THE SELF-CONSISTENT DETERMINATION OF THE ION AND NEUTRAL MOLECULE WAVEFUNCTIONS IN A THEORY OF ELECTRON AFFINITIES AND IONIZATION POTENTIALS

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Received 4 December 1973

In this paper, we discuss the validity of our earlier derivation of a theory of molecular electron affinities and ionization potentials. We show how one can improve upon our original derivation, which was not entirely consistent, by iteratively calculating both the ion and neutral molecule wavefunctions. Most importantly, we demonstrate that the electron affinities and ionization potentials which are obtained by using our original theory are correct through third order, even though the derivation of this theory contains an inconsistency.

1. Introduction

In recent publications [1, 2], we demonstrated how an approximate solution of the Heisenberg equation of motion [3] (EOM), which has previously been used to calculate molecular electronic excitation energies and oscillator strengths [4–10], could be employed to compute molecular electron affinities, ionization potentials, and first-order density matrices. In these papers we made the assumption that the ground-state wavefunction $|g\rangle$ of the neutral molecule could be adequately approximated by using first-order Rayleigh–Schrödinger (RS) perturbation theory [11]#. We felt that, although the RS wavefunction might not yield a very accurate energy for the neutral molecule, its use in the calculation of ion–neutral energy differences was strongly supported by McKoy's success in employing such wavefunctions in his calculations of electronic excitation energies. As McKoy and others have pointed out, the success of these direct-calculation methods is linked to the fact that the full complexity of $|g\rangle$ is neither displayed nor required in the computed energy difference. With these reasons in mind, the RS function was chosen as a well-defined and computationally tractable first approximation to $|g\rangle$. Of course, it is very natural and important to ask whether we could devise a scheme for obtaining an "improved" approximation to $|g\rangle$, which is fully consistent, in the sense described by McKoy [7], with the derivation of our theory of electron affinities and ionization potentials. In section 2 of this paper, we show how the necessary components of this consistent wavefunction $|g_C\rangle$ can be obtained in a computationally useful manner. We develop a rapidly convergent iterative procedure which permits the self-consistent calculation of both $|g_C\rangle$ and the excitation operator Ω_g^+ which generates the negative-ion state by operating on $|g_C\rangle$. Finally, we demonstrate that electron affinities which are accurate through third order in the electron repulsions r_{ij}^{-1} can be obtained by using a simplified non-iterative technique in which $|g_C\rangle$ is approximated by the first-order RS wavefunction $|g_{RS}\rangle$. Thus, we have shown that the results of our original theory are entirely valid *if* one is satisfied with calculating all quantities to third order; the self-consistent computation developed herein is unnecessary. Section 3 contains our concluding remarks.

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‡ Alfred P. Sloan Foundation Fellow.

Because we have not allowed for the possibility of singly excited configurations in $|g\rangle$, we are restricted to closed-shell ground states.

2. The calculation of $|g_C\rangle$

In the EOM theory of electron affinities and ionization potentials derived in ref. [1], the excitation operator Ω_λ^+, which generates the, in principle exact, eigenstate $|\lambda_-\rangle$ of the negative ion when operating on the true neutral-molecule ground state $|g\rangle$,

$$\Omega_\lambda^+|g\rangle = |\lambda_-\rangle\,, \tag{1}$$

is approximated in terms of the second-quantized Hartree–Fock orbital creation $\{C_i^+\}$ and annihilation $\{C_i\}$ operators as follows ‡.

$$\Omega_\lambda^+ = \sum_i X_i(\lambda)\,C_i^+ + \sum_{m<n,\alpha} Y_{n\alpha m}(\lambda)\,C_n^+ C_\alpha\, C_m^+ + \sum_{\alpha<\beta,m} Y_{\alpha m\beta}(\lambda)\,C_\alpha^+ C_m\, C_\beta^+\,. \tag{2}$$

The operator C_i^+ (C_i) creates (destroys) an electron in the Hartree–Fock spin-orbital φ_i. Greek indices α, β, γ label "occupied" Hartree–Fock spin-orbitals, m, n, p, q label "unoccupied" spin-orbitals, and i, j, k, l label either set. The $X_i(\lambda)$, $Y_{n\alpha m}(\lambda)$, and $Y_{\alpha m\beta}(\lambda)$ are expansion coefficients which are determined by making use of the EOM theory of ref. [1] whose pertinent aspects are briefly reviewed below. An analogous expansion for the operator Ω_μ which generates positive-ion eigenstates # when operating on $|g\rangle$ is also given in ref. [1].

