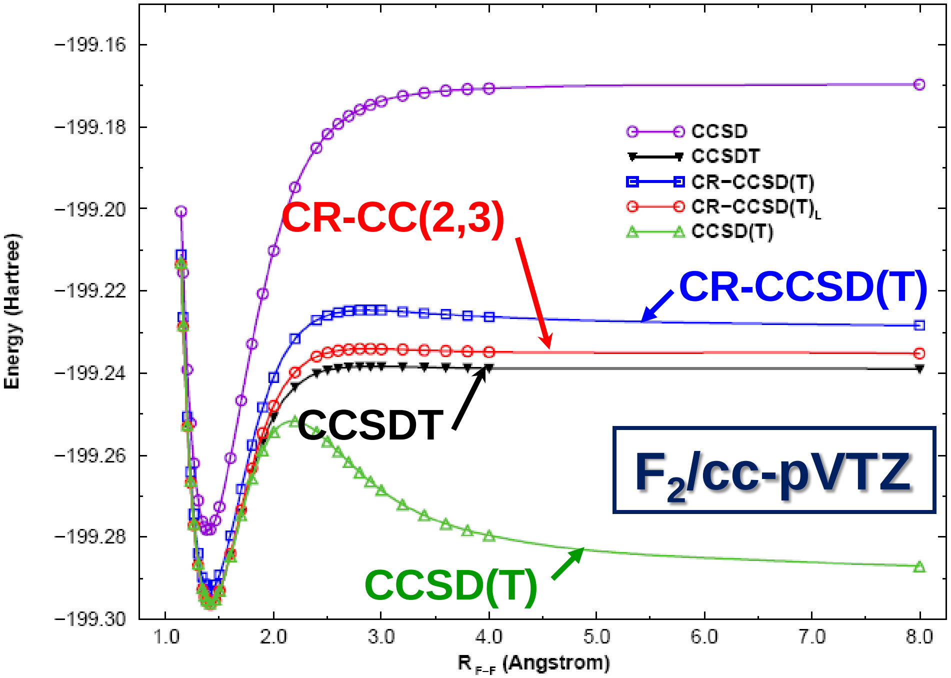
CR-CC(2,3)

Another example …



THE MMCC ENERGY FORMULA FOR GROUND AND EXCITED STATES

(original formulation; K. Kowalski and P. Piecuch, 2000, 2001, 2004; biorthogonal extension, P. Piecuch, M. Włoch, et al., 2005, 2006, 2009)

$$E_{\mu} = \langle \Psi_{\mu} | H R_{\mu}^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi_{\mu} | R_{\mu}^{(A)} e^{T^{(A)}} | \Phi \rangle$$

$$\delta_{\mu}^{(A)} \equiv E_{\mu} - E_{\mu}^{(A)}$$

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$$\boxed{\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N} \sum_{k=m_A+1}^{n} \langle \Psi_\mu | C_{n-k}(m_A)\, M_{\mu,k}(m_A) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle}$$

MMCC(2,3), MMCC(2,4), CR-EOMCCSD(T), etc.

$$M_{\mu,n}(m_A) = \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A)\, a^{a_1} \cdots a^{a_n} a_{i_n} \cdots a_{i_1}$$

$$\mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A) = \langle \Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle$$

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$$\mathfrak{M}_{\mu,a_1\ldots a_n}^{i_1\ldots i_n}(m_A) = \langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}|(\bar{H}^{(A)} R_\mu^{(A)})|\Phi\rangle$$

MMCC(2,3), MMCC(2,4), CR-EOMCCSD(T), etc.

CR-EOMCC(2,3), CR-EOMCC(2,4), etc.

$$\langle\Psi_\mu| = \langle\Phi|\mathscr{L}_\mu\, e^{-T^{(A)}}$$

$$\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N_{A,\mu}} \langle\Phi|\mathscr{L}_{\mu,n}\, M_{\mu,n}(m_A)|\Phi\rangle = \sum_{n=m_A+1}^{N_{A,\mu}} \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \ell_{\mu,i_1\ldots i_n}^{a_1\ldots a_n}\, \mathfrak{M}_{\mu,a_1\ldots a_n}^{i_1\ldots i_n}(m_A)$$

Example: CR-EOMCC(2,3), robust noniterative triples correction to EOMCCSD

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$E_\mu(2,3) = E_\mu^{(\mathrm{CCSD})} + \delta_\mu(2,3)$$

$$\delta_\mu(2,3) = \langle \Phi | \mathscr{L}_{\mu,3}(2) M_{\mu,3}(2) | \Phi \rangle \; = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}(2) \; \mathfrak{M}_{\mu,abc}^{ijk}(2)$$

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$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} (R_{\mu,0} + R_{\mu,1} + R_{\mu,2}) \middle| \Phi \right\rangle, \quad \langle \Phi | \mathscr{L}_\mu\, \overline{H}^{(\mathrm{CCSD})} = E_\mu\, \langle \Phi | \mathscr{L}_\mu$$

$$\overline{H}^{(\mathrm{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = \left(H e^{T_1 + T_2} \right)_C$$

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$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} (R_{\mu,0} + R_{\mu,1} + R_{\mu,2}) \middle| \Phi \right\rangle, \quad \langle \Phi | \mathscr{L}_\mu \, \overline{H}^{(\mathrm{CCSD})} = E_\mu \, \langle \Phi | \mathscr{L}_\mu$$

$$\overline{H}^{(\mathrm{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = \left(H e^{T_1 + T_2} \right)_C$$

$$\left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \, \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle + \sum_{l<m<n,d<e<f} \left\langle \Phi_{lmn}^{def} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \ell_{\mu,lmn}^{def}(2) = E_\mu^{(\mathrm{CCSD})} \, \ell_{\mu,ijk}^{abc}(2)$$

Example: CR-EOMCC(2,3), robust noniterative triples correction to EOMCCSD

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$E_\mu(2,3) = E_\mu^{(\mathrm{CCSD})} + \delta_\mu(2,3)$$

$$\delta_\mu(2,3) = \langle \Phi | \mathscr{L}_{\mu,3}(2) M_{\mu,3}(2) | \Phi \rangle = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}(2)\; \mathfrak{M}_{\mu,abc}^{ijk}(2)$$

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} \left(R_{\mu,0} + R_{\mu,1} + R_{\mu,2} \right) \middle| \Phi \right\rangle , \quad \langle \Phi | \mathscr{L}_\mu \; \overline{H}^{(\mathrm{CCSD})} = E_\mu \; \langle \Phi | \mathscr{L}_\mu$$

$$\overline{H}^{(\mathrm{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = \left(H e^{T_1 + T_2} \right)_C$$

$$\left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \; \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle + \sum_{l<m<n,d<e<f} \left\langle \Phi_{lmn}^{def} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \ell_{\mu,lmn}^{def}(2) = E_\mu^{(\mathrm{CCSD})} \; \ell_{\mu,ijk}^{abc}(2)$$

$$\ell_{\mu,ijk}^{abc}(2) = \left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \Big/ D_{\mu,abc}^{ijk}(2)$$

Example: CR-EOMCC(2,3), robust noniterative triples correction to EOMCCSD

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$E_\mu(2,3) = E_\mu^{(\mathrm{CCSD})} + \delta_\mu(2,3)$$

$$\delta_\mu(2,3) = \langle \Phi | \mathscr{L}_{\mu,3}(2) M_{\mu,3}(2) | \Phi \rangle = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}(2)\ \mathfrak{M}_{\mu,abc}^{ijk}(2)$$

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} \left(R_{\mu,0} + R_{\mu,1} + R_{\mu,2} \right) \middle| \Phi \right\rangle, \quad \langle \Phi | \mathscr{L}_\mu\ \overline{H}^{(\mathrm{CCSD})} = E_\mu\ \langle \Phi | \mathscr{L}_\mu$$

$$\overline{H}^{(\mathrm{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = \left(H e^{T_1 + T_2} \right)_C$$

$$\left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})}\ \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle + \sum_{l<m<n,d<e<f} \left\langle \Phi_{lmn}^{def} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \ell_{\mu,lmn}^{def}(2) = E_\mu^{(\mathrm{CCSD})}\ \ell_{\mu,ijk}^{abc}(2)$$

$$\ell_{\mu,ijk}^{abc}(2) = \left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \Big/ D_{\mu,abc}^{ijk}(2)$$

$$D_{\mu,abc}^{ijk}(2) = E_\mu^{(\mathrm{CCSD})} - \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \longrightarrow$$

CR-EOMCC(2,3),D

Example: CR-EOMCC(2,3), robust noniterative triples correction to EOMCCSD

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$\boxed{\begin{gathered} E_\mu(2,3) = E_\mu^{(\mathrm{CCSD})} + \delta_\mu(2,3) \\ \delta_\mu(2,3) = \langle \Phi | \mathscr{L}_{\mu,3}(2) M_{\mu,3}(2) | \Phi \rangle = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}(2)\, \mathfrak{M}_{\mu,abc}^{ijk}(2) \end{gathered}}$$

$$\mathfrak{M}_{\mu,abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} \left(R_{\mu,0} + R_{\mu,1} + R_{\mu,2}\right) \middle| \Phi \right\rangle , \quad \langle \Phi | \mathscr{L}_\mu \, \overline{H}^{(\mathrm{CCSD})} = E_\mu \, \langle \Phi | \mathscr{L}_\mu$$

$$\overline{H}^{(\mathrm{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = \left(H e^{T_1 + T_2} \right)_C$$

$$\left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \, \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle + \sum_{l<m<n,d<e<f} \left\langle \Phi_{lmn}^{def} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \ell_{\mu,lmn}^{def}(2) = E_\mu^{(\mathrm{CCSD})} \, \ell_{\mu,ijk}^{abc}(2)$$

$$\ell_{\mu,ijk}^{abc}(2) = \left\langle \Phi \middle| L_\mu^{(\mathrm{CCSD})} \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \Big/ D_{\mu,abc}^{ijk}(2)$$

$$D_{\mu,abc}^{ijk}(2) = E_\mu^{(\mathrm{CCSD})} - \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(\mathrm{CCSD})} \middle| \Phi_{ijk}^{abc} \right\rangle \longrightarrow \textbf{CR-EOMCC(2,3),D}$$

$$\downarrow$$

$$[\omega_\mu^{(\mathrm{CCSD})} - (\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k)]$$

$$\downarrow$$

CR-EOMCC(2,3),A = EOMCC(2)PT(2) of Hirata et al.

δ-CR-EOMCC(2,3): robust triples correction to EOMCCSD, which is size extensive in the ground state and size intensive for excitation energies

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$\omega_\mu^{(\text{CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu + \beta_\mu$$

$$\alpha_\mu = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2)$$

$$\beta_\mu = \sum_{i<j<k,a<b<c} \left(r_{\mu,0}\, \ell_{\mu,ijk}^{abc} - \ell_{0,ijk}^{abc} \right) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$$

δ-CR-EOMCC(2,3): robust triples correction to EOMCCSD, which is size extensive in the ground state and size intensive for excitation energies

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$\omega_\mu^{(\text{CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu + \beta_\mu$$

$$\alpha_\mu = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) \quad \longleftarrow \quad \textbf{size intensive}$$

$$\beta_\mu = \sum_{i<j<k,a<b<c} \left(r_{\mu,0}\, \ell_{\mu,ijk}^{abc} - \ell_{0,ijk}^{abc} \right) \mathfrak{M}_{0,abc}^{ijk}(2) \longleftarrow \textbf{size extensive}$$

$$\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$$

δ-CR-EOMCC(2,3): robust triples correction to EOMCCSD, which is size extensive in the ground state and size intensive for excitation energies

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$\omega_\mu^{(\text{CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu + \cancel{\beta_\mu}$$

$$\alpha_\mu = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2)$$

size intensive

$$\beta_\mu = \sum_{i<j<k,a<b<c} \left(r_{\mu,0}\, \ell_{\mu,ijk}^{abc} - \ell_{0,ijk}^{abc} \right) \mathfrak{M}_{0,abc}^{ijk}(2)$$

size extensive

$$\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$$

$$\omega_\mu^{(\delta\text{-CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu$$

$$\begin{aligned} E_\mu &= E_0^{(\text{CR-CC}(2,3))} + \omega_\mu^{(\delta\text{-CR-EOMCC}(2,3))} \\ &= E_\mu^{(\text{CCSD})} + \sum_{i<j<k,a<b<c} \ell_{0,ijk}^{abc}\, \mathfrak{M}_{0,abc}^{ijk}(2) + \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) \end{aligned}$$

δ-CR-EOMCC(2,3): robust triples correction to EOMCCSD, which is size extensive in the ground state and size intensive for excitation energies

iterative $n_o^2 n_u^4$ (N^6) + noniterative $n_o^3 n_u^4$ (N^7); CCTYP=CR-EOML in GAMESS

$$\omega_\mu^{(\text{CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu + \cancel{\beta_\mu}$$

$$\alpha_\mu = \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) \longleftarrow$$

size intensive

$$\beta_\mu = \sum_{i<j<k,a<b<c} \left(r_{\mu,0}\, \ell_{\mu,ijk}^{abc} - \ell_{0,ijk}^{abc} \right) \mathfrak{M}_{0,abc}^{ijk}(2) \longleftarrow$$

size extensive

$$\tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$$

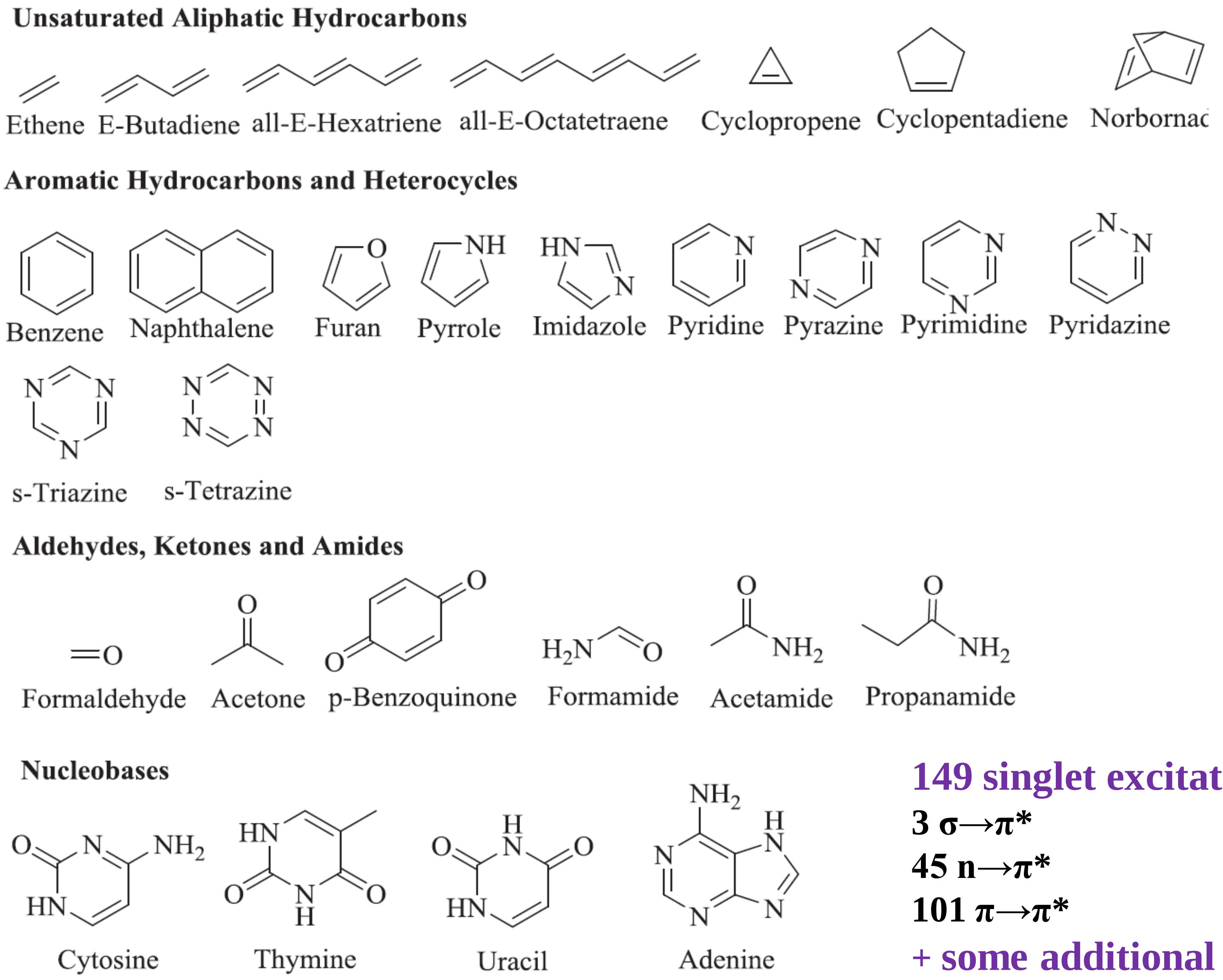
$$\omega_\mu^{(\delta\text{-CR-EOMCC}(2,3))} = \omega_\mu^{(\text{CCSD})} + \alpha_\mu$$

$$\begin{aligned} E_\mu &= E_0^{(\text{CR-CC}(2,3))} + \omega_\mu^{(\delta\text{-CR-EOMCC}(2,3))} \\ &= E_\mu^{(\text{CCSD})} + \sum_{i<j<k,a<b<c} \ell_{0,ijk}^{abc} \mathfrak{M}_{0,abc}^{ijk}(2) + \sum_{i<j<k,a<b<c} \ell_{\mu,ijk}^{abc}\, \tilde{\mathfrak{M}}_{\mu,abc}^{ijk}(2) \end{aligned}$$

δ-CR-EOMCC(2,3),A = EOMCCSD($\tilde{T}$) or Watts and Bartlett for excitation energies and EOMCCSD(2)$_T$ of Hirata et al. for total energies

Benchmark Molecules

[W. Thiel et al.]



149 singlet excitations

3 $\sigma \rightarrow \pi^*$

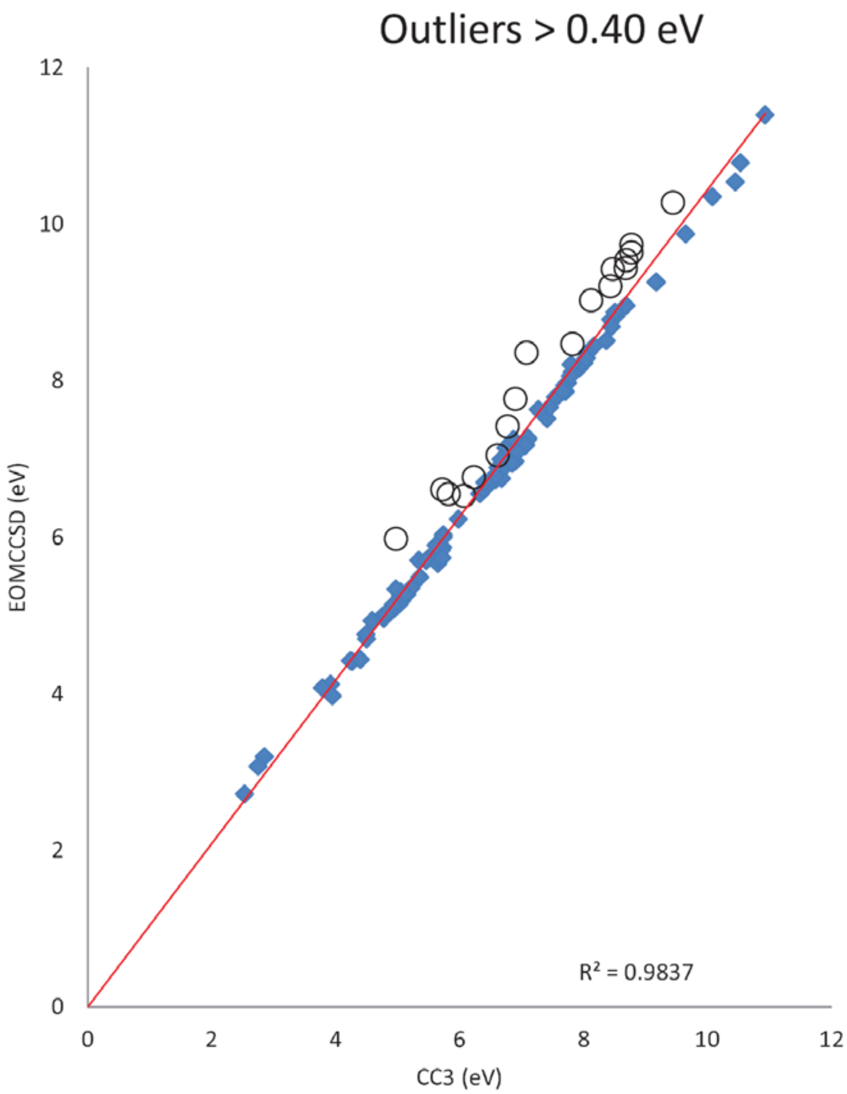
45 $n \rightarrow \pi^*$

101 $\pi \rightarrow \pi^*$

+ some additional states

EOMCCSD (iterative N^6) vs CC3 (iterative N^7)

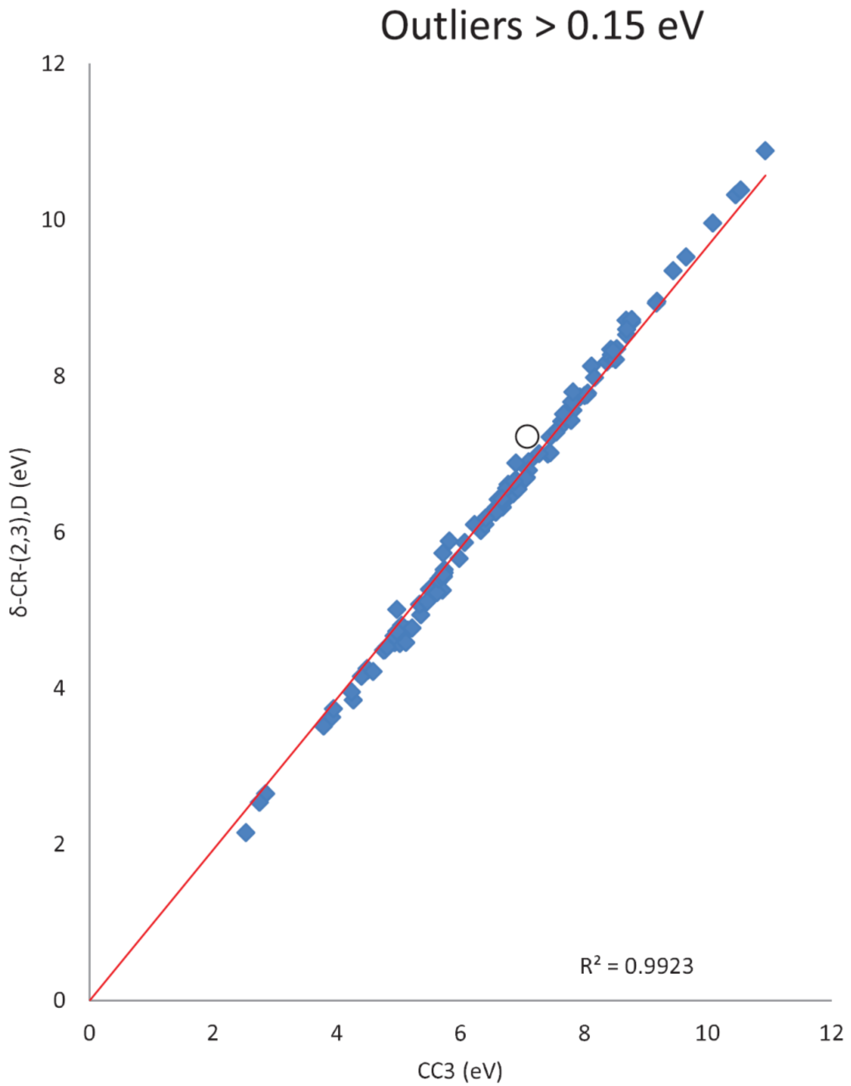
[A. Ayala, J.A. Hansen, and P. Piecuch, in preparation]



State	CC3 (eV)	EOMCCSD (eV)	REL
$2\ ^1A_g(\pi\rightarrow\pi^*)$	6.77	7.42	1.219
$2\ ^1A_g(\pi\rightarrow\pi^*)$	5.72	6.61	1.225
$2\ ^1A_g(\pi\rightarrow\pi^*)$	4.97	5.98	1.211
$2\ ^1A_1(\pi\rightarrow\pi^*)$	6.61	7.05	1.153
$2\ ^1E_{2g}(\pi\rightarrow\pi^*)$	8.43	9.21	1.166
$1\ ^1B_{1g}(\pi\rightarrow\pi^*)$	6.07	6.53	1.109
$3\ ^1A_g(\pi\rightarrow\pi^*)$	6.90	7.77	1.154
$3\ ^1B_{3u}(\pi\rightarrow\pi^*)$	8.12	9.03	1.177
$4\ ^1A_1(\pi\rightarrow\pi^*)$	8.68	9.44	1.140
$3\ ^1B_2(\pi\rightarrow\pi^*)$	8.77	9.64	1.172
$1\ ^1B_{3g}(\pi\rightarrow\pi^*)$	8.77	9.74	1.180
$2\ ^1A_g(\pi\rightarrow\pi^*)$	8.69	9.54	1.160
$2\ ^1E''(n\rightarrow\pi^*)$	7.80	8.21	1.110
$2\ ^1E'(\pi\rightarrow\pi^*)$	9.44	10.28	1.155
$2\ ^1B_{2g}(n\rightarrow\pi^*)$	6.23	6.77	1.123
$3\ ^1B_{1g}(n\rightarrow\pi^*)$	7.08	8.36	1.157
$2\ ^1B_{3g}(\pi\rightarrow\pi^*)$	8.47	9.43	1.169
$1\ ^1B_{3u}(n\rightarrow\pi^*)$	5.82	6.55	1.120
$2\ ^1A'(\pi\rightarrow\pi^*)$	7.82	8.47	1.103
$2\ ^1A'(\pi\rightarrow\pi^*)$	10.93	11.40	1.100

δ-CR-EOMCC(2,3),D (iterative N^6 + noniterative N^7) vs CC3 (iterative N^7)

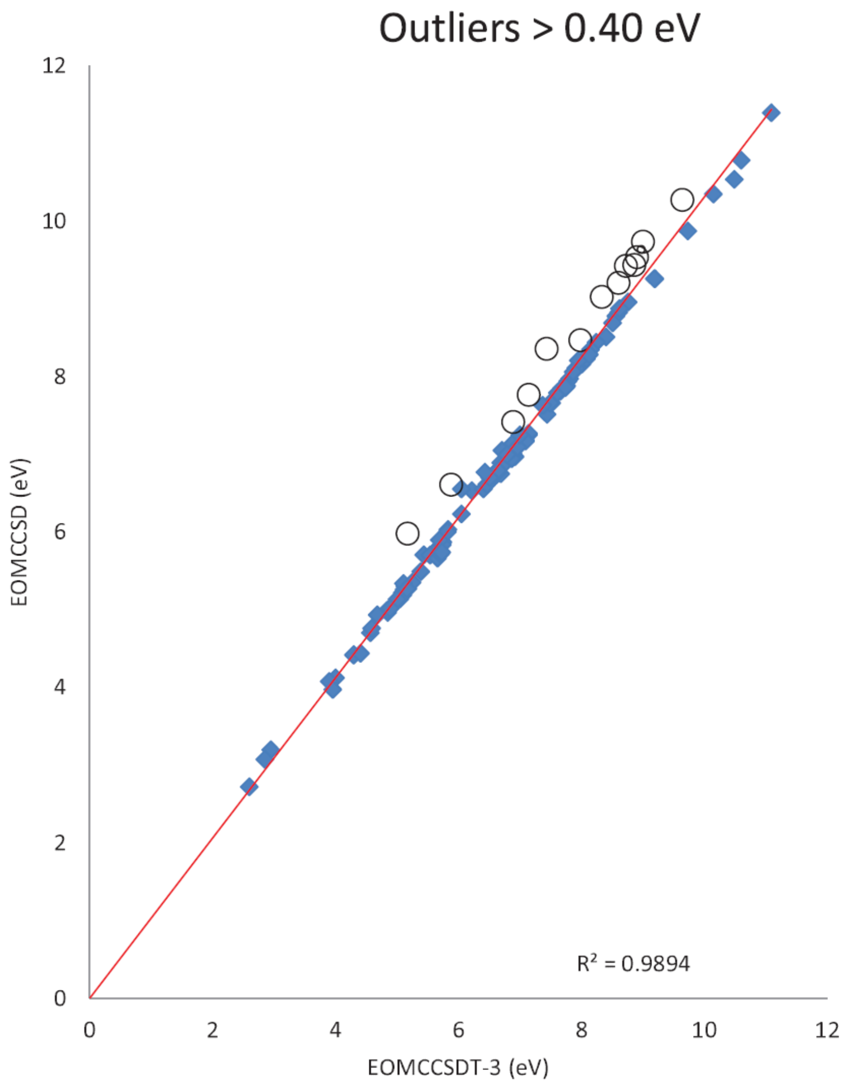
[A. Ayala, J.A. Hansen, and P. Piecuch, in preparation]



State	CC3 (eV)	δ-CR-(2,3),D (eV)	REL
3 $^1B_{1g}(n \to \pi^*)$	7.08	7.23	1.157

EOMCCSD (iterative N^6) vs EOMCCSDT-3 (iterative N^7)

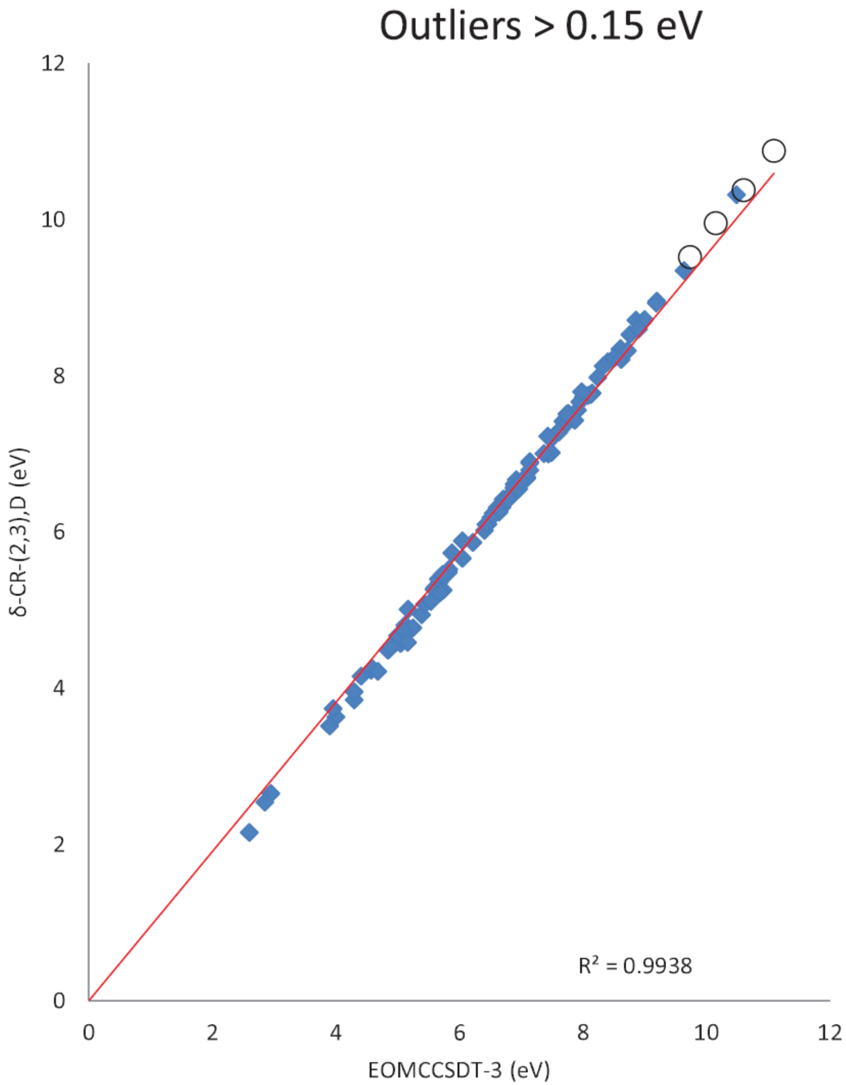
[A. Ayala, J.A. Hansen, and P. Piecuch, in preparation]



State	EOMCCSDT-3 (eV)	EOMCCSD (eV)	REL
2 $^1A_g(\pi\rightarrow\pi^*)$	6.89	7.42	1.219
2 $^1A_g(\pi\rightarrow\pi^*)$	5.88	6.61	1.225
2 $^1A_g(\pi\rightarrow\pi^*)$	5.17	5.98	1.211
2 $^1E_{2g}(\pi\rightarrow\pi^*)$	8.60	9.21	1.166
3 $^1A_g(\pi\rightarrow\pi^*)$	7.14	7.77	1.154
3 $^1B_{3u}(\pi\rightarrow\pi^*)$	8.33	9.03	1.177
4 $^1A_1(\pi\rightarrow\pi^*)$	8.86	9.44	1.140
3 $^1B_2(\pi\rightarrow\pi^*)$	8.97	9.64	1.172
1 $^1B_{3g}(\pi\rightarrow\pi^*)$	9.00	9.74	1.180
2 $^1A_g(\pi\rightarrow\pi^*)$	8.90	9.54	1.160
2 $^1E'(\pi\rightarrow\pi^*)$	9.64	10.28	1.155
3 $^1B_{1g}(n\rightarrow\pi^*)$	7.43	8.36	1.157
2 $^1B_{3g}(\pi\rightarrow\pi^*)$	8.72	9.43	1.169
1 $^1B_{3u}(n\rightarrow\pi^*)$	6.05	6.55	1.120
2 $^1A'(\pi\rightarrow\pi^*)$	7.98	8.47	1.103

