The Journal of Chemical Physics

Second-order, two-electron Dyson propagator theory: Comparisons for vertical double ionization potentials

Cite as: J. Chem. Phys. **129**, 084105 (2008); https://doi.org/10.1063/1.2973533
Submitted: 23 June 2008 . Accepted: 29 July 2008 . Published Online: 28 August 2008

T. Ida, and J. V. Ortiz

View Online Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Dyson orbitals for ionization from the ground and electronically excited states within equation-of-motion coupled-cluster formalism: Theory, implementation, and examples
The Journal of Chemical Physics **127**, 234106 (2007); https://doi.org/10.1063/1.2805393

Assessment of transition operator reference states in electron propagator calculations
The Journal of Chemical Physics **127**, 134106 (2007); https://doi.org/10.1063/1.2784638

Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen
The Journal of Chemical Physics **90**, 1007 (1989); https://doi.org/10.1063/1.456153

AIP Publishing

© 2008 American Institute of Physics.

Second-order, two-electron Dyson propagator theory: Comparisons for vertical double ionization potentials

T. Ida[1,2,a)] and J. V. Ortiz[1,b)]
[1]*Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312, USA*
[2]*Department of Chemistry, Kanazawa University, Kanazawa 920-1192, Japan*

(Received 23 June 2008; accepted 29 July 2008; published online 28 August 2008)

The second-order, two-electron Dyson propagator is derived using superoperator theory with a spin-adapted formulation. To include certain ladder diagrams to all orders, the shifted-denominator (SD2) approximation is made. Formal and computational comparisons with other approximations illustrate the advantages of the SD2 procedure. Vertical double ionization potentials (DIPs) for a set of closed-shell molecules are evaluated with the second-order propagator and the SD2 method. The results of the SD2 approximation are in good agreement with experiment. To systematically examine the quality of the results, we compared SD2 and equation-of-motion, coupled-cluster predictions. The average absolute discrepancy is 0.26 eV for 36 doubly ionized states. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2973533]

I. INTRODUCTION

Double ionization energies have been studied extensively using a variety of experimental techniques. Auger electron spectroscopy has been the most widely used method to investigate the doubly ionized states of molecules.[1–6] During the last few decades, other techniques with higher resolution such as double charge transfer (DCT),[7–14] threshold photoelectron coincidence (TPEsCO),[15] photoelectron-photoelectron coincidence[16] (PEPECO), and so on also have been developed.

In theoretical investigation of double ionization processes, the electronic energy-difference method based on configuration interaction (ΔCI) has been one of the most accurate methods. Many vertical double ionization potentials (DIPs) and properties for dicationic states have been evaluated with this technique.[12,17,18] However ΔCI calculations often cannot be carried out for systems of chemical interest because a very large matrix eigenvalue problem must be solved, even for small molecules.

On the other hand, electron propagator theory underlies many methods for calculating single-electron binding and excitation energies.[19–26] Improved accuracy and computational efficiency have been realized through use of recently derived approximations for vertical, single-electron detachment energies.[27–29] Electron propagator methods provide energy differences directly, without evaluation of total energies of initial and final states. Therefore, a number of approximations to the exact two-electron (two-particle or particle-particle) propagator, which obey the Bethe–Salpeter (BS) equation,[30] have been developed and used to study double ionization processes.

We have already reported a two-electron propagator method corrected by first-order perturbation theory with a closed-shell, single-determinantal reference state to study Auger spectra.[31] This efficient method for the calculation of DIPs has been improved by employment of complete active space self-consistent field (SCF) reference states,[32] by the introduction of Dyson orbitals from the one-electron propagator in the reference state[33] and by the GW approximation.[34–36]

The algebraic diagrammatic construction (ADC) approach has been the foundation of the most widely used theoretical methods for the study of double ionization processes in molecules.[37–45] The ADC(2) methods are based on an analysis of the Feynman diagrams which describe the second-order perturbation expansion of the propagator with respect to Hartree–Fock (HF) reference states. In the particle-particle ADC(2) method, the $(N-2)$ electron and $(N+2)$-electron parts in the spectral form of Green's function are treated separately, i.e., the ADC(2) propagator is not a Dyson propagator, but one of the propagators in the BS equation. This method is a so-called non-Dyson ADC approximation and has been described in detail.[46] The formulations of the propagator corrected by a second- or higher-order perturbation expansion are different from the standard Dyson propagator. A comparison of the Dyson and non-Dyson approaches is given in Sec. III.

In this paper, the second-order, two-electron Dyson propagator is derived with superoperator theory, and relationships with the ADC(2) method are described. (Superoperator theory is closely related to equation-of-motion techniques.) To include contributions from certain ladder diagrams in all orders from intermediate configurations, the shifted-denominator (SD2) approximation is applied to the second-order propagator. Formal and computational comparisons with other approximations illustrate the advantages of the SD2 procedure. Finally, numerical results on DIPs of typical, closed-shell molecules produced by the SD2 method will be compared to ΔCISD, ΔCCSD(T), equation-of-motion

[a)]Electronic mail: ida_t@wriron1.s.kanazawa-u.ac.jp.
[b)]Electronic mail: ortiz@auburn.edu.

 © 2008 American Institute of Physics

coupled-cluster singles and doubles (EOM-CCSD), and ADC(2) data and the advantages of the new procedure will be discussed.

II. THEORY

A. Superoperator theory

The physical content of the two-electron propagator resides chiefly in its poles and residues. In its spectral form, the pq,rs element of the two-electron propagator matrix is

$$G_{pq,rs}(E) = \lim_{\eta\to 0}\left[\sum_m \frac{\langle N|a_q^\dagger q_p^\dagger|N-2,m\rangle\langle N-2,m|a_r a_s|N\rangle}{E+E_n(N-2)-E_0(N)-i\eta} - \sum_n \frac{\langle N|a_r a_s|N+2,n\rangle\langle N+2,n|a_q^\dagger a_p^\dagger|N\rangle}{E+E_0(N)-E_m(N+2)+i\eta}\right]. \quad (1)$$

The limit with respect to η is taken because of integration techniques required in a Fourier transform from the time-dependent representation. Matrix elements of the corresponding field operator products, $a_q^\dagger a_p^\dagger$ and $a_r a_s$, depend on the N-electron reference state $|N\rangle$ and final states with $N\pm 2$ electrons labeled by the indices m and n. The propagator matrix is energy dependent; poles occur when E equals a DIP or a double electron affinity (DEA). Corresponding residues are related to the Feynman–Dyson amplitudes.

The superoperator metric[19,25] is defined by

$$(\mu|\nu) = \langle N|[\mu^\dagger,\nu]|N\rangle, \quad (2)$$

where μ and ν are field operator products that change the number of electrons by 2. The identity superoperator $\hat{I}$ obeys

$$\hat{I}\nu = \nu. \quad (3)$$

The Hamiltonian superoperator $\hat{H}$ is defined by

$$\hat{H}\nu = [\nu,H], \quad (4)$$

where the Hamiltonian reads

$$H = \sum_{pq} h_{pq}a_p^\dagger a_q + \tfrac{1}{4}\sum_{pqrs}\langle pq\,\|\,rs\rangle a_p^\dagger a_q^\dagger a_s a_r, \quad (5)$$

and where $\langle pq\|rs\rangle$ is an antisymmetrized Coulomb repulsion integral such that

$$\langle pq\,\|\,rs\rangle = V_{pq,rs} - V_{pq,sr}, \quad (6)$$

with

$$V_{pq,rs} = \iint \frac{\phi_p^*(\mathbf{r})\phi_\mathbf{q}^*(\mathbf{r}')\phi_\mathbf{r}(\mathbf{r})\phi_\mathbf{s}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \quad (7)$$

It is possible to express the pq, rs element of the two-electron propagator matrix as

$$G_{pq,rs}(E) = (a_p a_q|(E\hat{I}-\hat{H})^{-1}a_r a_s). \quad (8)$$

In matrix notation, Eq. (8) is rewritten as

$$\mathbf{G}(\mathbf{E}) = (\mathbf{aa}|(\mathbf{E}\hat{\mathbf{I}}-\hat{\mathbf{H}})^{-1}\mathbf{aa}). \quad (9)$$

To avoid treatment of the inverse operator, an inner projection is effected, where

$$\mathbf{G}(\mathbf{E}) = (\mathbf{aa}|\mathbf{h})(\mathbf{h}|(\mathbf{E}\hat{\mathbf{I}}-\hat{\mathbf{H}})\mathbf{h})^{-1}(\mathbf{h}|\mathbf{aa}), \quad (10)$$

and where $\mathbf{h}$ is the vector of all ν field operator products, i.e.,

$$\mathbf{h} = \{\mathbf{aa},\mathbf{a}^\dagger\mathbf{aaa},\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{aaaa},\ldots\}. \quad (11)$$

