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ANALYSIS OF THE EQUATION-OF-MOTION THEORY OF ELECTRON AFFINITIES AND IONIZATION POTENTIALS

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An analysis of the equation-of-motion (EOM) method for computing molecular electron affinities and ionization potentials is presented. The method is compared with the Dyson equation approach of Green function theory. Particular emphasis is devoted to clarifying the similarities between these two theories when carried out to second and to third order. The Epstein–Nesbet hamiltonian and the notion of diagonal scattering renormalization have been used to systematize this comparison.

1. Introduction

Until recently, most of the theoretical studies of molecular electron affinities (EA) were based on separate calculations of the energies of the neutral and ion species; the EA would then be obtained from the difference of these two quantities. As discussed by one of us in ref. [1] (hereafter referred to as EOM-I), simple calculations based on Koopmans' theorem [2] or on separate Hartree–Fock (HF) treatments of both the neutral and the ion frequently result in poor EAs due to the inadequacy of such approaches in dealing with charge redistribution and the change in electron correlation energy associated with adding the "extra" electron. The conventional approach for overcoming these difficulties has been to perform more accurate calculations by some form of perturbation theory or configuration interaction (CI) on the two species and to then compute the energy difference. As a result, one frequently has to subtract two numbers of almost equal magnitude. Furthermore, it is found that many identical terms appear in the neutral and ion energy expressions and therefore cancel when the difference is considered [3]. Therefore, a direct calculation technique which is aimed at the significant aspects of the problem is to be preferred. The EOM method as developed by Rowe [4] and applied by McKoy [5] and other authors [6–13] to atomic and molecular problems provides a means for directly calculating excitation energies, transition moments, and other quantities of interest. This method is capable of providing highly accurate results without explicitly requiring calculations of correlated ground and excited state wavefunctions.

Recently, several papers [1, 14, 15] have appeared in which the EOM theory has been developed and applied to the problems of molecular ionization potentials (IP) and EAs. In addition to these ion–neutral energy differences one can also obtain other useful information including the one-particle density matrix

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of the parent closed-shell species. Further, just as in the case of electronic excitation energies, there is a close connection between the Green function [16–27] and EOM treatments. One of the goals of this paper is to establish this connection.

In section 2, we present expressions for the various hamiltonians used in the development of our theory. In section 3, we summarize the well-known results of the Dyson equation approach. Finally, in sections 4 and 5, we establish the connections between the EOM and the perturbational treatment of one-particle Green functions [16, 18, 22–25, 28, 29].

2. The hamiltonian

The hamiltonian describing the electronic structure of molecules (neglecting relativistic effects and invoking the Born–Oppenheimer approximation) is

$$H = H^0_{\mathrm{HF}} + W_{\mathrm{HF}} + \langle 0|H|0\rangle , \tag{1}$$

where

$$H^0_{\mathrm{HF}} = \sum_i \epsilon_i N[C_i^\dagger C_i] , \tag{2}$$

and

$$W_{\mathrm{HF}} = \tfrac{1}{4} \sum_{i,j,k,l} (ij|v|kl) N[C_i^\dagger C_j^\dagger C_l C_k] . \tag{3}$$

The ϵ_i's are spin–orbital energies in the Hartree–Fock (HF) approximation and W_{HF} is the perturbational part of the hamiltonian. Note that we have expressed the zeroth-order approximation H^0_{HF} and the residual perturbation part W_{HF} in normal product form [30]. The third term in eq. (1) is the expectation value of the hamiltonian for the zeroth-order approximation to the ground state of the neutral molecule. We have adopted the convention for two-electron integrals that $(ij|v|kl) \equiv \langle ij|v|kl\rangle - \langle ij|v|lk\rangle$, i.e., the integrals involve direct and exchange terms. The partitioning of H described in eqs. (1)–(3) is widely used in the current literature in the application of perturbation theory to correlation problems. There is another partitioning scheme, proposed by Epstein and Nesbet [31] (EN) which is also used in this article, and which we now describe.

The EN decomposition of H is defined as follows:

$$H = H_{\mathrm{EN}} + W_{\mathrm{EN}} + \langle 0|H|0\rangle , \tag{4}$$

where

$$H_{\mathrm{EN}} = H^0_{\mathrm{HF}} + V_{\mathrm{d}} , \tag{5}$$

and

$$V_{\mathrm{d}} = \tfrac{1}{4} \sum_{i,j} (ij|v|ij) N[C_i^\dagger C_j^\dagger C_j C_i] \tag{6}$$

and

$$W_{\mathrm{EN}} = W_{\mathrm{HF}} - V_{\mathrm{d}} . \tag{7}$$

The zeroth order of the EN hamiltonian differs from the H^0_{HF} in eq. (2) by the diagonal scattering term V_{d}. The perturbation term W_{EN} is the same as W_{HF} when the diagonal scattering term is omitted. The operator H_{EN} has the following diagonal properties. For a general p-particle h-hole vector $|A\rangle$,

$$|A\rangle = C^\dagger_{m_1} C^\dagger_{m_2} \dots C^\dagger_{m_p} C_{\alpha_1} C_{\alpha_2} \dots C_{\alpha_h} |0\rangle . \tag{8}$$

The expectation value of H_{EN} is given by

$$\langle A|H_{\mathrm{EN}}|A\rangle = \sum_{i=1}^{p} \epsilon_{m_i} - \sum_{i=1}^{h} \epsilon_{\alpha_1} + \sum_{i,j\in(m_i,\alpha_j)} a_{ij} (ij|v|ij) , \tag{9}$$

where

$$a_{ij} = \begin{cases} 1 & \text{if } i, j \text{ are both particle states or both hole states,} \\ -1 & \text{otherwise ,} \end{cases} \tag{10}$$

and

$$\langle A_1|H_{\mathrm{EN}}|A_2\rangle = 0 , \qquad \text{if } |A_1\rangle \neq |A_2\rangle . \tag{11}$$

For convenience in using the EN hamiltonian in subsequent sections, we introduce the following short hand notation for diagonal scattering terms:

$$(ij|v|ij) \equiv [ij] , \tag{12}$$

and for non-diagonal scattering terms:

$$(ij|v|kl) \equiv [ij|kl] , \qquad (i \neq k, j \neq l) , \tag{13}$$

and in general (without distinguishing the diagonal and non-diagonal):

$$(ij|v|kl) \equiv (ij|kl) . \tag{14}$$

In the EOM method, as described in ref. [1] and briefly outlined later, H_{EN} is treated as the zeroth order approximation and W_{EN} is considered as the perturbation. However, in the Green function development, the introduction of H_{EN} and W_{EN} is avoided in the perturbation expansion, but the notion of diagonal scattering terms is found to be very useful (see refs. [32, 40]). With this discussion of the two decompositions of H completed, let us now turn to a review of Green function theory and then to the connections with our EOM theory.

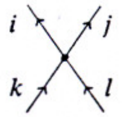
3. Many-body Green functions

The perturbational approach to Green functions is now well-established [16, 18, 22–25, 28, 29]. The Dyson equation may be formulated as a pseudo-eigenvalue problem [33],

$$\sum_j [\epsilon_j \delta_{ij} + M_{ij}(\Delta E)] X_j = \Delta E X_i , \qquad (15)$$

where the matrix elements $M_{ij}(\Delta E)$ of the mass operator or self-energy $\mathsf{M}(\Delta E)$ are represented by the sets of Hugenholtz diagrams in figs. 1 and fig. 2 in second and third orders, respectively [23]. The rules for assigning contributions to each of these diagrams depend on whether the diagonal scattering renormalization (DSR) [32] is used. For the case where renormalization is neglected, the rules are well-known [34], and are given, along with their DSR generalizations as follows:

Rule (1): To each vertex in a diagram,



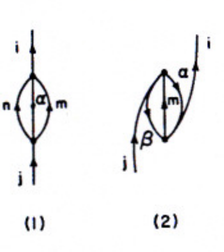


Fig. 1. Second order Hugenholtz diagrams.