By assuming that $|g\rangle$ and $|\lambda_-\rangle$ exactly obey the following Schrödinger equations

$$H|g\rangle = E|g\rangle\,, \tag{3a}$$

and

$$H|\lambda_-\rangle = E_\lambda^-|\lambda_-\rangle\,, \tag{3b}$$

one immediately obtains the basic equations of motion

$$[H, \Omega_\lambda^+]\,|g\rangle = (E_\lambda^- - E)\,\Omega_\lambda^+|g\rangle\,, \tag{3c}$$

which were used in ref. [1] to derive the following matrix pseudo-eigenvalue problem involving the electron affinity and the coefficients $X_i(\lambda)$

$$\sum_j H_{ij}(\Delta E_\lambda)\,X_j(\lambda) = \Delta E_\lambda\, X_i(\lambda)\,, \tag{4}$$

where ΔE_λ is $E_\lambda^- - E$. This result can be derived by using the approximation to Ω_λ^+ given in eq. (2) and the RS approximation to $|g\rangle$

$$|g_{\mathrm{RS}}\rangle = N_0^{-1/2}\left[|0\rangle + \sum_{m<n,\alpha<\beta} \frac{\langle mn|\alpha\beta\rangle}{\epsilon_\alpha+\epsilon_\beta-\epsilon_m-\epsilon_n} \times C_m^+\, C_n^+ C_\beta\, C_\alpha|0\rangle\right] \tag{5}$$

in eq. (3c). The coefficients $Y_{n\alpha m}(\lambda)$ and $Y_{\alpha m\beta}(\lambda)$ have been eliminated by partitioning the resulting equations. In eq. (5), N_0 is a normalization constant, ϵ_i is the Hartree–Fock energy of spin-orbital φ_i, and the $\langle mn|\alpha\beta\rangle$ are antisymmetrized two-electron integrals over the spin-orbitals $\varphi_m, \varphi_n, \varphi_\alpha$, and φ_β. The Hartree–Fock wavefunction of the neutral parent is represented by $|0\rangle$. The elements of the matrix $H_{ij}(\Delta E_\lambda)$ are given in eq. (37) of ref. [1] as

$$H_{ij}(\Delta E_\lambda) = A_{ij} + \sum_{\alpha<\beta,m} \frac{B_{i,\alpha m\beta}\,B^*_{j,\alpha m\beta}}{E^m_{\alpha\beta}+\Delta E_\lambda} - \sum_{N+1<n,\alpha} \frac{B_{i,n\alpha N+1}\,B^*_{j,n\alpha N+1}}{E_\alpha^{N+1\,n}-\Delta E_\lambda} - \sum_{N+1<m<n,\alpha} \frac{B_{i,n\alpha m}\,B^*_{j,n\alpha m}}{E_\alpha^{mn}-\Delta E_\lambda} \tag{1-37}$$

and the quantities appearing in this equation are defined in eqs. (31d)–(35) of ref. [1] which are reproduced here for the sake of completeness

$$A_{ij} = \delta_{ij}\,\epsilon_i + \sum_{k,l} \langle ik|jl\rangle F_{kl}\,, \tag{1-31d}$$

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‡ For a good description of the properties of such Fermion creation and annihilation operators, see ref. [12]. The effect of Ω_λ^+ on $|g\rangle$ is relatively easy to understand. The term $X_i(\lambda)\,C_i^+$ simply adds, in a weighted manner, an electron to the spin-orbital φ_i; while $Y_{n\alpha m}(\lambda)\,C_n^+ C_\alpha C_m^+$ adds an electron to φ_m and promotes another electron from φ_α to φ_n. Finally, the term $Y_{\alpha m\beta}(\lambda)\,C_\alpha^+ C_m\, C_\beta^+$ adds an electron to φ_β and moves another electron from φ_m to φ_α.