Superoperator matrix elements are evaluated with respect to the exact ground state. After partitioning $\mathbf{h}$ into a primary space of simple field operator products $\mathbf{aa}$ and a secondary space of field operator products that is orthogonal to the primary space $\mathbf{f}$, the propagator matrix may be expressed by

$$\mathbf{G}(\mathbf{E}) = [\mathbf{1}\ \mathbf{0}]\begin{bmatrix} E\mathbf{1}-(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa}) & (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}) \\ (\mathbf{f}|\mathbf{Haa}) & E\mathbf{1}-(\mathbf{f}|\hat{\mathbf{H}}\mathbf{f}) \end{bmatrix}^{-1}\begin{bmatrix}\mathbf{1}\\ \mathbf{0}\end{bmatrix}. \quad (12)$$

From the above expression, one may extract

$$\mathbf{G}^{-1}(\mathbf{E}) = E\mathbf{1}-(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})-(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f})\{\mathbf{E1}-(\mathbf{f}|\hat{\mathbf{H}}\mathbf{f})\}^{-1}(\mathbf{f}|\hat{\mathbf{H}}\mathbf{aa}) \quad (13)$$

which may also be written as the inverse form of the Dyson equation,

$$\mathbf{G}^{-1}(\mathbf{E}) = \mathbf{G}_0^{-1}(\mathbf{E})-\mathbf{\Sigma}(\mathbf{E}), \quad (14)$$

where the zeroth order propagator reads

$$\mathbf{G}_0^{-1}(\mathbf{E}) = E\mathbf{1}-(\mathbf{aa}|\hat{\mathbf{H}}_0\mathbf{aa})_{\mathbf{HF}}, \quad (15)$$

and the self-energy is given by

$$\mathbf{\Sigma}(\mathbf{E}) = (\mathbf{aa}|\hat{\mathbf{V}}\mathbf{aa})_{\mathrm{HF}}+(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_{\mathrm{corr}} + (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f})\{\mathbf{E1}-(\mathbf{f}|\hat{\mathbf{H}}\mathbf{f})\}^{-1}(\mathbf{f}|\hat{\mathbf{H}}\mathbf{aa}). \quad (16)$$

The HF subscript in the zeroth-order propagator restricts operator averages in the ground state to the HF contributions; the corr subscript in the self-energy part refers to the correlation (non-HF) contribution only. The usual Møller–Plesset partitioning of the Hamiltonian defines $\hat{H}_0$ and $\hat{V}$. The dimension of the propagator matrices and of the self-energy matrix, $\mathbf{\Sigma}(\mathbf{E})$, is equal to the rank of the primary space. A diagonalization only of the relatively small primary space is needed. Pole searches based on the Dyson equation usually converge rapidly with respect to E.

B. Approximate superoperator Hamiltonian matrices

Several propagators can be defined in terms of superoperator Hamiltonian matrix elements. Poles corresponding to the second-order self-energy equal eigenvalues of the matrix

$$\hat{\mathbf{H}} = \begin{bmatrix} (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})^{(2)} & (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_4)^{(1)} \\ (\mathbf{f}_4|\hat{\mathbf{H}}\mathbf{aa})^{(1)} & (\mathbf{f}_4|\mathbf{Hf}_4)^{(0)} \end{bmatrix}, \quad (17)$$

where $\mathbf{f}_4$ is a vector of three-hole, one-particle ($3hp$), and three-particle, one-hole ($3hp$) field operators and where the superscripts in parentheses stand for the orders through which the elements are evaluated. For example, the primary operator block evaluated through second order has constituents in each order according to

TABLE I. Elements of zeroth- and first-order $\hat{\mathbf{H}}$ blocks for the two-electron propagator.

Block	Element	Formula
$(\mathbf{aa}\|\hat{\mathbf{H}}\mathbf{aa})$		
$\hat{\mathbf{H}}^{(1)}_{2h-2h}$	$\hat{\mathbf{H}}_{ij,kl}$	$\delta_{ik}\delta_{jl}(\epsilon_i+\epsilon_j)-\langle ij\|\|kl\rangle$
$\hat{\mathbf{H}}^{(1)}_{2h-2p}$	$\hat{\mathbf{H}}_{ij,ab}$	$\langle ij\|\|ab\rangle$
$\hat{\mathbf{H}}^{(1)}_{2p-2h}$	$\hat{\mathbf{H}}_{ab,ij}$	$\langle ab\|\|ij\rangle$
$\hat{\mathbf{H}}^{(1)}_{2p-2p}$	$\hat{\mathbf{H}}_{ab,cd}$	$\delta_{ac}\delta_{bd}(\epsilon_a+\epsilon_b)-\langle ab\|\|cd\rangle$
$(\mathbf{aa}\|\hat{\mathbf{H}}\mathbf{f_4})$		
$\hat{\mathbf{H}}^{(1)}_{2h-3hp}$	$\hat{\mathbf{H}}_{ij,klma}$	$(1-P_{ij})(1-P_{kl}-P_{lm})\delta_{jl}\langle ia\|\|km\rangle$
$\hat{\mathbf{H}}^{(1)}_{2h-3ph}$	$\hat{\mathbf{H}}_{ij,kabc}$	0
$\hat{\mathbf{H}}^{(1)}_{2p-3hp}$	$\hat{\mathbf{H}}_{ab,ijkc}$	0
$\hat{\mathbf{H}}^{(1)}_{2p-3ph}$	$\hat{\mathbf{H}}_{ab,icde}$	$(1-P_{ab})(1-P_{cd}-P_{de})\delta_{bd}\langle ai\|\|ce\rangle$
$(\mathbf{f_4}\|\hat{\mathbf{H}}\mathbf{f_4})$		
$\hat{\mathbf{H}}^{(1)}_{3hp-3hp}$	$\hat{\mathbf{H}}_{ijka,lmnb}$	$\delta_{il}\delta_{jm}\delta_{kn}\delta_{ab}(\epsilon_i+\epsilon_j+\epsilon_k-\epsilon_a)$ $+(1-P_{ij}-P_{jk})(1-P_{lm}-P_{mn})$ $\times\{\delta_{il}\delta_{kn}\langle jb\|\|ma\rangle-\delta_{ab}\delta_{jm}\langle jk\|\|ln\rangle\}$
$\hat{\mathbf{H}}^{(1)}_{3hp-3ph}$	$\hat{\mathbf{H}}_{ijka,lbcd}$	0
$\hat{\mathbf{H}}^{(1)}_{3ph-3ph}$	$\hat{\mathbf{H}}_{iabc,jdef}$	$\delta_{ij}\delta_{ad}\delta_{be}\delta_{cf}(\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_i)$ $+(1-P_{ab}-P_{bc})(1-P_{de}-P_{ef})$ $\times\{\delta_{ad}\delta_{cf}\langle bj\|\|ei\rangle-\delta_{ij}\delta_{be}\langle ac\|\|df\rangle\}$

$$(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})^{(2)}=(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_0+(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_1+(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_2, \quad (18)$$

where $(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_0$, the zeroth-order part, corresponds to $(\mathbf{aa}|\hat{\mathbf{H}}_0\mathbf{aa})_{\mathrm{HF}}$ in Eq. (15), the first-order part corresponds to $(\mathbf{aa}|\hat{\mathbf{V}}\mathbf{aa})_{\mathrm{HF}}$ in Eq. (16) and the second-order part is a constituent of $(\mathbf{aa}|\hat{\mathbf{H}}\mathbf{aa})_{\mathrm{corr}}$.

Table I displays formulas for each block of zeroth- and first-order $\hat{\mathbf{H}}$ in the canonical HF orbital basis. $2h$ and $2p$ subscripts of the primary block refer to two-hole and two-particle field operators, and the indices $i,j,k,\ldots$ and $a,b,c,\ldots$ stand for occupied and virtual spin orbitals, respectively. First-order $2h$-$3ph$ and $2p$-$3hp$ matrix elements vanish. These results indicate that intermediate $3ph$ and $3hp$ operators do not affect calculations on two-hole and two-particle final states, respectively, up to third order. If only $2h$ ($2p$) operators are included in the primary space, $3ph$ ($3hp$) operators can be neglected in calculations on DIPs (DEAs) because of the first-order $2h$-$3ph$ ($2p$-$3hp$) decoupling. Therefore, it is possible to truncate the superoperator Hamiltonian matrix for the second-order Dyson propagator with respect to the DIP ($\hat{\mathbf{H}}^-$) and the DEA ($\hat{\mathbf{H}}^+$) parts by repartitioning, such that

$$\hat{\mathbf{H}}^-=\begin{bmatrix}\hat{\mathbf{H}}^{(2)}_{2h,2h} & \hat{\mathbf{H}}^{(1)}_{2h,2p} & \hat{\mathbf{H}}^{(1)}_{2h,3hp}\\ \mathbf{H}^{(1)}_{2p,2h} & \mathbf{H}^{(0)}_{2p,2p} & 0\\ \mathbf{H}^{(1)}_{3hp,2h} & 0 & \hat{\mathbf{H}}^{(0)}_{3hp,3hp}\end{bmatrix}, \quad (19)$$

$$\hat{\mathbf{H}}^+=\begin{bmatrix}\hat{\mathbf{H}}^{(2)}_{2p,2p} & \hat{\mathbf{H}}^{(1)}_{2p,2h} & \hat{\mathbf{H}}^{(1)}_{2p,3ph}\\ \mathbf{H}^{(1)}_{2h,2p} & \mathbf{H}^{(0)}_{2h,2h} & 0\\ \mathbf{H}^{(1)}_{3ph,2p} & 0 & \hat{\mathbf{H}}^{(0)}_{3ph,3ph}\end{bmatrix}. \quad (20)$$

These two expressions are produced by neglecting $2p$-$3ph$ or $2h$-$3hp$ couplings in the former and latter cases, respectively. This simplification has the advantage of reducing the dimension of the matrices to the size that is characteristic of the ADC(2) method. We will henceforth treat only the DIP part of the approximate, superoperator Hamiltonian matrix. An inversion of occupied and virtual indices leads to the corresponding treatment of DEAs.