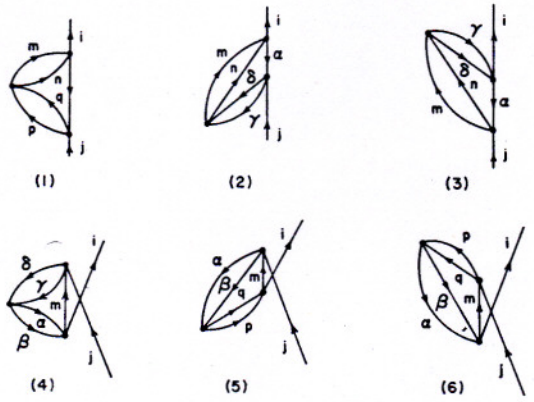


Fig. 2a.

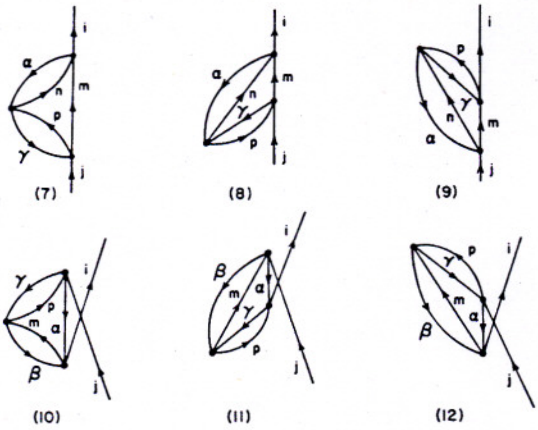


Fig. 2b.

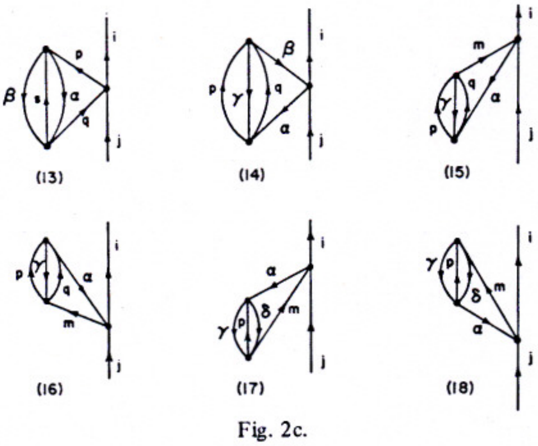


Fig. 2c.

Fig. 2. Third order Hugenholtz diagrams.

Table 1
Second order contribution to Green function and EOM

	Green function			Equation-of-motion					
Diagram I	Numerical factor II	Denominator [a] III	Term IV	Numerical factor V	Denominator [a] VI	Numerator VII	Case I VIII	Case II IX	Case III X
1	1/2	E^{mn}_{α}	(1) $\begin{bmatrix}0&0\\0&3\end{bmatrix}$ $\{3\}$ $\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	1/2	E^{mn}_{α}	$(i\alpha\|mn)(mn\|j\alpha)$	*	*	*
2	−1/2	$E^{m}_{\alpha\beta}$	(2) $\begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}$ $\{\bar{3}\}$ $\begin{bmatrix}0&0\\\bar{3}&1'\end{bmatrix}$	−1/2	$E^{m}_{\alpha\beta}$	$(im\|\alpha\beta)(\alpha\beta\|jm)$	*	*	*
			(3) $\begin{bmatrix}0&0\\1&5\end{bmatrix}$ $\{5\}$ $\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/8	$E^{mij}_{\alpha\beta}$				*

[a] For the energy denominators in tables 1 and 2, the following notation is employed:

$$\epsilon^{mn\ldots pq}_{\alpha\beta\ldots\gamma\delta} = (\epsilon_\alpha + \epsilon_\beta + \ldots + \epsilon_\gamma + \epsilon_\delta) - (\epsilon_m + \epsilon_n + \ldots + \epsilon_p + \epsilon_q),$$

$$E^{mn\ldots pq}_{\alpha\beta\ldots\gamma\delta} = (\epsilon_\alpha + \epsilon_\beta + \ldots + \epsilon_\gamma + \epsilon_\delta) - (\epsilon_m + \epsilon_n + \ldots + \epsilon_p + \epsilon_q) + \{\mathrm{sgn}(n_p - n_h)\}\,\Delta E + \sum_{i,j} b_{ij}[ij]\,,$$

where i and j run through the set of indices $\{m, n, \ldots, p, q, \alpha, \beta, \ldots, \gamma, \delta\}$, n_p and n_h are the number of particle and hole lines, respectively, and

$b_{ij} = -1$ if i, j are both particle or both hole states,
$\phantom{b_{ij}} = 1$ otherwise.

Table 2
Third order contributions to Green function and EOM

	Green function				Equations-of-motion				Case		
Diagram I	Numerical factor II	Denominators III	 IV	Term V	Numerical factors VI	Denominators VII	 VIII	Numerator IX	I X	II XI	III XII
1	1/4	E^{mn}_{α}	E^{pq}_{α}	(1) $\begin{bmatrix}0&0\\1&3\end{bmatrix}$ $\{3\}(3\ 3')\{3'\}$ $\begin{bmatrix}0&0\\3'&1'\end{bmatrix}$	1/4	E^{mn}_{α}	E^{pq}_{α}	$(i\alpha\|mn)[mn\|pq](pq\|j\alpha)$	*	*	*
2	1/4	E^{mn}_{α}	$E^{mnj}_{\gamma\delta}$	(2) $\begin{bmatrix}0&0\\1&3\end{bmatrix}$ $\{3\}$ $\begin{bmatrix}0&1\\3&1'\end{bmatrix}$	1/4	E^{mn}_{α}	$\epsilon^{mn}_{\gamma\delta}$	$(i\alpha\|mn)(mn\|\gamma\delta)(\gamma\delta\|j\alpha)$	*	*	*
				(3) $\begin{bmatrix}0&0\\1&3\end{bmatrix}$ $\{3\}(3\ 5)\{5\}$ $\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	1/8	E^{mn}_{α}	$E^{mnj}_{\gamma\delta}$				*
3	1/4	$E^{mni}_{\gamma\delta}$	E^{mn}_{α}	(4) $\begin{bmatrix}1&0\\1&3\end{bmatrix}$ $\{3\}$ $\begin{bmatrix}0&0\\3&1\end{bmatrix}$	1/4	$\epsilon^{mn}_{\gamma\delta}$	E^{mn}_{α}	$(i\alpha\|\gamma\delta)(\gamma\delta\|mn)(mn\|j\alpha)$	*	*	*
				(5) $\begin{bmatrix}0&0\\1&5\end{bmatrix}$ $\{5\}(5\ 3)\{3\}$ $\begin{bmatrix}0&0\\3&1'\end{bmatrix}$							*
4	−1/4	$E^{mij}_{\gamma\delta}$	$E^{mij}_{\alpha\beta}$	(6) $\begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}$ $\{\bar{3}\}(\bar{3}\ 3)$ $\{\bar{3}'\}$ $\begin{bmatrix}0&0\\\bar{3}'&1'\end{bmatrix}$	−1/4	$E^{m}_{\gamma\delta}$	$E^{m}_{\alpha\beta}$	$(im\|\alpha\beta)[\alpha\beta\|\gamma\delta](\gamma\delta\|jm)$	*	*	*