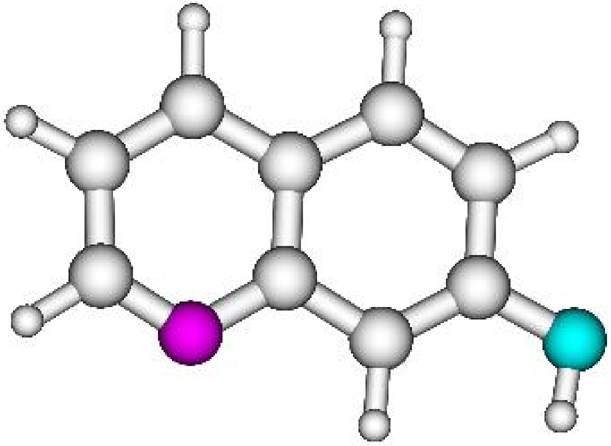
δ-CR-EOMCC(2,3) (iterative N^6 + noniterative N^7) vs EOMCCSDT-3 (iterative N^7)

[A. Ayala, J.A. Hansen, and P. Piecuch, in preparation]



State	EOMCCSDT-3 (eV)	δ-CR-(2,3),D (eV)	REL
$3\ ^1A'(\pi \rightarrow \pi^*)$	10.60	10.38	1.088
$3\ ^1A'(\pi \rightarrow \pi^*)$	10.15	9.96	1.089
$3\ ^1A'(\pi \rightarrow \pi^*)$	11.09	10.89	1.100
$2\ ^1A_1(\pi \rightarrow \pi^*)$	9.73	9.53	1.089

Vertical excitation energies of cis-7-hydroxyquinoline in various molecular environments



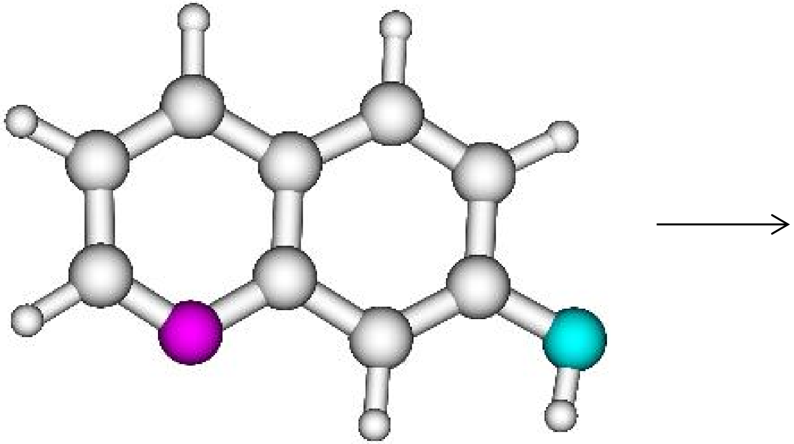
an aromatic system with first excited-state dominated by a π → π* electronic transition

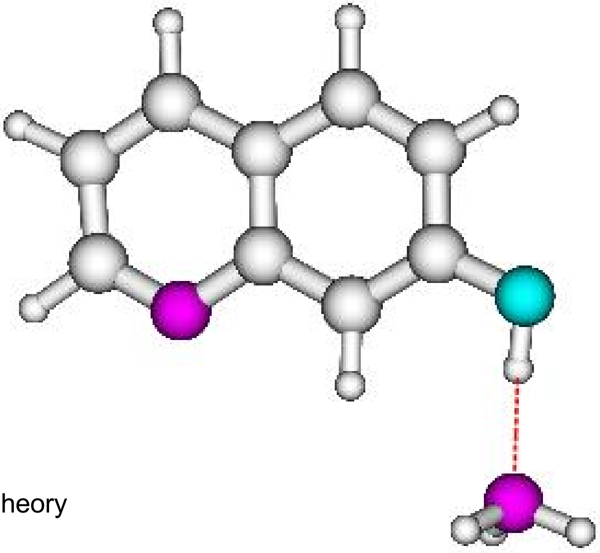
Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011. *Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008*

(Values in cm^{-1} obtained using 6-311+G(d)/6-31+G(d) basis set; 350 cm-1 ≈ 1 kcal/mol)

Environment	**Exp.**	**EOMCCSD**	**Error**	**δ-CR-EOMCC(2,3)**	**Error**
bare	30830	35046	4216	30711	-119

Vertical excitation energies of cis-7-hydroxyquinoline in various molecular environments



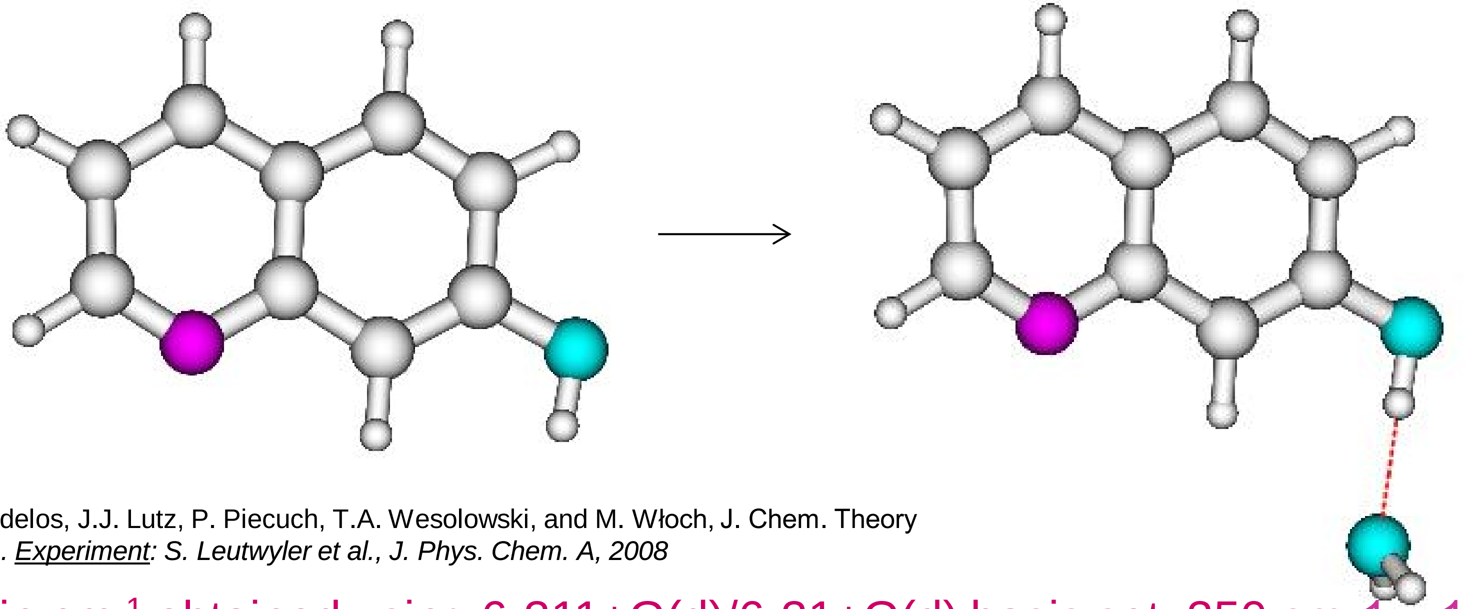


Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011. *Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008*

(Values in cm^{-1} obtained using 6-311+G(d)/6-31+G(d) basis set; 350 cm-1 ≈ 1 kcal/mol)

Environment	**Exp.**	**EOMCCSD**	**Error**	**δ-CR-EOMCC(2,3)**	**Error**
bare	30830	35046	4216	30711	-119
NH_3	29925	34263	4338	29922	-3

Vertical excitation energies of cis-7-hydroxyquinoline in various molecular environments

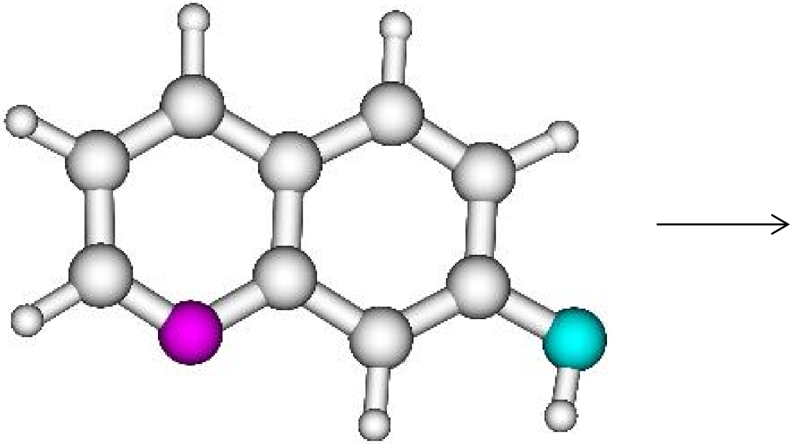


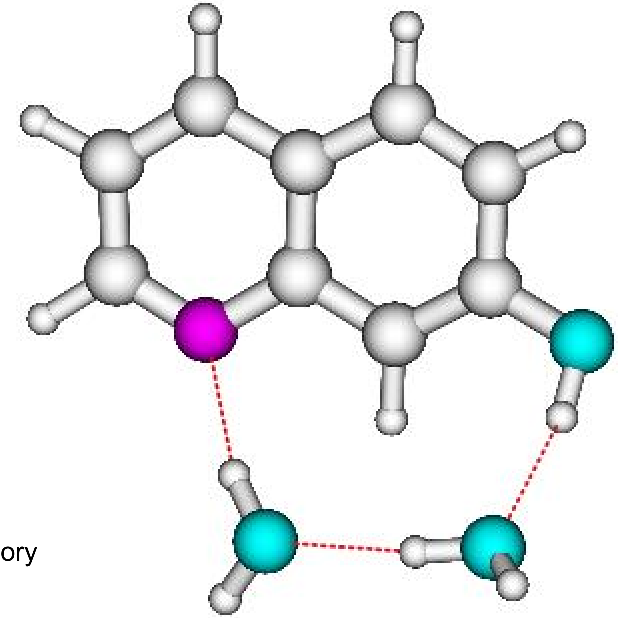
Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011. *Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008*

(Values in cm^{-1} obtained using 6-311+G(d)/6-31+G(d) basis set; 350 cm-1 ≈ 1 kcal/mol)

Environment	**Exp.**	**EOMCCSD**	**Error**	**δ-CR-EOMCC(2,3)**	**Error**
bare	30830	35046	4216	30711	-119
NH_3	29925	34263	4338	29922	-3
H_2O	30240	34500	4260	30199	-41

Vertical excitation energies of cis-7-hydroxyquinoline in various molecular environments



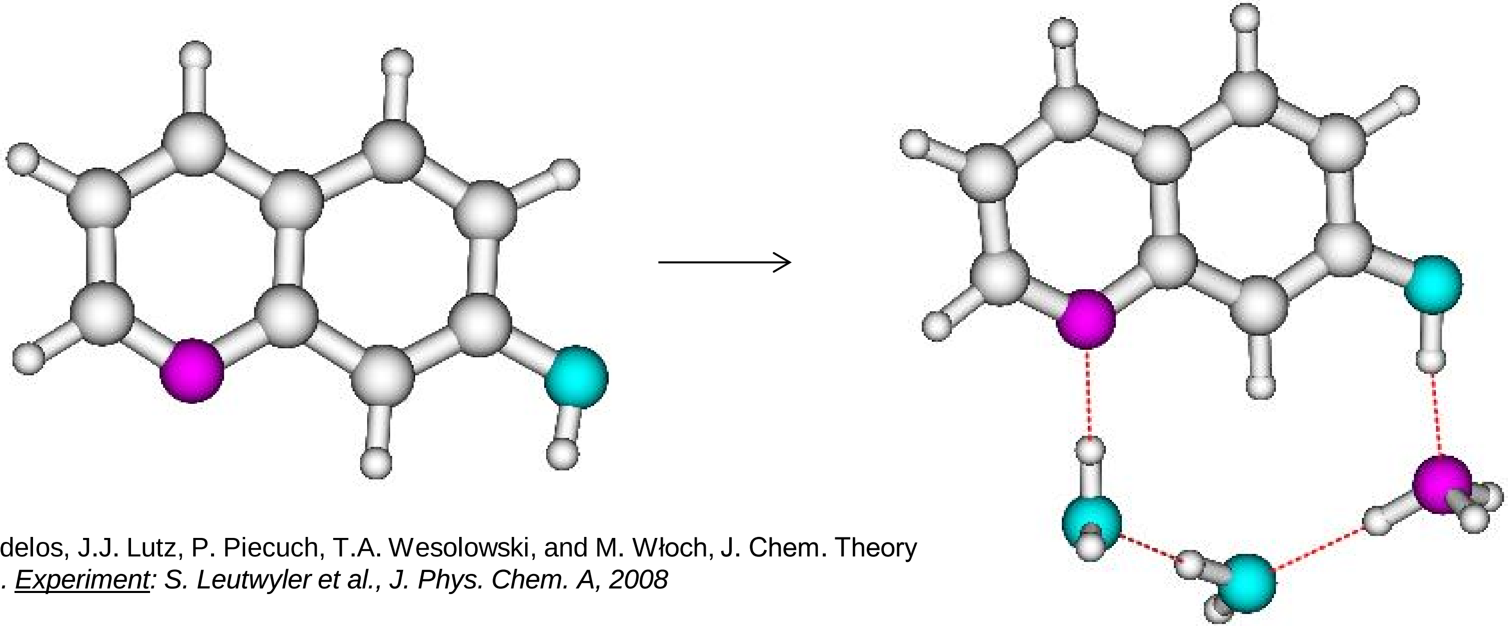


Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011. *Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008*

(Values in cm^{-1} obtained using 6-311+G(d)/6-31+G(d) basis set; 350 cm-1 ≈ 1 kcal/mol)

Environment	**Exp.**	**EOMCCSD**	**Error**	**δ-CR-EOMCC(2,3)**	**Error**
bare	30830	35046	4216	30711	-119
NH_3	29925	34263	4338	29922	-3
H_2O	30240	34500	4260	30199	-41
$H_2O + H_2O$	29193	33699	4506	29378	185

Vertical excitation energies of cis-7-hydroxyquinoline in various molecular environments



Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011. *Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008*

(Values in cm^{-1} obtained using 6-311+G(d)/6-31+G(d) basis set; 350 cm-1 ≈ 1 kcal/mol)

Environment	**Exp.**	**EOMCCSD**	**Error**	**δ-CR-EOMCC(2,3)**	**Error**
bare	30830	35046	4216	30711	-119
NH_3	29925	34263	4338	29922	-3
H_2O	30240	34500	4260	30199	-41
$H_2O + H_2O$	29193	33699	4506	29378	185
$NH_3 + H_2O + H_2O$	28340	33218	4878	28863	523

Excitation energy shifts for cis-7-hydroxyquinoline in various molecular environments (in cm^{-1})

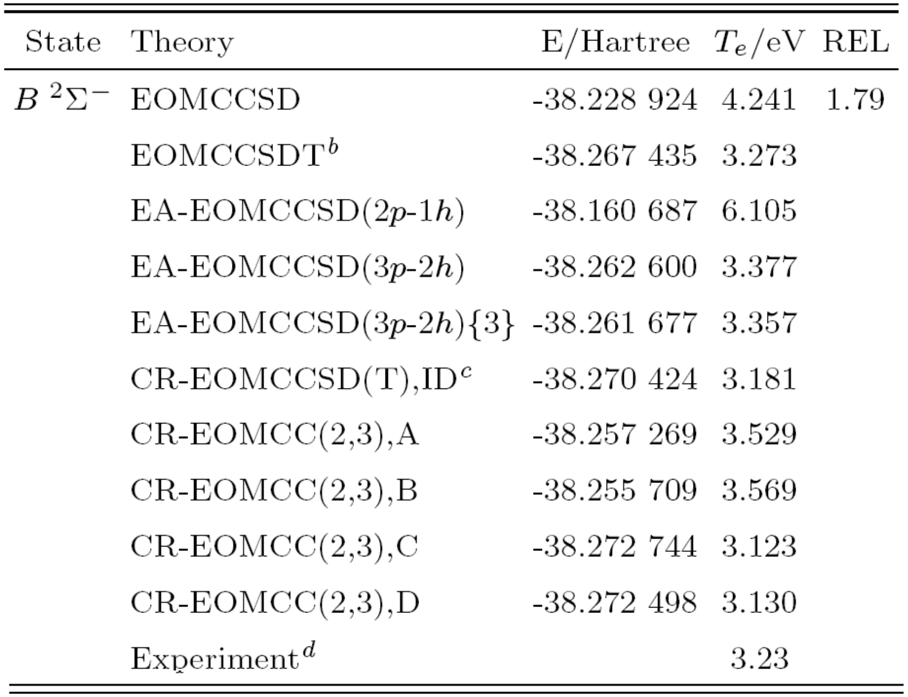
Theory: G. Fradelos, J.J. Lutz, P. Piecuch, T.A. Wesolowski, and M. Włoch, J. Chem. Theory Comput., 2011.
Experiment: S. Leutwyler et al., J. Phys. Chem. A, 2008

Environment	**Exp.**	**δ-CR-EOMCC(2,3)**	**TDDFT**
NH_3	**-905**	-820 (9%)	-1222 (35%)
H_2O	**-590**	-562 (5%)	-944 (60%)
$H_2O + H_2O$	**-1637**	-1446 (12%)	-2280 (39%)
CH_3OH	**-467**	-396 (15%)	-805 (72%)
HCOOH	**-1014**	-743 (27%)	-1569 (55%)
$NH_3 + H_2O + H_2O$	**-2490**	-1969 (21%)	-2838 (14%)
$NH_3 + H_2O + NH_3$	**-2136**	-1780 (17%)	-2594 (21%)
$NH_3 + NH_3 + H_2O$	**-2482**	-2055 (17%)	-2899 (17%)
Average error		15%	39%

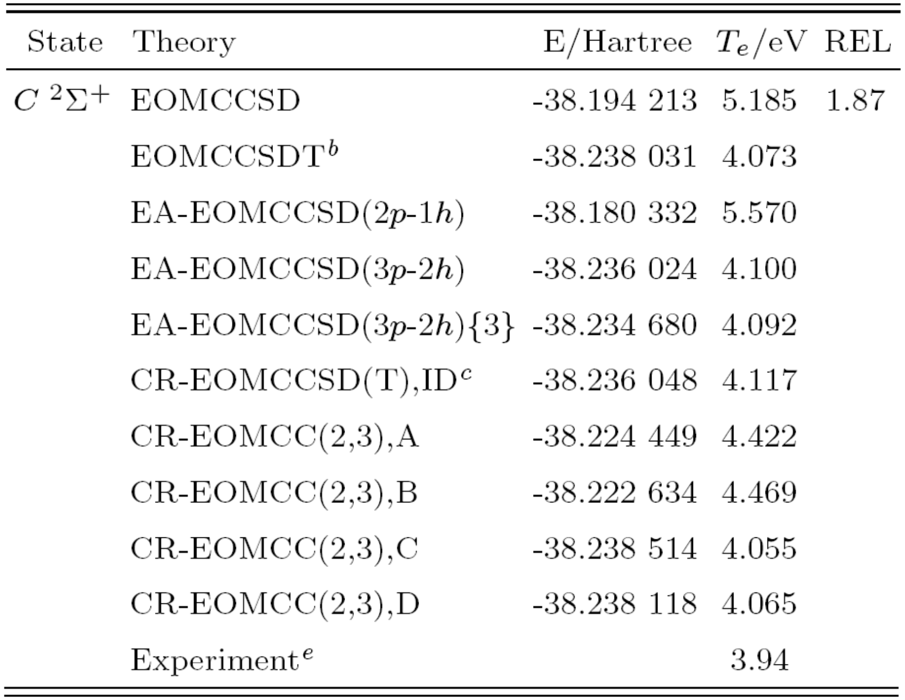
ADIABATIC EXCITATIONS IN CH, CNC, C_2N

CH

[Piecuch, Gour, Włoch, IJQC (2009)]



State	Theory	E/Hartree	T_e/eV	REL
$B\ ^2\Sigma^-$	EOMCCSD	-38.228 924	4.241	1.79
	EOMCCSDT[b]	-38.267 435	3.273	
	EA-EOMCCSD(2p-1h)	-38.160 687	6.105	
	EA-EOMCCSD(3p-2h)	-38.262 600	3.377	
	EA-EOMCCSD(3p-2h){3}	-38.261 677	3.357	
	CR-EOMCCSD(T),ID[c]	-38.270 424	3.181	
	CR-EOMCC(2,3),A	-38.257 269	3.529	
	CR-EOMCC(2,3),B	-38.255 709	3.569	
	CR-EOMCC(2,3),C	-38.272 744	3.123	
	CR-EOMCC(2,3),D	-38.272 498	3.130	
	Experiment[d]		3.23	



State	Theory	E/Hartree	T_e/eV	REL
$C\ ^2\Sigma^+$	EOMCCSD	-38.194 213	5.185	1.87
	EOMCCSDT[b]	-38.238 031	4.073	
	EA-EOMCCSD(2p-1h)	-38.180 332	5.570	
	EA-EOMCCSD(3p-2h)	-38.236 024	4.100	
	EA-EOMCCSD(3p-2h){3}	-38.234 680	4.092	
	CR-EOMCCSD(T),ID[c]	-38.236 048	4.117	
	CR-EOMCC(2,3),A	-38.224 449	4.422	
	CR-EOMCC(2,3),B	-38.222 634	4.469	
	CR-EOMCC(2,3),C	-38.238 514	4.055	
	CR-EOMCC(2,3),D	-38.238 118	4.065	
	Experiment[e]		3.94	

ADIABATIC EXCITATIONS IN CH, CNC, C$_2$N

CH

[Piecuch, Gour, Włoch, IJQC (2009)]

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[Piecuch, Gour, Włoch, IJQC (2009)]

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ADIABATIC EXCITATIONS IN CH, CNC, C_2N

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	CR-EOMCC(2,3),C	-38.272 744	3.123			CR-EOMCC(2,3),C	-38.238 514	4.055	
	CR-EOMCC(2,3),D	-38.272 498	3.130	(<0.1 eV error)		CR-EOMCC(2,3),D	-38.238 118	4.065	
	Experiment^d		3.23			Experiment^e		3.94	

ADIABATIC EXCITATIONS IN CH, CNC, C$_2$N

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[Piecuch, Gour, Włoch, IJQC (2009)]

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ADIABATIC EXCITATIONS IN CH, CNC, C_2N

CH

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	Experiment[d]		3.23				Experiment[e]		3.94	

CNC, C_2N

[Piecuch, Gour, Włoch, IJQC (2009); Ehara, Gour, Piecuch, Mol. Phys. (2009); Hansen, Piecuch, Lutz, Gour, Phys. Scr. (2011)]

			EA-EOMCCSD					CR-EOMCC(2,3)				
Molecule	State	REL	(2p-1h)	(3p-2h)	(3p-2h){4}	EOMCCSD	CR-EOMCCSD(T),ID	A	B	C	D	Experiment[b]
CNC	$A\ ^2\Delta_u$	1.099	7.206	4.105	4.085	4.291	4.339	4.400	4.397	4.395	4.395	3.761
	$B\ ^2\Sigma_u^+$	1.979	7.639	4.718	4.704	7.123	4.675	5.432	5.595	4.582	4.599	4.315
C_2N	$A\ ^2\Delta$	1.090	6.190	3.055	3.028	3.191	3.344	3.377	3.368	3.389	3.388	2.636
	$B\ ^2\Sigma^-$	1.856	7.856	3.677	3.648	5.514	3.351	4.018	4.160	3.091	3.110	2.779
	$C\ ^2\Sigma^+$	1.897	6.722	3.809	3.788	6.358	4.023	4.741	4.901	3.799	3.824	3.306

ADIABATIC EXCITATIONS IN CH, CNC, C_2N

CH

[Piecuch, Gour, Włoch, IJQC (2009)]

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			EA-EOMCCSD					CR-EOMCC(2,3)				
Molecule	State	REL	(2*p*-1*h*)	(3*p*-2*h*)	(3*p*-2*h*){4}	EOMCCSD	CR-EOMCCSD(T),ID	A	B	C	D	Experiment[b]
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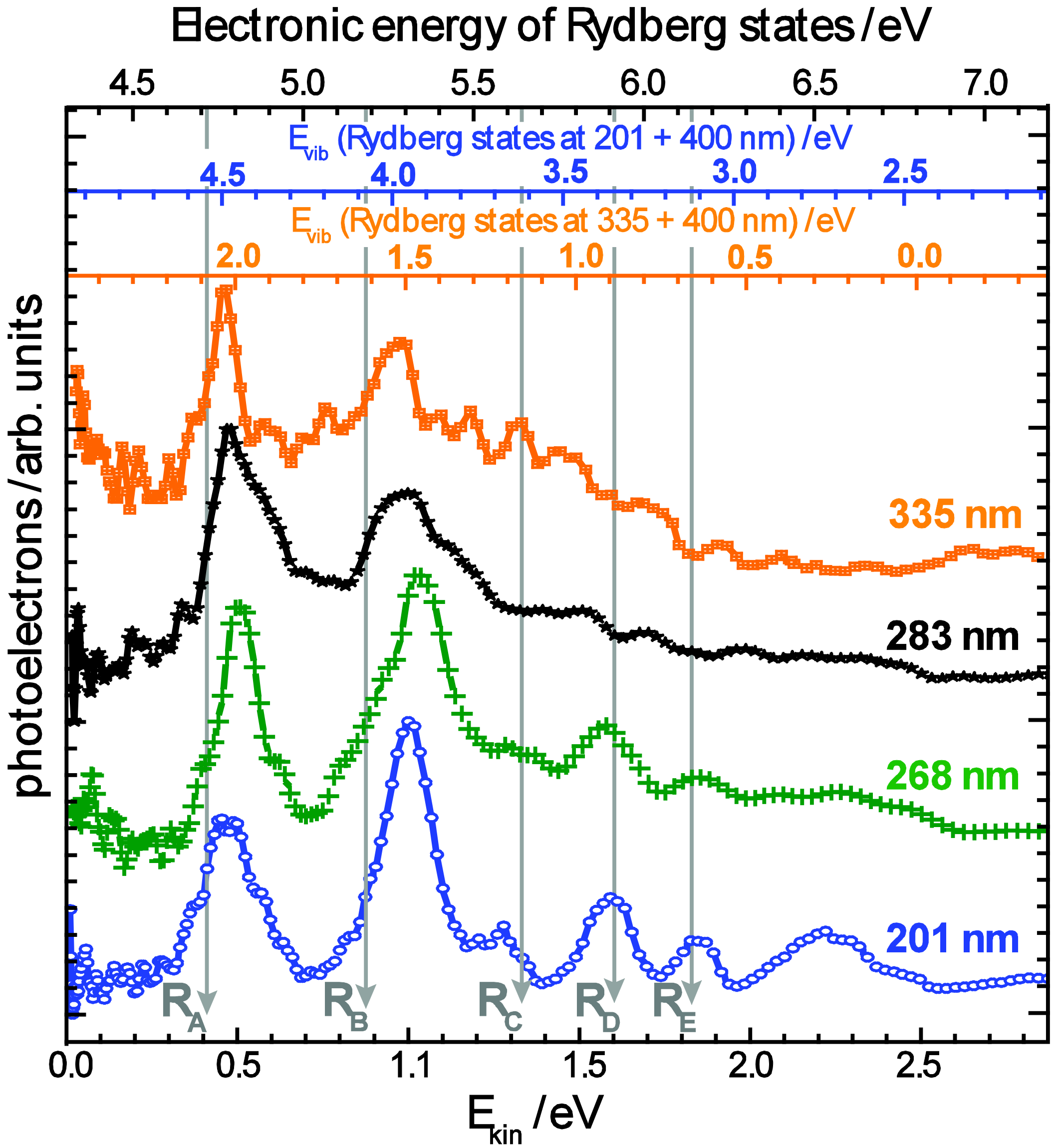
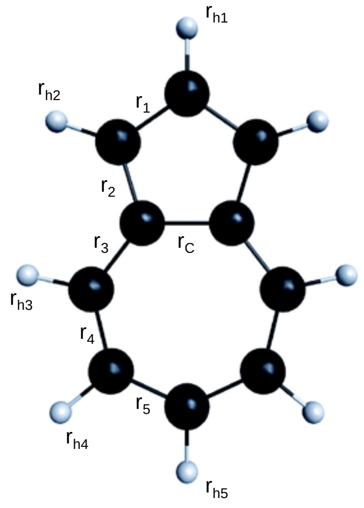
ELECTRONIC SPECTRUM OF AZULENE: DISCOVERY OF THE DOUBLY EXCITED STATE THAT MEDIATES THE 1+2' PHOTOIONIZATION OF AZULENE

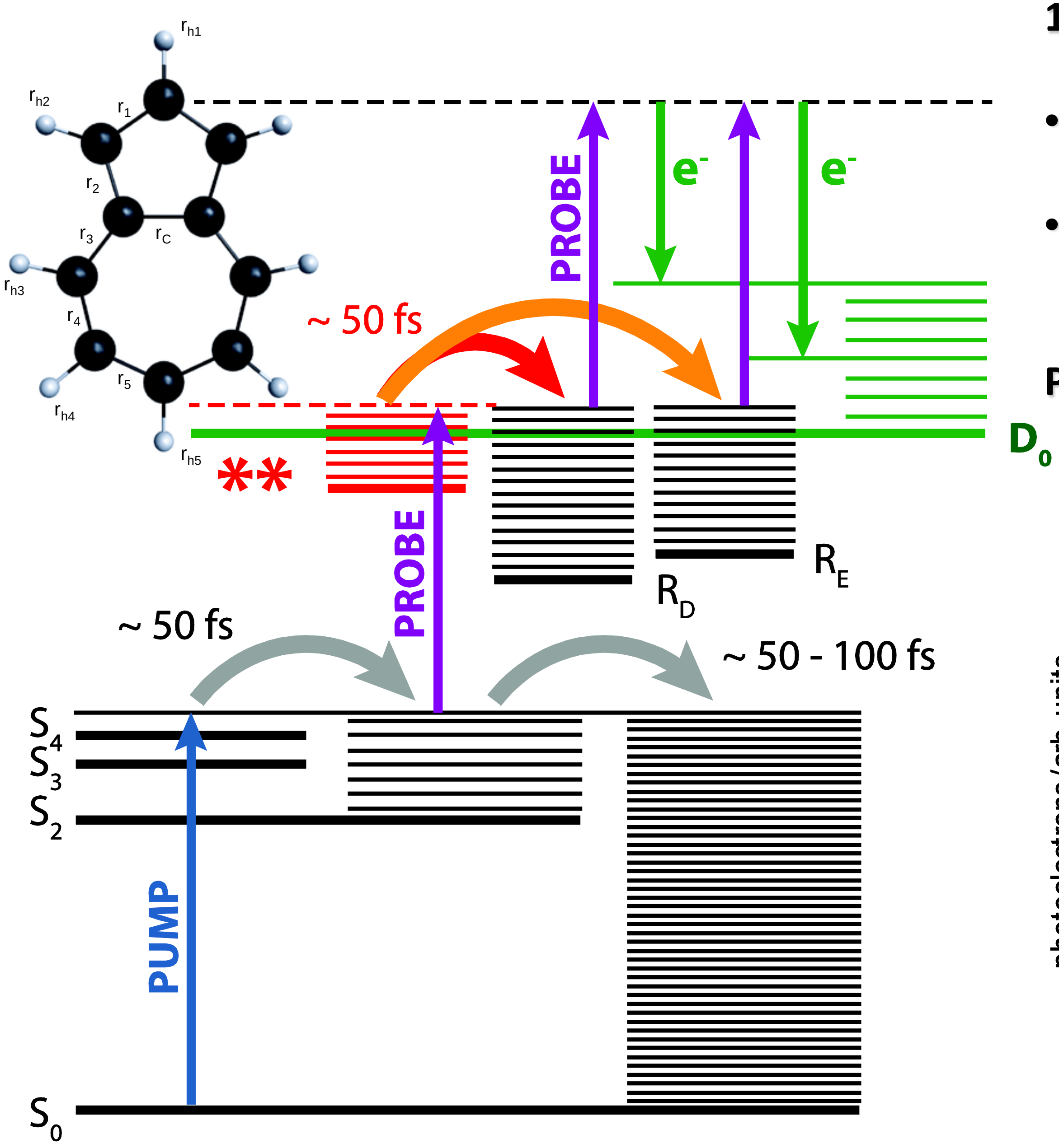
[P. Piecuch, J.A. Hansen, D. Staedter, S. Faure, and V. Blanchet, J. Chem. Phys., 2013]





J. Chem. Phys. **138**, 201102 (2013)

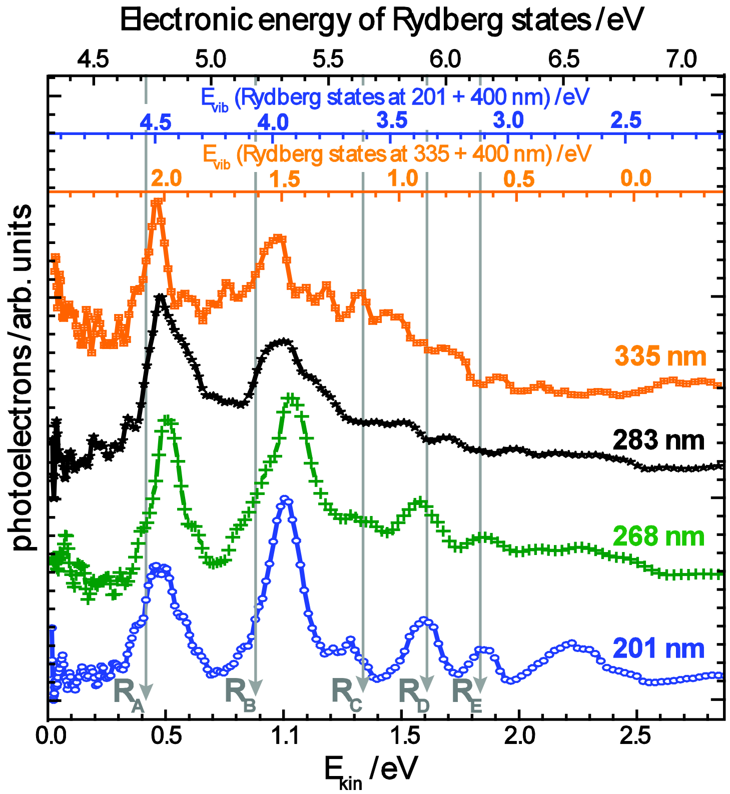
V. Blanchet, et al. J. Chem. Phys. **128**, 164318 (2008)



1+2' photoionization spectra are invariant with respect to

- **the pump-probe time delay varied between 120 and 500 fs**
- **the pump wavelength varied between 201 and 335 nm (3.71-6.18 eV)**