C. Expression of second-order self-energy

All zeroth- and first-order superoperator matrix elements have been evaluated with the HF reference state. To derive the second-order, two-electron propagator, the second-order $\hat{\mathbf{H}}_{2h,2h}$ block is needed. The second-order ij,kl element is

$$(a_ia_j|\hat{H}a_ka_l)_2=\langle\Psi^{(1)}|[a_j^\dagger a_i^\dagger,[a_ka_l,V]]|\Psi^{(0)}\rangle + \langle\Psi^{(0)}|[a_j^\dagger a_j^\dagger,[a_ka_l,V]]|\Psi^{(1)}\rangle \quad (21)$$

$$=\tfrac{1}{2}(1-P_{ij})(1-P_{kl})\delta_{jl}\sum_{m,ab}\langle km\,\|\,ab\rangle t_{im,ab}, \quad (22)$$

where

$$|\Psi^{(1)}\rangle=\sum_{ij,ab}t_{ij,ab}a_ia_ja_a^\dagger a_b^\dagger|\Psi^{(0)}\rangle \quad (23)$$

and

$$t_{ij,ab}=\frac{\langle ab\,\|\,ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}. \quad (24)$$

$\Psi^{(0)}$ is the HF determinantal wavefunction. From Eq. (22) one may suspect that the second-order expression is non-Hermitian. Because the $2h$ operator space is not orthonormal in all orders of the fluctuation potential, it is necessary to replace a_ia_j by its symmetrically orthogonalized[47] counterpart f_{ij}, where

$$f_{ij}=a_ia_j-\tfrac{1}{2}\sum_{kl}(a_ka_l|a_ia_j)a_ka_l - \tfrac{1}{2}\sum_{klma}(a_a^\dagger a_ka_la_m|a_ia_j)a_a^\dagger a_ka_la_m+\cdots. \quad (25)$$

Higher terms depend on second-order and higher-order terms in the superoperator overlap matrix. By using the symmetric orthogonalization, the complete second-order ij,kl element is given by

$$(f_{ij}|\hat{H}f_{kl})_2=(a_ia_j|\hat{H}_0a_ka_l)_2+(a_ia_j|\hat{V}a_ka_l)_1 - \tfrac{1}{2}\sum_{mn}(a_ia_j|a_ma_n)_2^*(a_ma_n|\hat{H}_0a_ka_l)_0 - \tfrac{1}{2}\sum_{mn}(a_ia_j|\hat{H}_0a_ma_n)_0(a_ma_n|a_ka_l)_2, \quad (26)$$

where the overlap matrix elements between the $2h$ and $3hp$ spaces vanish and terms of third and higher orders are omitted. In the canonical orbital basis, the simplifying relation

$$\hat{H}_0a_ia_j=(\epsilon_i+\epsilon_j)a_ia_j \quad (27)$$

implies that

$$(f_{ij}|\hat{H}f_{kl})_2 = (a_i a_j|\hat{V}a_k a_l)_1 - \tfrac{1}{2}(\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l)(a_i a_j|a_k a_l)_2. \tag{28}$$

$(a_i a_j|\hat{V}a_k a_l)_1$ has been evaluated in Eq. (22), and the remaining term is given by

$$\begin{aligned}(a_i a_j|a_k a_l)_2 &= \langle\Psi^{(1)}|[a_j^\dagger a_i^\dagger, a_k a_l]|\Psi^{(1)}\rangle \\ &+ \langle\Psi^{(0)}|[a_j^\dagger a_i^\dagger, a_k a_l]|\Psi^{(2)}\rangle \\ &+ \langle\Psi^{(2)}|[a_j^\dagger a_i^\dagger, a_k a_l]|\Psi^{(0)}\rangle \\ &= -\tfrac{1}{2}(1 - P_{ij})(1 - P_{kl})\delta_{jl}\sum_{m,ab} t_{im,ab} t^*_{km,ab}. \end{aligned} \tag{29}$$

Substitution of the terms in Eqs. (22) and (29) into Eq. (28) yields

$$\begin{aligned}(f_{ij}|\hat{H}f_{kl})_2 &= \tfrac{1}{4}(1 - P_{ij})(1 - P_{kl}) \\ &\times \sum_{m,ab} \delta_{jl}[\langle km \| ab\rangle t_{im,ab} + \langle ab \| im\rangle t^*_{km,ab}]. \end{aligned} \tag{30}$$

Inserting the expression for the individual matrix elements of Eq. (30) and those shown in Table I into Eq. (16) gives the following expression for the second-order, self-energy matrix element of the two-electron Dyson propagator

$$\begin{aligned}[\boldsymbol{\Sigma}^{(2)}(\mathbf{E})]_{ij,kl} &= -\langle ij \| kl\rangle + \frac{1}{4}(1 - P_{ij})(1 - P_{kl})\sum_{m,ab} \delta_{jl}[\langle km \| ab\rangle t_{im,ab} + \langle ab \| im\rangle t^*_{km,ab}] \\ &+ \frac{1}{2}\sum_{ab}\left[\frac{\langle ij \| ab\rangle\langle ab \| kl\rangle}{E - \epsilon_a - \epsilon_b}\right] + (1 - P_{ij})(1 - P_{kl})\frac{1}{2}\delta_{jl} \\ &\times \sum_{mn,a} \frac{\langle ia \| mn\rangle\langle mn \| ka\rangle}{E - (\epsilon_j + \epsilon_m + \epsilon_n - \epsilon_a)} - (1 - P_{ij})(1 - P_{kl})\sum_{m,a} \frac{\langle ia \| lm\rangle\langle jm \| ka\rangle}{E - (\epsilon_j + \epsilon_l + \epsilon_m - \epsilon_a)}. \end{aligned} \tag{31}$$

The expression for the self-energy matrix elements in Eq. (31) resembles that of the ADC(2) method,[37,38,48] except for the third term,

$$\frac{1}{2}\sum_{ab}\left[\frac{\langle ij \| ab\rangle\langle ab \| kl\rangle}{E - \epsilon_a - \epsilon_b}\right], \tag{32}$$

which corresponds to a contribution from the $2p$ space. In the ADC(2) method, the $2p$ operators are decoupled; analogous ladder-diagram terms were included in the energy-independent self-energy part as

$$\tfrac{1}{4}\sum_{ab}[\langle kl \| ab\rangle t_{ij,ab} + \langle ab \| ij\rangle t^*_{kl,ab}]. \tag{33}$$

In another two-particle propagator study, Liegener reported[33] that neglect of the contribution of the energy-dependent term of Eq. (32) is a good approximation. However, this approximation gives rise to an average deviation of ~1–2 eV in the calculation of DIPs and will be discussed later.