Table 2 (continued)

	Green function				Equations-of-motion						
Diagram I	Numerical factor II	Denominators III	IV	Term V	Numerical factors VI	Denominators VII	VIII	Numerator IX	Case I X	II XI	III XII
				$(7)\ \begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}(\bar{3}\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/8	$E^{m}_{\gamma\delta}$	$E^{mij}_{\alpha\beta}$				*
				$(8)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ \bar{3})\{3\}\begin{bmatrix}0&0\\\bar{3}&1'\end{bmatrix}$	−1/8	$E^{mij}_{\gamma\delta}$	$E^{m}_{\alpha\beta}$				*
				$(9)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/16	$E^{mij}_{\gamma\delta}$	$E^{mij}_{\alpha\beta}$				*
5	-1/4	$E^{mij}_{\alpha\beta}$	$E^{pqj}_{\alpha\beta}$	$(10)\ \begin{bmatrix}0&1\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}\begin{bmatrix}0&0\\\bar{3}&1\end{bmatrix}$	−1/4	$E^{m}_{\alpha\beta}$	$\epsilon^{pq}_{\alpha\beta}$	$(im\mid pq)(pq\mid\alpha\beta)(\alpha\beta\mid jm)$	*	*	*
				$(11)\ \begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}(\bar{3}\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/8	$E^{m}_{\alpha\beta}$	$E^{pqj}_{\alpha\beta}$				*
				$(12)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ 5')\{5'\}\begin{bmatrix}0&0\\5'&1'\end{bmatrix}$	−1/16	$E^{mij}_{\alpha\beta}$	$E^{pqj}_{\alpha\beta}$				*
6	−1/4	$E^{pqi}_{\alpha\beta}$	$E^{mij}_{\alpha\beta}$	$(13)\ \begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}\begin{bmatrix}1&0\\\bar{3}&1\end{bmatrix}$	−1/4	$\epsilon^{pq}_{\alpha\beta}$	$E^{m}_{\alpha\beta}$	$(im\mid\alpha\beta)(\alpha\beta\mid pq)(pq\mid jm)$	*	*	*
				$(14)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ \bar{3})\{\bar{3}\}\begin{bmatrix}0&0\\\bar{3}&1'\end{bmatrix}$	−1/8	$E^{pqi}_{\alpha\beta}$	$E^{m}_{\alpha\beta}$				*
				$(15)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ 5')\{5'\}\begin{bmatrix}0&0\\5'&1\end{bmatrix}$	−1/16	$E^{pqi}_{\alpha\beta}$	$E^{mij}_{\alpha\beta}$				*
7	1	E^{mn}_{α}	E^{mp}_{γ}	$(16)\ \begin{bmatrix}0&0\\1&3\end{bmatrix}\ \{3\}(3\ 3')\{3'\}\begin{bmatrix}0&0\\3'&1'\end{bmatrix}$	1	E^{mn}_{α}	E^{mp}_{γ}	$(i\alpha\mid mn)[n\gamma\mid p\alpha](mp\mid j\gamma)$	*	*	*
8	1	E^{mn}_{α}	$E^{pnj}_{\alpha\gamma}$	$(17)\ \begin{bmatrix}0&0\\1&3\end{bmatrix}\ \{3\}\begin{bmatrix}0&1\\3&1'\end{bmatrix}$	1	E^{mn}_{α}	$\epsilon^{pn}_{\alpha\gamma}$	$(i\alpha\mid mn)(pn\mid\alpha\gamma)(m\gamma\mid jp)$	*	*	*
				$(18)\ \begin{bmatrix}0&0\\1&3\end{bmatrix}\ \{3\}(3\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	1/2	E^{mn}_{α}	$E^{pnj}_{\alpha\gamma}$				*
9	1	$E^{pni}_{\alpha\gamma}$	E^{mn}_{α}	$(19)\ \begin{bmatrix}1&0\\1&3\end{bmatrix}\ \{3\}\begin{bmatrix}0&0\\3&1\end{bmatrix}$	1	$\epsilon^{pn}_{\alpha\gamma}$	E^{mn}_{α}	$(ip\mid m\gamma)(\alpha\gamma\mid np)(mn\mid j\alpha)$	*	*	*
				$(20)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ 3)\{3\}\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	1/2	$E^{pni}_{\alpha\gamma}$	E^{mn}_{α}				*
10	−1	$E^{pij}_{\alpha\gamma}$	$E^{mij}_{\alpha\beta}$	$(21)\ \begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}(\bar{3}\ \bar{3}')\{\bar{3}'\}\begin{bmatrix}0&0\\\bar{3}'&1'\end{bmatrix}$	−1	$E^{p}_{\alpha\gamma}$	$E^{m}_{\alpha\beta}$	$(im\mid\alpha\beta)[\beta p\mid\gamma m](\alpha\gamma\mid jp)$	*	*	*
				$(22)\ \begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}(\bar{3}\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/2	$E^{p}_{\alpha\gamma}$	$E^{mij}_{\alpha\beta}$				*
				$(23)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ \bar{3})\{\bar{3}\}\begin{bmatrix}0&0\\\bar{3}&1'\end{bmatrix}$	−1/2	$E^{pij}_{\alpha\gamma}$	$E^{m}_{\alpha\beta}$				*
				$(24)\ \begin{bmatrix}0&0\\1&5\end{bmatrix}\ \{5\}(5\ \bar{5})\{\bar{5}\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/4	$E^{pij}_{\alpha\gamma}$	$E^{mij}_{\alpha\beta}$				*
11	−1	$E^{mij}_{\alpha\beta}$	$E^{pmj}_{\beta\gamma}$	$(25)\ \begin{bmatrix}0&1\\1&\bar{3}\end{bmatrix}\ \{\bar{3}\}\begin{bmatrix}0&0\\\bar{3}&1\end{bmatrix}$	−1	$E^{m}_{\alpha\beta}$	$\epsilon^{pm}_{\beta\gamma}$	$(i\gamma\mid\alpha p)(mp\mid\gamma\beta)(\alpha\beta\mid jm)$	*	*	*

Table 2 (continued)