Probe was fixed at 400 nm (3.10 eV)



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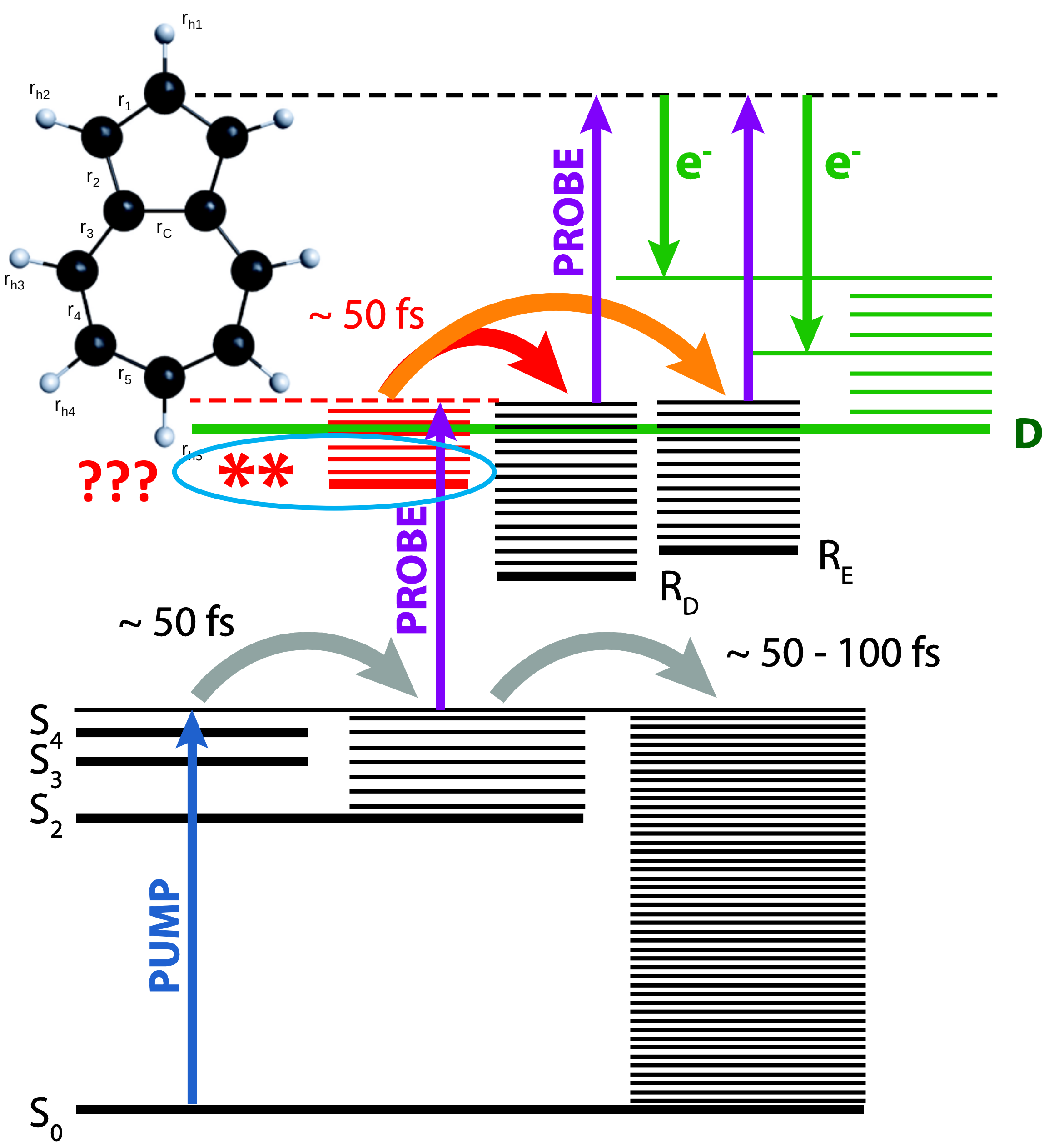

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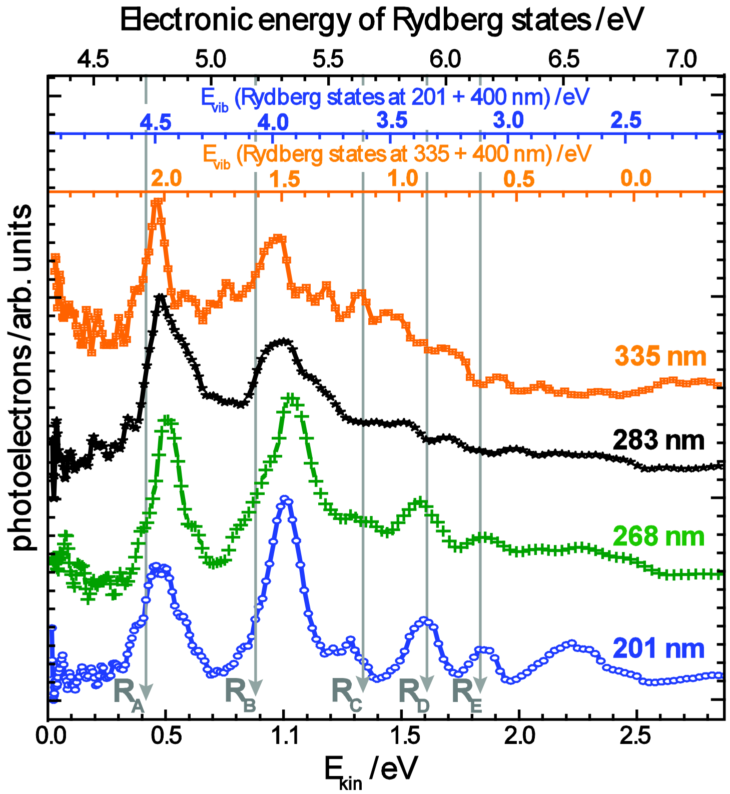

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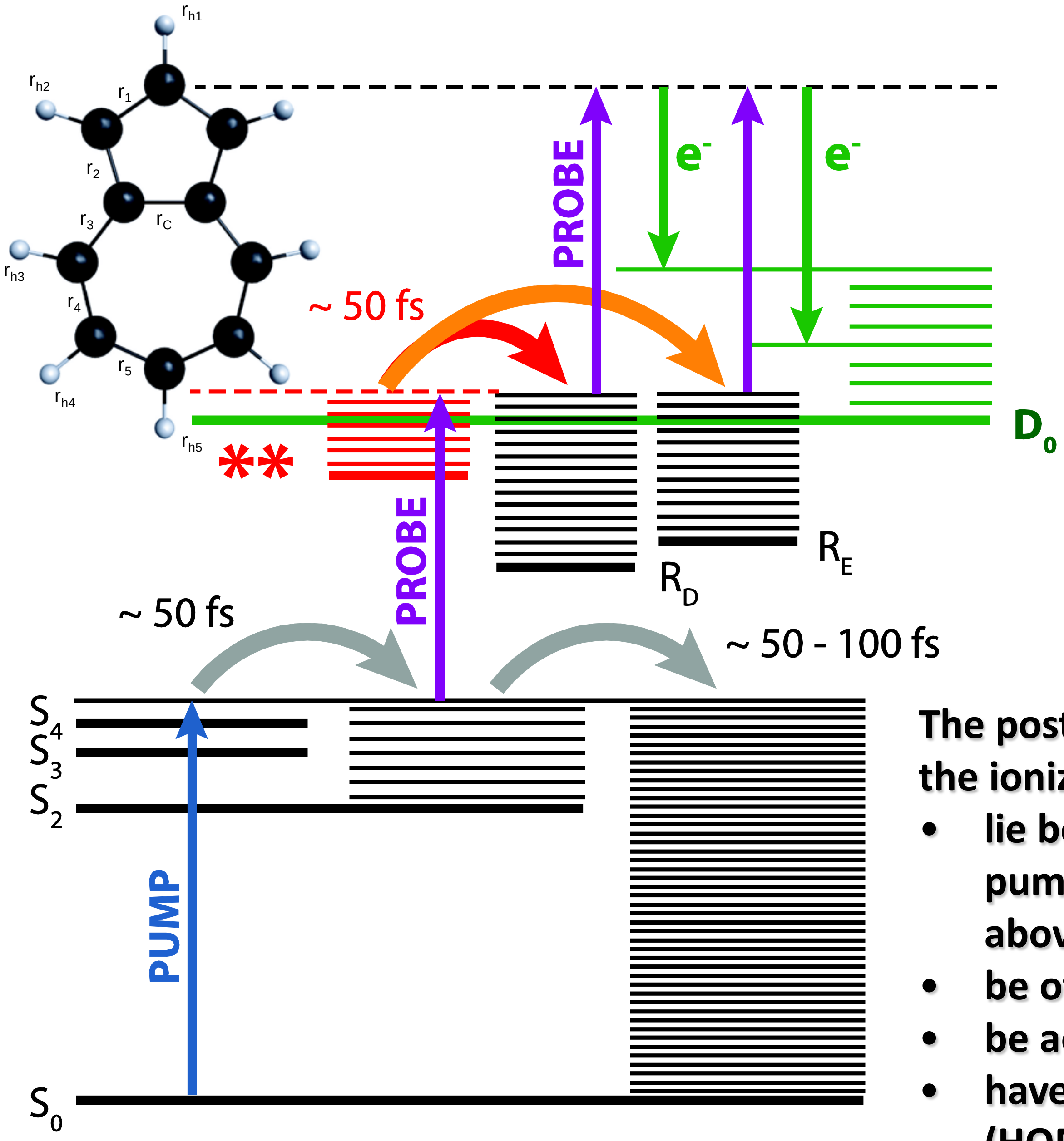

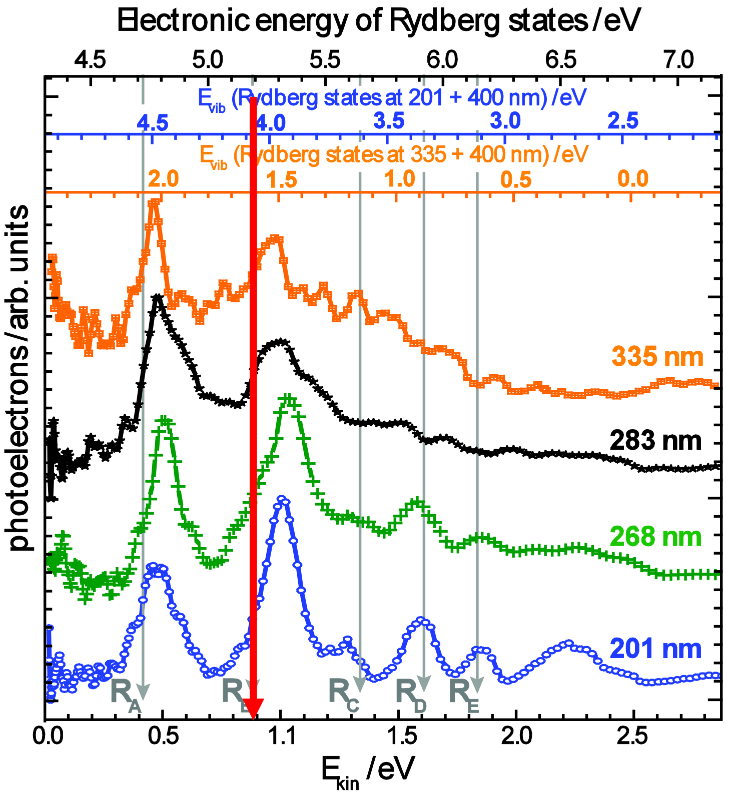

The postulated doubly excited state below the ionization threshold (7.41 eV) should

- **lie below 6.81 eV (the lowest-energy pump at 335 nm + 400 nm probe) and above R_B = 5.19 eV**
- **be of $^1A_1$ symmetry**
- **be accessible from the S_2 state**
- **have electronic structure dominated by $(HOMO)^2 \rightarrow (LUMO+1)^2$ and $(HOMO-1)^2 \rightarrow (LUMO)^2$ transitions.**

J. Chem. Phys. **138**, 201102 (2013)

State	Basis	REL	EOMCCSD	δ-CR-EOMCC(2,3)	CAS(10,10)	CASPT2(10,10)	Experiment
$S_1(B_1)$	6-31G(d)	1.105	2.290	1.691	1.97	1.96	1.77
	cc-pVDZ	1.105	2.224	1.618			
$S_2(A_1)$	6-31G(d)	1.089	4.192	3.570	4.45	3.81	3.56
	cc-pVDZ	1.090	4.037	3.414			
$S_3(B_1)$	6-31G(d)	1.109	4.897	4.220	4.62	4.15	4.23
	cc-pVDZ	1.110	4.760	4.083			
$S_4(A_1)$	6-31G(d)	1.097	5.567	4.954	5.50	4.94	4.40
	cc-pVDZ	1.097	5.387	4.770			
$S_5(B_1)$	6-31G(d)	1.107	6.424	5.792			4.72
	cc-pVDZ	1.107	6.237	5.607			
$S_6(A_1)$	6-31G(d)	1.146	6.671	5.824			5.19
	cc-pVDZ	1.143	6.509	5.674			
$S_7(B_2)$	6-31G(d)	1.093	6.543	6.010			6.15
	cc-pVDZ	1.095	6.421	5.888			
$S_8(A_1)$	6-31G(d)	1.140	7.378	6.473			6.33
	cc-pVDZ	1.138	7.187	6.298			
$S_9(A_1)$	6-31G(d)	1.879	10.708	6.787			
	cc-pVDZ	1.893	10.652	6.578			
$S_{10}(A_2)$	6-31G(d)	1.092	7.348	6.810			
	cc-pVDZ	1.094	7.186	6.648			

J. Chem. Phys. **138**, 201102 (2013)

V. Blanchet, et al. J. Chem. Phys. **128**, 164318 (2008)
A. Murakami, et al. J. Chem. Phys. **120**, 1245 (2004)

State	Basis	REL	EOMCCSD	δ-CR-EOMCC(2,3)	CAS(10,10)	CASPT2(10,10)	Experiment
$S_1(B_1)$	6-31G(d)	1.105	2.290	1.691	1.97	1.96	1.77
	cc-pVDZ	1.105	2.224	1.618			
$S_2(A_1)$	6-31G(d)	1.089	4.192	3.570	4.45	3.81	3.56
	cc-pVDZ	1.090	4.037	3.414			
$S_3(B_1)$	6-31G(d)	1.109	4.897	4.220	4.62	4.15	4.23
	cc-pVDZ	1.110	4.760	4.083			
$S_4(A_1)$	6-31G(d)	1.097	5.567	4.954	5.50	4.94	4.40
	cc-pVDZ	1.097	5.387	4.770			
$S_5(B_1)$	6-31G(d)	1.107	6.424	5.792			4.72
	cc-pVDZ	1.107	6.237	5.607			
$S_6(A_1)$	6-31G(d)	1.146	6.671	5.824			5.19
	cc-pVDZ	1.143	6.509	5.674			
$S_7(B_2)$	6-31G(d)	1.093	6.543	6.010			6.15
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$S_8(A_1)$	6-31G(d)	1.140	7.378	6.473			6.33
	cc-pVDZ	1.138	7.187	6.298			
$S_9(A_1)$	6-31G(d)	1.879	10.708	6.787			
	cc-pVDZ	1.893	10.652	6.578			
$S_{10}(A_2)$	6-31G(d)	1.092	7.348	6.810			
	cc-pVDZ	1.094	7.186	6.648			

V. Blanchet, et al. J. Chem. Phys. **128**, 164318 (2008)
A. Murakami, et al. J. Chem. Phys. **120**, 1245 (2004)

J. Chem. Phys. **138**, 201102 (2013)

State	Basis	REL	EOMCCSD	δ-CR-EOMCC(2,3)	CAS(10,10)	CASPT2(10,10)	Experiment
$S_1(B_1)$	6-31G(d)	1.105	2.290	1.691	1.97	1.96	1.77
	cc-pVDZ	1.105	2.224	1.618			
$S_2(A_1)$	6-31G(d)	1.089	4.192	3.570	4.45	3.81	3.56
	cc-pVDZ	1.090	4.037	3.414			
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1. Lies between 5.19 – 6.81 eV ✓
2. Is of $^1A_1$ symmetry ✓

J. Chem. Phys. **138**, 201102 (2013)

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EOMCCSD Oscillator Strengths

State	Basis	$S_0(A_1)$	$S_1(B_1)$	$S_2(A_1)$	$S_3(B_1)$	$S_4(A_1)$
$S_1(B_1)$	6-31G(d)	0.007				
	cc-pVDZ	0.007				
	Exp.	0.009				
$S_2(A_1)$	6-31G(d)	0.003	0.000			
	cc-pVDZ	0.003	0.000			
	Exp.	0.08				
$S_3(B_1)$	6-31G(d)	0.064	0.022	0.001		
	cc-pVDZ	0.062	0.022	0.001		
$S_4(A_1)$	6-31G(d)	1.309	0.008	0.001	0.000	
	cc-pVDZ	1.307	0.008	0.001	0.000	
	Exp.	1.10				
$S_9(A_1)$	6-31G(d)	0.001	0.043	0.005	0.052	0.190
	cc-pVDZ	0.000	0.043	0.004	0.038	0.212

J. Chem. Phys. **138**, 201102 (2013)

R. Pariser J. Chem. Phys. **25**, 1112 (1956)

EOMCCSD Oscillator Strengths

State	Basis	$S_0(A_1)$	$S_1(B_1)$	$S_2(A_1)$	$S_3(B_1)$	$S_4(A_1)$
$S_1(B_1)$	6-31G(d)	0.007				
	cc-pVDZ	0.007				
	Exp.	0.009				
$S_2(A_1)$	6-31G(d)	0.003	0.000			
	cc-pVDZ	0.003	0.000			
	Exp.	0.08				
$S_3(B_1)$	6-31G(d)	0.064	0.022	0.001		
	cc-pVDZ	0.062	0.022	0.001		
$S_4(A_1)$	6-31G(d)	1.309	0.008	0.001	0.000	
	cc-pVDZ	1.307	0.008	0.001	0.000	
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$S_9(A_1)$	6-31G(d)	0.001	0.043	0.005	0.052	0.190
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1. Lies between 5.19 – 6.81 eV ✓
2. Is of $^1A_1$ symmetry ✓
3. Accessible from the S_2 state ✓

J. Chem. Phys. **138**, 201102 (2013)

R. Pariser J. Chem. Phys. **25**, 1112 (1956)

Dominant Electronic Transitions

State	Basis	$r_{\mu,0}$	Leading $r_{\mu,1}$ and $r_{\mu,2}$ amplitudes			
S_9 (A_1)	**6-31G(d)**	**0.15**	**$3b_2 \rightarrow 6b_2$ (0.10)**	**$1a_2 2a_2 \rightarrow 3a_2^2$ (0.12)**	**$3b_2^2 \rightarrow 4b_2^2$ (0.41)**	**$3b_2 2a_2 \rightarrow 4b_2 3a_2$ (0.23)**
				$2a_2^2 \rightarrow 4b_2^2$ (0.11)	**$2a_2^2 \rightarrow 3a_2^2$ (0.42)**	**$3b_2 2a_2 \rightarrow 3a_2 4b_2$ (0.28)**
	cc-pVDZ	**0.15**		**$1a_2 2a_2 \rightarrow 3a_2^2$ (0.12)**	**$3b_2^2 \rightarrow 4b_2^2$ (0.41)**	**$3b_2 2a_2 \rightarrow 4b_2 3a_2$ (0.23)**
				$2a_2^2 \rightarrow 4b_2^2$ (0.11)	**$2a_2^2 \rightarrow 3a_2^2$ (0.42)**	**$3b_2 2a_2 \rightarrow 3a_2 4b_2$ (0.28)**

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				$2a_2^2 \rightarrow 4b_2^2$ (0.11)	**$2a_2^2 \rightarrow 3a_2^2$ (0.42)**	**$3b_2 2a_2 \rightarrow 3a_2 4b_2$ (0.28)**
	cc-pVDZ	**0.15**		**$1a_2 2a_2 \rightarrow 3a_2^2$ (0.12)**	**$3b_2^2 \rightarrow 4b_2^2$ (0.41)**	**$3b_2 2a_2 \rightarrow 4b_2 3a_2$ (0.23)**
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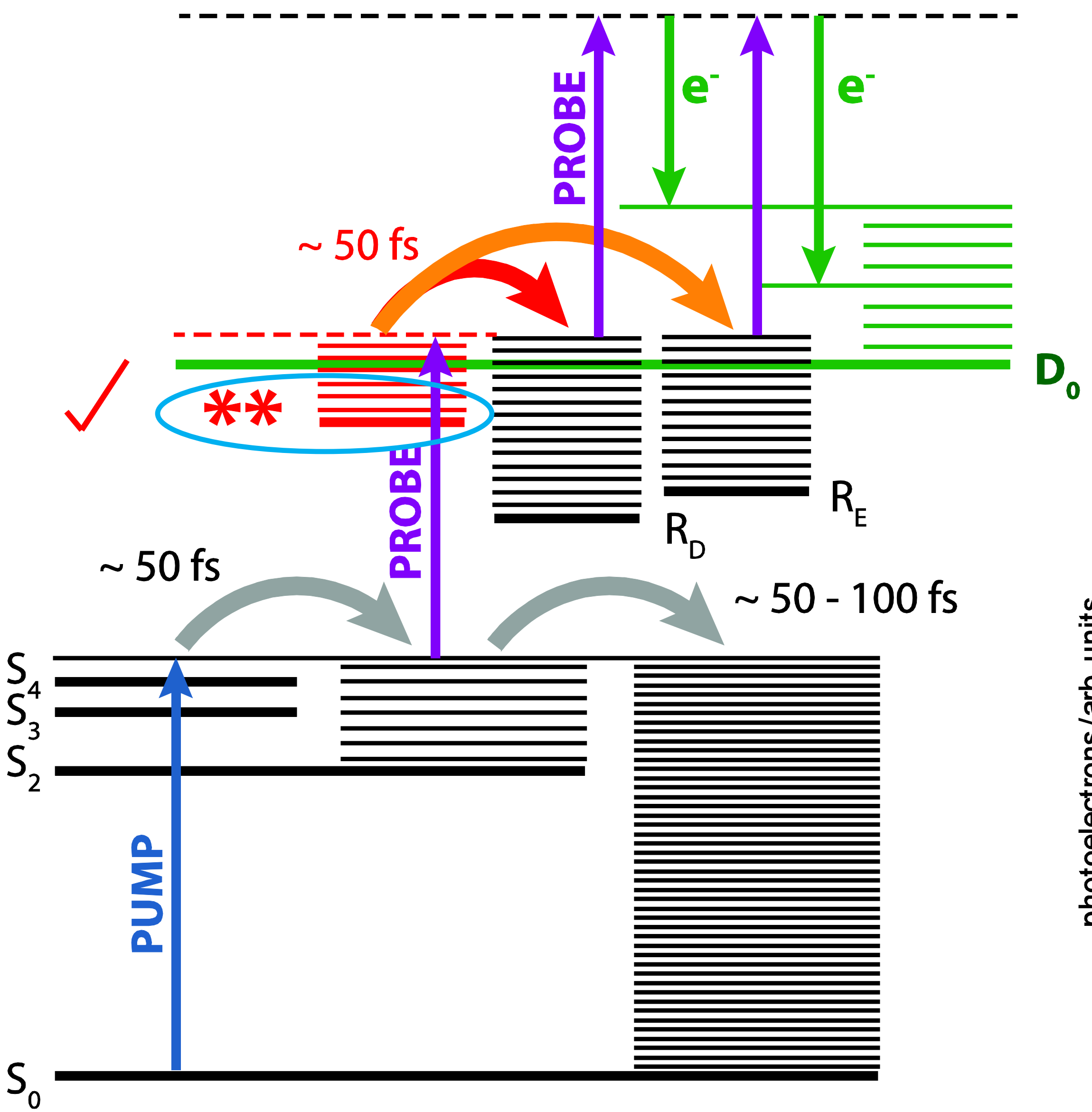
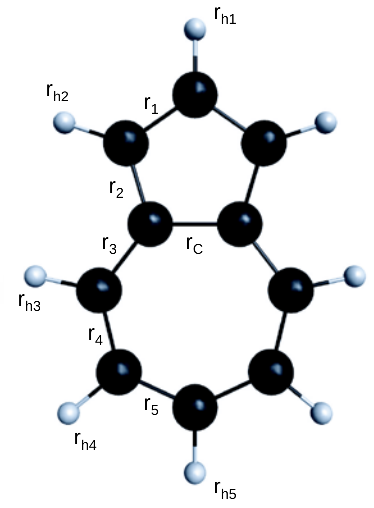
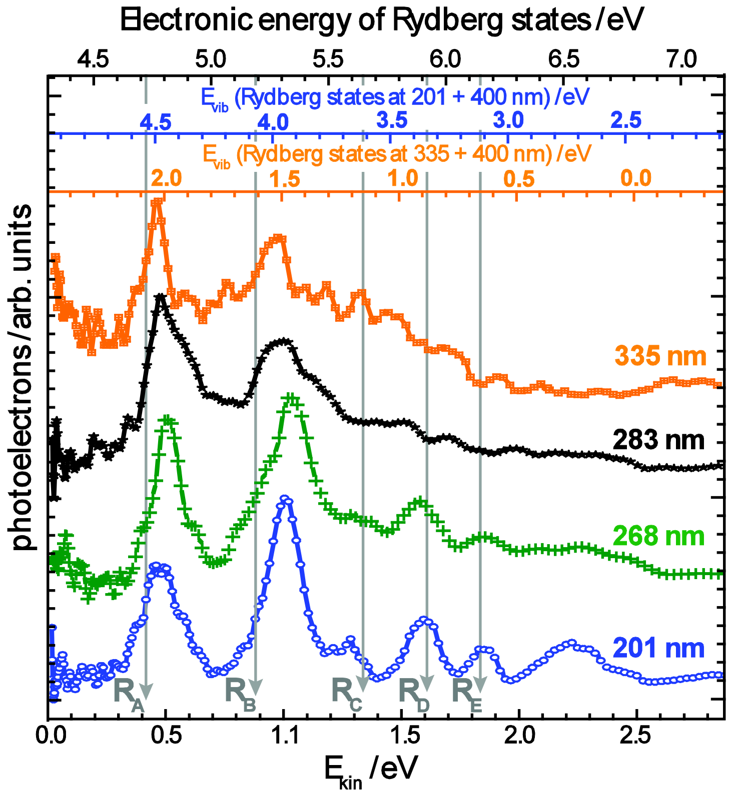
1. Lies between 5.19 – 6.81 eV ✓
2. Is of $^1A_1$ symmetry ✓
3. Is accessible from the S_2 state ✓
4. Has electronic structure dominated by $(\text{HOMO})^2 \rightarrow (\text{LUMO+1})^2$ $[(2a_2)^2 \rightarrow (3a_2)^2]$ and $(\text{HOMO-1})^2 \rightarrow (\text{LUMO})^2$ $[(3b_2)^2 \rightarrow (4b_2)^2]$ transitions ✓

J. Chem. Phys. **138**, 201102 (2013)



J. Chem. Phys. **138**, 201102 (2013)



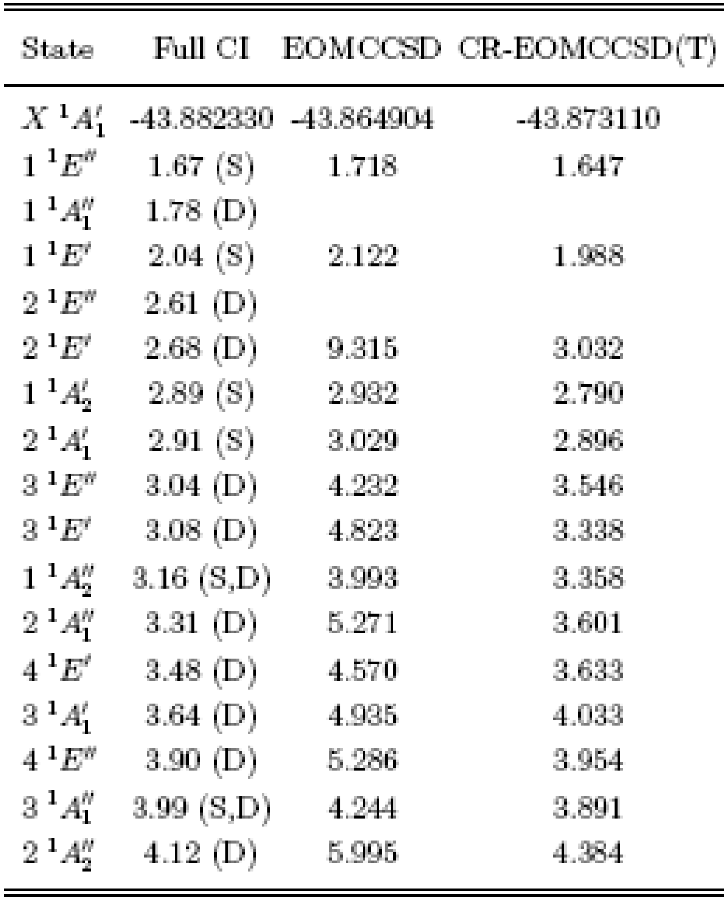


V. Blanchet, et al. J. Chem. Phys. **128**, 164318 (2008)

Completely renormalized CC/EOMCC methods can offer great help … but there are situations where this is not sufficient …

Example: excited states of metallic clusters (Be_3)

(K. Kowalski et al., J. Chem. Phys. 2005, P. Piecuch et al., Int. J. Quantum Chem., 2006)



State	Full CI	EOMCCSD	CR-EOMCCSD(T)
$X\ {}^1A_1'$	-43.882330	-43.864904	-43.873110
$1\ {}^1E''$	1.67 (S)	1.718	1.647
$1\ {}^1A_1''$	1.78 (D)		
$1\ {}^1E'$	2.04 (S)	2.122	1.988
$2\ {}^1E''$	2.61 (D)		
$2\ {}^1E'$	2.68 (D)	9.315	3.032
$1\ {}^1A_2'$	2.89 (S)	2.932	2.790
$2\ {}^1A_1'$	2.91 (S)	3.029	2.896
$3\ {}^1E''$	3.04 (D)	4.232	3.546
$3\ {}^1E'$	3.08 (D)	4.823	3.338
$1\ {}^1A_2''$	3.16 (S,D)	3.993	3.358
$2\ {}^1A_1''$	3.31 (D)	5.271	3.601
$4\ {}^1E'$	3.48 (D)	4.570	3.633
$3\ {}^1A_1'$	3.64 (D)	4.935	4.033
$4\ {}^1E''$	3.90 (D)	5.286	3.954
$3\ {}^1A_1''$	3.99 (S,D)	4.244	3.891
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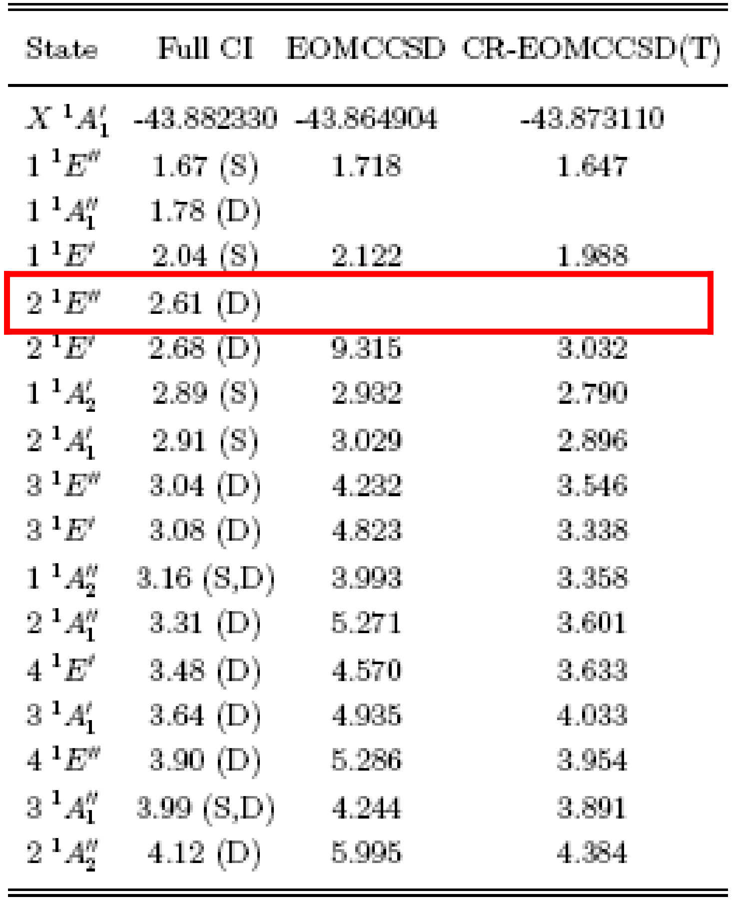

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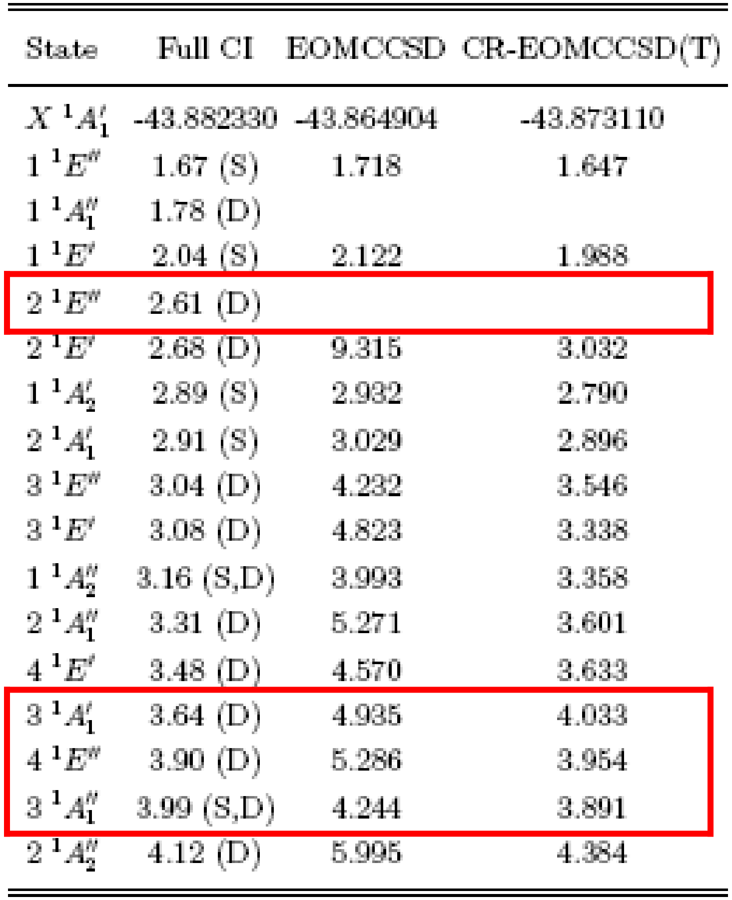

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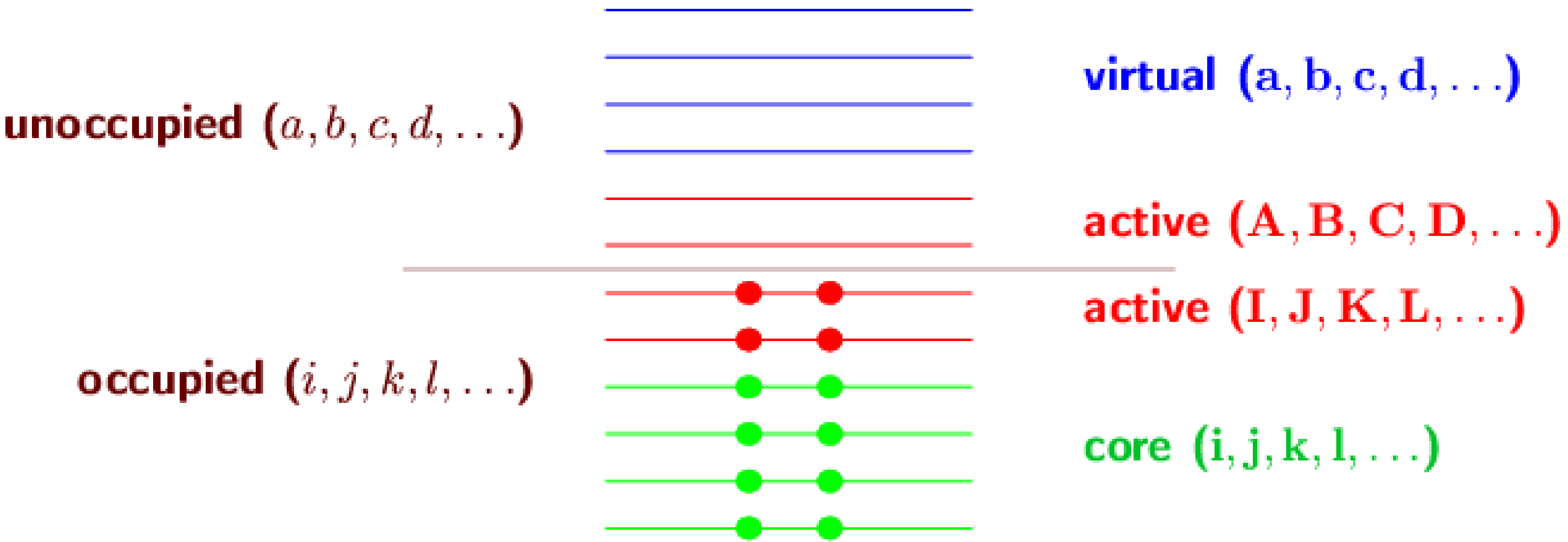
ACTIVE-SPACE CC/EOMCC APROACHES FOR QUASI-DEGENERATE STATES (CCSDt, CCSDtq, EOMCCSDt, etc.)