D. Shifted-denominator approximation

The particle-particle ADC(2) method has been extended to include first-order terms in the $3hp$-$3hp$ block.[37,48] This additional correction produces an approximate superoperator Hamiltonian matrix,

$$\hat{\mathbf{H}}^- = \begin{bmatrix} \hat{\mathbf{H}}^{(2)}_{2h,2h} & \hat{\mathbf{H}}^{(1)}_{2h,2p} & \hat{\mathbf{H}}^{(1)}_{2h,3hp} \\ \hat{\mathbf{H}}^{(1)}_{2p,2h} & \hat{\mathbf{H}}^{(0)}_{2p,2p} & 0 \\ \hat{\mathbf{H}}^{(1)}_{3hp,2h} & 0 & \hat{\mathbf{H}}^{(1)}_{3hp,3hp} \end{bmatrix}. \tag{34}$$

This superoperator Hamiltonian matrix resembles that of the Tamm–Dancoff approximation[20] and incorporates some third- or higher-order self-energy terms in the propagator. Eigenvalues of the Hamiltonian matrix in the ADC(2) method have been applied to making quantitative assignments of Auger spectra.[40–45]

In pole searches with the Dyson propagator, the second-order self-energy with the first-order, $3hp$ correction may be rewritten as

$$\boldsymbol{\Sigma}(\mathbf{E}) = (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\}^{-1}(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}. \tag{35}$$

We expand, as usual, the inverse matrix to second- and third-order terms to avoid a full matrix inversion so that

$$\begin{aligned}\boldsymbol{\Sigma}(\mathbf{E}) &= (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_0\}^{-1}(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)} \\ &+ (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_0\}^{-1} \\ &\times (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_1\{E1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_0\}^{-1} \\ &\times (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}, \end{aligned} \tag{36}$$

where $(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_0$ has only diagonal elements expressed in terms of orbital energies.

On the other hand, an expansion of the first-order, $3hp$-$3hp$ block about the diagonal and off-diagonal parts according to

$$(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)} = \{(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\}_{\gamma,\gamma} + \{(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}\}_{\gamma,\gamma'}, \tag{37}$$

where γ and κ refer to $3hp$ indices and $\gamma \neq \kappa$, shows that certain third- and higher-order terms are retained by the approximation

$$\begin{aligned}\boldsymbol{\Sigma}(\mathbf{E}) = \sum_{\gamma} (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma} \{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma,\gamma}\}^{-1} \\ \times (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}_{\gamma} + \sum_{\gamma\neq\kappa} (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma} \\ \times \{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma,\gamma}\}^{-1} (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma,\kappa} \\ \times \{E1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\kappa,\kappa}\}^{-1} (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}_{\kappa}.\end{aligned} \tag{38}$$

Neglect of the off-diagonal term of Eq. (37) produces the following, simplified, self-energy matrix,

$$\begin{aligned}\boldsymbol{\Sigma}(\mathbf{E}) &= \sum_{\gamma} (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma} \\ &\quad \times \{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}f_{3hp})^{(1)}_{\gamma,\gamma}\}^{-1} (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}_{\gamma} \\ &= \sum_{\gamma} (\mathbf{aa}|\hat{\mathbf{H}}\mathbf{f}_{3hp})^{(1)}_{\gamma} \{\mathbf{E}1 - (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_0 \\ &\quad - \{(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_1\}_{\gamma,\gamma}\}^{-1} (\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{aa})^{(1)}_{\gamma}.\end{aligned} \tag{39}$$

One can see that this self-energy is identical to the second-order self-energy term in Eq. (16) except for the shifted denominator arising from the term $\{(\mathbf{f}_{3hp}|\hat{\mathbf{H}}\mathbf{f}_{3hp})_1\}_{\gamma,\gamma}$. The first-order, diagonal element from the $3hp$ configuration gives certain ladder diagrams up to infinite order. One also avoids performing a double loop over the $3hp$ indices in the calculation of primary matrix elements. Therefore, DIPs can be obtained with the same effort of the second-order propagator method with a single evaluation of the diagonal elements of the first-order $3hp$-$3hp$ matrix. Because many terms beyond second order are included in this approximation, it is denoted by the abbreviation SD2. Comparison of the calculated DIPs using the self-energy of Eq. (36) and of the SD2 method is presented in the following section. Explicit expressions for the self-energy are discussed in the Appendix.

TABLE II. Singlet- and triplet-adapted $3hp$ operators.

Basis	Element	Formula
Singlet		
$\mathbf{f}^{(\mathrm{I})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}\neq\mathbf{ja}}$	$2^{-1/2}(a^\dagger_a a_i a_j \bar{a}_k + \bar{a}^\dagger_a \bar{a}_i a_j \bar{a}_k)$
$\mathbf{f}^{(\mathrm{II})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}<\mathbf{j}<\mathbf{ka}}$	$2^{-1}(a^\dagger_a \bar{a}_i a_j a_k - a^\dagger_a a_i a_j \bar{a}_k - \bar{a}^\dagger_a a_i \bar{a}_j \bar{a}_k + \bar{a}^\dagger_a \bar{a}_i \bar{a}_j a_k)$
$\mathbf{f}^{(\mathrm{III})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}<\mathbf{j}<\mathbf{ka}}$	$12^{-1/2}(-a^\dagger_a \bar{a}_i a_j a_k + 2a^\dagger_a a_i \bar{a}_j a_k - a^\dagger_a a_i a_j \bar{a}_k + \bar{a}^\dagger_a a_i \bar{a}_j \bar{a}_k - 2\bar{a}^\dagger_a \bar{a}_i a_j \bar{a}_k + \bar{a}^\dagger_a \bar{a}_i a_j a_k)$
Triplet		
$\mathbf{f}^{(\mathrm{I})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}\neq\mathbf{ja}}$	$2^{-1/2}(a^\dagger_a a_i a_j \bar{a}_k - \bar{a}^\dagger_a \bar{a}_i a_j \bar{a}_k)$
$\mathbf{f}^{(\mathrm{II})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}<\mathbf{j}<\mathbf{ka}}$	$2^{-1/2}(a^\dagger_a \bar{a}_i a_j a_k + \bar{a}^\dagger_a a_i \bar{a}_j \bar{a}_k)$
$\mathbf{f}^{(\mathrm{III})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}<\mathbf{j}<\mathbf{ka}}$	$2^{-1/2}(a^\dagger_a a_i \bar{a}_j a_k + \bar{a}^\dagger_a \bar{a}_i a_j \bar{a}_k)$
$\mathbf{f}^{(\mathrm{IV})}_{\mathbf{3hp}}$	$\mathbf{f}_{\mathbf{i}<\mathbf{j}<\mathbf{ka}}$	$2^{-1/2}(a^\dagger_a a_i a_j \bar{a}_k + \bar{a}^\dagger_a \bar{a}_i a_j a_k)$

E. Spin-adapted basis

So far, the matrix element formulas of the second-order, two-electron Dyson propagator have referred to a nondegenerate ground state assumed to have a closed-shell HF representation. Final states may be singlets or triplets. Therefore, one may factorize the propagator into singlet and triplet parts by introducing spin-adapted operators. In general, $(N\pm 2)$-electron configurations corresponding to a field operator product acting on a closed-shell, determinantal reference state are not eigenfunctions of the spin-operator S^2. For example, the operation of S^2 on a $3hp$ configuration which is an eigenfunction of S_z yields

$$S^2 a^\dagger_a a_i a_j \bar{a}_k |\Psi^{(0)}\rangle \equiv S^2 |a^\dagger_a a_i a_j \bar{a}_k\rangle \tag{40}$$

$$\begin{aligned}&= 2|a^\dagger_a a_i a_j \bar{a}_k\rangle + |a^\dagger_a a_i \bar{a}_j a_k\rangle + |a^\dagger_a \bar{a}_i a_j a_k\rangle \\ &\quad - |\bar{a}^\dagger_a \bar{a}_i a_j \bar{a}_k\rangle - |\bar{a}^\dagger_a a_i \bar{a}_j \bar{a}_k\rangle,\end{aligned} \tag{41}$$

where subscript indices label spatial orbitals and a bar over a field operator distinguishes spin β from spin α. Equation (41) indicates that a basis of $3hp$ operators has singlet, triplet, and quintet components. Therefore, we employ the following spin-adapted $2h$ $(2p)$ operator basis:

$$\{\mathbf{aa}\}_{\mathbf{pq}} = \{2(1+\delta_{pq})\}^{-1/2} (a_p \bar{a}_q \mp \bar{a}_p a_q)], \tag{42}$$

where indices (p,q) stand for general spatial orbitals. The upper sign refers to singlets $(p \leqslant q)$, and the lower sign refers to triplets $(p<q)$.

The three singlet and four triplet, spin-adapted $3hp$ operators are shown in Table II. The lone quintet operator is neglected in this paper. Use of these operators factorizes the propagator for the singlet and triplet parts. Here, only the superoperator Hamiltonian for the singlet state is presented,

$$\hat{\mathbf{H}}^{-}_{\mathrm{singlet}} = \begin{bmatrix} \hat{\mathbf{H}}^{(2)}_{2h,2h} & \hat{\mathbf{H}}^{(1)}_{2h,2p} & \hat{\mathbf{H}}^{(1)(\mathrm{I})}_{2h,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{II})}_{2h,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{III})}_{2h,3hp} \\ \hat{\mathbf{H}}^{(1)}_{2p,2h} & \hat{\mathbf{H}}^{(0)}_{2p,2p} & 0 & 0 & 0 \\ \hat{\mathbf{H}}^{(1)(\mathrm{I})}_{3hp,2h} & 0 & \hat{\mathbf{H}}^{(1)(\mathrm{I-I})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{I-II})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{I-III})}_{3hp,3hp} \\ \hat{\mathbf{H}}^{(1)(\mathrm{II})}_{3hp,2h} & 0 & \hat{\mathbf{H}}^{(1)(\mathrm{II-I})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{II-II})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{II-III})}_{3hp,3hp} \\ \hat{\mathbf{H}}^{(1)(\mathrm{III})}_{3hp,2h} & 0 & \hat{\mathbf{H}}^{(1)(\mathrm{III-I})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{III-II})}_{3hp,3hp} & \hat{\mathbf{H}}^{(1)(\mathrm{III-III})}_{3hp,3hp} \end{bmatrix}. \tag{43}$$

TABLE III. Molecular geometries and the SCF total energies.