The conclusions reached in this paper are obtained by considering the states of the negative ion. Analogous results can be deduced by carrying through the development with the positive-ion states $\Omega_\mu|g\rangle$.

$$B_{i\alpha m\beta} = -\langle im|\alpha\beta\rangle - \tfrac{1}{2}\sum_{p,q} \langle im|pq\rangle K^{pq}_{\alpha\beta}$$

$$+\sum_{\gamma,p} [\langle i\gamma|p\alpha\rangle K^{mp}_{\beta\gamma} - \langle i\gamma|p\beta\rangle K^{mp}_{\alpha\gamma}] \,, \qquad (1\text{-}31\text{e})$$

$$B_{i,n\alpha m} = \langle i\alpha|mn\rangle + \tfrac{1}{2}\sum_{\gamma\delta} \langle i\alpha|\delta\gamma\rangle K^{mn}_{\delta\gamma}$$

$$+\sum_{\gamma p} [\langle ip|\gamma n\rangle K^{mp}_{\alpha\gamma} - \langle ip|\gamma m\rangle K^{np}_{\alpha\gamma}] \,, \qquad (1\text{-}31\text{f})$$

$$F_{kl} \equiv \sum_{\alpha<\beta,p} K^{pk}_{\alpha\beta} K^{pl}_{\alpha\beta} - \sum_{p<q,\alpha} K^{pq}_{\alpha l} K^{pq}_{\alpha k} \,, \qquad (1\text{-}32)$$

$$E^{mn}_{\alpha} = \epsilon_m + \epsilon_n - \epsilon_\alpha - \langle \alpha m|\alpha m\rangle - \langle \alpha n|\alpha n\rangle + \langle mn|mn\rangle, \qquad (1\text{-}34)$$

$$E^{p}_{\delta\gamma} = \epsilon_p - \epsilon_\delta - \epsilon_\gamma - \langle \delta p|\delta p\rangle - \langle \gamma p|\gamma p\rangle + \langle \delta\gamma|\delta\gamma\rangle \,, \qquad (1\text{-}35)$$

and

$$K^{pq}_{\alpha\beta} = \langle pq|\alpha\beta\rangle (\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)^{-1} \,. \qquad (1\text{-}15)$$

Although the above quantities are rather complicated, it should be kept in mind that a knowledge of the orbital energies $\{\epsilon_i\}$ and two-electron integrals $\langle ij|kl\rangle$ is sufficient to permit the formation of $H_{ij}(\Delta E_\lambda)$. The physical content of the terms in the above expression for $H_{ij}(\Delta E)$, which is discussed more completely in ref. [1], can be summarized as follows.

(i) The second sum in eq. (1-37) contributes to the ion–neutral Hartree–Fock energy difference; therefore, this term contains the effects of charge redistribution on the calculated electron affinities.

(ii) The third sum approximates the correlation energy of an electron in φ_{N+1} interacting with all other electrons.

(iii) The first sum gives the approximate change in correlation energy of the parent's N electrons caused by the "extra" electron.

Eq. (4) can be solved iteratively for the coefficients $X_i(g)$ and the pseudo-eigenvalue ΔE_g which belong to the ground state of the negative ion. The other solutions $X_i(\lambda)$, ΔE_λ to eq. (4) correspond to excited states of the negative-ion and to positive-ion states[‡]. Once the $X_i(g)$ have been calculated in the manner discussed above, the $Y_{n\alpha m}(g)$ and $Y_{\alpha m\beta}(g)$ can be obtained from the equations

$$Y_{\alpha m\beta}(g) = \sum_i (\Delta E_g + E^{m}_{\alpha\beta})^{-1} B^{*}_{i,\alpha m\beta} X_i(g) \qquad (6\text{a})$$

and

$$Y_{n\alpha m}(g) = \sum_i (\Delta E_g - E^{mn}_{\alpha})^{-1} B^{*}_{i,n\alpha m} X_i(g) \,, \qquad (6\text{b})$$

which result from the partitioning of the original equations of motion [eq. (3c)] mentioned above. Thus, the solution of eq. (4) yields all the information needed to describe the excitation operator given in eq. (2), and, hence, all the information needed to specify the approximate negative-ion ground state $\Omega^{+}_{g}|g_{\mathrm{RS}}\rangle$.