[~ state-selective MRCC methods exploiting a single-reference formalism]

[Key concepts: Oliphant and Adamowicz, 1991; Piecuch, Oliphant, and Adamowicz, 1993; Piecuch and Adamowicz, 1994; Piecuch, Kucharski, and Bartlett, 1999; Kowalski and Piecuch, 2000-2001; Gour, Piecuch, and Włoch, 2005-2006; Shen and Piecuch, 2013-2014; cf., also, CASCC work by Adamowicz et al.]



unoccupied $(a, b, c, d, \ldots)$

virtual $(\mathrm{a}, \mathrm{b}, \mathrm{c}, \mathrm{d}, \ldots)$

active $(\mathrm{A}, \mathrm{B}, \mathrm{C}, \mathrm{D}, \ldots)$

active $(\mathrm{I}, \mathrm{J}, \mathrm{K}, \mathrm{L}, \ldots)$

occupied $(i, j, k, l, \ldots)$

core $(\mathrm{i}, \mathrm{j}, \mathrm{k}, \mathrm{l}, \ldots)$

$$|\Psi\rangle = e^{T}|\Phi\rangle, \quad T = T^{\mathrm{int}} + T^{\mathrm{ext}}, \quad [T^{\mathrm{int}}, T^{\mathrm{ext}}] = 0$$

$$|\Psi\rangle = e^{T^{\mathrm{ext}}}|\Phi^{\mathrm{int}}\rangle, \quad |\Phi^{\mathrm{int}}\rangle = e^{T^{\mathrm{int}}}|\Phi\rangle$$ ← **(CAS)**

T^{int} – **nondynamic correlation,** T^{ext} – **dynamic correlation**

(long-range correlations) **(short-range correlations)**

REPRESENTATIVE APPROXIMATIONS:
CCSDt OR SSMRCCSD(T) AND EOMCCSDt

$$T^{\text{int}} = T_1^{\text{int}} + T_2^{\text{int}} + T_3^{\text{int}}, \quad T^{\text{ext}} = T_1^{\text{ext}} + T_2^{\text{ext}} + T_3^{\text{ext}}\left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array}\right)$$

$$T^{\text{CCSDt}} = T_1 + T_2 + T_3\left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array}\right), \quad R_K^{\text{CCSDt}} = R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3}\left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array}\right)$$

$$\bar{\mathbf{H}}^{\text{CCSDt}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} & \bar{\mathbf{H}}_{\mathbf{St}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} & \bar{\mathbf{H}}_{\mathbf{Dt}} \\ \bar{\mathbf{H}}_{\mathbf{tS}} & \bar{\mathbf{H}}_{\mathbf{tD}} & \bar{\mathbf{H}}_{\mathbf{tt}} \end{pmatrix}, \quad \bar{H} = e^{-T} H e^{T} = (He^{T})_C$$

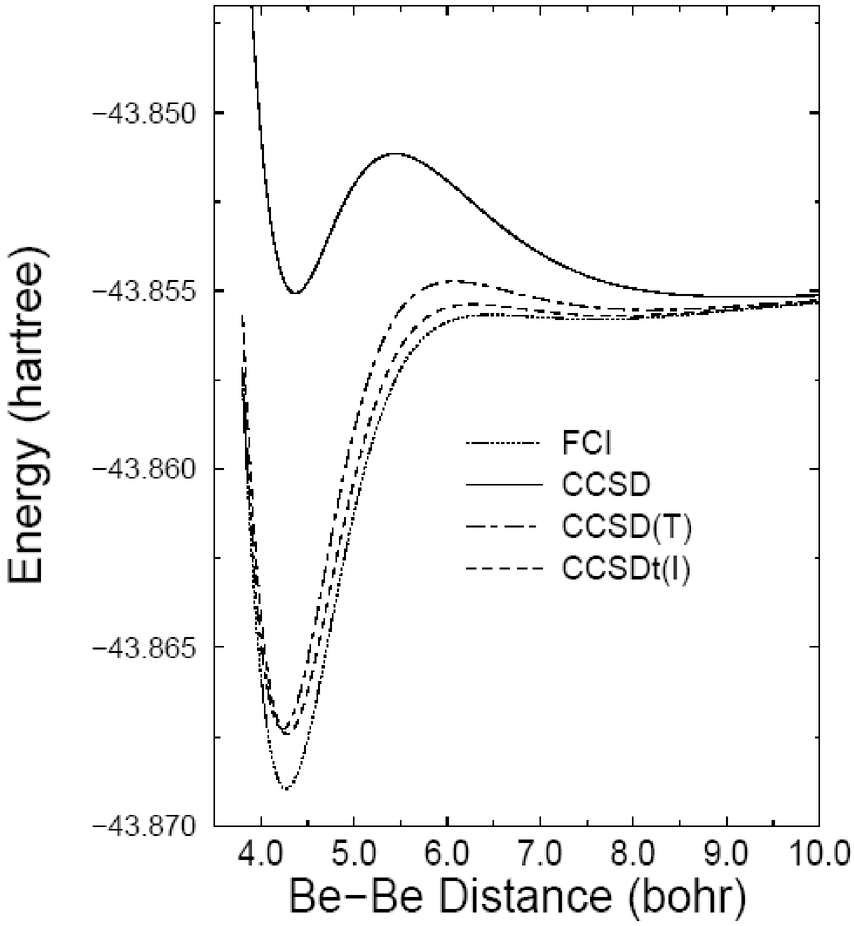
Other approximations: SSMRCCSD(TQ) or CCSDtq, EOMCCSDtq, etc.

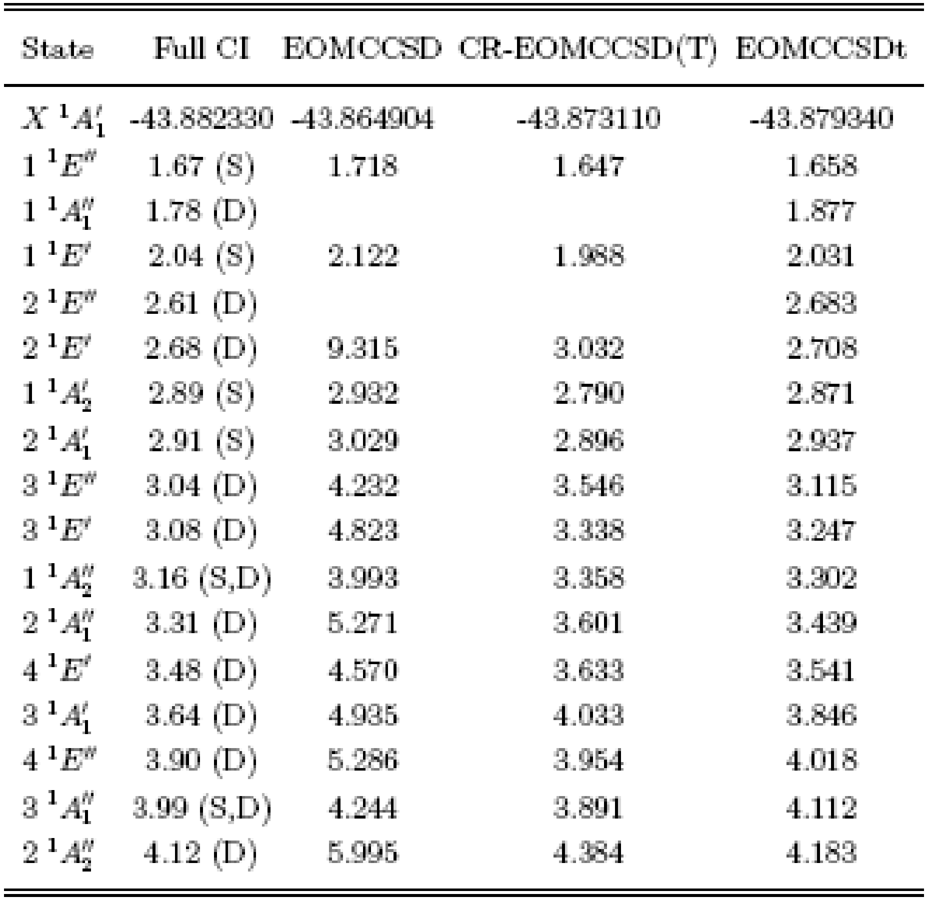
Because of the use of active orbitals, the numbers of t, q, … excitations are small fractions (~10-30 %) of all T, Q, … excitations.

The most expensive CPU steps of (EOM)CCSDt and (EOM)CCSDtq scale as ~$N_oN_u\mathit{n}_o^2\mathit{n}_u^4$ and ~$N_o^2N_u^2\mathit{n}_o^2\mathit{n}_u^4$, respectively.

Ground and excited states of Be_3

(K. Kowalski et al., J. Chem. Phys. 2005, P. Piecuch et al., Int. J. Quantum Chem., 2006)





State	Full CI	EOMCCSD	CR-EOMCCSD(T)	EOMCCSDt
$X\,^1A_1'$	-43.882330	-43.864904	-43.873110	-43.879340
$1\,^1E''$	1.67 (S)	1.718	1.647	1.658
$1\,^1A_1''$	1.78 (D)			1.877
$1\,^1E'$	2.04 (S)	2.122	1.988	2.031
$2\,^1E''$	2.61 (D)			2.683
$2\,^1E'$	2.68 (D)	9.315	3.032	2.708
$1\,^1A_2'$	2.89 (S)	2.932	2.790	2.871
$2\,^1A_1'$	2.91 (S)	3.029	2.896	2.937
$3\,^1E''$	3.04 (D)	4.232	3.546	3.115
$3\,^1E'$	3.08 (D)	4.823	3.338	3.247
$1\,^1A_2''$	3.16 (S,D)	3.993	3.358	3.302
$2\,^1A_1''$	3.31 (D)	5.271	3.601	3.439
$4\,^1E'$	3.48 (D)	4.570	3.633	3.541
$3\,^1A_1'$	3.64 (D)	4.935	4.033	3.846
$4\,^1E''$	3.90 (D)	5.286	3.954	4.018
$3\,^1A_1''$	3.99 (S,D)	4.244	3.891	4.112
$2\,^1A_2''$	4.12 (D)	5.995	4.384	4.183

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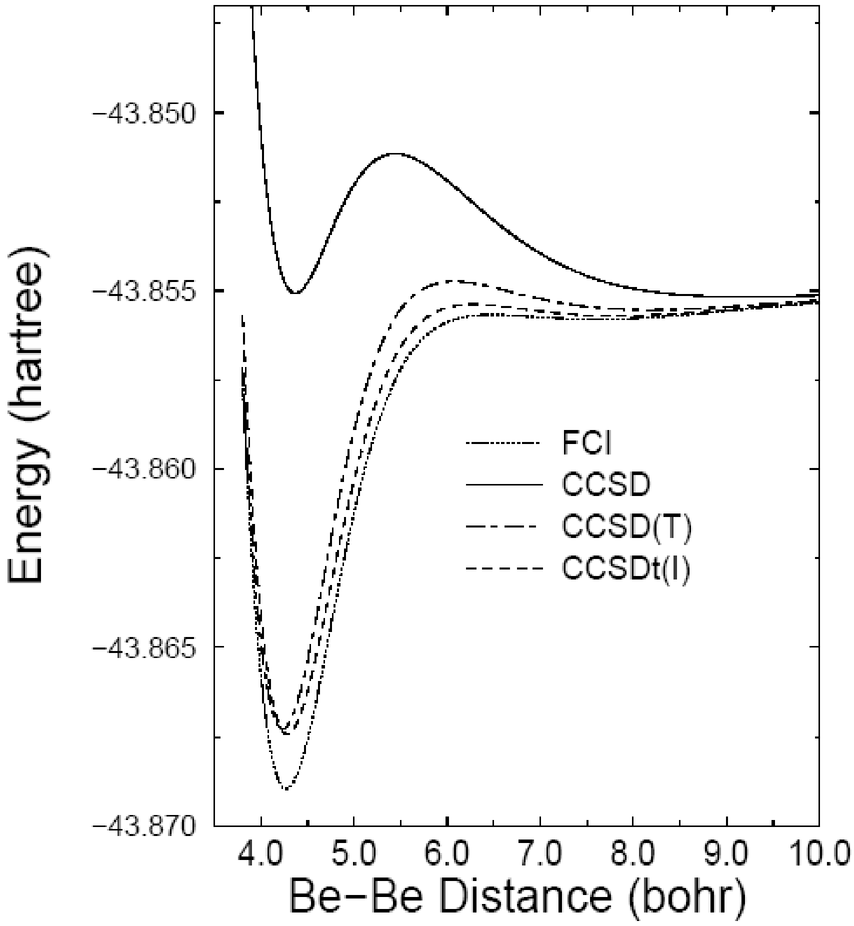

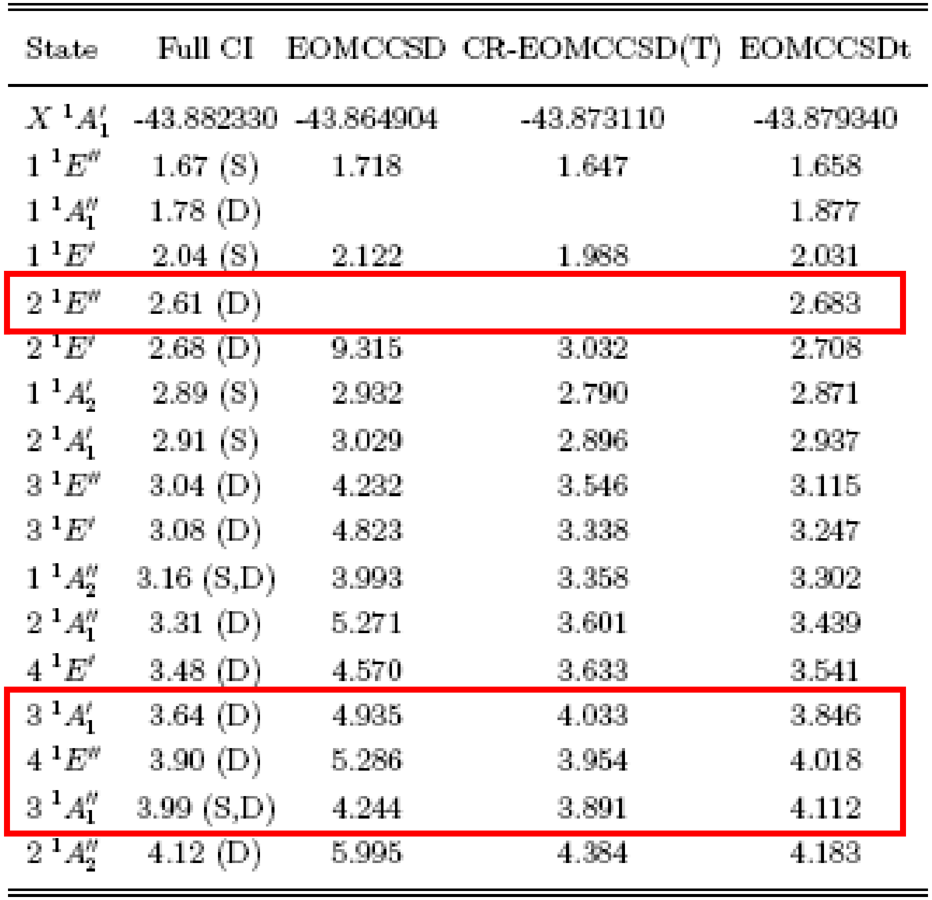

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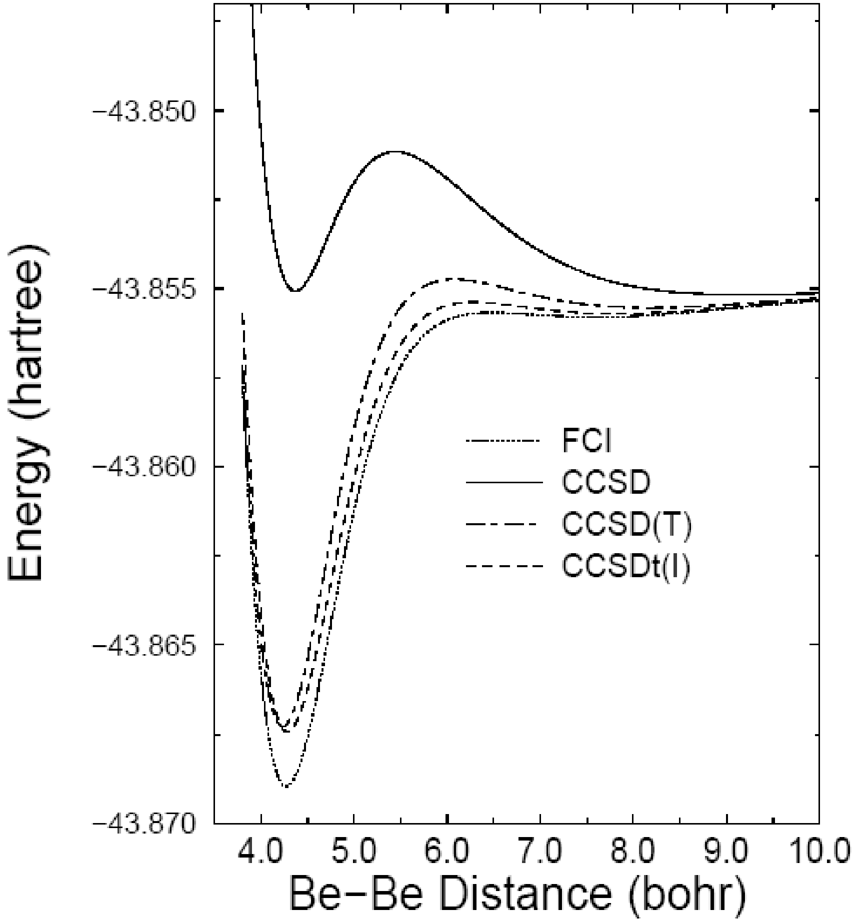

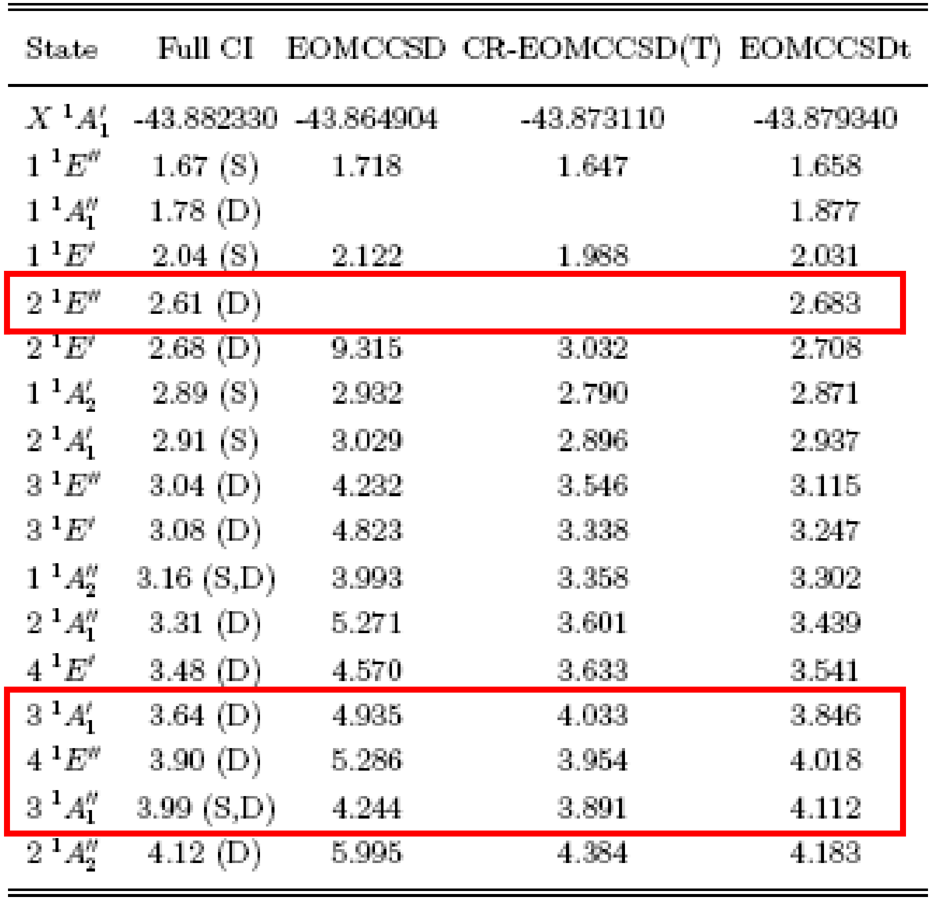

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$2\,^1A_2''$	4.12 (D)	5.995	4.384	4.183

Average errors (eV): 1.33 0.20 0.08

Radicals via the active-space electron-attached (EA) and ionized (IP) EOMCC

(J.R. Gour, P. Piecuch, and M. Włoch, J. Chem. Phys., 2005; Int. J. Quantum Chem., 2006, J.R. Gour and P. Piecuch, J. Chem. Phys., 2006; Piecuch et al., 2007-2011)

$$(\bar{H}_{N,\text{open}} R_{\mu}^{(N\pm1)}(\text{CCSDt}))_C|\Phi\rangle = \omega_{\mu}{}^{(N\pm1)} R_{\mu}^{(N\pm1)}(\text{CCSDt})|\Phi\rangle$$

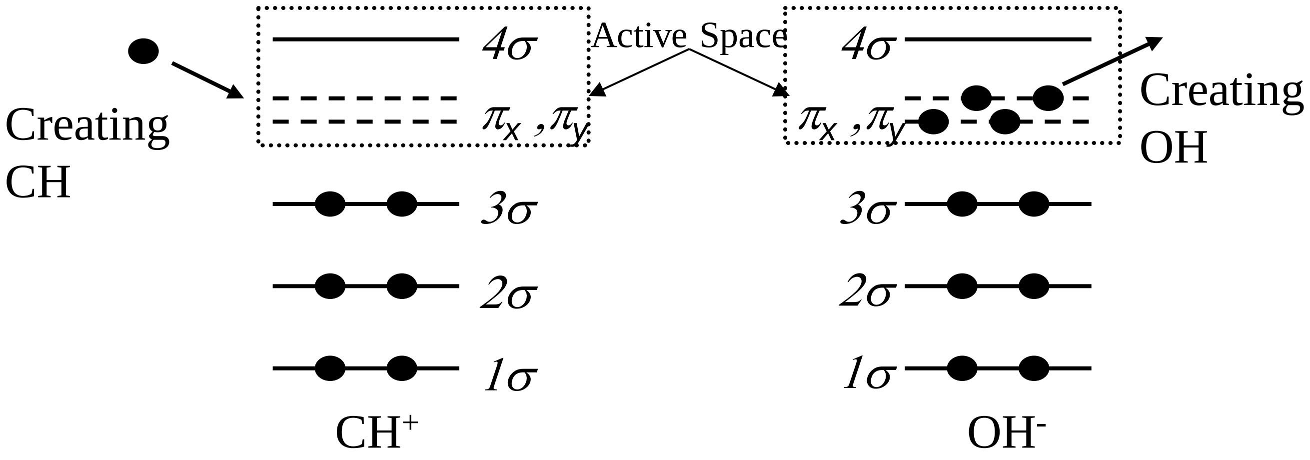
$$R_{\mu}^{(N+1)}(\text{CCSDt}) = R_{\mu,1p} + R_{\mu,2p\text{-}1h} \boxed{+ r_{\mu,3p\text{-}2h}}$$

$$R_{\mu}^{(N-1)}(\text{CCSDt}) = R_{\mu,1h} + R_{\mu,2h\text{-}1p} \boxed{+ r_{\mu,3h\text{-}2p}}$$

where

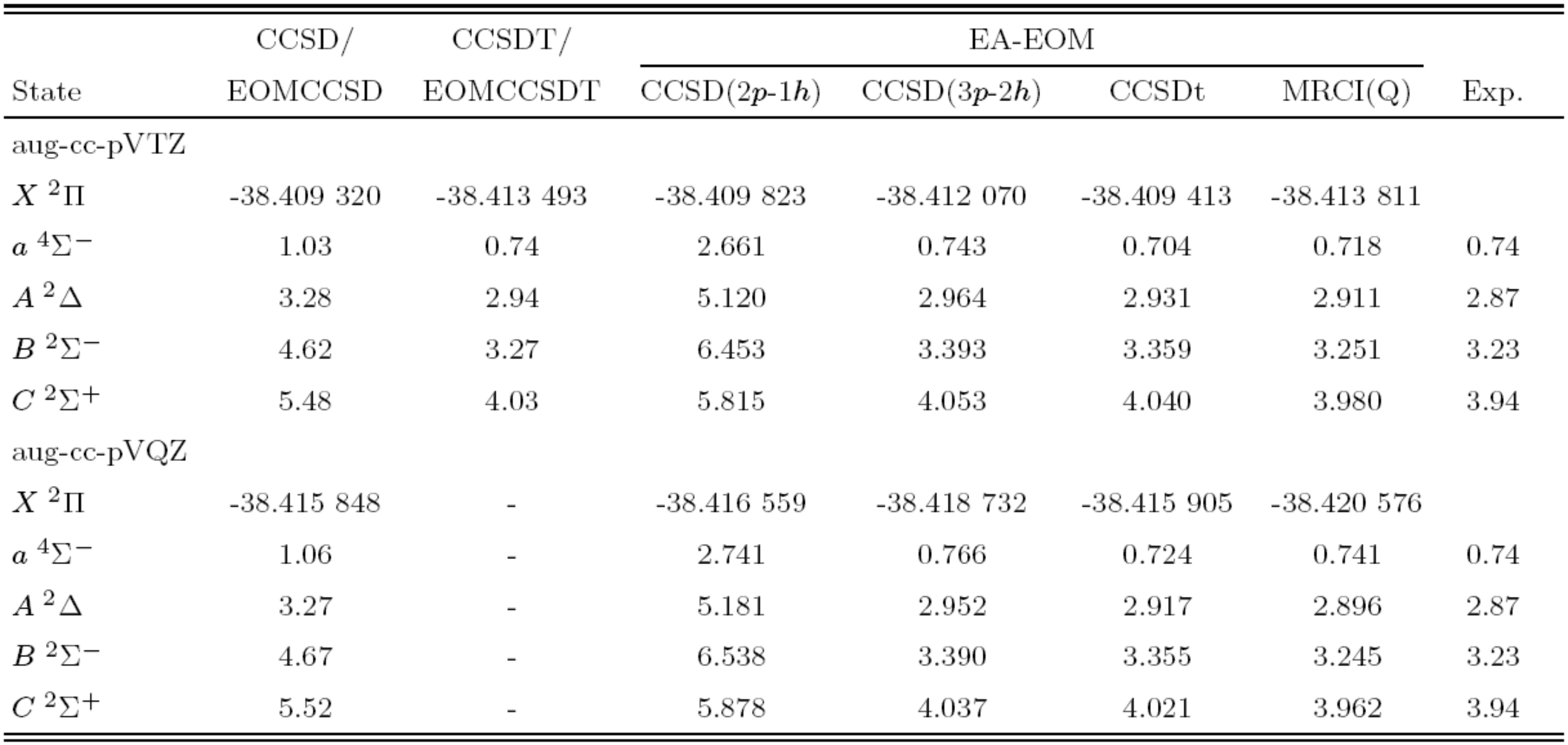
$$r_{\mu,3p\text{-}2h} = \sum_{j>k,\mathbf{A}<b<c} r_{\boxed{\mathbf{A}}bc}^{jk}\, a^{\mathbf{A}} a^{b} a^{c} a_{k} a_{j},$$

$$r_{\mu,3h\text{-}2p} = \sum_{\mathbf{I}>j>k,b<c} r_{bc}^{\boxed{\mathbf{I}}jk}\, a^{b} a^{c} a_{k} a_{j} a_{\mathbf{I}}.$$



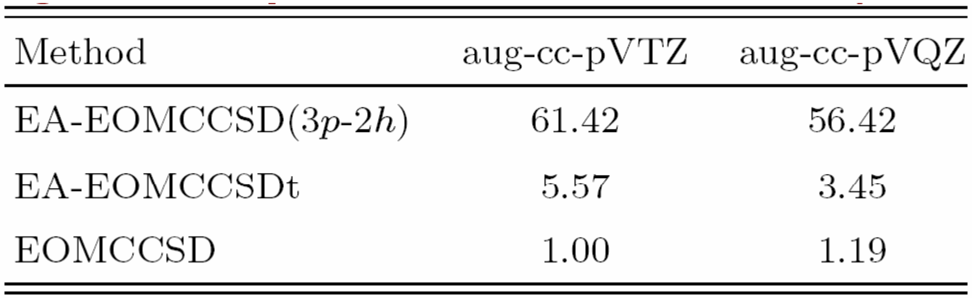
(CCTYP=EA-EOM3A and IP-EOM3A, respectively, in GAMESS)

Adiabatic Excitation Energies of CH (in eV)



State	CCSD/ EOMCCSD	CCSDT/ EOMCCSDT	EA-EOM CCSD($2p$-$1h$)	EA-EOM CCSD($3p$-$2h$)	EA-EOM CCSDt	MRCI(Q)	Exp.
aug-cc-pVTZ							
$X\ ^2\Pi$	-38.409 320	-38.413 493	-38.409 823	-38.412 070	-38.409 413	-38.413 811	
$a\ ^4\Sigma^-$	1.03	0.74	2.661	0.743	0.704	0.718	0.74
$A\ ^2\Delta$	3.28	2.94	5.120	2.964	2.931	2.911	2.87
$B\ ^2\Sigma^-$	4.62	3.27	6.453	3.393	3.359	3.251	3.23
$C\ ^2\Sigma^+$	5.48	4.03	5.815	4.053	4.040	3.980	3.94
aug-cc-pVQZ							
$X\ ^2\Pi$	-38.415 848	-	-38.416 559	-38.418 732	-38.415 905	-38.420 576	
$a\ ^4\Sigma^-$	1.06	-	2.741	0.766	0.724	0.741	0.74
$A\ ^2\Delta$	3.27	-	5.181	2.952	2.917	2.896	2.87
$B\ ^2\Sigma^-$	4.67	-	6.538	3.390	3.355	3.245	3.23
$C\ ^2\Sigma^+$	5.52	-	5.878	4.037	4.021	3.962	3.94

Timings in Multiples of the EA-EOMCCSD(*2p-1h*) Time



Method	aug-cc-pVTZ	aug-cc-pVQZ
EA-EOMCCSD($3p$-$2h$)	61.42	56.42
EA-EOMCCSDt	5.57	3.45
EOMCCSD	1.00	1.19