Molecule	Length (Å)	Angle (°)	Energy (a.u.)
NH_3	1.0170	107.80	−56.205 29
H_2O	0.9584	104.45	−76.041 91
C_2H_2	C–C 1.2030		−76.828 43
	C–H 1.0587		
C_2H_4	C–C 1.3390	H–C–H 117.60	−78.043 43
	C–H 1.0856		
CO	1.1280		−112.755 62
H_2CO	C–O 1.2078	H–C–H 116.50	−113.885 12
	C–H 1.0587		

The spin-adapted expressions of each block are shown in the Appendix.

III. RESULTS AND DISCUSSION

A. Comparison of approximate self-energy terms

The four lowest DIPs for NH_3 and H_2O were calculated with the sum of two occupied orbital energies which corresponds to a zeroth-order, two-electron propagator, the first-order propagator, the second-order propagator, the self-energy of Eq. (36), and the SD2 approximation. Molecular geometries based on experimental data shown in Table III were used. All calculations were performed with Dunning's augmented, correlation-consistent, polarized-valence, double-ζ basis (aug-cc-pVDZ) (Ref. 49) using a modified version of the NWCHEM 5.0 program package.[50]

Numerical results of the DIPs with experimental values from Auger spectroscopy[1,2] are listed in Table IV. The second-order propagator overcorrects the DIPs of the first column. It is especially noteworthy that the DIPs for $^3B_1$ and $^1A_1$ dicationic states in H_2O are misordered in the zeroth-order approximation. The propagator results include not only electron correlation and orbital relaxation effects but also Coulomb interactions between the two holes. ^3E and ^1E in NH_3^{2+} are degenerate at the zeroth-order level, but are separated by 1.36 eV in the second-order column. In comparison with the experimental values, however, the second-order Dyson method is inadequate for performing a quantitative analysis of Auger spectra.

The self-energy of Eq. (36) includes third-order $3hp$ terms. Calculated DIPs are underestimated due to overcorrection by the third-order self-energy. The SD2 self-energy produces results that are in good agreement with experiment. Ladder diagrams in all orders from $3hp$ configurations considerably improve the second-order propagator. Contributions of off-diagonal elements of the first-order $3hp$-$3hp$ matrix are much smaller than those of the diagonal elements. As mentioned in the shifted-denominator approximation section, the SD2 method avoids double loops over $3hp$ indices. Therefore, the SD2 method is an accurate and efficient approximation for calculating vertical DIPs of molecules.

B. Numerical results on vertical DIPs

DIPs for NH_3, H_2O, C_2H_2, C_2H_4, CO, and H_2CO were calculated by the second and SD2 methods. To compare with other theories, we also calculated DIPs by indirect energy-difference methods including CI singles and doubles (ΔCISD) and CCSD[51] with perturbative triples corrections[52] (ΔCCSD(T)). An EOM-CCSD approach[53,54] also was examined. In this approximation, CCSD calculations are performed on the molecule and the lowest singlet and triplet states of the dication to obtain the first DIPs for each final-state multiplicity. To infer higher singlet and triplet DIPs, EOM-CCSD excitation energies for the dication are calculated using the reference state with the same multiplicity. Our numerical results, ADC(2) reports, and experimental values from Auger spectroscopy, DCT, TPEsCO, and PEPECO are listed in Table V–X for each molecule.

SD2 results are in good agreement with experimental values. To systematically examine the quality of the SD2 results, we compare to DIPs from ΔCISD, ΔCCSD(T), and EOM-CCSD. For 12 DIPs, the SD2 method yields average absolute deviations from ΔCISD and ΔCCSD(T) of 0.44 and 0.31 eV, respectively. For 36 DIPs, the SD2 method generates an average absolute error from EOM-CCSD of only 0.26 eV. The largest discrepancy of SD2 and the other methods occurs for the first $^1A_{1g}$ state of $C_2H_4^{2+}$. This final state has two holes in the reference state's highest occupied molecular orbital. The use of a more accurate reference state

TABLE IV. Vertical DIPs (eV) for NH_3 and H_2O calculated with sum of orbital energies ($\epsilon_i+\epsilon_j$), the first-order propagator, the second-order propagator, the self-energy terms of Eq. (36), and the SD2 method. Experimental values are from Auger electron spectroscopy.

No.	State	$\epsilon_i+\epsilon_j$	First	Second	Eq. (36)	SD2	Exp.[a]
NH_3							
1	$^1A_1$	23.14	39.53	30.98	26.09	35.81	35.36
2	^3E	28.67	41.95	33.55	29.39	37.87	
3	^1E	28.67	43.39	34.91	30.19	39.58	40.09
4	$^3A_2$	34.19	46.87	39.35	35.21	43.47	
H_2O							
1	$^3B_1$	29.78	46.30	33.77	27.82	39.76	39.1
2	$^1A_1$	27.70	47.27	34.35	27.93	41.34	41.3
3	$^1B_1$	29.78	48.41	35.82	29.78	42.38	
4	$^3A_2$	33.40	49.38	39.08	32.55	43.82	

[a]References 1 and 2.

TABLE V. Vertical DIPs (eV) of ammonia (NH_3).

No.	State	This work					ADC(2)[a]	Auger[b]	DCT[c] H^+/F^+
		Second	SD2	CISD	CCSD(T)	EOM			
1	$^1A_1$	30.98	35.81	35.17	35.42	35.33	34.19	35.36	35.5
2	^3E	33.55	37.87	37.67	37.96	37.87	36.69		38.0
3	^1E	34.91	39.58			39.53	38.35	40.09	39.4
4	$^3A_2$	39.35	43.47			43.65	42.59		43.7
5	^1E	40.69	45.39				44.37	46.08	44.7
6	$^1A_1$	42.34	47.54				45.00	48.81	

[a]Reference 40.
[b]Reference 1.
[c]Reference 7.

may reduce SD2's errors. However, most results of the SD2 method are in good agreement with EOM-CCSD.

From the tables, it can be seen that the ADC(2) method underestimates DIPs by ~1–2 eV. The main difference between SD2 and ADC(2) is the treatment of the self-energy term arising from the $2p$ operator space, as mentioned in previous section. The SD2 method employs an energy-dependent self-energy term, whereas the ADC(2) method has an energy-independent term.

IV. CONCLUSIONS

We have formulated the second-order, two-electron Dyson propagator using superoperator theory and the shifted-denominator approximation (SD2). The spin-adapted superoperator Hamiltonian was presented by introducing a spin-adapted basis for singlet and triplet states. Numerical tests for vertical DIPs showed that the results from the SD2 method were in good agreement with experiment. To systematically examine the quality of the results, we compared DIPs calculated with the SD2 and EOM-CCSD methods. The average absolute error was 0.26 eV for 36 doubly ionized states. This remarkable outcome is likely to arise from cancellation of basis set and correlation errors; nonetheless, the SD2 method has considerable promise. Because the SD2 method, like the P3 and NR2 approximations of electron propagator theory,[27,28] has no parameters, it can be applied in an unbiased manner for the prediction of double electron binding energies.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-0451810 to Auburn University.

APPENDIX A: MATRIX ELEMENT FORMULAS

1. Approximate self-energy terms

In this appendix, explicit expressions of the self-energy terms including first-order $3hp$ corrections are evaluated. As mentioned in the Theory section, the second-order self-energy matrix in Eq. (31) can be separated into three parts as

$$\mathbf{\Sigma}^{(2)}(\mathbf{E}) = \mathbf{\Sigma}^{(2)}(\infty) + \mathbf{\Sigma}^{(2)}_{\mathbf{2p}}(\mathbf{E}) + \mathbf{\Sigma}^{(2)}_{\mathbf{3hp}}(\mathbf{E}), \tag{A1}$$

where $\mathbf{\Sigma}^{(2)}(\infty)$ contains the first and second terms of Eq. (31), $\mathbf{\Sigma}^{(2)}_{\mathbf{2p}}(\mathbf{E})$ is the third term and $\mathbf{\Sigma}^{(2)}_{\mathbf{3hp}}(\mathbf{E})$ corresponds to the fourth and fifth terms. The third-order self-energy formulas for the two-electron propagator were evaluated with an analysis of the Feynman diagrams by Tarantelli and

TABLE VI. Vertical DIPs (eV) of water (H_2O).