	Green function				Equations-of-motion						
Diagram	Numerical factor	Denominators		Term	Numerical factors	Denominators		Numerator	Case		
I	II	III	IV	V	VI	VII	VIII	IX	I X	II XI	III XII
				(26) $\begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\{\bar{3}\}(\bar{3}\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	$-1/2$	$E^{m}_{\alpha\beta}$	$E^{pmj}_{\beta\gamma}$				*
				(27) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ 5')\{5'\}\begin{bmatrix}0&0\\5'&1'\end{bmatrix}$	$-1/4$	$E^{mij}_{\alpha\beta}$	$E^{pmj}_{\beta\gamma}$				*
12	-1	$E^{pmi}_{\beta\gamma}$	$E^{mij}_{\alpha\beta}$	(28) $\begin{bmatrix}0&0\\1&\bar{3}\end{bmatrix}\{\bar{3}\}\begin{bmatrix}1&0\\\bar{3}&1\end{bmatrix}$	-1	$\epsilon^{pm}_{\beta\gamma}$	$E^{m}_{\alpha\beta}$	$(im\mid\alpha\beta)(\gamma\beta\mid mp)(\alpha p\mid j\gamma)$	*	*	*
				(29) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ \bar{3})\{\bar{3}\}\begin{bmatrix}0&0\\\bar{3}&1'\end{bmatrix}$	$-1/2$	$E^{pmi}_{\beta\gamma}$	$E^{m}_{\alpha\beta}$				*
				(30) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ 5')\{5'\ \begin{bmatrix}0&0\\5'&1\end{bmatrix}$	$-1/4$	$E^{pmi}_{\beta\gamma}$	$E^{mij}_{\alpha\beta}$				*
13	$1/2$	$E^{psi}_{\alpha\beta}$	$E^{qsj}_{\alpha\beta}$	(31) $\begin{bmatrix}1&1\\1&1'\end{bmatrix}$	$1/2$	$\epsilon^{ps}_{\alpha\beta}$	$\epsilon^{qs}_{\alpha\beta}$	$(ip\mid jq)(sp\mid\alpha\beta)(\alpha\beta\mid sq)$ a)	*	*	*
				(32) $\begin{bmatrix}1&0\\1&5\end{bmatrix}\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	$1/4$	$\epsilon^{psi}_{\alpha\beta}$	$E^{qsj}_{\alpha\beta}$	$[ip\mid jq](sp\mid\alpha\beta)(\alpha\beta\mid sq)$			*
				(33) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}\begin{bmatrix}0&1\\5&1'\end{bmatrix}$	$1/4$	$E^{psi}_{\alpha\beta}$	$\epsilon^{qs}_{\alpha\beta}$				*
				(34) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ 5')\{5'\}\begin{bmatrix}0&0\\5'&1'\end{bmatrix}$	$1/8$	$E^{psi}_{\alpha\beta}$	$E^{qsj}_{\alpha\beta}$				*
14	$-1/2$	$E^{pqi}_{\beta\gamma}$	$E^{pqj}_{\alpha\gamma}$	(35) $\begin{bmatrix}1&1\\1&1'\end{bmatrix}$	$-1/2$	$\epsilon^{pq}_{\beta\gamma}$	$\epsilon^{pq}_{\alpha\gamma}$	$(i\alpha\mid j\beta)(\gamma\alpha\mid pq)(pq\mid\gamma\beta)$ b)	*	*	*
				(36) $\begin{bmatrix}1&0\\1&5\end{bmatrix}\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	$-1/4$	$\epsilon^{pq}_{\beta\gamma}$	$E^{pqj}_{\alpha\gamma}$	$[i\alpha\mid j\beta](\gamma\alpha\mid pq)(pq\mid\gamma\beta)$			*
				(37) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}\begin{bmatrix}0&1\\5&1'\end{bmatrix}$	$-1/4$	$E^{pqi}_{\beta\gamma}$	$\epsilon^{pq}_{\alpha\gamma}$				*
				(38) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ 5')\{5'\}\begin{bmatrix}0&0\\5'&1'\end{bmatrix}$	$1/8$	$E^{pqi}_{\beta\gamma}$	$E^{pqj}_{\alpha\gamma}$				*
15	$1/2$	E^{mj}_{α}	$E^{pqj}_{\alpha\gamma}$	(39) $\begin{bmatrix}0&0\\1&3\end{bmatrix}\{3\}\begin{bmatrix}0&1\\3&1'\end{bmatrix}$	$1/4$	E^{mj}_{α}	$\epsilon^{pq}_{\alpha\gamma}$	$(i\alpha\mid jm)(\alpha m\mid pq)(pq\mid\gamma\alpha)$	*	*	*
				(40) $\begin{bmatrix}0&2\\1&1'\end{bmatrix}$	$1/4$	ϵ^{m}_{α}	$\epsilon^{pq}_{\alpha\gamma}$			*	*
				(41) $\begin{bmatrix}0&0\\1&3\end{bmatrix}\{3\}(3\ 5)\{5\}\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	$1/4$	E^{mj}_{α}	$E^{pqj}_{\alpha\gamma}$				*
16	$1/2$	$E^{pqi}_{\alpha\gamma}$	E^{mi}_{α}	(42) $\begin{bmatrix}1&0\\1&3\end{bmatrix}\{3\}\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	$1/4$	$\epsilon^{pq}_{\alpha\gamma}$	E^{mi}_{α}	$(im\mid j\alpha)(pq\mid\gamma m)(\gamma\alpha\mid pq)$	*	*	*
				(43) $\begin{bmatrix}2&0\\1&1'\end{bmatrix}$	$1/4$	$\epsilon^{pq}_{\alpha\gamma}$	ϵ^{m}_{α}			*	*
				(44) $\begin{bmatrix}0&0\\1&5\end{bmatrix}\{5\}(5\ 3)\{3\}\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	$1/4$	$E^{pqi}_{\alpha\gamma}$	E^{mi}_{α}				*

Table 2 (continued)

	Green function				Equations-of-motion						
Diagram	Numerical factor	Denominators		Term	Numerical factors	Denominators		Numerator	Case		
									I	II	III
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
17	−1/2	E_{α}^{mj}	$E_{\gamma\delta}^{pmj}$	(45) $\begin{bmatrix}0&0\\1&3\end{bmatrix}$ $\{3\}$ $\begin{bmatrix}0&1\\3&1'\end{bmatrix}$	−1/4	E_{α}^{mj}	$\epsilon_{\gamma\delta}^{pm}$	$(i\alpha\vert jm)(\gamma\delta\vert p\alpha)(pm\vert\gamma\delta)$	*	*	*
				(46) $\begin{bmatrix}0&2\\1&1'\end{bmatrix}$	−1/4	ϵ_{α}^{m}	$\epsilon_{\gamma\delta}^{pm}$			*	*
				(47) $\begin{bmatrix}0&0\\1&3\end{bmatrix}$ $\{3\}(3\,5)\{5\}$ $\begin{bmatrix}0&0\\5&1'\end{bmatrix}$	−1/4	E_{α}^{mj}	$E_{\gamma\delta}^{pmj}$				*
18	−1/2	$E_{\gamma\delta}^{pmi}$	E_{α}^{mi}	(48) $\begin{bmatrix}1&0\\1&3\end{bmatrix}$ $\{3\}$ $\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	−1/4	$\epsilon_{\gamma\delta}^{pm}$	E_{α}^{mi}	$(im\vert j\alpha)(p\alpha\vert\gamma\delta)(\gamma\delta\vert pm)$	*	*	*
				(49) $\begin{bmatrix}2&0\\1&1'\end{bmatrix}$	−1/4	$\epsilon_{\gamma\delta}^{pm}$	ϵ_{α}^{m}			*	*
				(50) $\begin{bmatrix}0&0\\1&5\end{bmatrix}$ $\{5\}(5\;3)\{3\}$ $\begin{bmatrix}0&0\\3&1'\end{bmatrix}$	−1/4	$E_{\gamma\delta}^{pmi}$	E_{α}^{mi}				*

[a] In the case of Green function, the numerator should be $[ip\vert jq]\,(sp\vert\alpha\beta)(\alpha\beta\vert sq)$.

[b] In the case of Green function, the numerator should be $[i\alpha\vert j\beta]\,(\gamma\alpha\vert pq)(pq\vert\gamma\beta)$.

assign a factor $(ij|kl)$ for the case without DSR; a factor $[ij|kl]$ with DSR.

Rule (2): To each vertical cut between two neighboring vertices, assign an energy denominator equal to

$$\sum_{\alpha}(\text{hole line energies}) - \sum_{p}(\text{particle line energies}) + C$$

where

$$C = \{\operatorname{sgn}(n_p - n_h)\}\,\Delta E\,,$$

for the case without DRS, where n_p and n_h are the number of particle and hole lines, respectively; and

$$C = \sum_{i,j} b_{ij}[ij] + \{\operatorname{sgn}(n_p - n_h)\}\,\Delta E\,,$$

for the case with DSR, where i, j are line indices belonging to this vertical cut, and

$$b_{ij} = -1 \qquad \text{if } i, j \text{ are both particle indices or both hole indices,}$$
$$= 1 \qquad \text{otherwise.}$$

Rule (3): Assign a sign factor $(-1)^{n_h + l}$ where l is the number of closed loops [35].