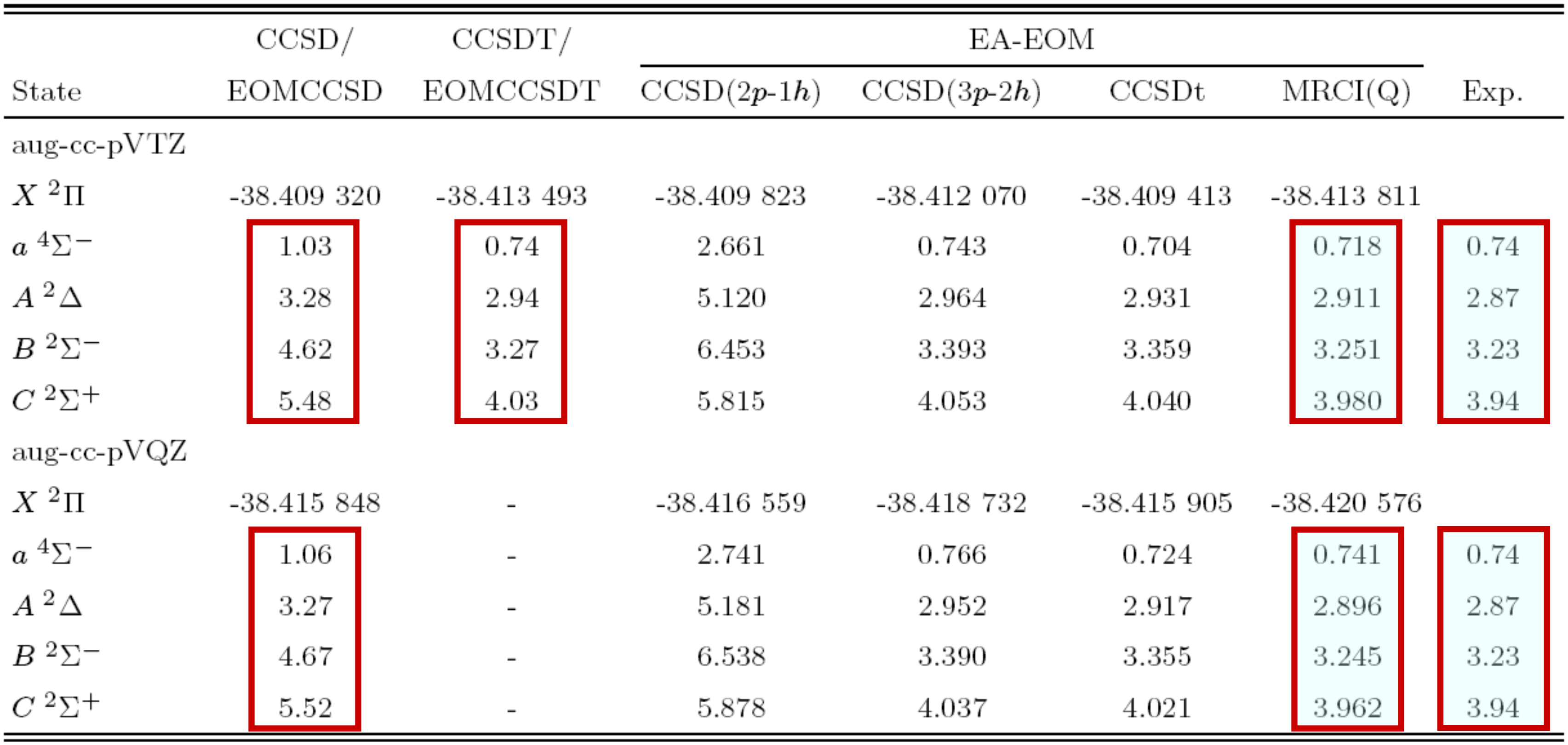
~ $n_o^2 n_u^5$

~$N_u\, n_o^2 n_u^4$

~$n_o^2 n_u^4$

Active orbitals in EA-EOMCCSDt:
$1\pi_x$, $1\pi_y$, 4σ

Adiabatic Excitation Energies of CH (in eV)



State	CCSD/ EOMCCSD	CCSDT/ EOMCCSDT	EA-EOM CCSD(2*p*-1*h*)	EA-EOM CCSD(3*p*-2*h*)	EA-EOM CCSDt	MRCI(Q)	Exp.
aug-cc-pVTZ							
$X\ ^2\Pi$	-38.409 320	-38.413 493	-38.409 823	-38.412 070	-38.409 413	-38.413 811	
$a\ ^4\Sigma^-$	1.03	0.74	2.661	0.743	0.704	0.718	0.74
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aug-cc-pVQZ							
$X\ ^2\Pi$	-38.415 848	-	-38.416 559	-38.418 732	-38.415 905	-38.420 576	
$a\ ^4\Sigma^-$	1.06	-	2.741	0.766	0.724	0.741	0.74
$A\ ^2\Delta$	3.27	-	5.181	2.952	2.917	2.896	2.87
$B\ ^2\Sigma^-$	4.67	-	6.538	3.390	3.355	3.245	3.23
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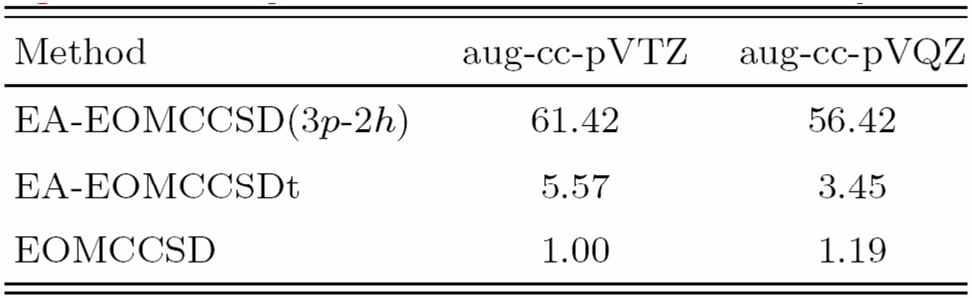
Timings in Multiples of the EA-EOMCCSD(*2p-1h*) Time



Method	aug-cc-pVTZ	aug-cc-pVQZ
EA-EOMCCSD(3*p*-2*h*)	61.42	56.42
EA-EOMCCSDt	5.57	3.45
EOMCCSD	1.00	1.19

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Active orbitals in EA-EOMCCSDt: $1\pi_x$, $1\pi_y$, 4σ

Adiabatic Excitation Energies of CH (in eV)

	CCSD/	CCSDT/	EA-EOM				
State	EOMCCSD	EOMCCSDT	CCSD($2p$-$1h$)	CCSD($3p$-$2h$)	CCSDt	MRCI(Q)	Exp.
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Adiabatic Excitation Energies of CH (in eV)

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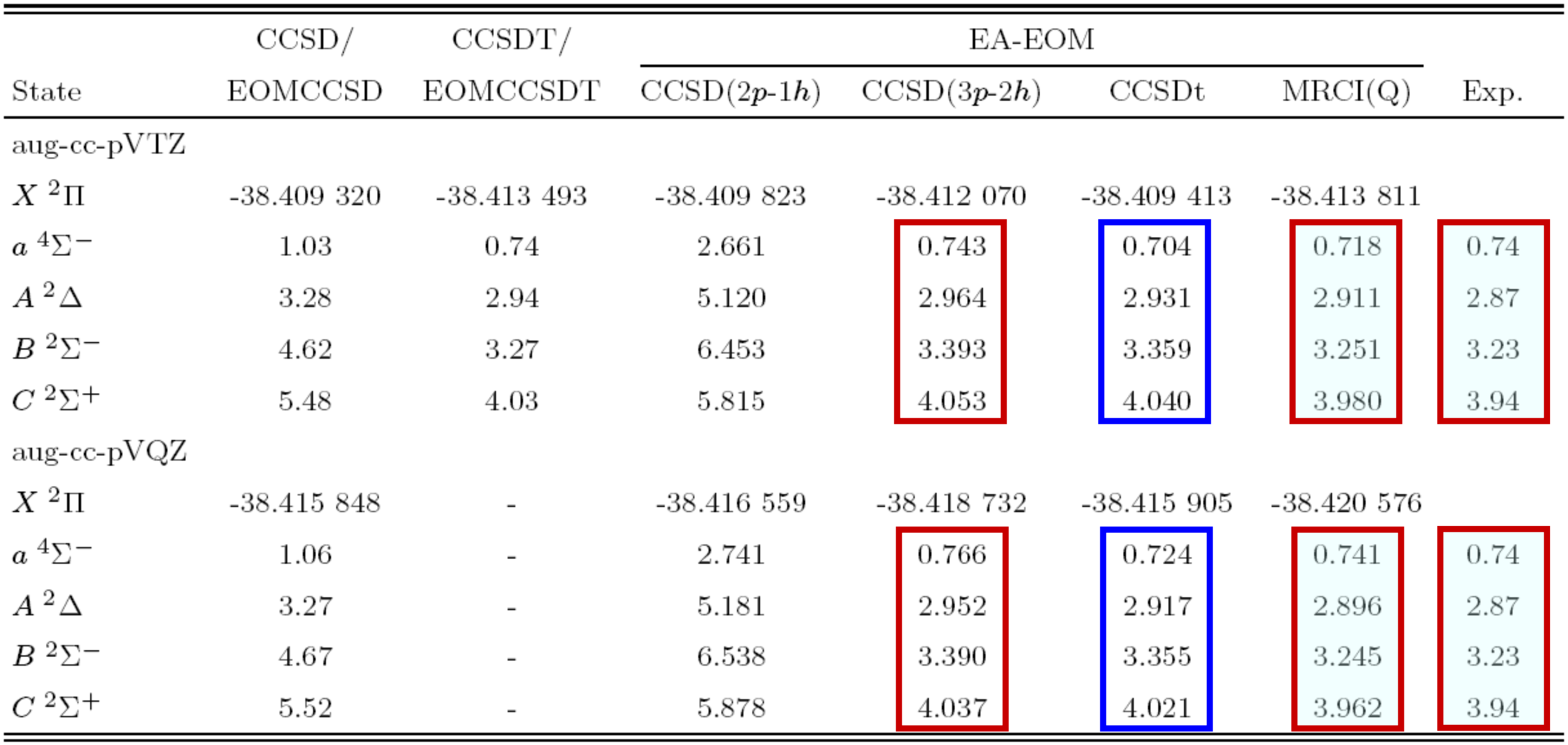

	CCSD/	CCSDT/	EA-EOM				
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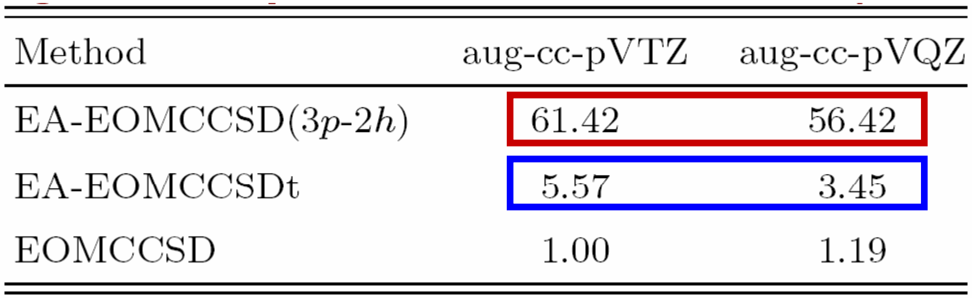

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Active orbitals in EA-EOMCCSDt: $1\pi_x$, $1\pi_y$, 4σ

Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

M. Nooijen and R.J. Bartlett, 1997; M. Nooijen, 2002; K.W. Sattetmeyer, H.F. Schaefer III, and J.F. Stanton, 2003; M. Musiał, R.J. Bartlett, et al., 2011-2013; T. Kuś and A.I. Krylov, 2011-2012; …

$$R_\mu^{(N+2)}\{N_u\} = R_{\mu,2p} + R_{\mu,3p\text{-}1h} + r_{\mu,4p\text{-}2h}$$

$$R_\mu^{(N-2)}\{N_o\} = R_{\mu,2h} + R_{\mu,3h\text{-}1p} + r_{\mu,4h\text{-}2p}$$

$$r_{\mu,4p\text{-}2h} = \sum_{k>l,\mathbf{A}<\mathbf{B}<c<d} r_{\mathbf{AB}cd}^{\;\;\;\;\;kl}(\mu)\, a^{\mathbf{A}} a^{\mathbf{B}} a^c a^d a_l a_k$$

$$r_{\mu,4h\text{-}2p} = \sum_{\mathbf{I}>\mathbf{J}>k>l,c<d} r^{\mathbf{IJ}kl}_{\;\;\;\;\;cd}(\mu)\, a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

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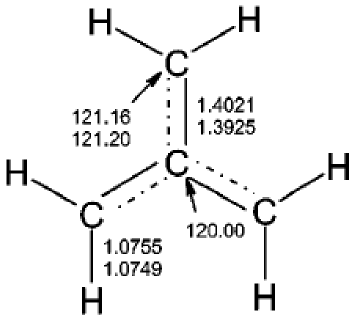
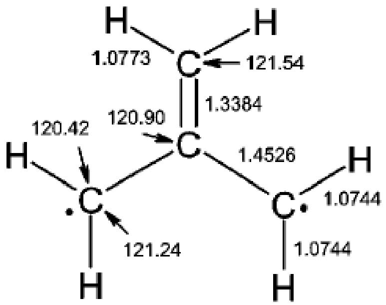
$$r_{\mu,4h\text{-}2p} = \sum_{\mathbf{I}>\mathbf{J}>k>l,c<d} r^{\mathbf{IJ}kl}_{\;\;\;\;\;\;cd}(\mu)\, a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

Example: Singlet-triplet gap in trimethylenemethane (TMM)



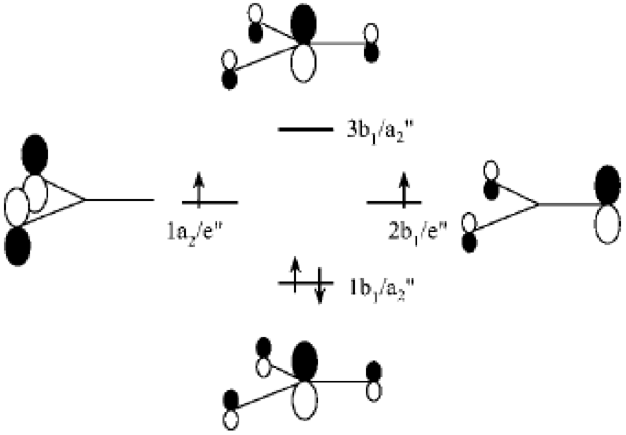
E_{nuc}=106.2361
106.7954

D_{3h} symmetry
$^3A_2'$



E_{nuc}=105.6092

C_{2v} symmetry, planar
$^1A_1$



Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

M. Nooijen and R.J. Bartlett, 1997; M. Nooijen, 2002; K.W. Sattetmeyer, H.F. Schaefer III, and J.F. Stanton, 2003; M. Musiał, R.J. Bartlett, et al., 2011-2013; T. Kuś and A.I. Krylov, 2011-2012; …

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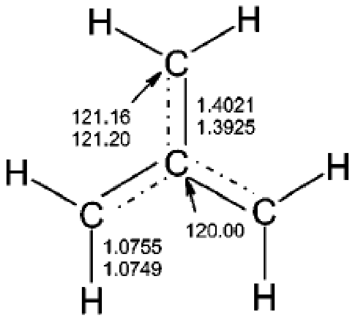

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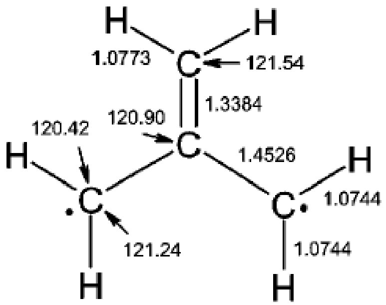

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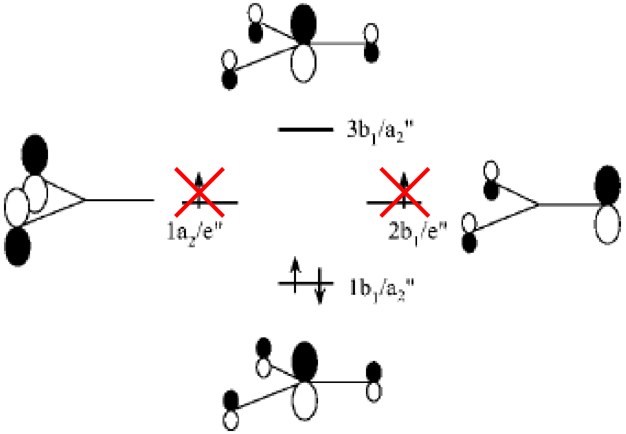

$n_o^2 n_u^6$

DEA: TMM^{2+}

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(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

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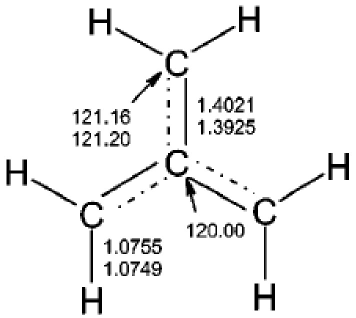

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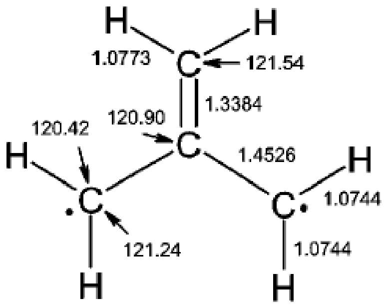

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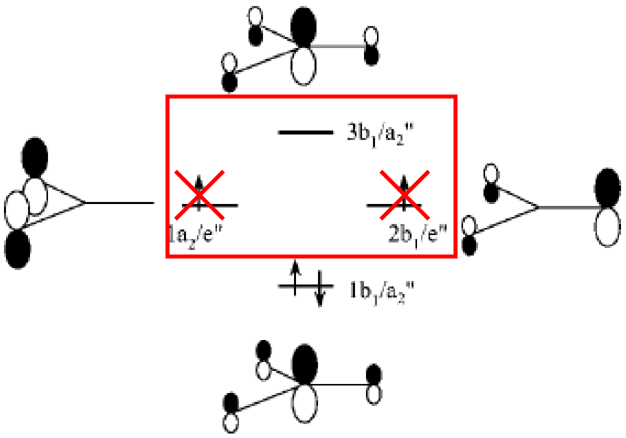

$n_o^2 n_u^6 \rightarrow N_u^2 n_o^2 n_u^4$

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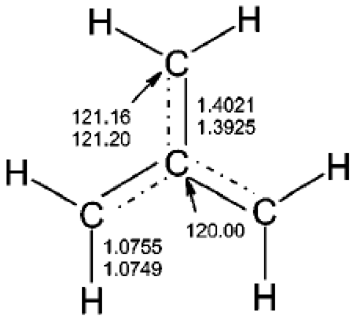
Example: Singlet-triplet gap in trimethylenemethane (TMM)



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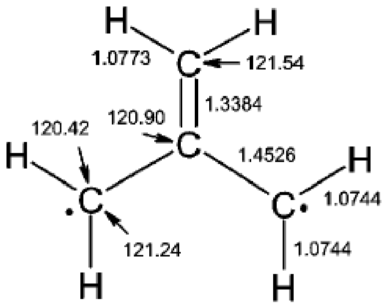

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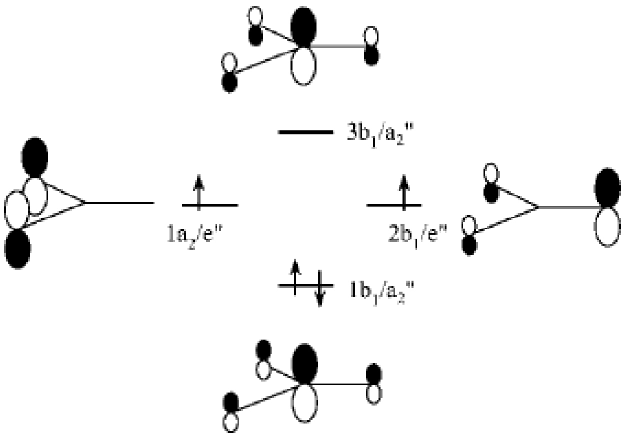

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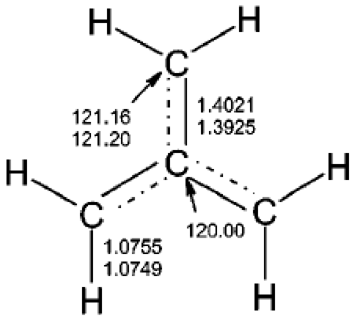
Example: Singlet-triplet gap in trimethylenemethane (TMM)



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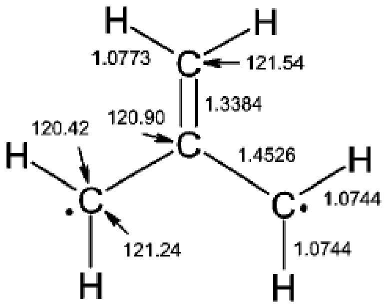
106.7954
D_{3h} symmetry
$^3A_2'$



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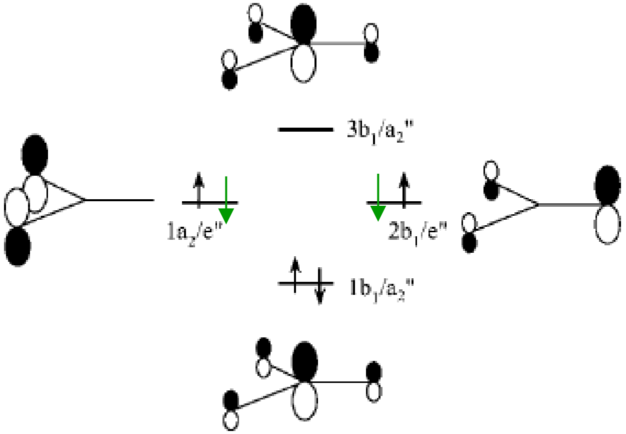

DIP: TMM^{2-}

$n_o^4 n_u^4$

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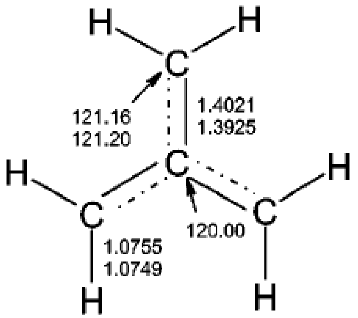
Example: Singlet-triplet gap in trimethylenemethane (TMM)



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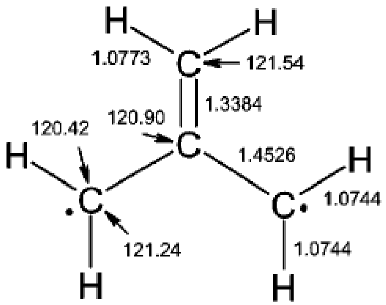
$^3A_2'$



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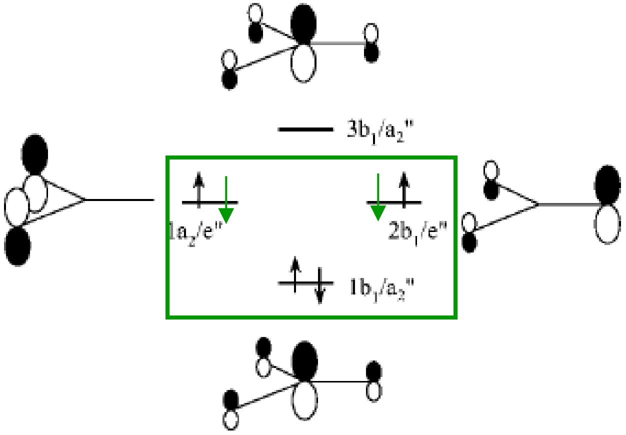

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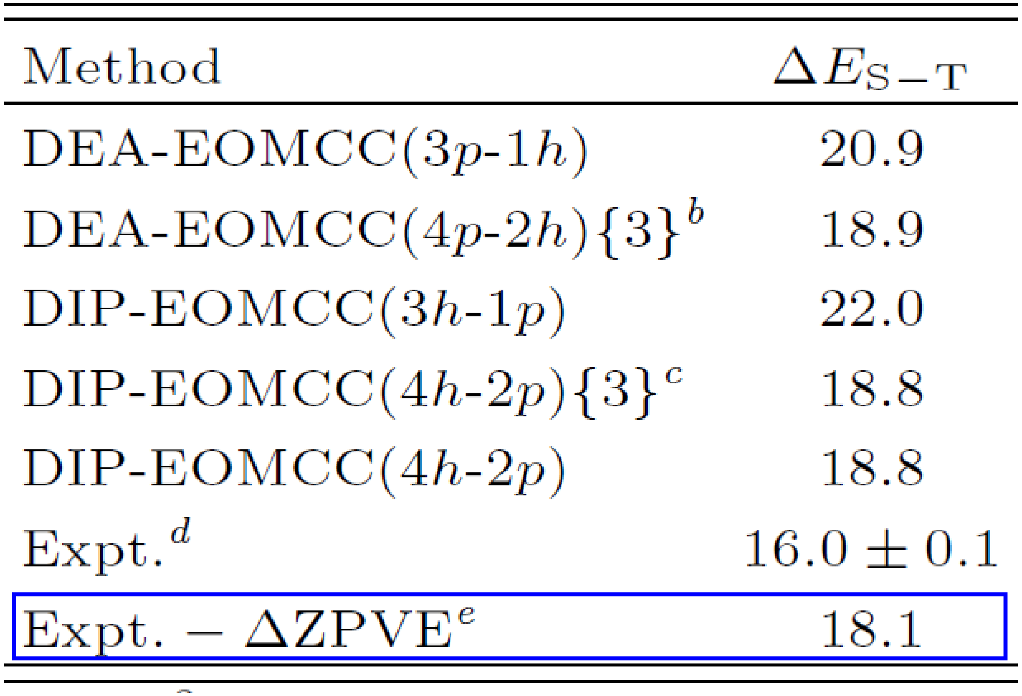
(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)



Method	$\Delta E_{\mathrm{S-T}}$
DEA-EOMCC(3p-1h)	20.9
DEA-EOMCC(4p-2h){3}[b]	18.9
DIP-EOMCC(3h-1p)	22.0
DIP-EOMCC(4h-2p){3}[c]	18.8
DIP-EOMCC(4h-2p)	18.8
Expt.[d]	16.0 ± 0.1
Expt. − ΔZPVE[e]	18.1

Example: Singlet-triplet gap in trimethylenemethane (TMM), in kcal/mol

[geometries from L.V. Slipchenko and A.I. Krylov,
J. Chem. Phys. **117**, 4694 (2002)]

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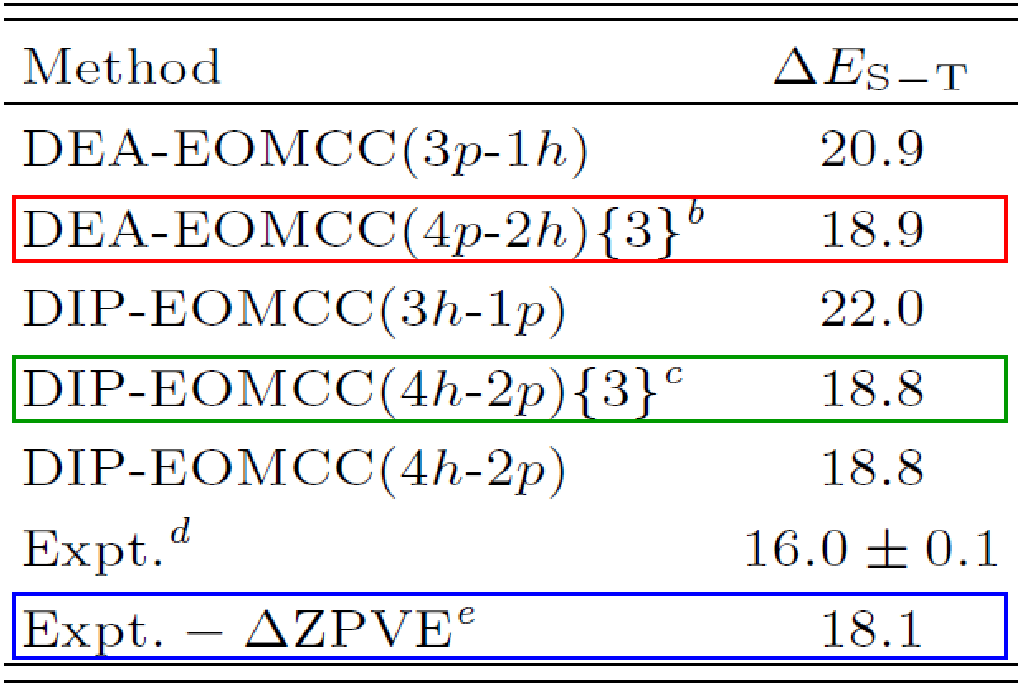

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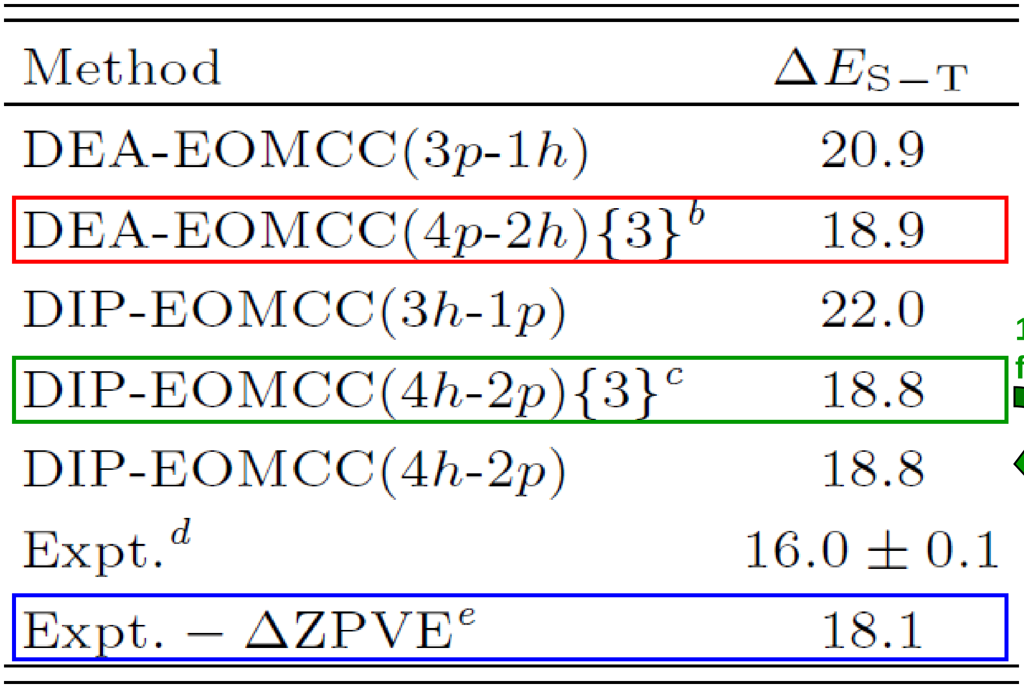

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15 times faster

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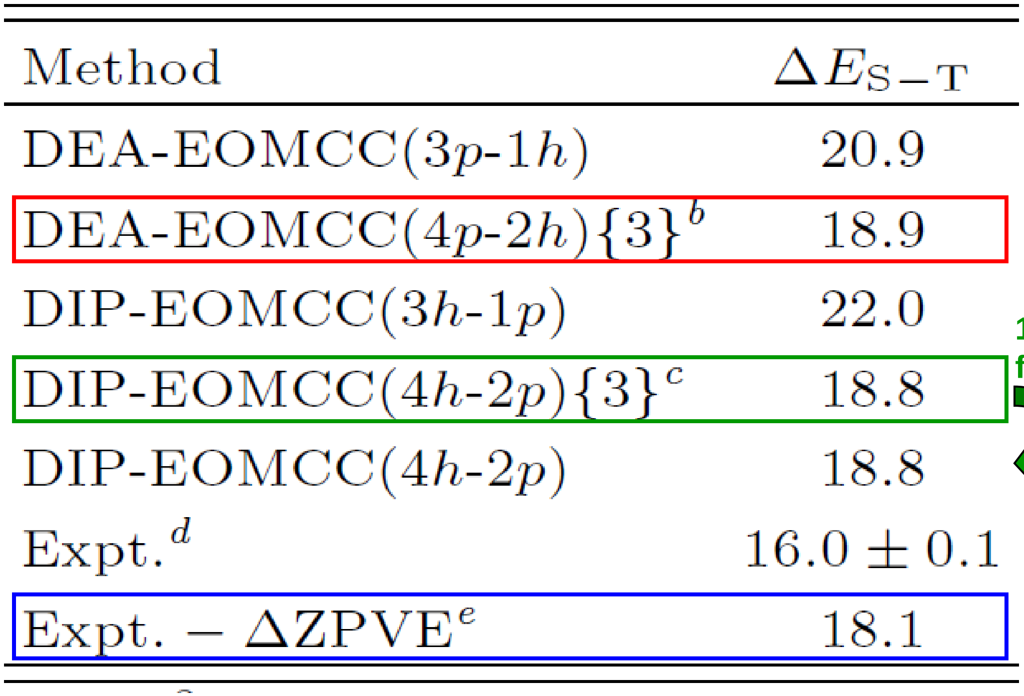