No.	State	This work					ADC(2)[a]	Auger[b]	DCT[c] H^+	DCT[d] F^+/OH^+
		Second	SD2	CISD	CCSD(T)	EOM				
1	$^3B_1$	33.77	39.76	39.62	39.93	39.83	38.5	39.1		40.06
2	$^1A_1$	34.35	41.34	40.96	41.16	41.10	39.6	41.3	41.4	
3	$^1B_1$	35.82	42.38			42.54	41.2			
4	$^3A_2$	39.08	43.82			44.09	42.0			43.2
5	$^1A_1$	39.11	45.79				44.3	46.3	45.5	
6	$^1A_2$	39.69	45.76			46.04	44.8			
7	$^3B_2$	41.17	45.60			46.08	44.8			45.5
8	$^1B_2$	41.98	47.98				47.0			
9	$^1A_1$	47.13	53.25				52.1	53.2		

[a]Reference 41.
[b]Reference 2.
[c]Reference 8.
[d]Reference 9.

TABLE VII. Vertical DIPs (eV) of acetylene (C_2H_2).

		This work								
No.	State	Second	SD2	CISD	CCSD(T)	EOM	ADC(2)[a]	Auger[b]	DCT[c] H^+	DCT[d] OH^+
1	$^3\Sigma_g^-$	29.20	32.48	31.57	32.17	31.95	31.35			32.7
2	$^1\Delta_g$	30.22	33.74	32.94	33.38	33.21	32.47	33	33.7	
3	$^1\Sigma_g^+$	31.15	34.91				33.24			
4	$^3\Pi_u$	34.75	37.68			37.43	36.75			37.9
5	$^1\Pi_u$	35.41	38.61			38.24	37.64	37.6	38.4	
6	$^3\Pi_g$	36.37	39.31			39.02	38.15			39.6
7	$^1\Pi_g$	38.26	40.80			40.27	39.62	39.3	41	
8	$^1\Sigma_g^+$	41.71	44.34				43.30	42.6	45.9	
9	$^3\Sigma_u^-$	42.82	44.75				43.81			
10	$^3\Pi_u$	41.76	46.23				44.58			

[a]Reference 42.
[b]Reference 3.
[c]Reference 10.
[d]Reference 11.

Cederbaum.[38] Because many diagrams were involved in the third-order BS equation, they presented only orbital forms for the energy-independent part of the self-energy. The formulas correspond to $\mathbf{\Sigma}^{(3)}(\infty)$ and $\mathbf{\Sigma}_{\mathbf{2p}}^{(3)}(\mathbf{E})$ in the two-electron Dyson propagator. Therefore, a new derivation of the energy-dependent self-energy $\mathbf{\Sigma}_{\mathbf{3hp}}^{(3)}(\mathbf{E})$ is useful for introducing various approximations for the propagator.

Using the first-order $3hp$-$3hp$ Hamiltonian matrix element in Table I the spin-orbital forms of the third-order self-energies of Eq. (36) are expanded into

$$\{\mathbf{\Sigma}_{\mathbf{3hp}}^{(3)}(\mathbf{E})\}_{\mathbf{ij,kl}} = \{\mathbf{\Sigma}_{\mathbf{3hp}}^{(2)}(\mathbf{E})\}_{\mathbf{ij,kl}} + (1-P_{ij})(1-P_{kl})\Bigg[\frac{1}{4}\sum_{pq,ab}\frac{\langle ia\|pq\rangle\langle jb\|la\rangle\langle pq\|kb\rangle}{(E-\epsilon_{jpq,a})(E-\epsilon_{lpq,b})} + \frac{1}{2}\sum_{pq,ab}\frac{\langle ia\|lp\rangle\langle jb\|qa\rangle\langle pq\|kb\rangle}{(E-\epsilon_{jlp,a})(E-\epsilon_{lpq,b})} + \text{H.c.}$$
$$-\frac{1}{2}\sum_{pq,ab}\frac{\langle ia\|lp\rangle\langle pb\|qa\rangle\langle jq\|kb\rangle}{(E-\epsilon_{jlp,a})(E-\epsilon_{jlq,b})} + \frac{1}{2}\sum_{pqr,a}\frac{\langle ia\|lp\rangle\langle jp\|qr\rangle\langle qr\|ka\rangle}{(E-\epsilon_{jlp,a})(E-\epsilon_{lqr,a})} + \text{H.c.} - \sum_{pqr,a}\frac{\langle ia\|pq\rangle\langle jq\|lr\rangle\langle pr\|ka\rangle}{(E-\epsilon_{jpq,a})(E-\epsilon_{lpr,a})}$$
$$-\frac{1}{4}\delta_{jl}\sum_{pqrs,a}\frac{\langle ia\|pq\rangle\langle pq\|rs\rangle\langle rs\|ka\rangle}{(E-\epsilon_{jpq,a})(E-\epsilon_{lrs,a})} + \frac{1}{2}\delta_{jl}\sum_{pqr,ab}\frac{\langle ia\|pq\rangle\langle qb\|ra\rangle\langle pr\|kb\rangle}{(E-\epsilon_{jpq,a})(E-\epsilon_{lpr,b})}\Bigg], \tag{A2}$$

TABLE VIII. Vertical DIPs (eV) of ethylene (C_2H_4).

		This work								
No.	State	Second	SD2	CISD	CCSD(T)	EOM	ADC(2)[a]	Auger[b]	DCT[c] H^+	DCT[d] OH^+
1	^1A_g	28.35	31.23	30.14	30.72	30.51	29.46	30.1	29.4	
2	^3A_g	29.29	31.50	31.45	31.76	31.72	30.65			31.4
3	^1A_g	29.74	32.11			32.07	31.19		32.2	
4	$^3B_{3u}$	30.95	33.89			33.93	32.78			
5	^1A_g	32.66	34.76				33.93	34.5	34.0	
6	$^1B_{3u}$	31.80	34.93			34.72	33.81		34.0	
7	$^3B_{1g}$	32.41	35.17			34.80	33.73			34.9
8	$^3B_{3g}$	33.23	35.71			35.84	34.96			
9	$^1B_{1g}$	33.28	36.11				34.87		35.2	
10	$^3B_{1u}$	34.93	36.61			36.51	35.92			
11	$^1B_{3g}$	34.38	37.14				36.31		37.0	
12	$^3B_{2g}$	35.59	38.43			38.14	36.87			38.2
13	$^3B_{2u}$	36.35	39.32				38.31			
14	^1A_g	N.C.[e]	39.54				38.37	38.5	40.0	
15	$^1B_{2u}$	36.97	39.62				38.57			

[a]Reference 43.
[b]Reference 4.
[c]Reference 12.
[d]Reference 13.
[e]No convergence.

TABLE IX. Vertical DIPs (eV) of carbon monoxide (CO).

		This work								
No.	State	Second	SD2	CISD	CCSD(T)	EOM	ADC(2)[a]	Auger[b]	DCT[c] H^+	TPEsCO[d]
1	$^3\Pi$	39.03	41.34	40.86	41.27	41.17	41.13			41.29
2	$^1\Sigma^+$	39.12	41.58	41.64	41.01	41.43	40.86		41.52	41.70
3	$^1\Pi$	39.66	42.16			42.16	41.68	42.2		41.81
4	$^3\Sigma^+$	41.15	43.27				42.93	43.7		43.57
5	$^1\Sigma^+$	42.13	45.78			45.91	44.36	45.8	45.51	45.48
6	$^3\Sigma^-$	41.24	46.33			45.56	44.96			
7	$^1\Delta$	42.74	48.24				46.80	48.1		
8	$^3\Pi$	42.77	48.32				47.32			

[a]Reference 44.
[b]Reference 5.
[c]Reference 14.
[d]Reference 15.

where

$$\epsilon_{ijk,a} = \epsilon_j + \epsilon_j + \epsilon_k - \epsilon_a, \tag{A3}$$

the indices $i,j,\ldots$ and $p,q,\ldots$ stand for occupied spin orbitals, and a,b refer to virtual spin orbitals. H.c. means the Hermitian conjugate term. From Eq. (A2), the third-order self-energy terms are included in multiloop structures with more than four indices. The multiloops arise from double $3hp$ indices and cause an increase in computational time.

The formulation of the self-energy in Eq. (38) is given by replacing the denominators of Eq. (A2) with

$$\epsilon_{ijk,a} \rightarrow \epsilon_{ijk,a} + W_{ijk,a}, \tag{A4}$$

where

$$W_{ijk,a} = (1 + P_{ij} + P_{jk})[\langle ja \| ja\rangle - \langle ik \| ik\rangle]. \tag{A5}$$

The shifted denominator with the first-order diagonal $3hp$-$3hp$ element considerably improves the second-order propagator, but multiloop structures remain in this self-energy term.