Rule (4): Assign a factor 2^{-e}, where e is the number of pairs of equivalent lines in the given diagram.

Rule (5): Multiply all the factors assigned above, and sum over all the internal line indices.

For convenience, we have written the contributions to the second and third-order Green function diagrams in the tables 1 and 2. To aid in our comparison with the EOM method, discussed in the next section, we have also listed the contributions of each second and third order diagram to the effective hamiltonian $H_{ij}(\Delta E)$ of our EOM theory. As can be seen from tables 1 and 2, the principal differences, between the two approaches is the assignment of energy denominators to each diagram and the overall numerical factor multiplying each diagram. Before going further into the comparison, we now give a brief outline of various approximations which are made to generate working EOM theories of molecular electron affinities.

4. The equation-of-motion method

Following the formulation of Rowe [4] and

McKoy [5], we consider a Fermion operator $\Omega_\lambda^\dagger$ which is constructed from products of odd numbers of creation and annihilation operators, describing the addition of an electron to the ground state $|g^N\rangle$ of an N-electron closed-shell molecule. As shown by Rowe and in ref. [1], one can obtain the basic EOM in symmetrized [36] "double commutator" form,

$$\langle g^N|\{\delta\Omega_\lambda, H, \Omega_\lambda^\dagger\}|g^N\rangle = \Delta E_\lambda \langle g^N|\{\delta\Omega_\lambda, \Omega_\lambda^\dagger\}|g^N\rangle , \tag{16}$$

where the commutators are defined as

$$\{x, y, z\} \equiv \tfrac{1}{2}\{x, [y, z]\} + \tfrac{1}{2}\{[x, y], z\} , \tag{17}$$

$$\{A, B\} \equiv AB + BA , \tag{18}$$

$$[A, B] \equiv AB - BA , \tag{19}$$

and $\Delta E_\lambda \equiv E_g^N - E_\lambda^{N+1}$ is the vertical EA (E_λ^{N+1} is the electronic energy of the λth state of the negative ion and E_g^N the ground state energy of the neutral species.) Generally, the Fermion operator $\Omega_\lambda^\dagger$ is taken to be a truncated linear combination of products of odd numbers of creation and annihilation operators,

$$\Omega_\lambda^\dagger \approx XC^\dagger + YC^\dagger CC^\dagger + ZC^\dagger CC^\dagger CC^\dagger + \dots . \tag{20}$$

The operator $\delta\Omega_\lambda$ is then the adjoint of any operator within the space in which $\Omega_\lambda^\dagger$ is expressed

$$\delta\Omega_\lambda \approx C, CC^\dagger C, CC^\dagger CC^\dagger C, \dots . \tag{21}$$

In practice, the criteria by which the important components in the truncated operator $\Omega_\lambda^\dagger$ are chosen and the requirements for the input ground state wavefunction $|g^N\rangle$ to be comparable in accuracy to a chosen $\Omega_\lambda^\dagger$ are not clear. This is an inherent difficulty of the EOM approach. Furthermore, the dimensionality of the EOM shown in eq. (16) is often very large. The problem of large dimensionality can be avoided by using the partitioning technique and perturbation theory [38] to cast the original eigenvalue problem into a new effective pseudo-eigenvalue problem of much smaller dimension. Such an approach can be very convenient provided the convergence of the perturbation expansion of the elements of the new effective hamiltonian matrix is fast enough to permit the inclusion of only second and third order terms (the probable limit of our present computing facilities). Based upon the assumption that calculations which are carried out through third order will be adequate to yield EAs to an accuracy of ± 0.2 eV, we shall use the notion of order in perturbation theory to determine whether various components in $\Omega_\lambda^\dagger$ and in $|g^N\rangle$ are going to contribute to the effective eigenvalue problem through third order. Following this line of thought, we have found that, in order to include all the second and third order effects in the effective pseudo-eigenvalue problem, we must choose the truncated operator $\Omega_\lambda^\dagger$ as follows [39]

$$\begin{aligned}\Omega^\dagger = {} & \sum_i X_i C_i^\dagger + \sum_{\substack{m<n\\ \alpha}} Y_{n\alpha m} C_n^\dagger C_\alpha C_m^\dagger \\ & + \sum_{\substack{\alpha<\beta\\ m}} Y_{\alpha m\beta} C_\alpha^\dagger C_m C_\beta^\dagger \\ & + \sum_{\substack{p<q<r\\ \gamma<\delta}} Y_{r\delta q\gamma p} C_r^\dagger C_\delta C_q^\dagger C_\gamma C_p^\dagger \\ \equiv {} & \sum_i X_i C_i^\dagger + \sum_{\substack{m<n\\ \alpha}} Y_{n\alpha m} d_{n\alpha m}^\dagger + \sum_{\substack{\alpha<\beta\\ m}} Y_{\alpha m\beta} d_{\alpha m\beta}^\dagger \\ & + \sum_{\substack{p<q<r\\ \gamma<\delta}} Y_{r\delta q\gamma p} d_{r\delta q\gamma p}^\dagger ,\end{aligned} \tag{22}$$

and the ground state wave function $|g^N\rangle$, apart from a normalization factor, as *

$$|g^N\rangle = |0\rangle + |1\rangle + |2\rangle , \tag{23}$$

where we have introduced the shorthand notation

$$|1\rangle \equiv \frac{1}{4} \sum_{\substack{\mu,\nu\\ p,q}} \frac{(pq|\mu\nu)}{\epsilon_{\mu\nu}^{pq}} C_p^\dagger C_q^\dagger C_\nu C_\mu |0\rangle , \tag{24}$$

$$\begin{aligned}|2\rangle \equiv \frac{1}{2}\Bigg(& \sum_{\substack{m,\alpha\\ p,q,\gamma}} \frac{(\gamma m|pq)(qp|\gamma\alpha)}{\epsilon_\alpha^m \, \epsilon_{\alpha\gamma}^{pq}} \\ & - \sum_{\substack{m,\alpha\\ p,\gamma,\delta}} \frac{(p\alpha|\gamma\delta)(\gamma\delta|pm)}{\epsilon_\alpha^m \, \epsilon_{\gamma\delta}^{pm}} \Bigg) C_m^\dagger C_\alpha |0\rangle .\end{aligned} \tag{25}$$

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* In EOM-I, monoexcited configurations were not included in the ground state; as a consequence of this EOM-I neglects the terms (40), (43), (46), and (49) shown in table 2 of this paper. There are also second order bi-excited components which are not included because they do not contribute until fourth order to the ionization potential or electron affinity.