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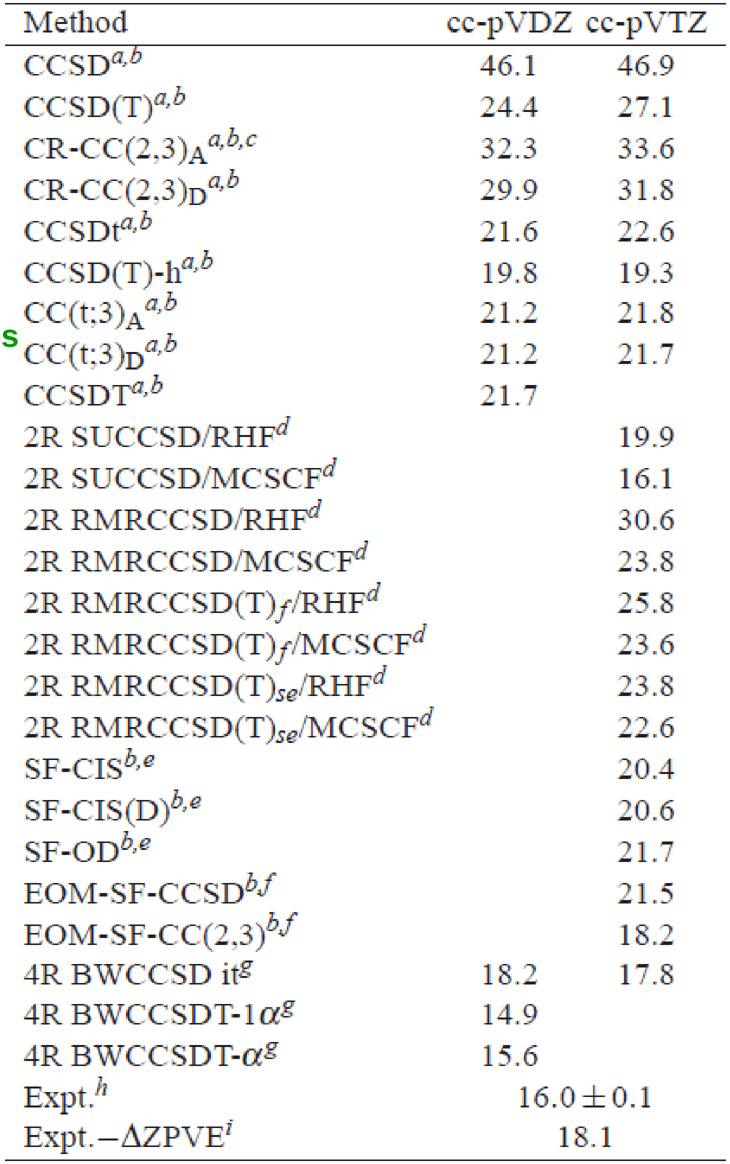

Method	cc-pVDZ	cc-pVTZ
CCSD[a,b]	46.1	46.9
CCSD(T)[a,b]	24.4	27.1
CR-CC(2,3)$_{\mathrm{A}}$[a,b,c]	32.3	33.6
CR-CC(2,3)$_{\mathrm{D}}$[a,b]	29.9	31.8
CCSDt[a,b]	21.6	22.6
CCSD(T)-h[a,b]	19.8	19.3
CC(t;3)$_{\mathrm{A}}$[a,b]	21.2	21.8
CC(t;3)$_{\mathrm{D}}$[a,b]	21.2	21.7
CCSDT[a,b]	21.7	
2R SUCCSD/RHF[d]		19.9
2R SUCCSD/MCSCF[d]		16.1
2R RMRCCSD/RHF[d]		30.6
2R RMRCCSD/MCSCF[d]		23.8
2R RMRCCSD(T)$_f$/RHF[d]		25.8
2R RMRCCSD(T)$_f$/MCSCF[d]		23.6
2R RMRCCSD(T)$_{se}$/RHF[d]		23.8
2R RMRCCSD(T)$_{se}$/MCSCF[d]		22.6
SF-CIS[b,e]		20.4
SF-CIS(D)[b,e]		20.6
SF-OD[b,e]		21.7
EOM-SF-CCSD[b,f]		21.5
EOM-SF-CC(2,3)[b,f]		18.2
4R BWCCSD it[g]	18.2	17.8
4R BWCCSDT-1α[g]	14.9	
4R BWCCSDT-α[g]	15.6	
Expt.[h]	16.0 ± 0.1	
Expt.−ΔZPVE[i]	18.1	

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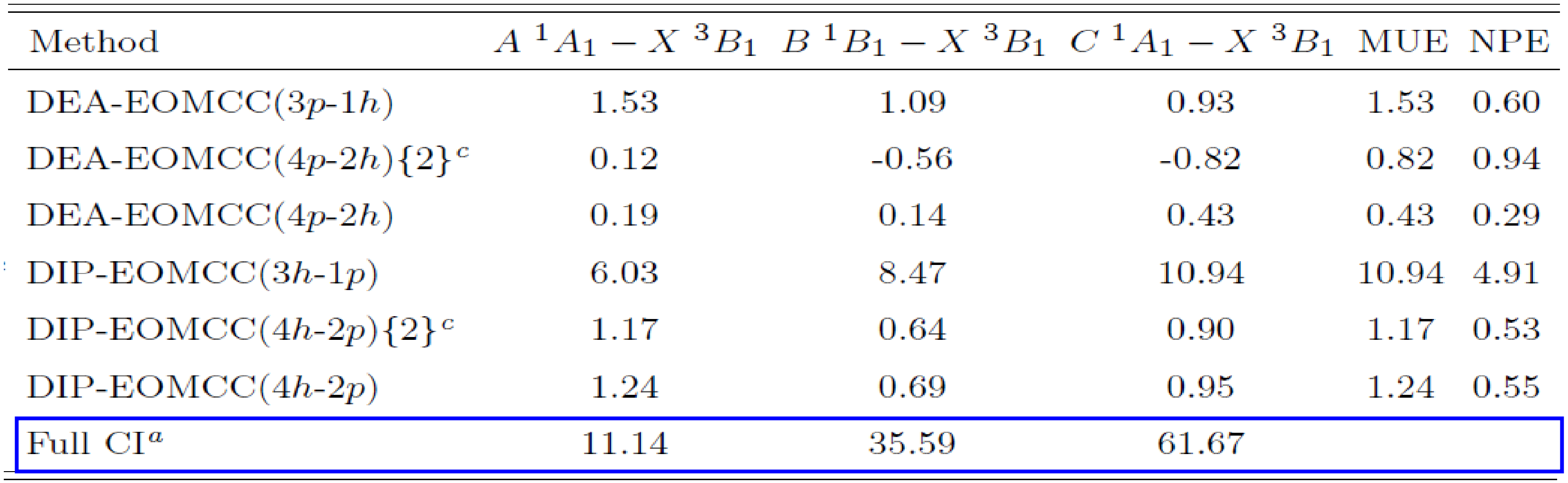
(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

Another example: Adiabatic excitation energies characterizing the low-lying states of methylene (TZ2P basis, errors relative to full CI, in kcal/mol)

$$X\ {}^3B_1,\ B\ {}^1B_1 \sim (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^1(1b_1)^1}$$

$$A\ {}^1A_1,\ C\ {}^1A_1 \sim (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^2(1b_1)^0},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^2}$$



Method	$A\ {}^1A_1 - X\ {}^3B_1$	$B\ {}^1B_1 - X\ {}^3B_1$	$C\ {}^1A_1 - X\ {}^3B_1$	MUE	NPE
DEA-EOMCC(3*p*-1*h*)	1.53	1.09	0.93	1.53	0.60
DEA-EOMCC(4*p*-2*h*){2}[c]	0.12	-0.56	-0.82	0.82	0.94
DEA-EOMCC(4*p*-2*h*)	0.19	0.14	0.43	0.43	0.29
DIP-EOMCC(3*h*-1*p*)	6.03	8.47	10.94	10.94	4.91
DIP-EOMCC(4*h*-2*p*){2}[c]	1.17	0.64	0.90	1.17	0.53
DIP-EOMCC(4*h*-2*p*)	1.24	0.69	0.95	1.24	0.55
Full CI[a]	11.14	35.59	61.67		

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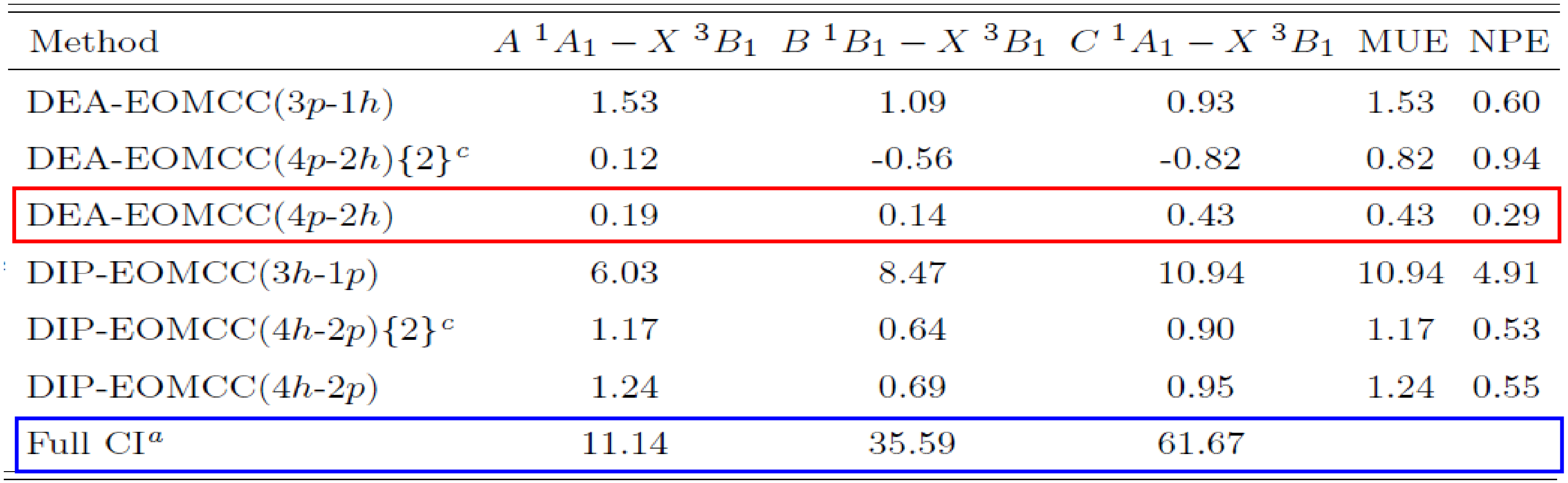
$$A\ {}^1A_1,\ C\ {}^1A_1 \sim (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^2(1b_1)^0},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^2}$$

DEA : $\mathbf{CH_2^{2+}},\ (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^0(1b_1)^0$ $n_o^2 n_u^6$



Method	$A\ {}^1A_1 - X\ {}^3B_1$	$B\ {}^1B_1 - X\ {}^3B_1$	$C\ {}^1A_1 - X\ {}^3B_1$	MUE	NPE
DEA-EOMCC(3p-1h)	1.53	1.09	0.93	1.53	0.60
DEA-EOMCC(4p-2h){2}^{c}	0.12	-0.56	-0.82	0.82	0.94
DEA-EOMCC(4p-2h)	0.19	0.14	0.43	0.43	0.29
DIP-EOMCC(3h-1p)	6.03	8.47	10.94	10.94	4.91
DIP-EOMCC(4h-2p){2}^{c}	1.17	0.64	0.90	1.17	0.53
DIP-EOMCC(4h-2p)	1.24	0.69	0.95	1.24	0.55
Full CI^a	11.14	35.59	61.67		

Biradicals via the active-space DEA- and DIP-EOMCC

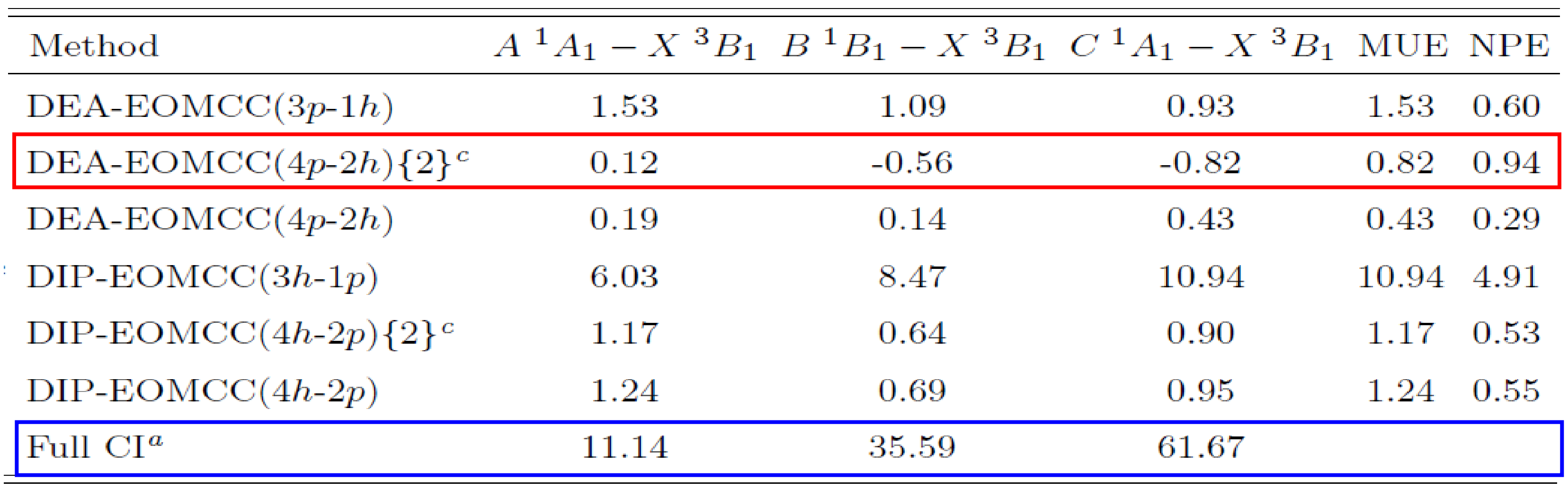
(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

Another example: Adiabatic excitation energies characterizing the low-lying states of methylene (TZ2P basis, errors relative to full CI, in kcal/mol)

$$X\ {}^3B_1,\ \ B\ {}^1B_1 \sim (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^1(1b_1)^1}$$

$$A\ {}^1A_1,\ \ C\ {}^1A_1 \sim (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^2(1b_1)^0},\ \ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^2}$$

DEA : $\mathbf{CH_2^{2+}},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^0}$ $\quad n_o^{\,2}n_u^{\,6} \rightarrow N_u^{\,2}\,n_o^{\,2}n_u^{\,4}$



Method	$A\ {}^1A_1 - X\ {}^3B_1$	$B\ {}^1B_1 - X\ {}^3B_1$	$C\ {}^1A_1 - X\ {}^3B_1$	MUE	NPE
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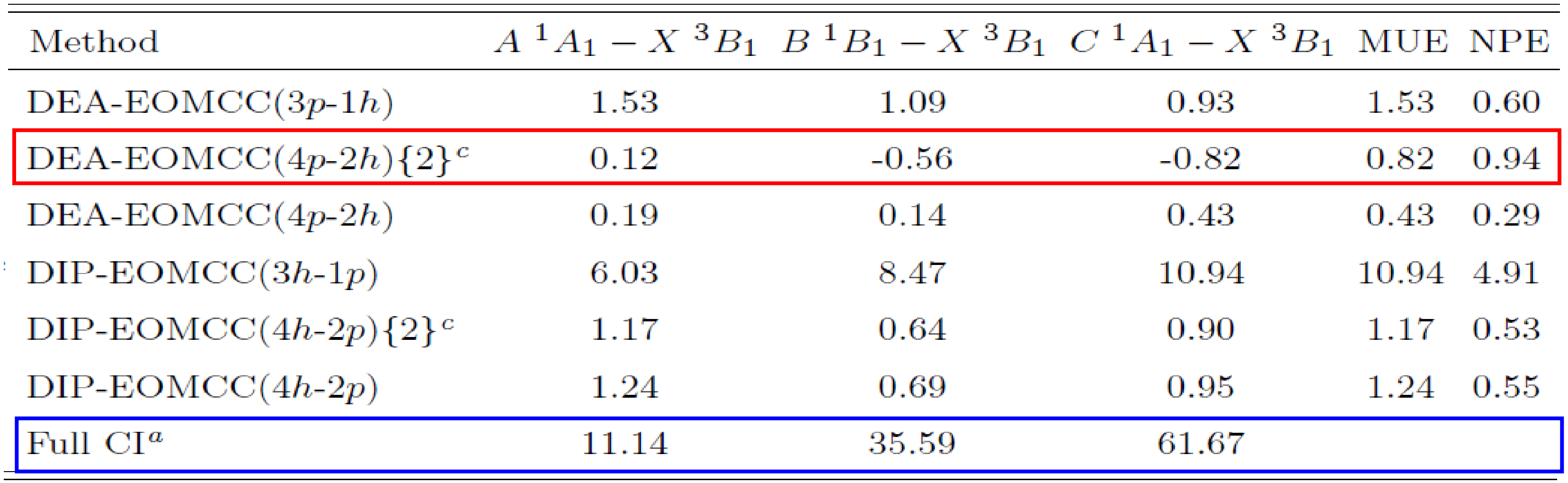
DEA : $\mathrm{CH}_2^{2+},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^0}$ $\quad n_o^2 n_u^6 \rightarrow N_u^2\, n_o^2 n_u^4$



Method	$A\ {}^1A_1 - X\ {}^3B_1$	$B\ {}^1B_1 - X\ {}^3B_1$	$C\ {}^1A_1 - X\ {}^3B_1$	MUE	NPE	
DEA-EOMCC(3p-1h)	1.53	1.09	0.93	1.53	0.60	**2 s/iter**
DEA-EOMCC(4p-2h){2}[c]	0.12	-0.56	-0.82	0.82	0.94	**6 s/iter.**
DEA-EOMCC(4p-2h)	0.19	0.14	0.43	0.43	0.29	**2621 s/iter.**
DIP-EOMCC(3h-1p)	6.03	8.47	10.94	10.94	4.91	
DIP-EOMCC(4h-2p){2}[c]	1.17	0.64	0.90	1.17	0.53	
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DEA : $\mathrm{CH}_2^{2+},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^0(1b_1)^0}$ $n_o^2 n_u^6 \rightarrow N_u^2 n_o^2 n_u^4$

DIP : $\mathrm{CH}_2^{2-},\ (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ $n_o^4 n_u^4$

Method	$A\ ^1A_1 - X\ ^3B_1$	$B\ ^1B_1 - X\ ^3B_1$	$C\ ^1A_1 - X\ ^3B_1$	MUE	NPE	
DEA-EOMCC(3*p*-1*h*)	1.53	1.09	0.93	1.53	0.60	2 s/iter
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DIP : $\mathrm{CH}_2^{2-},\ (1a_1)^2(2a_1)^2(1b_2)^2\boxed{(3a_1)^2(1b_1)^2}$ $\quad n_o^4 n_u^4 \rightarrow N_o^2 n_o^2 n_u^4$

Method	$A\ {}^1A_1 - X\ {}^3B_1$	$B\ {}^1B_1 - X\ {}^3B_1$	$C\ {}^1A_1 - X\ {}^3B_1$	MUE	NPE	
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Full CI[a]	11.14	35.59	61.67			

MERGING ACTIVE-SPACE AND RENORMALIZED COUPLED-CLUSTER METHODS, CC(*P*;*Q*), CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), ETC. SCHEMES

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

Key idea: Replace the previously developed moment expansions, which aim at describing the differences between the exact (full CI) energies E_μ and the corresponding CC/EOMCC energies obtained using conventional truncation schemes for the cluster operator *T* and, in the case of excited states, excitation operator R_μ by the expansions that enable us to correct the energies obtained with arbitrary truncations of *T* and R_μ for the selected higher-order correlation effects of interest.

Examples (and motivation):

Correct the results of CCSDt calculations, where $T \approx T^{(\mathrm{CCSDt})} = T_1 + T_2 + t_3$, for the remaining triples effects neglected in CCSDt calculations, or correct EOMCCSDtq energies, obtained with $T \approx T^{(\mathrm{CCSDtq})} = T_1 + T_2 + t_3 + t_4$ and and $R_\mu \approx R_\mu^{(\mathrm{CCSDtq})} = R_1 + R_2 + r_3 + r_4$ for the remaining triples and quadruples.

CC(*P*;*Q*) HIERARCHY.

CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. schemes

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys, 2012]

$$E_\mu^{(P+Q)} \equiv E_\mu^{(P)} + \delta_\mu(P;Q), \qquad \delta_\mu(P;Q) = \sum_{\substack{|\Phi_K\rangle \in \mathscr{H}^{(Q)} \\ \mathrm{rank}(|\Phi_K\rangle) \leq \min(N_\mu^{(P)}, \Xi^{(Q)})}} \ell_{\mu,K}(P)\, \mathfrak{M}_{\mu,K}(P)$$

$$\mathfrak{M}_{\mu,K}(P) = \langle \Phi_K | (\bar{H}^{(P)} R_\mu^{(P)}) | \Phi \rangle, \qquad \bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C$$

$$\ell_{\mu,K}(P) = \langle \Phi | L_\mu^{(P)} \bar{H}^{(P)} | \Phi_K \rangle / D_{\mu,K}(P), \quad D_{\mu,K}(P) = E_\mu^{(P)} - \langle \Phi_K | \bar{H}^{(P)} | \Phi_K \rangle$$

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$$\left.\begin{array}{l} E_\mu^{(\mathrm{CC(t;3)})} = E_\mu^{(\mathrm{CCSDt})} + \delta_\mu(\mathrm{t};3) \\ \delta_\mu(\mathrm{t};3) = \displaystyle\sum_{|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(\mathrm{T})} \ominus \mathscr{H}^{(\mathrm{t})}} \ell_{\mu,ijk}^{abc}(\mathrm{CCSDt})\, \mathfrak{M}_{\mu,abc}^{ijk}(\mathrm{CCSDt}) \end{array}\right\} \Rightarrow \mathrm{CC(t;3)}$$

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$$\left.\begin{aligned} E_\mu^{(\mathrm{CC(t,q;3)})} &= E_\mu^{(\mathrm{CCSDtq})} + \delta_\mu(\mathrm{t,q};3) \\ \delta_\mu(\mathrm{t,q};3) &= \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(\mathrm{T})} \ominus \mathscr{H}^{(\mathrm{t})}} \ell_{\mu,ijk}^{abc}(\mathrm{CCSDtq})\, \mathfrak{M}_{\mu,abc}^{ijk}(\mathrm{CCSDtq}). \end{aligned}\right\} \Rightarrow \text{CC(t,q;3)}$$

CC(*P*;*Q*) HIERARCHY.

CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. schemes

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➡ **CC(t;3)**

$$E_\mu^{(\mathrm{CC(t,q;3)})} = E_\mu^{(\mathrm{CCSDtq})} + \delta_\mu(\mathrm{t},\mathrm{q};3)$$

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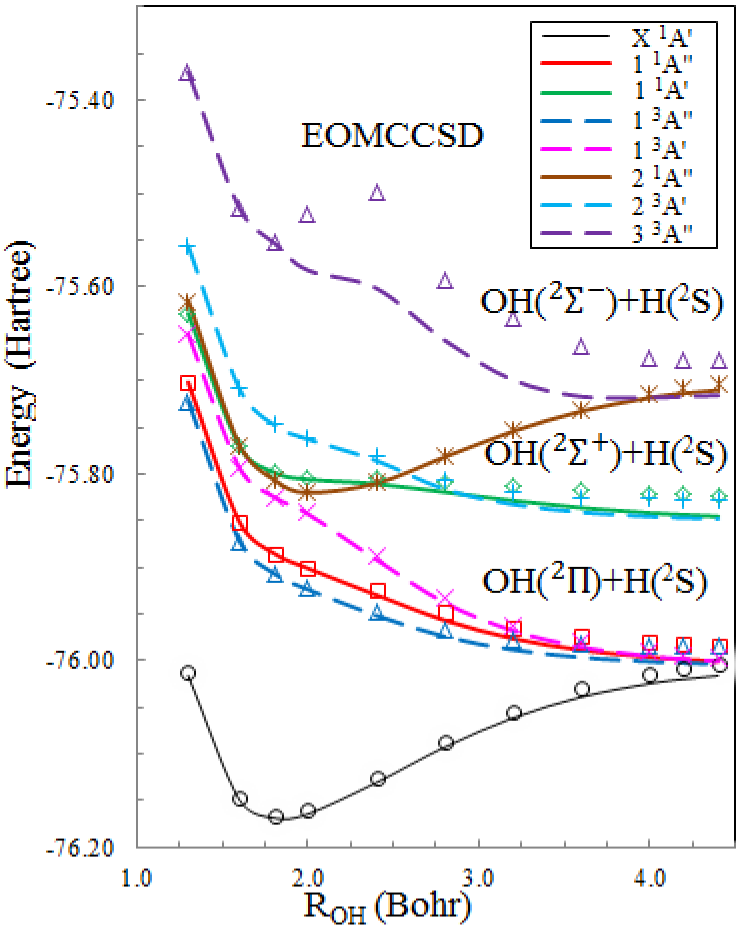
$$E_\mu^{(\mathrm{CC(t,q;3,4)})} = E_\mu^{(\mathrm{CCSDtq})} + \delta_\mu(\mathrm{t},\mathrm{q};3,4)$$

$$\begin{aligned}\delta_\mu(\mathrm{t},\mathrm{q};3,4) \; = \; & \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(\mathrm{T})} \ominus \mathscr{H}^{(\mathrm{t})}} \ell_{\mu,ijk}^{abc}(\mathrm{CCSDtq})\,\mathfrak{M}_{\mu,abc}^{ijk}(\mathrm{CCSDtq}) \\ & + \sum_{|\Phi_{ijkl}^{abcd}\rangle \in \mathscr{H}^{(\mathrm{Q})} \ominus \mathscr{H}^{(\mathrm{q})}} \ell_{\mu,ijkl}^{abcd}(\mathrm{CCSDtq})\,\mathfrak{M}_{\mu,abcd}^{ijkl}(\mathrm{CCSDtq})\end{aligned}$$

➡ **CC(t,q;3,4)**

EXCITED-STATE POTENTIAL ENERGY SURFACES OF THE WATER MOLECULE

[J. Shen and P. Piecuch, in preparation; cf., also, J.J. Lutz and P. Piecuch, Comput. Theor. Chem., 2014]



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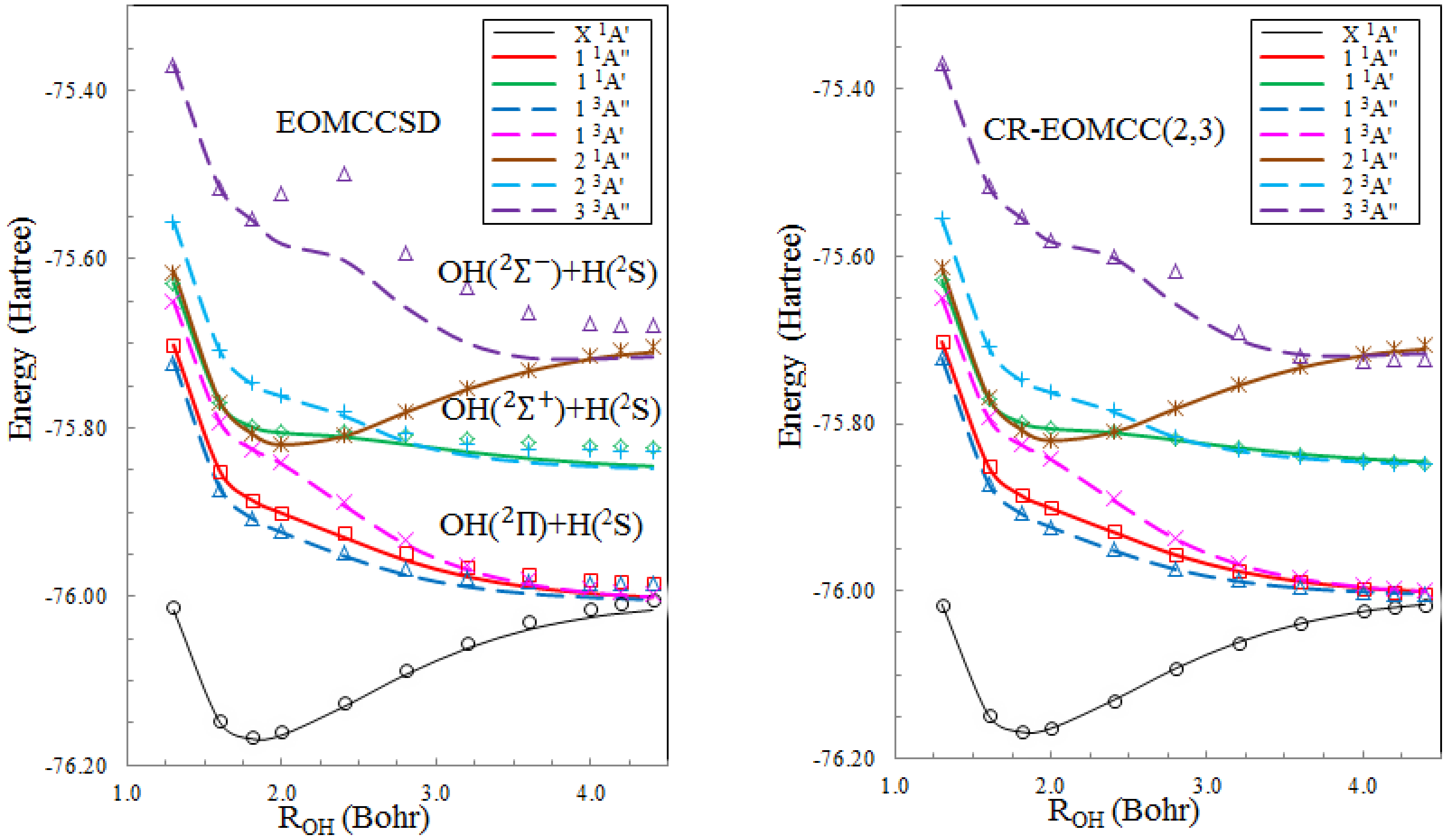

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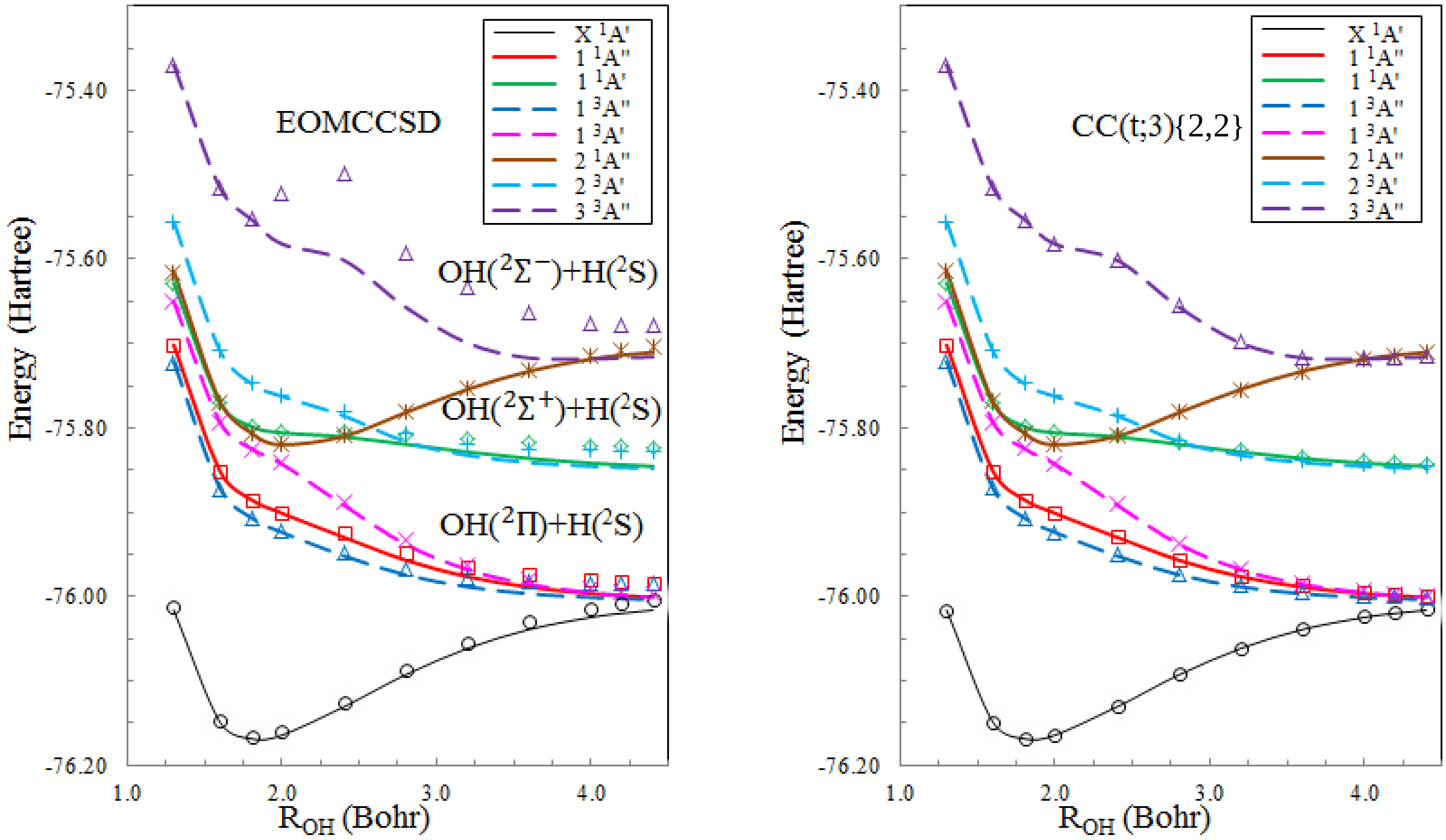

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Mean unsigned errors (MUEs) rel. to full CI, in mH, for the A' and A″ excited states

STATE	7R-SU-CCSD [1]	EOMCCSD	CR-EOMCC(2,3)	CC(t;3)
1 $^1A'$	3.94	10.80	0.88	1.10
2 $^1A'$	3.12	15.59	1.89	1.61
3 $^1A'$	12.44	14.86	3.86	2.12
1 $^3A'$	4.25	3.03	1.31	0.92
2 $^3A'$	4.15	9.67	0.68	1.25
3 $^3A'$	6.48	11.09	4.89	2.08
AVERAGE MUE	**5.73**	**10.84**	**3.38**	**1.51**

STATE	4R-SU-CCSD [1]	(8,4)-CCSD [1]	EOMCCSD	CR-EOMCC(2,3)	CC(t;3)
1 $^1A''$	2.85	1.32	8.31	0.87	0.99
2 $^1A''$	6.22	3.80	1.54	0.89	0.19
1 $^3A''$	3.88	2.82	8.53	0.58	1.19
2 $^3A''$	12.62	1.95	8.95	4.13	0.63
AVERAGE MUE	**6.39**	**2.47**	**6.83**	**1.62**	**0.75**

[1] X. Li and J. Paldus, *J. Chem. Phys.* 133, 024102 (2010).