In the SD2 approximation, the multiloops can be avoided by neglect of the off-diagonal elements of the first-order $3hp$-$3hp$ matrix. The self-energy term from the $3hp$ configuration is

$$\{\boldsymbol{\Sigma}^{(\mathrm{SD2})}_{\mathbf{3hp}}(\mathbf{E})\}_{\mathbf{ij,kl}} = (1 - P_{ij})(1 - P_{kl}) \times \left[\frac{1}{2}\delta_{jl}\sum_{mn,a}\frac{\langle ia \| mn\rangle\langle mn \| ka\rangle}{E - \epsilon_{jmn,a} - W_{jmn,a}} - \sum_{m,a}\frac{\langle ia \| lm\rangle\langle jm \| ka\rangle}{E - \epsilon_{jlm,a} - W_{jlm,a}}\right]. \tag{A6}$$

This improvement facilitates the calculation of self-energy matrix elements and yields accurate DIPs as described in Sec. III.

2. Spin-adapted superoperator Hamiltonian matrix elements

We present explicit expressions of the spin-adapted elements of the superoperator Hamiltonian matrix for the SD2 method. Spin-adapted operators were displayed in Eq. (42)

TABLE X. Vertical DIPs (eV) of formaldehyde (H_2CO).

		This work							
No.	State	Second	SD2	CISD	CCSD(T)	EOM	ADC(2)[a]	Auger[b]	PEPECO[c]
1	$^1A_1$	28.57	32.67	33.14	32.89	33.04	31.69	33.8	33.0
2	$^3A_2$	31.06	35.26			35.19	34.16		35.5
3	$^3B_2$	31.51	36.23				35.48		
4	$^1A_2$	32.35	36.46			36.78	35.47	37.0	
5	$^3A_1$	34.22	36.55	36.46	37.08	36.74	35.83		36.964
6	$^1B_2$	33.23	38.19			38.67	37.23	39.3	38.5
7	$^1A_1$	35.08	40.04			39.95	39.07	40.4	
8	$^3B_2$	38.39	40.93				40.10		
9	$^3B_1$	35.86	40.96				39.53		40.5
10	$^1B_2$	40.18	41.80				40.63		
11	$^3A_2$	38.27	41.56				40.54		
12	$^1A_1$	36.90	42.20				40.26	42.3	
13	$^3B_2$	39.19	42.50				41.86		

[a]Reference 45.
[b]Reference 6.
[c]Reference 16.

TABLE XI. Singlet matrix elements of spin-adapted first-order $\hat{\mathbf{H}}$ blocks. The diagonal orbital energy terms are omitted. $\langle ij||kl\rangle^{\pm}=V_{ij,kl}\pm V_{ij,lk}$.

Block	Element	Formula
$(\mathbf{aa}\|\hat{\mathbf{H}}_{\mathbf{aa}})$		
$\hat{\mathbf{H}}^{(1)}_{2h-2h}$	$\hat{\mathbf{H}}_{i\leqslant j,k\leqslant l}$	$-N_{ij}N_{kl}\langle ij\|\|kl\rangle^{+}$
$\hat{\mathbf{H}}^{(1)}_{2h-2p}$	$\hat{\mathbf{H}}_{i\leqslant j,a\leqslant b}$	$-N_{ij}N_{ab}\langle ij\|\|ab\rangle^{+}$
$(\mathbf{aa}\|\hat{\mathbf{H}}\mathbf{f}_{\mathbf{4}})$		
$\hat{\mathbf{H}}^{(1)(\mathrm{I})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i\leqslant j,k\neq la}$	$2^{1/2}N_{ij}(1+P_{ij})\{\delta_{jl}(V_{ia,lk}-\langle ia\|\|kl\rangle^{-})-\delta_{jk}V_{ia,ll}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{II})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i\leqslant j,k<l<ma}$	$-N_{ij}(1+P_{ij})\{\delta_{jl}\langle ia\|\|km\rangle^{+}$ $-(1+P_{km})\delta_{jm}(\langle ia\|\|kl\rangle^{-}+V_{ia,kl})\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{III})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i\leqslant j,k<l<ma}$	$3^{1/2}N_{ij}(1+P_{ij})\{\delta_{jl}\langle ia\|\|km\rangle^{-}+(1-P_{km})\delta_{jk}V_{ia,lm}\}$
$(\mathbf{f}_{\mathbf{4}}\|\hat{\mathbf{H}}\mathbf{f}_{\mathbf{4}})$		
$\hat{\mathbf{H}}^{(1)(\mathrm{I-I})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{i\neq ja}$	$-(1-P_{ia}-P_{ja})\{\langle ij\|\|ij\rangle^{-}+V_{ij,ij}\}+\langle ia\|\|ia\rangle^{+}$
$\hat{\mathbf{H}}^{(1)(\mathrm{II-II})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{i<j<ka}$	$-2^{-1}(1+P_{ik})\{\langle ij\|\|ij\rangle^{-}+V_{ij,ij}-\langle ia\|\|ia\rangle^{-}-V_{ia,ia}\}$ $+(\langle ja\|\|ja\rangle^{-}-V_{ja,aj})-\langle ik\|\|ik\rangle^{+}$
$\hat{\mathbf{H}}^{(1)(\mathrm{III-III})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{i<j<ka}$	$-2^{-1}(1+P_{ik})\{\langle ij\|\|ij\rangle^{+}+V_{ij,ij}-2\langle ia\|\|ia\rangle^{-}+V_{ia,ai}\}$ $+V_{ja,ja}-\langle ik\|\|ik\rangle^{-}$

TABLE XII. Triplet matrix elements of spin-adapted first-order $\hat{\mathbf{H}}$ blocks. The diagonal orbital energy terms are omitted.

Block	Element	Formula
$(\mathbf{aa}\|\hat{\mathbf{H}}_{\mathbf{aa}})$		
$\hat{\mathbf{H}}^{(1)}_{2h-2h}$	$\hat{\mathbf{H}}_{i<j,k\leqslant l}$	$-\langle ij\|\|kl\rangle^{-}$
$\hat{\mathbf{H}}^{(1)}_{2h-2p}$	$\hat{\mathbf{H}}_{i<j,a<b}$	$-\langle ij\|\|ab\rangle^{-}$
$(\mathbf{aa}\|\hat{\mathbf{H}}\mathbf{f}_{\mathbf{4}})$		
$\hat{\mathbf{H}}^{(1)(\mathrm{I})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i<j,k\neq la}$	$(1-P_{ij})\{\delta_{jk}V_{ia,ll}-\delta_{jl}V_{ia,kl}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{II})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i<j,k<l<ma}$	$(1-P_{ij})\{\delta_{jm}\langle ia\|\|lk\rangle^{-}+(1-P_{kl})\delta_{jk}V_{ia,ml}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{III})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i<j,k<l<ma}$	$(1-P_{ij})\{\delta_{jl}\langle ia\|\|km\rangle^{-}+(1-P_{km})\delta_{jm}V_{ia,lk}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{IV})}_{2h-3hp}$	$\hat{\mathbf{H}}_{i<j,k<l<ma}$	$(1-P_{ij})\{\delta_{jk}\langle ia\|\|ml\rangle^{-}+(1-P_{lm})\delta_{jl}V_{ia,km}\}$
$(\mathbf{f}_{\mathbf{4}}\|\hat{\mathbf{H}}\mathbf{f}_{\mathbf{4}})$		
$\hat{\mathbf{H}}^{(1)(\mathrm{I-I})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{i\neq ja}$	$-(1-P_{ia})\{\langle ij\|\|ij\rangle^{-}+V_{ij,ij}\}-V_{jj,ij}+V_{ia,ia}$
$\hat{\mathbf{H}}^{(1)(\mathrm{II-II})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{j<j<ka}$	$-(1-P_{ia}-P_{ja})\{\langle ij\|\|ij\rangle^{-}-V_{ka,ka}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{III-III})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{j<j<ka}$	$-(1-P_{ia}-P_{ka})\{\langle ik\|\|ik\rangle^{-}-V_{ja,ja}\}$
$\hat{\mathbf{H}}^{(1)(\mathrm{IV-IV})}_{3hp-3hp}$	$\hat{\mathbf{H}}_{j<j<ka}$	$-(1-P_{ja}-P_{ka})\{\langle jk\|\|jk\rangle^{-}-V_{ia,ia}\}$

and Table II. Expressing second-order elements of the $2h$-$2h$ superoperator Hamiltonian matrix over spin-adapted functions yields the following expression;

$$\begin{aligned}\{\hat{\mathbf{H}}^{(2)}_{2h,2h}\}_{ij,kl} &= N_{ij}N_{kl}(a_i\bar{a}_j \mp \bar{a}_i a_j|\hat{H}a_k\bar{a}_l \mp \bar{a}_k a_l)_2 \\ &= N_{ij}N_{kl}[(a_i\bar{a}_j|\hat{H}a_k\bar{a}_l)_2 \mp (\bar{a}_i a_j|\hat{H}a_k\bar{a}_l)_2 \\ &\quad \mp (a_i\bar{a}_j|\hat{H}\bar{a}_k a_l)_2 + (\bar{a}_i a_j|\hat{H}\bar{a}_k a_l)_2], \end{aligned} \tag{A7}$$

where the normalization constant is

$$N_{ij} = \begin{cases} [2(1+\delta_{ij})]^{-1/2} & (\text{for singlet}) \\ 2^{-1/2} & (\text{for triplet}). \end{cases} \tag{A8}$$