It has been pointed out by McKoy [4] and others [1, 9] that the derivation of the working equations of any EOM theory are valid only if the excitation operator (Ω^{+}_{λ}) and the parent wavefunction ($|g\rangle$) are consistent. In the case under consideration here, this consistency condition is based upon the requirement that the functions $\Omega_\lambda|g\rangle$ should vanish identically[#]

$$\Omega_\lambda|g\rangle = 0 \,, \quad \text{for all } \lambda \,. \qquad (7)$$

That is, it was assumed in the derivation of eq. (4) that Ω^{+}_{λ} and $|g\rangle$ obey eq. (7). It can easily be shown

[‡] It can be shown that eq. (4) yields a complementary set of expansion coefficients $X_i(\mu)$, $Y_{n\alpha m}(\mu)$, $Y_{\alpha m\beta}(\mu)$ which relate $|g\rangle$ to positive-ion states $|\mu_+\rangle = \Omega_\mu|g\rangle$ and that Ω_μ obeys the equation $[H, \Omega_\mu]|g\rangle = (E^{+}_{\mu} - E)\,\Omega_\mu|g\rangle$. It can also be shown that the positive- and negative-ion excitation operators obey the following important orthogonality relations: $\langle g|\Omega^{+}_{\mu}\Omega_\lambda|g\rangle = 0$, $\langle g|\Omega_\mu\Omega^{+}_{\lambda}|g\rangle = 0$. Because these relations hold for all negative-ion states $|\lambda_-\rangle$ and all positive-ion states $|\mu_+\rangle$, they imply that the functions $\Omega_\lambda|g\rangle$ and $\Omega^{+}_{\mu}|g\rangle$ are identically zero. These observations will be used shortly.

[#] See the last parts of footnote ‡. In deriving the working equation (4) from the fundamental Heisenberg equation (3c), the assumption that $\Omega_\lambda|g\rangle = 0$ allowed us to rewrite $\langle g|\Omega_\lambda[H, \Omega^{+}_{\lambda}]|g\rangle = \Delta E_\lambda\langle g|\Omega_\lambda\Omega^{+}_{\lambda}|g\rangle$ in a form which gives a hermitian matrix $H_{ij}(\Delta E_\lambda)$ when eq. (2) is substituted for Ω^{+}_{λ} and the $Y_{n\alpha m}(\lambda)$ and $Y_{\alpha m\beta}(\lambda)$ are eliminated by partitioning. The above rewriting is given by $\langle g|\{\Omega_\lambda, [H, \Omega^{+}_{\lambda}]\}|g\rangle = \Delta E_\lambda\langle g|\{\Omega_\lambda, \Omega^{+}_{\lambda}\}|g\rangle$, where the anticommutator is defined as $\{A,B\} \equiv AB + BA$.

that the first-order RS ground state $|g_{RS}\rangle$, which has been employed in the development of our original EOM theory, is not consistent with the excitation operator given in eq. (2). Thus, there is a shadow of doubt cast upon the derivation of the working equations of ref. [1]. In an attempt to remove this inconsistency in our derivation and, thus, in the resultant theory, we herein develop a technique which makes use of eq. (7) to calculate a new wavefunction $|g_C\rangle$ which is consistent with the negative-ion excitation operator Ω^+_λ given in eq. (2). It is shown that, although $|g_C\rangle$ differs from $|g_{RS}\rangle$ in a significant fashion, the electron affinities and ionization potentials which are obtained in our original theory remain valid through third order in the electron repulsions.

As an initial step toward overcoming the above inconsistency, the excitation operator Ω^+_λ whose expansion coefficients $X_i(\lambda)$, $Y_{\alpha m\beta}(\lambda)$, $Y_{n\alpha m}(\lambda)$ are calculated within the (inconsistent) theory of ref. [1] can be used in eq. (7) to obtain a first approximation for $|g_C\rangle$. This "improved" wavefunction can be used in the development of a new eq. (4) which, in turn, will yield new coefficients $X_i(\lambda)$, $Y_{\alpha m\beta}(\lambda)$, $Y_{n\alpha m}(\lambda)$ and, via eq. (7), a new approximation to $|g_C\rangle$. The analog of such a self-consistent determination of Ω^+_λ and $|g_C\rangle$ has been successfully carried out by McKoy [6] and by Ostlund and Karplus [9] within an EOM theory of electronic excitation energies. From the results of his calculations, McKoy [6] has concluded both that self-consistency is usually reached after only one or two iterations and that the excitation energies obtained in the initial calculation, when $|g_{RS}\rangle$ is used, are very close to the converged results. Based upon these observations and the fact that the self-consistent determination of the excitation operator and $|g_C\rangle$ may be a time-consuming and costly problem, McKoy has decided that the use of $|g_{RS}\rangle$ within the non-iterative EOM theory is reasonably well justified.