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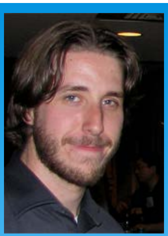

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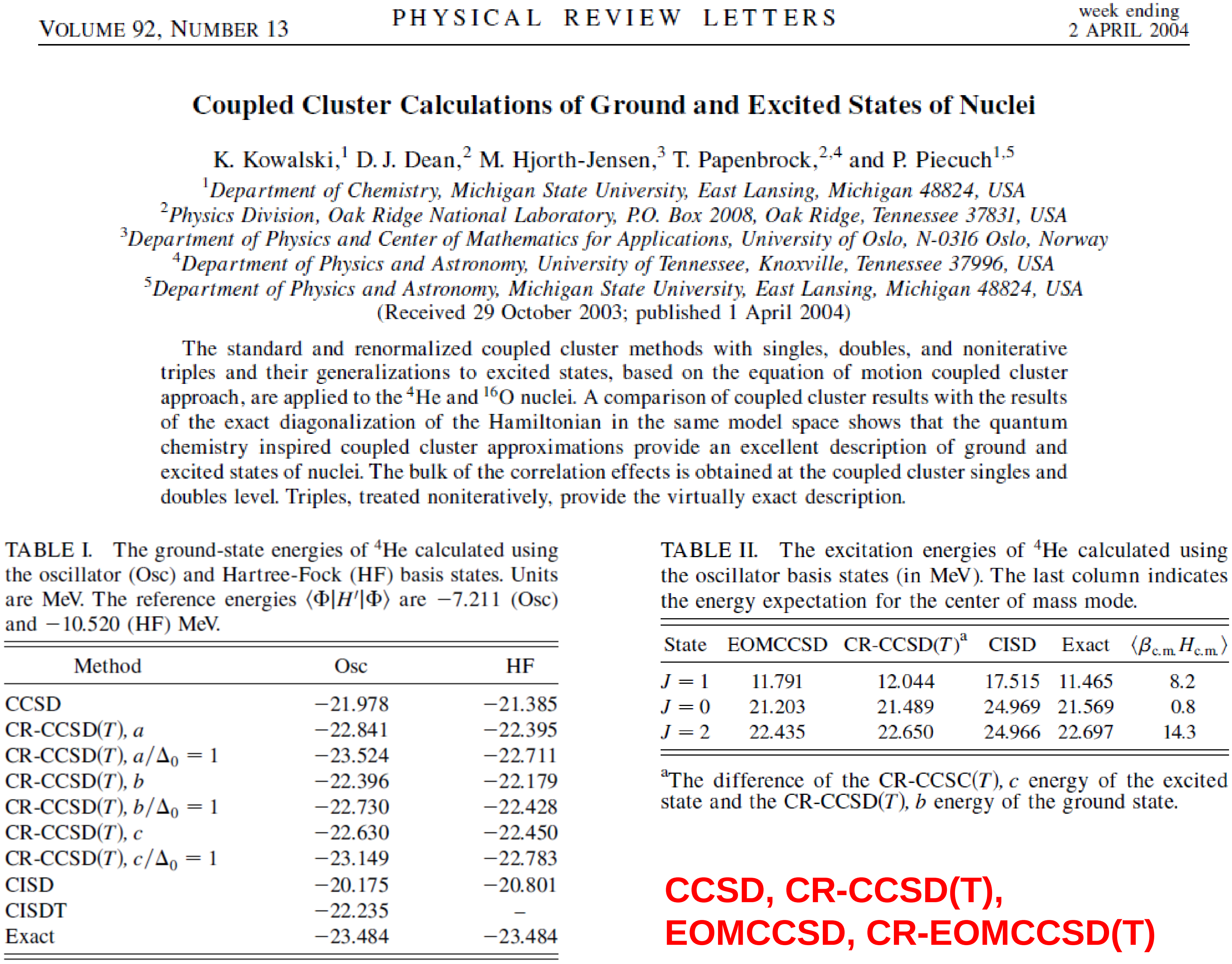
Collaborators (development, benchmarks, and applications – nuclear physics): Sven Binder, B. Alex Brown, David J. Dean, Gaute Hagen, Morten Hjorth-Jensen, Mihai Horoi, Thomas Papenbrock, Robert Roth.



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Coupled Cluster Calculations of Ground and Excited States of Nuclei

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The standard and renormalized coupled cluster methods with singles, doubles, and noniterative triples and their generalizations to excited states, based on the equation of motion coupled cluster approach, are applied to the ^{4}He and ^{16}O nuclei. A comparison of coupled cluster results with the results of the exact diagonalization of the Hamiltonian in the same model space shows that the quantum chemistry inspired coupled cluster approximations provide an excellent description of ground and excited states of nuclei. The bulk of the correlation effects is obtained at the coupled cluster singles and doubles level. Triples, treated noniteratively, provide the virtually exact description.

TABLE I. The ground-state energies of ^{4}He calculated using the oscillator (Osc) and Hartree-Fock (HF) basis states. Units are MeV. The reference energies $\langle\Phi|H'|\Phi\rangle$ are -7.211 (Osc) and -10.520 (HF) MeV.

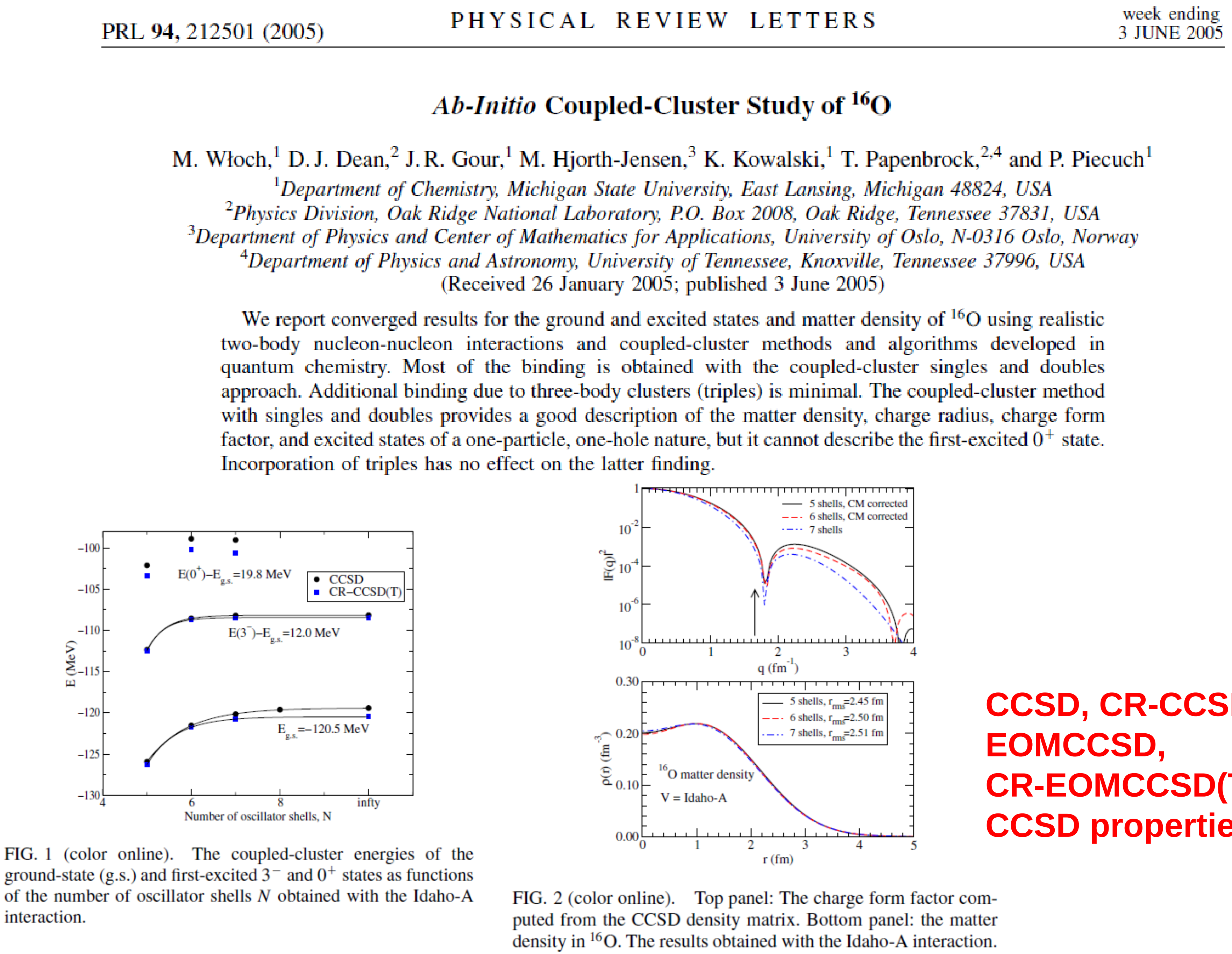
Method	Osc	HF
CCSD	-21.978	-21.385
CR-CCSD(T), a	-22.841	-22.395
CR-CCSD(T), $a/\Delta_0 = 1$	-23.524	-22.711
CR-CCSD(T), b	-22.396	-22.179
CR-CCSD(T), $b/\Delta_0 = 1$	-22.730	-22.428
CR-CCSD(T), c	-22.630	-22.450
CR-CCSD(T), $c/\Delta_0 = 1$	-23.149	-22.783
CISD	-20.175	-20.801
CISDT	-22.235	–
Exact	-23.484	-23.484

TABLE II. The excitation energies of ^{4}He calculated using the oscillator basis states (in MeV). The last column indicates the energy expectation for the center of mass mode.

State	EOMCCSD	CR-CCSD(T)[a]	CISD	Exact	$\langle\beta_{\text{c.m.}} H_{\text{c.m.}}\rangle$
$J = 1$	11.791	12.044	17.515	11.465	8.2
$J = 0$	21.203	21.489	24.969	21.569	0.8
$J = 2$	22.435	22.650	24.966	22.697	14.3

[a] The difference of the CR-CCSC(T), c energy of the excited state and the CR-CCSD(T), b energy of the ground state.

CCSD, CR-CCSD(T), EOMCCSD, CR-EOMCCSD(T)



PRL **94,** 212501 (2005) PHYSICAL REVIEW LETTERS week ending 3 JUNE 2005

Ab-Initio Coupled-Cluster Study of ^{16}O

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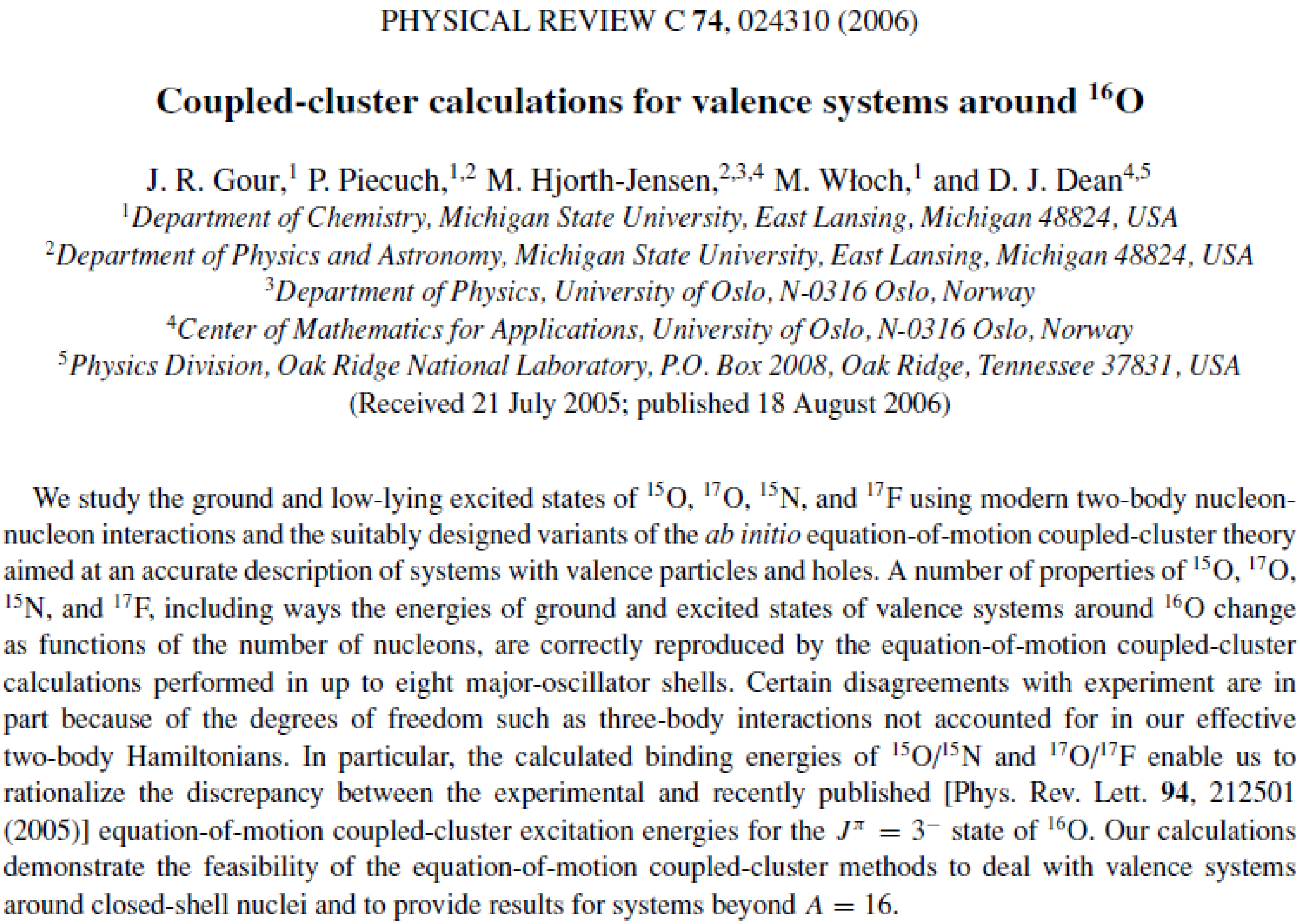
We report converged results for the ground and excited states and matter density of ^{16}O using realistic two-body nucleon-nucleon interactions and coupled-cluster methods and algorithms developed in quantum chemistry. Most of the binding is obtained with the coupled-cluster singles and doubles approach. Additional binding due to three-body clusters (triples) is minimal. The coupled-cluster method with singles and doubles provides a good description of the matter density, charge radius, charge form factor, and excited states of a one-particle, one-hole nature, but it cannot describe the first-excited 0^+ state. Incorporation of triples has no effect on the latter finding.

FIG. 1 (color online). The coupled-cluster energies of the ground-state (g.s.) and first-excited 3^- and 0^+ states as functions of the number of oscillator shells N obtained with the Idaho-A interaction.

FIG. 2 (color online). Top panel: The charge form factor computed from the CCSD density matrix. Bottom panel: the matter density in ^{16}O. The results obtained with the Idaho-A interaction.

CCSD, CR-CCSD(T), EOMCCSD, CR-EOMCCSD(T), CCSD properties



PHYSICAL REVIEW C **74**, 024310 (2006)

Coupled-cluster calculations for valence systems around ^{16}O

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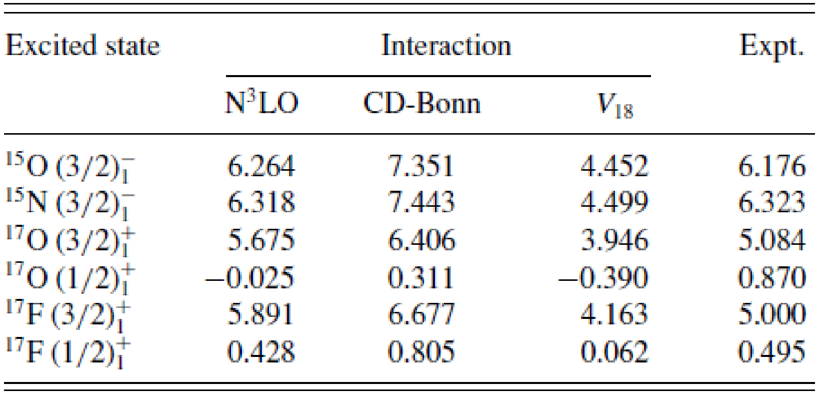
We study the ground and low-lying excited states of ^{15}O, ^{17}O, ^{15}N, and ^{17}F using modern two-body nucleon-nucleon interactions and the suitably designed variants of the *ab initio* equation-of-motion coupled-cluster theory aimed at an accurate description of systems with valence particles and holes. A number of properties of ^{15}O, ^{17}O, ^{15}N, and ^{17}F, including ways the energies of ground and excited states of valence systems around ^{16}O change as functions of the number of nucleons, are correctly reproduced by the equation-of-motion coupled-cluster calculations performed in up to eight major-oscillator shells. Certain disagreements with experiment are in part because of the degrees of freedom such as three-body interactions not accounted for in our effective two-body Hamiltonians. In particular, the calculated binding energies of ^{15}O/^{15}N and ^{17}O/^{17}F enable us to rationalize the discrepancy between the experimental and recently published [Phys. Rev. Lett. **94**, 212501 (2005)] equation-of-motion coupled-cluster excitation energies for the $J^\pi = 3^-$ state of ^{16}O. Our calculations demonstrate the feasibility of the equation-of-motion coupled-cluster methods to deal with valence systems around closed-shell nuclei and to provide results for systems beyond $A = 16$.



Excited state	Interaction			Expt.
	N^{3}LO	CD-Bonn	V_{18}	
^{15}O $(3/2)^-_1$	6.264	7.351	4.452	6.176
^{15}N $(3/2)^-_1$	6.318	7.443	4.499	6.323
^{17}O $(3/2)^+_1$	5.675	6.406	3.946	5.084
^{17}O $(1/2)^+_1$	−0.025	0.311	−0.390	0.870
^{17}F $(3/2)^+_1$	5.891	6.677	4.163	5.000
^{17}F $(1/2)^+_1$	0.428	0.805	0.062	0.495

**PA-EOMCCSD(2p1h),
PR-EOMCCSD(2h1p)**

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Coupled-cluster theory for three-body Hamiltonians

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We derive coupled-cluster equations for three-body Hamiltonians. The equations for the one- and two-body cluster amplitudes are presented in a factorized form that leads to an efficient numerical implementation. We employ low-momentum two- and three-nucleon interactions and calculate the binding energy of ^{4}He. The results show that the main contribution of the three-nucleon interaction stems from its density-dependent zero-, one-, and two-body terms that result from the normal ordering of the Hamiltonian in coupled-cluster theory. The residual three-body terms that remain after normal ordering can be neglected.

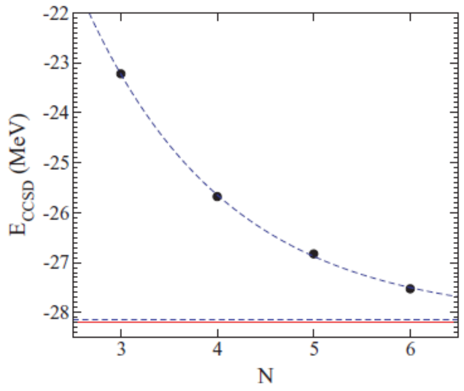


FIG. 6. (Color online) (Data points) CCSD results (taken at the $\hbar\omega$ minima) for the binding energy of ^{4}He with 3NFs as a function of the number of oscillator shells. (Dashed lines) Exponential fit to the data and asymptote of the fit. (Full line) Exact result.

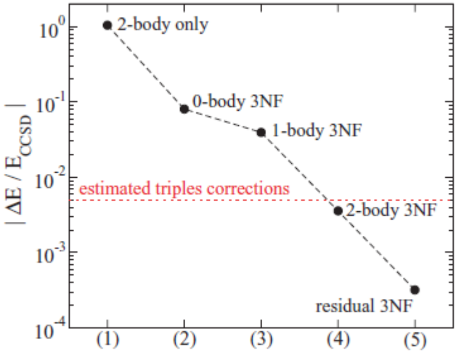
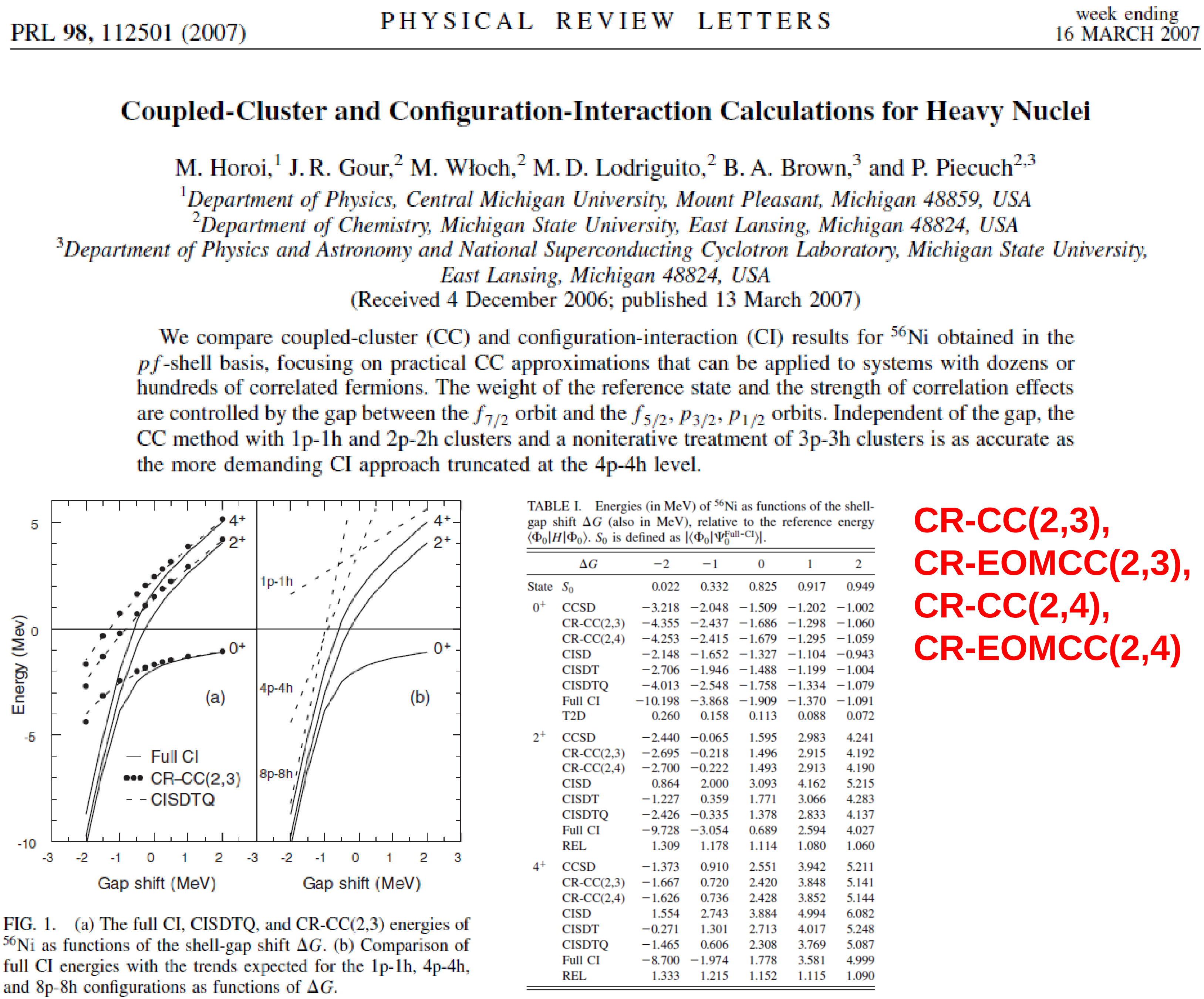


FIG. 7. (Color online) Relative contributions $|\Delta E/E|$ to the binding energy of ^{4}He at the CCSD level. The different points denote the contributions from (1) low-momentum NN interactions, (2) the vacuum expectation value of the 3NF, (3) the normal-ordered one-body Hamiltonian due to the 3NF, (4) the normal-ordered two-body Hamiltonian due to the 3NF, and (5) the residual 3NFs. The dotted line estimates the corrections due to omitted three-particle/three-hole clusters.

CCSD, NN+3N



PRL 98, 112501 (2007) PHYSICAL REVIEW LETTERS week ending 16 MARCH 2007

Coupled-Cluster and Configuration-Interaction Calculations for Heavy Nuclei

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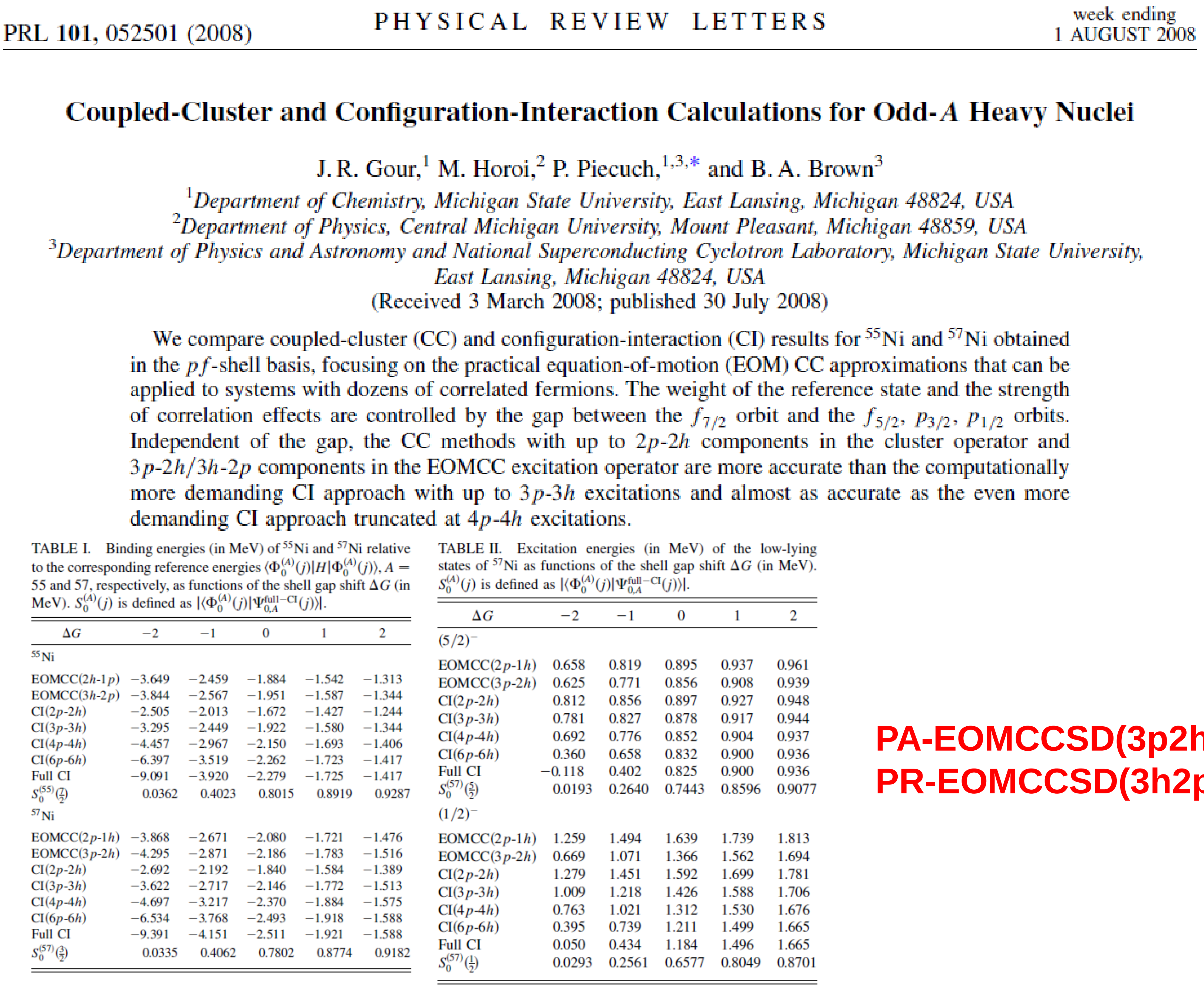
We compare coupled-cluster (CC) and configuration-interaction (CI) results for ^{56}Ni obtained in the pf-shell basis, focusing on practical CC approximations that can be applied to systems with dozens or hundreds of correlated fermions. The weight of the reference state and the strength of correlation effects are controlled by the gap between the $f_{7/2}$ orbit and the $f_{5/2}$, $p_{3/2}$, $p_{1/2}$ orbits. Independent of the gap, the CC method with 1p-1h and 2p-2h clusters and a noniterative treatment of 3p-3h clusters is as accurate as the more demanding CI approach truncated at the 4p-4h level.

FIG. 1. (a) The full CI, CISDTQ, and CR-CC(2,3) energies of ^{56}Ni as functions of the shell-gap shift ΔG. (b) Comparison of full CI energies with the trends expected for the 1p-1h, 4p-4h, and 8p-8h configurations as functions of ΔG.

TABLE I. Energies (in MeV) of ^{56}Ni as functions of the shell-gap shift ΔG (also in MeV), relative to the reference energy $\langle\Phi_0|H|\Phi_0\rangle$. S_0 is defined as $|\langle\Phi_0|\Psi_0^{\text{Full-CI}}\rangle|$.

	ΔG	−2	−1	0	1	2
State	S_0	0.022	0.332	0.825	0.917	0.949
0^+	CCSD	−3.218	−2.048	−1.509	−1.202	−1.002
	CR-CC(2,3)	−4.355	−2.437	−1.686	−1.298	−1.060
	CR-CC(2,4)	−4.253	−2.415	−1.679	−1.295	−1.059
	CISD	−2.148	−1.652	−1.327	−1.104	−0.943
	CISDT	−2.706	−1.946	−1.488	−1.199	−1.004
	CISDTQ	−4.013	−2.548	−1.758	−1.334	−1.079
	Full CI	−10.198	−3.868	−1.909	−1.370	−1.091
	T2D	0.260	0.158	0.113	0.088	0.072
2^+	CCSD	−2.440	−0.065	1.595	2.983	4.241
	CR-CC(2,3)	−2.695	−0.218	1.496	2.915	4.192
	CR-CC(2,4)	−2.700	−0.222	1.493	2.913	4.190
	CISD	0.864	2.000	3.093	4.162	5.215
	CISDT	−1.227	0.359	1.771	3.066	4.283
	CISDTQ	−2.426	−0.335	1.378	2.833	4.137
	Full CI	−9.728	−3.054	0.689	2.594	4.027
	REL	1.309	1.178	1.114	1.080	1.060
4^+	CCSD	−1.373	0.910	2.551	3.942	5.211
	CR-CC(2,3)	−1.667	0.720	2.420	3.848	5.141
	CR-CC(2,4)	−1.626	0.736	2.428	3.852	5.144
	CISD	1.554	2.743	3.884	4.994	6.082
	CISDT	−0.271	1.301	2.713	4.017	5.248
	CISDTQ	−1.465	0.606	2.308	3.769	5.087
	Full CI	−8.700	−1.974	1.778	3.581	4.999
	REL	1.333	1.215	1.152	1.115	1.090

CR-CC(2,3),
CR-EOMCC(2,3),
CR-CC(2,4),
CR-EOMCC(2,4)



PRL **101,** 052501 (2008) PHYSICAL REVIEW LETTERS week ending 1 AUGUST 2008

Coupled-Cluster and Configuration-Interaction Calculations for Odd-A Heavy Nuclei

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We compare coupled-cluster (CC) and configuration-interaction (CI) results for ^{55}Ni and ^{57}Ni obtained in the pf-shell basis, focusing on the practical equation-of-motion (EOM) CC approximations that can be applied to systems with dozens of correlated fermions. The weight of the reference state and the strength of correlation effects are controlled by the gap between the $f_{7/2}$ orbit and the $f_{5/2}$, $p_{3/2}$, $p_{1/2}$ orbits. Independent of the gap, the CC methods with up to $2p$-$2h$ components in the cluster operator and $3p$-$2h/3h$-$2p$ components in the EOMCC excitation operator are more accurate than the computationally more demanding CI approach with up to $3p$-$3h$ excitations and almost as accurate as the even more demanding CI approach truncated at $4p$-$4h$ excitations.

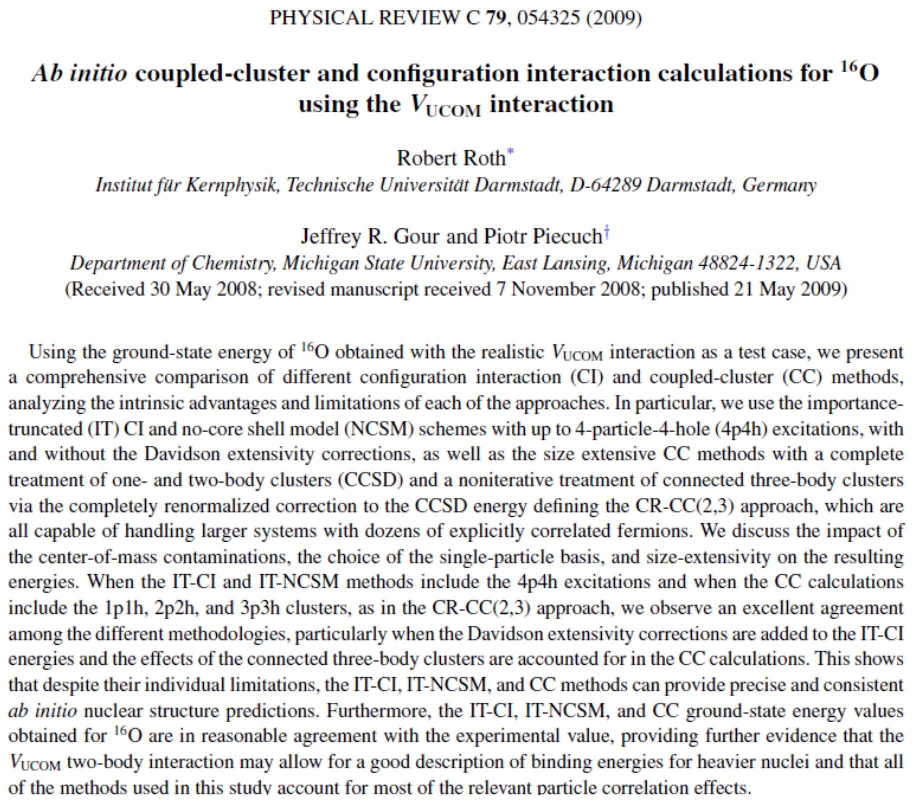
TABLE I. Binding energies (in MeV) of ^{55}Ni and ^{57}Ni relative to the corresponding reference energies $\langle\Phi_0^{(A)}(j)|H|\Phi_0^{(A)}(j)\rangle$, $A =$ 55 and 57, respectively, as functions of the shell gap shift ΔG (in MeV). $S_0^{(A)}(j)$ is defined as $|\langle\Phi_0^{(A)}(j)|\Psi_{0,A}^{\text{full}-\text{CI}}(j)\rangle|$.