The indices (i,j,k,l) refer to occupied spatial orbitals. The upper sign refers to singlets ($i\leqslant j$, $k\leqslant l$) and the lower sign refers to triplets ($i<j$, $k<l$). From Eq. (A7), the expression of the second-order element is given by

$$\begin{aligned}\{\hat{\mathbf{H}}^{(2)}_{2h,2h}\}_{ij,kl} &= \frac{1}{4}N_{ij}N_{kl}(1\pm P_{ij})(1\pm P_{kl})\sum_{m,ab}(1-\delta_{ab}/2) \\ &\quad \times[V_{im,ab}V_{km,ab}+V_{mi,ab}V_{mk,ab} \\ &\quad +\langle im\,\|\,ab\rangle\langle km\,\|\,ab\rangle] \\ &\quad \times\left[\frac{1}{\epsilon_i+\epsilon_m-\epsilon_a-\epsilon_b}+\frac{1}{\epsilon_k+\epsilon_m-\epsilon_a-\epsilon_b}\right]. \end{aligned} \tag{A9}$$

Spin-adapted expressions of other matrix elements are derived and listed in Tables XI and XII for singlet and triplet states, respectively. Expressions for the diagonal elements of the $3hp$-$3hp$ blocks also are reported.

[1] R. W. Shaw, Jr., J. S. Jen, and T. D. Thomas, J. Electron Spectrosc. Relat. Phenom. **11**, 91 (1977).
[2] H. Siegbahn, L. Asplund, and P. Kelfve, Chem. Phys. Lett. **35**, 330 (1975).
[3] M. Thompson, P. A. Hewitt, and D. S. Wooliscroft, Anal. Chem. **48**, 1336 (1976).
[4] R. R. Rye, T. E. Madey, J. E. Houston, and P. H. Holloway, J. Chem. Phys. **69**, 1504 (1978).
[5] W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. **55**, 2317 (1971); J. A. Kelber, D. R. Jennison, and R. R. Rye, *ibid.* **75**, 652 (1981).
[6] N. Correira, A. Naves de Brito, M. P. Keane, L. Karlsson, S. Svensson, C.-M. Liegener, A. Cesar, and H. Ågren, J. Chem. Phys. **95**, 5187 (1991).
[7] M. L. Langford, F. M. Harris, P. G. Fournier, and J. Fournier, Int. J. Mass Spectrom. Ion Process. **116**, 53 (1992).
[8] P. J. Richardson, J. H. D. Eland, P. G. Fournier, and D. L. Cooper, J. Chem. Phys. **84**, 3189 (1986).
[9] J. C. Severs, F. M. Harris, S. R. Andrews, and D. E. Parry, Chem. Phys. **175**, 467 (1993).
[10] J. H. D. Eland, S. D. Price, J. C. Cheney, P. Lablanquie, I. Nenner, and P. G. Fournier, Philos. Trans. R. Soc. London, Ser. A **324**, 247 (1988).
[11] S. R. Andrews, F. M. Harris, and D. E. Parry, Chem. Phys. **166**, 69 (1992).
[12] C. Benoit and J. A. Horsley, Mol. Phys. **30**, 557 (1975).
[13] W. J. Griffiths and F. M. Harris, Int. J. Mass Spectrom. Ion Process. **122**, 321 (1992).
[14] O. Furuhashi, T. Kinugawa, S. Masuda, C. Yamada, and S. Ohtani, Chem. Phys. Lett. **337**, 97 (2001).
[15] G. Dawber, A. G. McConkey, L. Avaldi, M. A. MacDonald, G. C. King, and R. I. Hall, J. Phys. B **27**, 2191 (1994).
[16] M. Hochlaf and J. H. D. Eland, J. Chem. Phys. **123**, 164314 (2005).
[17] T. J. Van Huis, S. S. Wesolowski, Y. Yamaguchi, and H. F. Schaefer III, J. Chem. Phys. **110**, 11856 (1999).
[18] A. Ben Houria, Z. Ben Lakhdar, M. Hochlaf, F. Kemp, and I. R. McNab, J. Chem. Phys. **122**, 54303 (2005).
[19] B. T. Pickup and O. Goscinski, Mol. Phys. **26**, 1013 (1973).
[20] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 206 (1977).
[21] J. Simons, Theor. Chem. Adv. Persp. **3**, 1 (1978).
[22] M. F. Herman, K. F. Freed, and D. L. Yeager, Adv. Chem. Phys. **48**, 1 (1981).
[23] Y. Öhrn and G. Born, Adv. Quantum Chem. **13**, 1 (1981).
[24] W. von Niessen, J. Schirmer, and L. S. Cederbaum, Comput. Phys. Rep. **1**, 57 (1984).
[25] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic, New York, 1981).
[26] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry*, 2nd ed. (Wiley Interscience, Hoboken, 2004).

[27] J. V. Ortiz, J. Chem. Phys. **104**, 7599 (1996).
[28] J. V. Ortiz, J. Chem. Phys. **108**, 1008 (1998).
[29] J. V. Ortiz, Adv. Quantum Chem. **35**, 33 (1999).
[30] M. Gell-Mann and F. Low, Phys. Rev. **84**, 350 (1951).
[31] J. V. Ortiz, J. Chem. Phys. **81**, 5873 (1984).
[32] R. L. Graham and D. L. Yeager, J. Chem. Phys. **94**, 2884 (1991).
[33] C.-M. Liegener, J. Chem. Phys. **104**, 2940 (1996).
[34] Y. Noguchi, Y. Kudo, S. Ishii, and K. Ohno, J. Chem. Phys. **123**, 144112 (2005).
[35] Y. Noguchi, S. Ishii, and K. Ohno, J. Chem. Phys. **125**, 114108 (2006).
[36] Y. Noguchi, S. Ishii, and K. Ohno, J. Electron Spectrosc. Relat. Phenom. **156–158**, 155 (2007).
[37] J. Schirmer and A. Barth, Z. Phys. A **317**, 267 (1984).
[38] A. Tarantelli and L. S. Cederbaum, Phys. Rev. A **39**, 1639 (1989); **39**, 1656 (1989).
[39] A. Tarantelli and L. S. Cederbaum, Phys. Rev. A **49**, 3407 (1994).
[40] F. Tarantelli, A. Tarantelli, A. Sgamellotti, J. Schirmer, and L. S. Cederbaum, Chem. Phys. Lett. **117**, 577 (1985).
[41] F. Tarantelli, A. Tarantelli, A. Sgamellotti, J. Schirmer, and L. S. Cederbaum, J. Chem. Phys. **83**, 4683 (1985).
[42] E. M.-L. Ohrendorf, F. Tarrantelli, and L. S. Cederbaum, J. Chem. Phys. **92**, 2984 (1990).
[43] E. Ohrendorf, H. Köppel, L. S. Cederbaum, F. Tarantelli, and A. Sgamellotti, J. Chem. Phys. **91**, 1734 (1989).
[44] L. S. Cederbaum, P. Campos, F. Tarantelli, and A. Sgamellotti, J. Chem. Phys. **95**, 6634 (1991).
[45] D. Minelli, F. Tarantelli, A. Sgamellotti, and L. S. Cederbaum, J. Chem. Phys. **99**, 6688 (1993).
[46] A. B. Trofimov and J. Schirmer, J. Chem. Phys. **123**, 144115 (2005).
[47] P. O. Löwdin, J. Chem. Phys. **97**, 7531 (1950).
[48] F. Tarantelli, Chem. Phys. **329**, 11 (2006).
[49] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[50] E. J. Bylaska, W. A. de Jong, K. Kowalski *et al.*, NWCHEM, A Computational Chemistry Package for Parallel Computers, Version 5.0 (2006), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA. A modified version.
[51] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[52] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[53] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem., Quantum Chem. Symp. **18**, 255 (1984); J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989); H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990); J. F. Stanton and R. J. Bartlett, *ibid.* **98**, 7029 (1993).
[54] The EOM-CC approach is similar to symmetry adapted cluster method. [H. Nakatsuji, Chem. Phys. Lett. **39**, 562 (1978)].