In these equations $|0\rangle$ is the HF ground-state wavefunction, $|1\rangle$ is the first order bi-excited component, $|2\rangle$ is the second order monoexcited component, and

$$\epsilon^{mn\dots pq}_{\alpha\beta\dots\mu\nu} = (\epsilon_\alpha + \epsilon_\beta + \dots + \epsilon_\mu + \epsilon_\nu) - (\epsilon_m + \epsilon_n + \dots + \epsilon_p + \epsilon_q) .$$

By using eq. (22) for $\Omega^\dagger$ and successively choosing $\delta\Omega$ as C_i, $C_m C^\dagger_\alpha C_n$, $C_\beta C^\dagger_m C_\alpha$, and $C_p C^\dagger_\gamma C_q C^\dagger_\delta C_r$, one obtains from eq. (16) a set of equations for the expansion coefficients X_i, $Y_{n\alpha m}$, $Y_{\alpha m\beta}$, and $Y_{r\delta q\gamma p}$, which in matrix form becomes

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{D} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Delta E \begin{pmatrix} \mathbf{1} & \mathbf{R} \\ \mathbf{R}^\dagger & \mathbf{S} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} . \tag{26}$$

Here, the coefficients X_i and $Y_{n\alpha m}$, $Y_{\alpha m\beta}$, $Y_{r\delta q\gamma p}$, appear in column vector form as X and Y, respectively. The elements of the submatrices in eq. (26) are

$$A_{ij} = \langle g^N | \{C_i, H, C^\dagger_j\} | g^N \rangle , \tag{27a}$$

$$B_{i,x} = \langle g^N | \{C_i, H, d^\dagger_x\} | g^N \rangle ,$$

$$(x = n\alpha m, \alpha m\beta, r\delta q\gamma p) , \tag{27b}$$

$$D_{x,y} = \langle g^N | \{d_x, H, d^\dagger_y\} | g^N \rangle ,$$

$$(x, y = n\alpha m, \alpha m\beta, r\delta q\gamma p) , \tag{27c}$$

$$R_{i,x} = \langle g^N | \{C_i, d^\dagger_x\} | g^N \rangle , \tag{27d}$$

$$S_{x,y} = \langle g^N | \{d_x, d^\dagger_y\} | g^N \rangle . \tag{27e}$$

The $d^\dagger_x$ have been introduced to represent $C^\dagger_n C_\alpha C^\dagger_m$, etc. The partitioning of eq. (26) to yield a pseudo-eigenvalue problem of smaller dimension is easily performed by rewriting eq. (26) in the form of simultaneous equations and eliminating the vector Y in favor of X. In this manner the following equations are obtained:

$$\mathbf{H}(\Delta E) X = \Delta E\, X , \tag{28a}$$

where

$$\mathbf{H}(\Delta E) \equiv \mathbf{A} + (\mathbf{B} - \Delta E\, \mathbf{R})(\Delta E\, \mathbf{S} - \mathbf{D})^{-1} (\mathbf{B}^\dagger - \Delta E\, \mathbf{R}^\dagger) . \tag{28b}$$

Eq. (28) is a pseudo-eigenvalue equation which is solved iteratively. It should be noted that the dimension of $\mathbf{H}(\Delta E)$ is equal to the dimension of the spin-orbital basis used to generate the HF orbitals. The most convenient way of evaluating the matrix elements of $\mathbf{A}, \mathbf{B}, \mathbf{D}, \mathbf{S}$ and $\mathbf{R}$ in eqs. (27)–(28) is to employ Wick's theorem and diagrammatic techniques [41] of many-body theory. This greatly simplifies the bookkeeping.

Two difficulties remain at this stage of the analysis. The calculation of the overlap matrices $\mathbf{S}$ and $\mathbf{R}$ involve the evaluation of 1-, 2-, 3- and 4-particle density matrices. It can be shown that $\mathbf{R}$ is at least of second order and $\mathbf{S}$ differs from the unit matrix $\mathbf{1}$ by second and higher order terms. The replacement of $\mathbf{S}$ by $\mathbf{1}$ causes a fourth order error in the second term on the right-hand side of eq. (28b) since $\mathbf{B}$ is at least first order while $\mathbf{D}$ is at least zeroth order. Since our objective is to obtain results accurate through third order, the approximation $\mathbf{S} \approx \mathbf{1}$ is made. Further, as in EOM-I, we make the approximation that $\mathbf{R} \approx \mathbf{O}$, turning later to the consequences of this approximation.

$$\mathbf{H}_\mathrm{I}(\Delta E) X = \Delta E X , \tag{29a}$$

$$\mathbf{H}_\mathrm{I}(\Delta E) \equiv \mathbf{A} + \mathbf{B} (\Delta E \mathbf{1} - \mathbf{D})^{-1} \mathbf{B}^\dagger . \tag{29b}$$

In EOM-I, we have made one additional approximation, namely, the replacement of H by H_EN to render the $\mathbf{D}$ matrix diagonal. This was done in order to avoid the very laborious calculation of the inverse matrix $(\Delta E \mathbf{1} - \mathbf{D})^{-1}$. As an improvement over this approximation, we employ the following expansion of the inverse matrix:

$$\begin{aligned} (\Delta E \mathbf{1} - \mathbf{D})^{-1} \cong{} & (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \\ & + (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \mathbf{D}_1 (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \\ & + (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \mathbf{D}_1 (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \mathbf{D}_1 (\Delta E \mathbf{1} - \mathbf{D}_\mathrm{EN})^{-1} \end{aligned} \tag{30}$$

where $\mathbf{D}$ is decomposed as

$$\mathbf{D} = \mathbf{D}_\mathrm{EN} + \mathbf{D}_1 , \tag{31}$$

with

$$(\mathbf{D}_\mathrm{EN})_{x,y} = \delta_{x,y} \langle g^N | \{d_x, H_\mathrm{EN}, d^\dagger_y\} | g^N \rangle , \tag{32}$$

$$(\mathbf{D}_1)_{x,y} = (1 - \delta_{x,y}) \langle g^N | \{d_x, W_\mathrm{EN}, d^\dagger_y\} | g^N \rangle . \tag{33}$$

In eqs. (32)–(33), the diagonal properties [eqs. (9)–(11)] of the EN hamiltonian have been fully exploited. Keeping in mind that we are only interested in keeping terms in $\mathbf{H}(\Delta E)$ through third order we need only retain the first and second terms on the right hand side of eq. (30). The improved effective hamiltonian operator $\mathsf{H}(\Delta E)$ thus becomes *

$$\mathsf{H}(\Delta E) = \mathsf{A} + \mathsf{B}(\Delta E\,\mathbf{1} - \mathsf{D}_{\mathrm{EN}})^{-1}\mathsf{B}^{\dagger} + \mathsf{B}(\Delta E\mathbf{1} - \mathsf{D}_{\mathrm{EN}})^{-1}\mathsf{D}_1(\Delta E\mathbf{1} - \mathsf{D}_{\mathrm{EN}})^{-1}\mathsf{B}^{\dagger}\,. \qquad (34)$$

To aid in the description of the various terms in eq. (34) we define the following quantities:

$$\begin{bmatrix} a\, b \\ i\, j \end{bmatrix} \equiv \langle a|\{C_i, W_{\mathrm{HF}}, C_j^{\dagger}\}|b\rangle\,, \qquad (35a)$$

$$\begin{bmatrix} a\, b \\ i\, x \end{bmatrix} \equiv \langle a|\{C_i, W_{\mathrm{HF}}, d_x^{\dagger}\}|b\rangle\,, \qquad (35b)$$

$$\{x\} \equiv [\langle 0|\{d_x, H_{\mathrm{EN}}, d_x^{\dagger}\}|0\rangle]^{-1}\,, \qquad (35c)$$

$$(xy) \equiv \langle 0|\{d_x, W_{\mathrm{EN}}, d_y^{\dagger}\}|0\rangle\,, \qquad (35d)$$

$$\begin{bmatrix} b\, a \\ x\, i \end{bmatrix} = \begin{bmatrix} a\, b \\ i\, x \end{bmatrix}^{*} \equiv \langle b|\{d_x, W_{\mathrm{HF}}, C_i^{\dagger}\}|a\rangle\,, \qquad (35e)$$

where $a, b = 0, 1, 2$ represent the zeroth, first, and second order components of $|g^N\rangle$ respectively. In addition, we shall use $1, 3, \bar{3}$, and 5 to denote collectively the indices i, $n\alpha m$, $\alpha m\beta$, and $r\delta q\gamma p$ respectively as shown in eqs. (27a)–(27c). With these notational simplifications, we can now write down the non-zero contributions to the matrix elements $H_{ij}(\Delta E)$ through third order. In the tables we have specialized to the case for which i and j are both particle states, that is the results are presented for an electron affinity calculation. For the sake of organization and clarity, we have presented the second- and third-order contributions together with the Green function results in tables 1 and 2. In zeroth order we obtain the Koopmans' theorem result from the A_{ij} term:

$$A_{i,j} = \langle g^N|\{C_i, H, C_j^{\dagger}\}|g^N\rangle = \epsilon_i\delta_{ij} + (\text{third and higher order terms})\,. \qquad (36)$$

In second order, as listed in table 1, the contributions come from the sum of the two Hugenholtz diagrams shown in fig. 1. To compute the contribution of each diagram to the self-energy of Green function theory (or the effective hamiltonian of the EOM theory) one must form the product of the numerical factors listed in columns II and VII (V and VII) and divide by the energy denominator listed in column III (VI). The numerical factors for the Green function contributions are a result of applying the diagram rules discussed in section 3, whereas the factors listed for the EOM case arise from using the diagram rules of section 3 to evaluate the symmetrized matrix elements given in eq. (27).