ΔG	−2	−1	0	1	2
^{55}Ni					
EOMCC($2h$-$1p$)	−3.649	−2.459	−1.884	−1.542	−1.313
EOMCC($3h$-$2p$)	−3.844	−2.567	−1.951	−1.587	−1.344
CI($2p$-$2h$)	−2.505	−2.013	−1.672	−1.427	−1.244
CI($3p$-$3h$)	−3.295	−2.449	−1.922	−1.580	−1.344
CI($4p$-$4h$)	−4.457	−2.967	−2.150	−1.693	−1.406
CI($6p$-$6h$)	−6.397	−3.519	−2.262	−1.723	−1.417
Full CI	−9.091	−3.920	−2.279	−1.725	−1.417
$S_0^{(55)}(\frac{7}{2})$	0.0362	0.4023	0.8015	0.8919	0.9287
^{57}Ni					
EOMCC($2p$-$1h$)	−3.868	−2.671	−2.080	−1.721	−1.476
EOMCC($3p$-$2h$)	−4.295	−2.871	−2.186	−1.783	−1.516
CI($2p$-$2h$)	−2.692	−2.192	−1.840	−1.584	−1.389
CI($3p$-$3h$)	−3.622	−2.717	−2.146	−1.772	−1.513
CI($4p$-$4h$)	−4.697	−3.217	−2.370	−1.884	−1.575
CI($6p$-$6h$)	−6.534	−3.768	−2.493	−1.918	−1.588
Full CI	−9.391	−4.151	−2.511	−1.921	−1.588
$S_0^{(57)}(\frac{3}{2})$	0.0335	0.4062	0.7802	0.8774	0.9182

TABLE II. Excitation energies (in MeV) of the low-lying states of ^{57}Ni as functions of the shell gap shift ΔG (in MeV). $S_0^{(A)}(j)$ is defined as $|\langle\Phi_0^{(A)}(j)|\Psi_{0,A}^{\text{full}-\text{CI}}(j)\rangle|$.

ΔG	−2	−1	0	1	2
$(5/2)^-$					
EOMCC($2p$-$1h$)	0.658	0.819	0.895	0.937	0.961
EOMCC($3p$-$2h$)	0.625	0.771	0.856	0.908	0.939
CI($2p$-$2h$)	0.812	0.856	0.897	0.927	0.948
CI($3p$-$3h$)	0.781	0.827	0.878	0.917	0.944
CI($4p$-$4h$)	0.692	0.776	0.852	0.904	0.937
CI($6p$-$6h$)	0.360	0.658	0.832	0.900	0.936
Full CI	−0.118	0.402	0.825	0.900	0.936
$S_0^{(57)}(\frac{5}{2})$	0.0193	0.2640	0.7443	0.8596	0.9077
$(1/2)^-$					
EOMCC($2p$-$1h$)	1.259	1.494	1.639	1.739	1.813
EOMCC($3p$-$2h$)	0.669	1.071	1.366	1.562	1.694
CI($2p$-$2h$)	1.279	1.451	1.592	1.699	1.781
CI($3p$-$3h$)	1.009	1.218	1.426	1.588	1.706
CI($4p$-$4h$)	0.763	1.021	1.312	1.530	1.676
CI($6p$-$6h$)	0.395	0.739	1.211	1.499	1.665
Full CI	0.050	0.434	1.184	1.496	1.665
$S_0^{(57)}(\frac{1}{2})$	0.0293	0.2561	0.6577	0.8049	0.8701

PA-EOMCCSD(3p2h),
PR-EOMCCSD(3h2p)



PHYSICAL REVIEW C **79**, 054325 (2009)

Ab initio coupled-cluster and configuration interaction calculations for ^{16}O using the V_{UCOM} interaction

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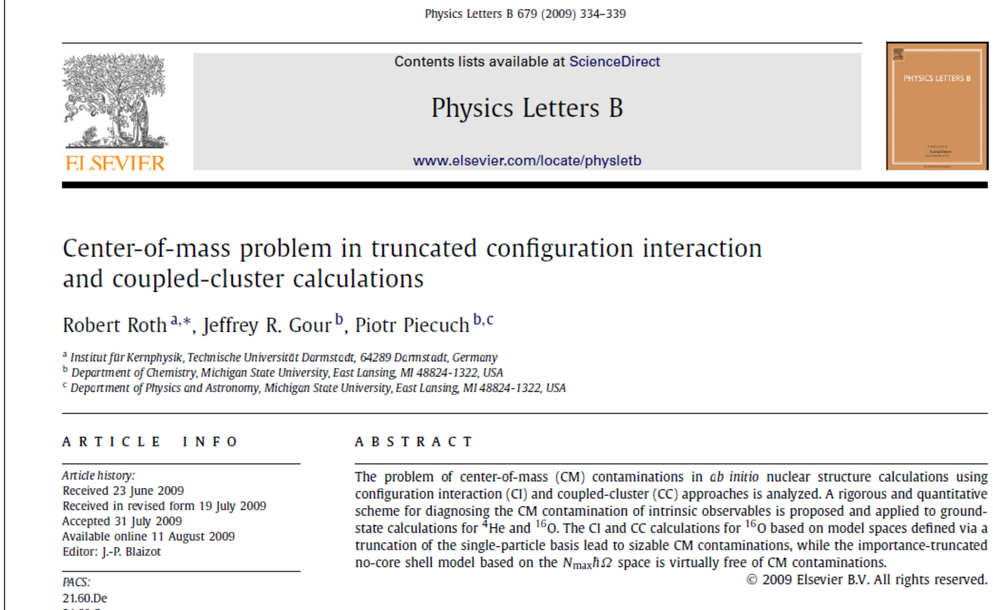
Using the ground-state energy of ^{16}O obtained with the realistic V_{UCOM} interaction as a test case, we present a comprehensive comparison of different configuration interaction (CI) and coupled-cluster (CC) methods, analyzing the intrinsic advantages and limitations of each of the approaches. In particular, we use the importance-truncated (IT) CI and no-core shell model (NCSM) schemes with up to 4-particle-4-hole (4p4h) excitations, with and without the Davidson extensivity corrections, as well as the size extensive CC methods with a complete treatment of one- and two-body clusters (CCSD) and a noniterative treatment of connected three-body clusters via the completely renormalized correction to the CCSD energy defining the CR-CC(2,3) approach, which are all capable of handling larger systems with dozens of explicitly correlated fermions. We discuss the impact of the center-of-mass contaminations, the choice of the single-particle basis, and size-extensivity on the resulting energies. When the IT-CI and IT-NCSM methods include the 4p4h excitations and when the CC calculations include the 1p1h, 2p2h, and 3p3h clusters, as in the CR-CC(2,3) approach, we observe an excellent agreement among the different methodologies, particularly when the Davidson extensivity corrections are added to the IT-CI energies and the effects of the connected three-body clusters are accounted for in the CC calculations. This shows that despite their individual limitations, the IT-CI, IT-NCSM, and CC methods can provide precise and consistent *ab initio* nuclear structure predictions. Furthermore, the IT-CI, IT-NCSM, and CC ground-state energy values obtained for ^{16}O are in reasonable agreement with the experimental value, providing further evidence that the V_{UCOM} two-body interaction may allow for a good description of binding energies for heavier nuclei and that all of the methods used in this study account for most of the relevant particle correlation effects.



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Center-of-mass problem in truncated configuration interaction and coupled-cluster calculations

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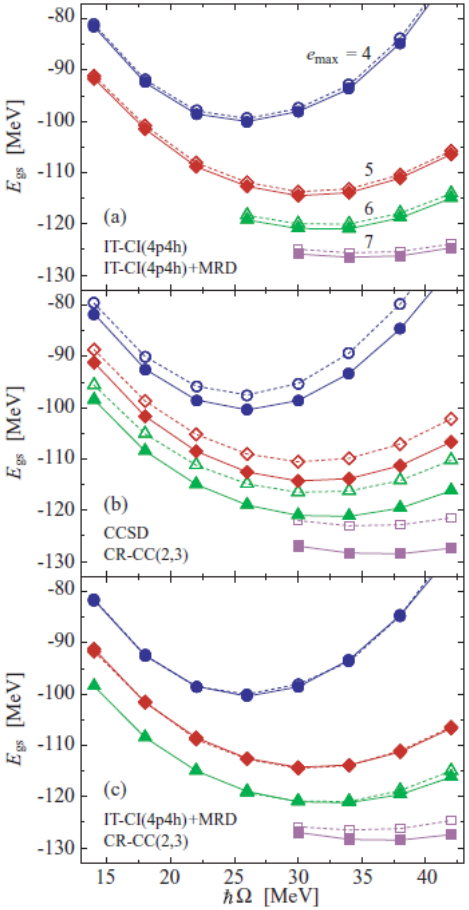
ABSTRACT

The problem of center-of-mass (CM) contaminations in *ab initio* nuclear structure calculations using configuration interaction (CI) and coupled-cluster (CC) approaches is analyzed. A rigorous and quantitative scheme for diagnosing the CM contamination of intrinsic observables is proposed and applied to ground-state calculations for ^{4}He and ^{16}O. The CI and CC calculations for ^{16}O based on model spaces defined via a truncation of the single-particle basis lead to sizable CM contaminations, while the importance-truncated no-core shell model based on the $N_{\max}\hbar\Omega$ space is virtually free of CM contaminations.



CR-CC(2,3), center-of-mass problem in CC

PHYSICAL REVIEW C **88**, 054319 (2013)

Extension of coupled-cluster theory with a noniterative treatment of connected triply excited clusters to three-body Hamiltonians

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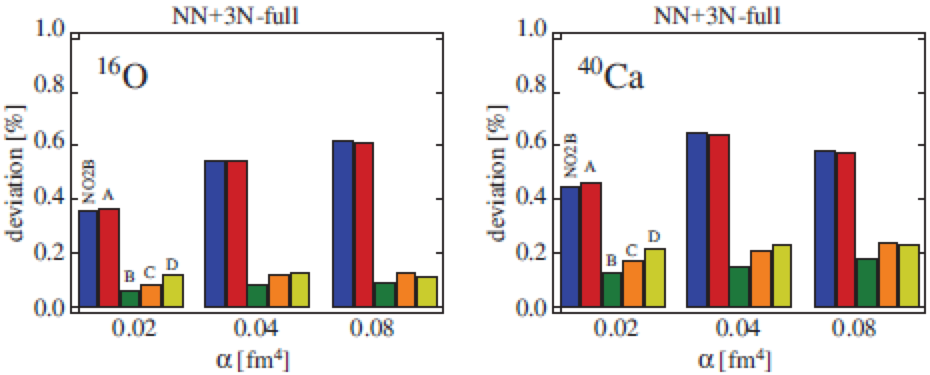
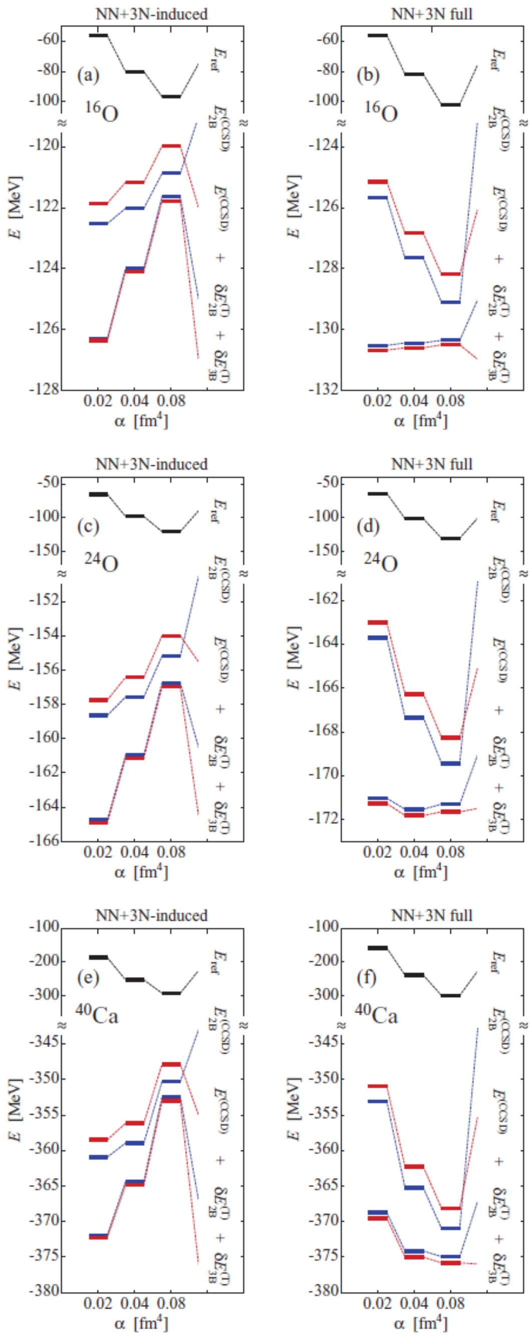
We generalize the coupled-cluster (CC) approach with singles, doubles, and the noniterative treatment of triples termed ΛCCSD(T) to Hamiltonians containing three-body interactions. The resulting method and the underlying CC approach with singles and doubles only (CCSD) are applied to the medium-mass closed-shell nuclei ^{16}O, ^{24}O, and ^{40}Ca. By comparing the results of CCSD and ΛCCSD(T) calculations with explicit treatment of three-nucleon interactions to those obtained using an approximate treatment in which they are included effectively via the zero-, one-, and two-body components of the Hamiltonian in normal-ordered form, we quantify the contributions of the residual three-body interactions neglected in the approximate treatment. We find these residual normal-ordered three-body contributions negligible for the ΛCCSD(T) method, although they can become significant in the lower-level CCSD approach, particularly when the nucleon-nucleon interactions are soft.





CCSD plus a noniterative correction due to T_3 extracted from CR-CC(2,3) with NN+3N

Bare Hamiltonian (N^3LO, Argonne V18, etc.)

Bare Hamiltonian (N^{3}LO, Argonne V18, etc.)

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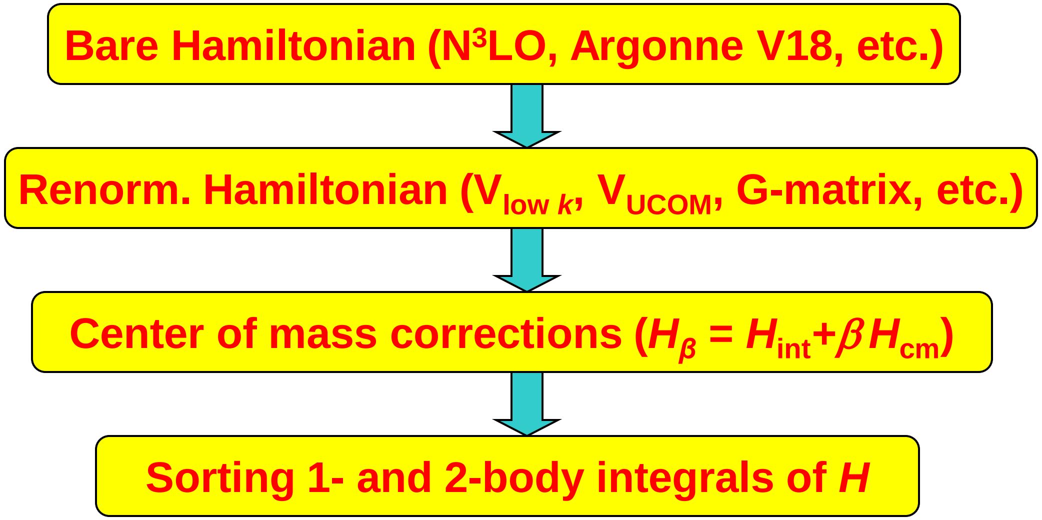
Renorm. Hamiltonian ($V_{\mathrm{low}\ k}$, V_{UCOM}, G-matrix, etc.)

Bare Hamiltonian (N^{3}LO, Argonne V18, etc.)

Renorm. Hamiltonian ($V_{\text{low }k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)



Bare Hamiltonian (N^3LO, Argonne V18, etc.)

Renorm. Hamiltonian ($V_{\text{low } k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)

Sorting 1- and 2-body integrals of H

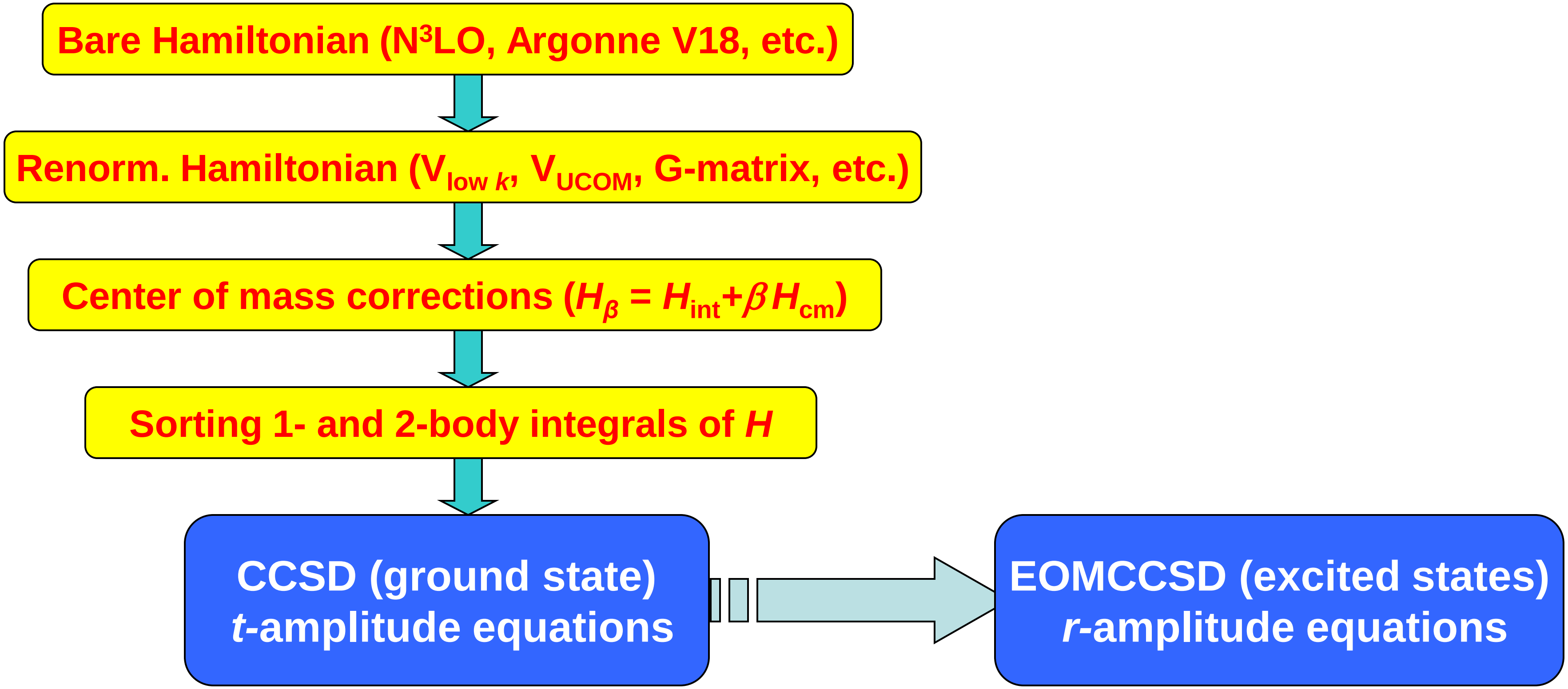
Bare Hamiltonian (N^{3}LO, Argonne V18, etc.)

Renorm. Hamiltonian ($V_{\text{low } k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)

Sorting 1- and 2-body integrals of *H*

CCSD (ground state)
***t*-amplitude equations**



Bare Hamiltonian (N^3LO, Argonne V18, etc.)

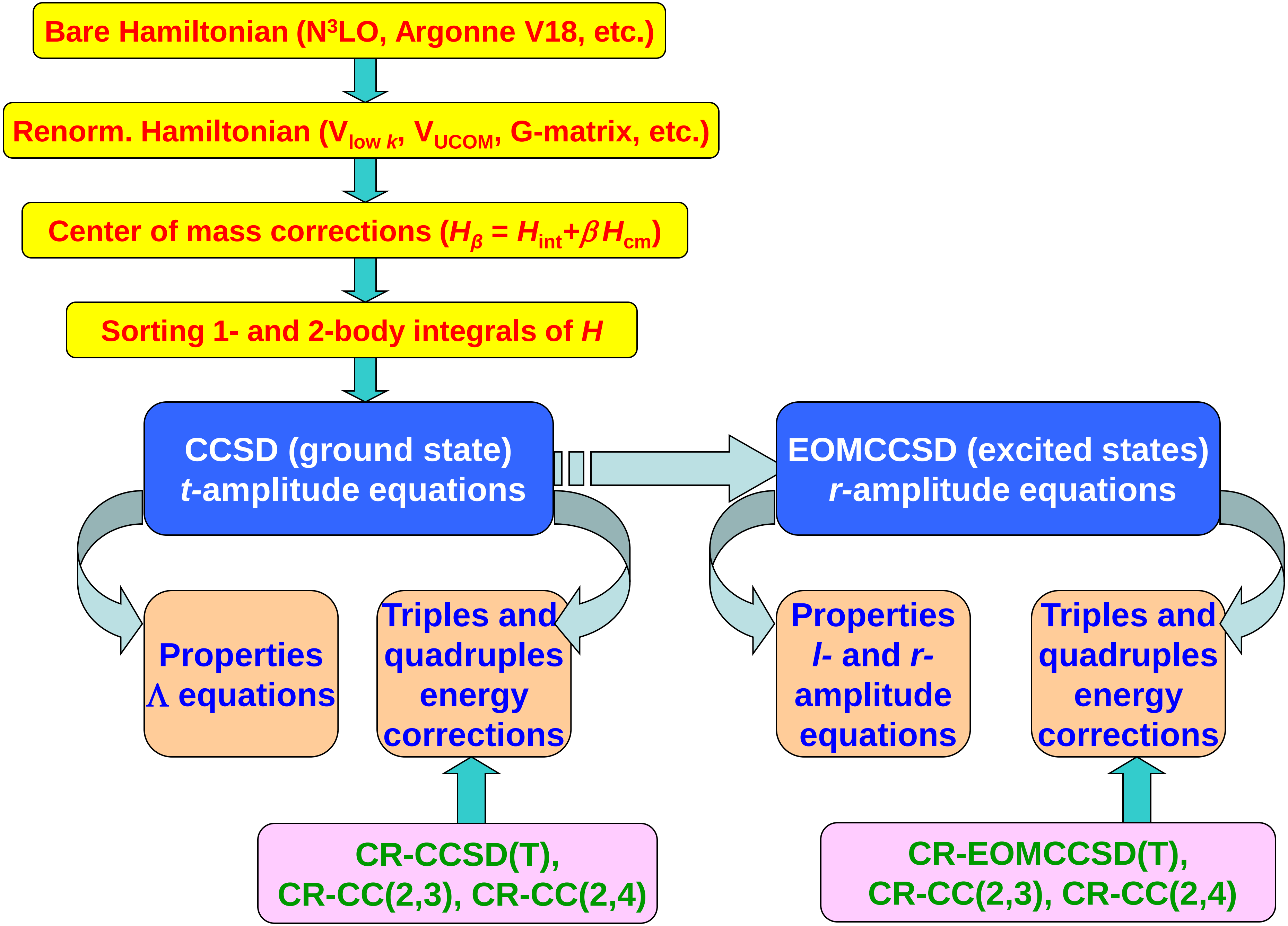
Renorm. Hamiltonian ($V_{\text{low } k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)

Sorting 1- and 2-body integrals of H

CCSD (ground state)
***t*-amplitude equations**

EOMCCSD (excited states)
***r*-amplitude equations**



Bare Hamiltonian (N^3LO, Argonne V18, etc.)

Renorm. Hamiltonian ($V_{\text{low } k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)

Sorting 1- and 2-body integrals of *H*

CCSD (ground state)
t-amplitude equations

EOMCCSD (excited states)
r-amplitude equations

Properties
Λ equations

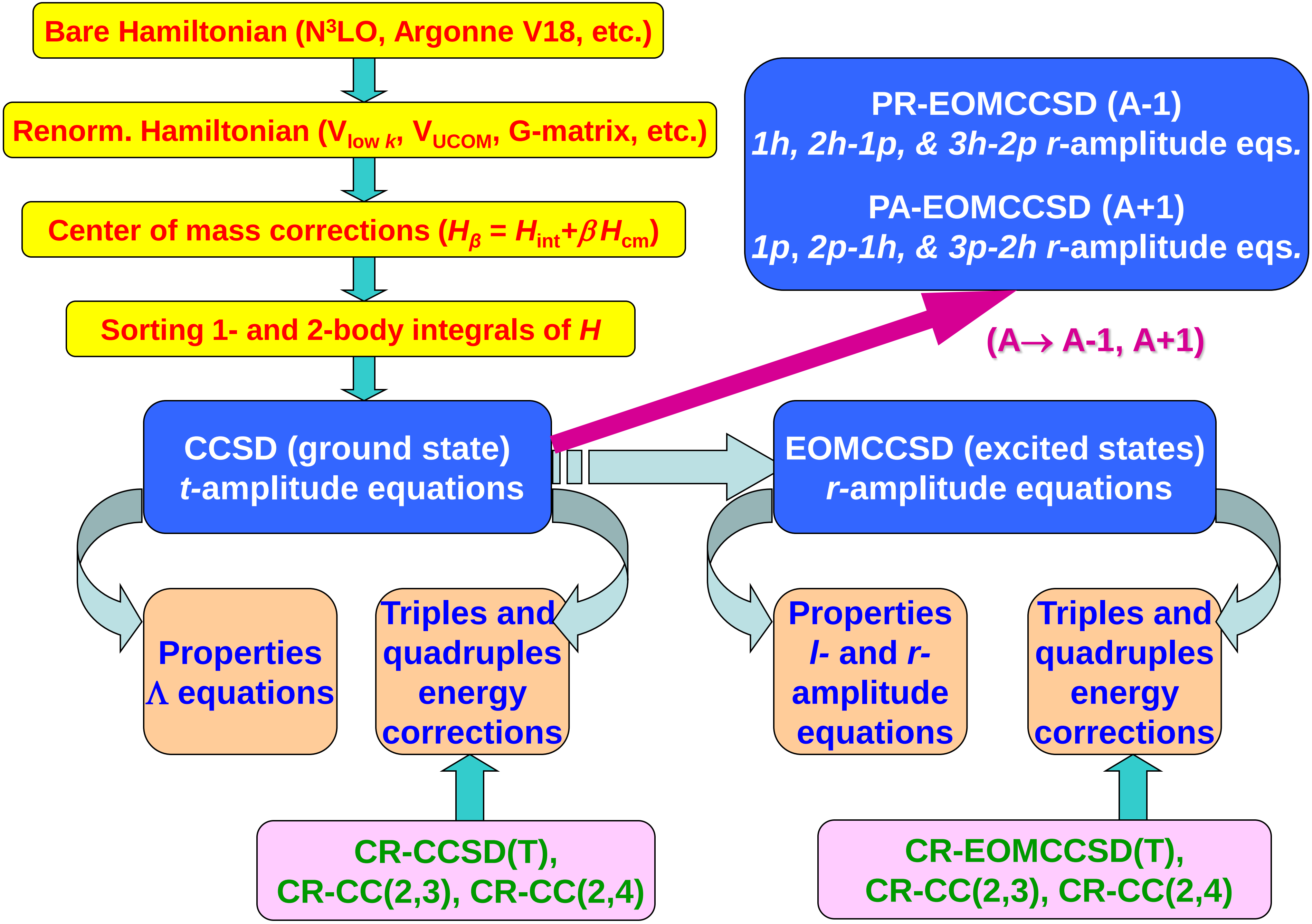
Triples and quadruples energy corrections

Properties
l- and *r*-amplitude equations

Triples and quadruples energy corrections

CR-CCSD(T),
CR-CC(2,3), CR-CC(2,4)

CR-EOMCCSD(T),
CR-CC(2,3), CR-CC(2,4)



Bare Hamiltonian (N^3LO, Argonne V18, etc.)

Renorm. Hamiltonian ($V_{\text{low }k}$, V_{UCOM}, G-matrix, etc.)

Center of mass corrections ($H_\beta = H_{\text{int}} + \beta H_{\text{cm}}$)

Sorting 1- and 2-body integrals of H

CCSD (ground state)
t-amplitude equations

EOMCCSD (excited states)
r-amplitude equations

PR-EOMCCSD (A-1)
1h, 2h-1p, & 3h-2p r-amplitude eqs.

PA-EOMCCSD (A+1)
1p, 2p-1h, & 3p-2h r-amplitude eqs.

(A→ A-1, A+1)

Properties
Λ equations

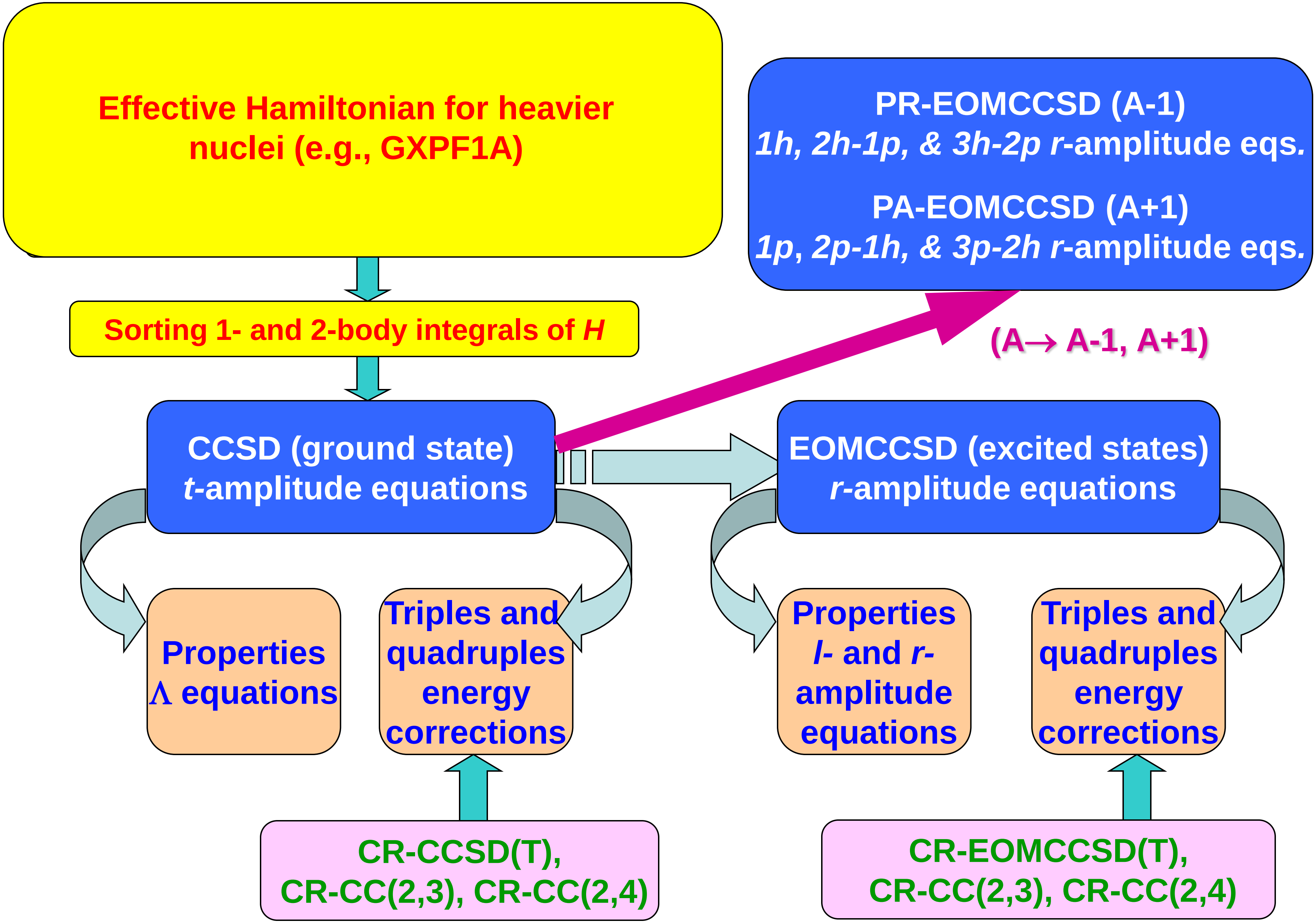
Triples and quadruples energy corrections

Properties
l- and *r*-amplitude equations

Triples and quadruples energy corrections

CR-CCSD(T),
CR-CC(2,3), CR-CC(2,4)

CR-EOMCCSD(T),
CR-CC(2,3), CR-CC(2,4)



Effective Hamiltonian for heavier nuclei (e.g., GXPF1A)

Sorting 1- and 2-body integrals of *H*

CCSD (ground state)
***t*-amplitude equations**

Properties
Λ equations

Triples and quadruples energy corrections

CR-CCSD(T),
CR-CC(2,3), CR-CC(2,4)

(A→ A-1, A+1)

PR-EOMCCSD (A-1)
***1h, 2h-1p, & 3h-2p r*-amplitude eqs.**

PA-EOMCCSD (A+1)
***1p, 2p-1h, & 3p-2h r*-amplitude eqs.**

EOMCCSD (excited states)
***r*-amplitude equations**

Properties
***l*- and *r*-amplitude equations**

Triples and quadruples energy corrections

CR-EOMCCSD(T),
CR-CC(2,3), CR-CC(2,4)

THANK YOU