The first point to be made concerning the relationship of EOM and Green function theories is that neglect of the $C_r^{\dagger}C_{\delta}C_q^{\dagger}C_{\gamma}C_p^{\dagger}$ terms in $\Omega_{\lambda}^{\dagger}$ leads to equivalence between the two approaches through second order (see table 1).

The third order terms listed in table 2 can be represented by the 18 Hugenholtz diagrams shown in fig. 2. For the Green function (EOM) theory, the contribution of each diagram is the product of the numerical factors given in columns II and IX (VI and IX) divided by the product of energy denominators given in columns III and IV (VII and VIII). The diagonal scattering form of the Green function is given; the more familiar form without renormalization of the energy denominators is obtained by omitting all two electron interaction terms appearing in the denominators (i.e., the $\epsilon_{\alpha\beta\ldots\gamma\delta}^{mn\ldots pq}$ form of the energy denominators should replace the $E_{\alpha\beta\ldots\gamma\delta}^{mn\ldots pq}$). In order to facilitate comparison between the two theories in third order, let us now specifically consider the following special cases within the general EOM theory discussed earlier in this section (recall that we have taken $\mathsf{R} \approx \mathsf{O}$ and $\mathsf{S} \approx \mathbf{1}$).

Case I: Only the first order component of $|g^N\rangle$ is retained:

$$|g^N\rangle \approx |0\rangle + |1\rangle\,,$$

and $\Omega_{\lambda}^{\dagger}$ is truncated by eliminating $d_{r\delta q\gamma p}^{\dagger}$:

$$\Omega_{\lambda}^{\dagger} = \sum_i X_i C_i^{\dagger} + \sum_{\substack{m<n \\ \alpha}} Y_{n\alpha m} d_{n\alpha m}^{\dagger} + \sum_{\substack{\alpha<\beta \\ m}} Y_{\alpha m\beta} d_{\alpha m\beta}^{\dagger}\,.$$

Case II: The full $|g^N\rangle$ of eq. (23) is used:

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* The referee has pointed out that this expression for $\mathsf{H}(\Delta E)$ has improper analytical properties as a function of ΔE and may give non-physical results if it were applied to "shake-up" processes. For a discussion of the use of GF methods as applied to shake-up processes, see: L.S. Cederbaum, J. Chem. Phys. 62 (1975) 2160, and L.T. Redmon, G. Purvis and Y. Ohrn, J. Chem. Phys. 63 (1975) 5011.

$$|g^N\rangle \approx |0\rangle + |1\rangle + |2\rangle , \tag{37}$$

but $\Omega_\lambda^\dagger$ is truncated:

$$\Omega_\lambda^\dagger = \sum_i X_i C_i^\dagger + \sum_{\substack{m<n \\ \alpha}} Y_{n\alpha m} d_{n\alpha m}^\dagger + \sum_{\substack{\alpha<\beta \\ m}} Y_{\alpha m\beta} d_{\alpha m\beta}^\dagger . \tag{38}$$

Case III: The full second order $|g^N\rangle$ is used:

$$|g^N\rangle \approx |0\rangle + |1\rangle + |2\rangle , \tag{39}$$

and $\Omega_\lambda^\dagger$ is not further truncated:

$$\Omega_\lambda^\dagger = \sum_i X_i C_i^\dagger + \sum_{\substack{n<m \\ \alpha}} Y_{n\alpha m} d_{n\alpha m}^\dagger + \sum_{\substack{\alpha<\beta \\ m}} Y_{\alpha m\beta} d_{\alpha m\beta}^\dagger + \sum_{\substack{p<q<r \\ \gamma<\delta}} Y_{r\delta q\gamma p} d_{r\delta q\gamma p}^\dagger . \tag{40}$$

In columns X, XI and XII of table 2, we have marked with an asterisk each term which contributes to the overall self-energy or effective hamiltonian under each of the above three special cases of the EOM theory. From this tabulation it is seen that Case II of the EOM bears the most similarity to the many-body Green function (MBGF) approach; the only difference between EOM Case II and the MBGF approach being the form of some of the energy denominators. For example, for term 2 of table 2 the MBGF denominator is $E_\alpha^{mn} E_{\gamma\delta}^{mnj}$ while the corresponding denominator in the EOM is $E_\alpha^{mn} \epsilon_{\gamma\delta}^{mn}$. Using the definitions given in eq. (12) we find

$$E_\alpha^{mn} = -\epsilon_m - \epsilon_n + \epsilon_\alpha - [mn] + [m\alpha] + [n\alpha] + \Delta E , \tag{41}$$

$$E_{\gamma\delta}^{mnj} = -\epsilon_m - \epsilon_n - \epsilon_j + \epsilon_\gamma + \epsilon_\delta - [mn] - [nj] - [mj] - [\gamma\delta] + [m\gamma] + [m\delta] + [n\gamma] + [n\delta] + [j\gamma] + [j\delta] + \Delta E , \tag{42}$$

$$\epsilon_{\gamma\delta}^{mn} = -\epsilon_m - \epsilon_n + \epsilon_\gamma + \epsilon_\delta . \tag{43}$$

From comparison of eqs. (42) and (43) we see that for term (2) of table 2 the EOM and MBGF energy denominators differ in two ways. First, two-electron matrix elements appear in eq. (42) but not in eq. (43) and secondly eq. (42) also contains a $\Delta E - \epsilon_j$ contribution lacking in eq. (43). From expansion of the energy denominator

$$\left(\epsilon_m + \epsilon_n + \epsilon_j - \epsilon_\gamma - \epsilon_\delta - \Delta E - \sum_{x,y} b_{xy}[x,y]\right)^{-1} \approx (\epsilon_m + \epsilon_n + \epsilon_j - \epsilon_\gamma - \epsilon_\delta - \Delta E)^{-1} \times \left(1 + \sum_{x,y} \frac{b_{xy}[x,y]}{\epsilon_m + \epsilon_n + \epsilon_j - \epsilon_\gamma - \epsilon_\delta - \Delta E}\right) \tag{44}$$

it is clear that the two electron renormalization terms contribute in fourth and higher orders of the interaction. If ΔE is also replaced by ϵ_j then we have agreement between the Case II EOM and MBGF representations of term (2) through third order. The replacement of ΔE by ϵ_j is precisely the first step to an iterative solution of the EOM. If a similar analysis is performed on the other entries in table 2, we find that through third order the MBGF and Case II EOM approaches agree. Consequently, Case II EOM represents a more consistent theory than do the Case I and Case III EOM approaches.

The extension of our operator set to include terms of the sort $C_r^\dagger C_\delta C_q^\dagger C_\delta C_p{}^\dagger$ causes the EOM to differ from the MBGF approach in second, third and higher orders. Thus, care must be taken to ensure that the operator set is consistent with the ground state approximation and other approximations introduced into the EOM. In fact, the discrepancy between the MBGF and EOM approaches that arises in second and third order when $C_r^\dagger C_\delta C_q^\dagger C_\gamma C_p^\dagger$ terms are included in the operator is due to the approximation $\mathsf{R} \approx \mathsf{O}$. Eq. (28) may be rewritten

$$[\mathsf{H}_\mathrm{I}(\Delta E) + \mathsf{m}(\Delta E)] X = \Delta E\, X , \tag{45}$$

where $\mathsf{H}_\mathrm{I}(\Delta E)$ is given by eq. (29) and

$$\mathsf{m}(\Delta E) = \mathsf{B}(\Delta E \mathsf{S} - \mathsf{D})^{-1} \mathsf{R}^\dagger + \mathsf{R}(\Delta E \mathsf{S} - \mathsf{D})^{-1} \mathsf{B}^\dagger - \Delta E\, \mathsf{R}(\Delta E \mathsf{S} - \mathsf{D})^{-1} \mathsf{R}^\dagger . \tag{46}$$

When $C_r^\dagger C_\delta C_q^\dagger C_\delta C_p^\dagger$ terms are included in the operator set they give rise to second and third order contributions to $\mathsf{m}(\Delta E)$. After considerable algebra involving expansion of energy denominators and the regrouping of terms, we find that these new terms cancel through third order the terms involving the $C^\dagger C C^\dagger C C^\dagger$ operators in tables 1 and 2. Apparently, we again have agreement between EOM and MBGF. However, it also turns out that the $C^\dagger C C^\dagger$ operators contribute to $\mathsf{m}(\Delta E)$ in third order due to the presence of single excitations in the ground state given in eq. (23). These new terms are represented by diagrams 15–18 in fig. 2 and their contribution causes a slight disagreement between the MBGF and EOM theories in third and higher orders. For example, let us consider the terms contributing to diagram 15. The new contribution from $\mathrm{m}(\Delta E)$ enters with a coefficient of $-1/8$ which means that the overall coefficient is 3/8 rather than the 1/2 of the MBGF approach [remember that term (41) containing the contribution from the five operator is cancelled through third order by the five operator contribution to $\mathrm{m}(\Delta E)$]. This disagreement is not serious since the contribution of these diagrams to molecular electron affinities and ionization potentials is small [23, 42].

5. Discussion

In this paper we have established the connections between the EOM and the one-particle Green function approaches to ionization potentials and electron affinities. The EOM derivation presented here has employed the symmetrized "double commutator" defined in eqs. (16)–(17). We note that in general

$$\langle g^N|\{C_i, [H, C_n^\dagger C_\alpha C_m^\dagger]\}|g^N\rangle$$
$$\neq \langle g^N|\{[C_i, H], C_n^\dagger C_\alpha C_m^\dagger\}|g^N\rangle,$$

since the exact ground state is not employed [42]. In the development of this paper we have employed the symmetrized double commutator

$$B_{i,n\alpha m} = \tfrac{1}{2}\{\langle g^N|\{[C_i, H], C_n^\dagger C_\alpha C_m^\dagger\}|g^N\rangle$$
$$+ \langle g^N|\{C_i, [H, C_n^\dagger C_\alpha C_m^\dagger]\}|g^N\rangle\}.$$

It is not obvious that the use of the symmetrized double commutator results in a more straightforward or consistent formulation of the EOM. In order to investigate this matter, we have also carried out the derivations of this paper using $B_{i,n\alpha m} = \langle g^N|\{C_i, [H, C_n^\dagger C_\alpha C_m^\dagger]\}|g^N\rangle$. The differences between this development and that of the text arises in the coefficients of the terms contributing to diagrams 15–18 of table 2. To illustrate the resulting changes, we will briefly discuss the various contributions to diagram 16 with the above unsymmetrized definition of B. Term (42) now appears with a coefficient of 1/2 rather than 1/4. Terms (43) and (44) still have coefficients of 1/4, and the contribution of the five operators in term (44) again is cancelled through third order due to the contribution from $\mathrm{m}(\Delta E)$. As before, the presence of the single excitations in the approximation to $|g^N\rangle$ also gives rise to a third order term due to $\mathrm{m}(\Delta E)$, however the coefficient is now $-1/4$ rather than $-1/8$. Thus, through third order, we now have agreement with the MBGF approach. Thus, if our object were to obtain a theory correct through third order, there is no need to include either the operators $C_r^\dagger C_\delta C_q^\dagger C_\gamma C_p^\dagger$ or the single excitations in the ground state $|g^N\rangle$. This finding suggests that the unsymmetrized version of the EOM approach may be preferable.

As with the EOM for excitation energies [43], many questions remain concerning the effects of various choices of $|g^N\rangle$ and $\Omega_\lambda^\dagger$. The role of terms such as $C_m^\dagger C_p C_n^\dagger$, $C_m^\dagger C_\beta C_\alpha^\dagger$, and $C_m^\dagger C_n C_\gamma^\dagger$ has not been established. Similarly the significance of second-order double excitations in $|g^N\rangle$ has not been explored. Our experience with the $C_r^\dagger C_\delta C_q^\dagger C_\gamma C_p^\dagger$ operators indicates that these questions do not have unambiguous answers. Whether a certain operator or ground state component contributes to a given order in the interaction depends on the other terms and ground state components present as well as to approximations made to $\mathbf{R}$ and $\mathbf{S}$ and whether symmetrized commutators are employed.

In this paper we have discussed various approximate EOM theories for ionization potentials and electron affinities. We have presented an EOM theory which is correct through third order and sums a large number of terms to all orders in Rayleigh–Schrödinger perturbation theory. This summation of a large number of terms to all orders is a property shared with the Green function approaches [23].

It is significant to note that even the EOM-I method, which neglects certain third order terms, gives good ionization potentials (usually within 0.2 eV of the experimental value). For perspective, in table 3 we compare IPs calculated via EOM-I [14, 15, 44] with the experimental values for HF, BH, BeH$^-$, OH$^-$, and CN$^-$ (for the BeH$^-$, OH$^-$, and CN$^-$ we are reporting the vertical detachment energies). We have also included our theoretical predictions [45, 46], as obtained from EOM-I, for the EAs of LiH, NaH, BeO, and LiF. We believe that these calculated EAs are cor-

Table 3
Equation-of-motion and Koopmans' theorem estimates of electron affinities and ionization potentials (eV)

Species	EA or IP	EOM	$-\epsilon_{LUMO}$	Exptl [14, 15, 44]
BeO	EA	1.769	1.414	...
LiH	EA	0.299	0.200	...
NaH	EA	0.362	0.290	...
LiF	EA	0.464	0.425	...
HF	IP	15.87	17.79	16.01
BH	IP	9.53	9.30	9.77
BeH^-	IP	0.77	0.51	0.74
OH^-	IP	1.76	3.06	1.825
CN^-	IP	3.69	5.21	3.82

rect to 0.1 eV. These studies on the negative ions of LiH, NaH, BeO, and LiF were undertaken in order to investigate the nature of the binding of electrons to highly polar molecules. Experimental electron affinities are not available for BeO, NaH, and LiH, and our studies have led us to conclude [46, 47] that the experimental EA of LiF is in error by about 0.9 eV.

We are currently applying the EOM method to the calculation of IPs and EAs for various polyatomic molecules. Although, the energies given in table 3 correspond to vertical processes, the method is capable of describing the geometrical rearrangements that occur upon ionization or electron attachment. So far, we have restricted our attention to positive electron affinities. We plan to investigate the usefulness of EOM methods for describing temporary negative ions of molecules such as ethylene and butadiene [48].

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