To investigate whether these conclusions can be carried over to our calculations of electron affinities, the excitation operator Ω^+_λ generated in the theory of ref. [1] can be used in eq. (7) to solve for the first approximation to $|g_C\rangle$. This, of course, is nothing but the first step toward the self-consistent calculation of Ω^+_λ and $|g_C\rangle$ discussed above. To carry out the solution of eq. (7), the wavefunction $|g_C\rangle$ is expanded in terms of the Hartree–Fock Slater determinant $|0\rangle$ and single-, double-, triple-, etc., excitations relative to $|0\rangle$:

$$|g_C\rangle = |0\rangle + \sum_{m,\alpha} K^m_\alpha C^+_m C_\alpha |0\rangle + \sum_{m<n}\sum_{\alpha<\beta} K^{mn}_{\alpha\beta} C^+_m C^+_n C_\beta C_\alpha |0\rangle + \dots . \tag{8}$$

The expansion coefficients K^m_α, $K^{mn}_{\alpha\beta}$, etc., are no longer taken from RS perturbation theory but are determined from eq. (7). In the remainder of this discussion, only the single- and double-excitations in $|g_C\rangle$ will be treated; triple and higher excitations can be shown to not contribute to $H_{ij}(\Delta E_\lambda)$ through third order‡. By applying the adjoint of Ω^+_λ [see eq. (2)] to the above $|g_C\rangle$ and equating to zero the coefficients of each independent function, a set of equations is obtained for the K^m_α, $K^{mn}_{\alpha\beta}$, etc. For example, the coefficient of the function $C_\alpha|0\rangle$ appearing in $\Omega_\lambda|g_C\rangle$ can be set equal to zero to yield

$$X^*_\alpha(\lambda) + \sum_m X^*_m(\lambda) K^m_\alpha + \sum_{m<n}\sum_\beta Y^*_{n\beta m}(\lambda) K^{mn}_{\alpha\beta} = 0 . \tag{9}$$

Similarly, by equating the coefficient of $C^+_m C_\beta C_\alpha|0\rangle$ to zero, a second set of equations is obtained:

$$-Y^*_{\alpha m\beta}(\lambda) - X^*_\beta(\lambda) K^m_\alpha + X^*_\alpha(\lambda) K^m_\beta + \sum_n X^*_n(\lambda) K^{nm}_{\alpha\beta} = 0. \tag{10}$$

Eqs. (9) and (10) can be solved for the K^m_α and $K^{mn}_{\alpha\beta}$ in terms of the expansion coefficients appearing in Ω^+_λ in the manner described below.

If the $X_i(\lambda)$ are thought of as forming a square matrix $\{X_{i\lambda}\}$ whose row index is i and whose column index is λ, the coefficient $K^{pm}_{\alpha\beta}$ can be extracted from eq. (10) by multiplying this equation on the right by $(X^{-1})^*_{\lambda p}$ and summing over the index λ

$$\sum_\lambda Y^*_{\alpha m\beta}(\lambda)\,(X^{-1})^*_{\lambda p} = K^{pm}_{\alpha\beta} . \tag{11}$$

In analogous fashion, the coefficients K^p_α can be obtained by multiplying eq. (9) on the right by $(X^{-1})^*_{\lambda p}$ and summing over λ.

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‡ As in ref. [1], our goal is to obtain results which are valid through third order; all higher-order terms are neglected.

$$K_\alpha^p = -\sum_{m<n} \sum_\beta K_{\alpha\beta}^{mn} \sum_\lambda Y_{n\beta m}^*(\lambda)\,(X^{-1})_{\lambda p}^* . \qquad (12)$$

From eq. (6a) one can see that $Y_{n\beta m}(\lambda)$ is at least first order in the electron interactions and, thus, that the contributions of single excitations to $|g_C\rangle$ are of one higher order than the double-excitation coefficients $K_{\alpha\beta}^{pm}$. Because single- and double-excitations can contribute to our effective hamiltonian matrix $H_{ij}(\Delta E_\lambda)$ only through terms involving an additional factor in the electron repulsions r_{ij}^{-1}, e.g.,

$$\langle 0|\{C_p, [V, C_m^+]\}\, C_p^+ C_\alpha |0\rangle\, K_\alpha^p \,,$$

the coefficients K_α^p and $K_{\alpha\beta}^{pm}$ need only be computed through second order to guarantee our goal of obtaining $H_{ij}(\Delta E_\lambda)$ through third order. Through second order, eqs. (11) and (12) reduce to

$$\begin{aligned} K_{\alpha\beta}^{pm} &= \langle pm|\alpha\beta\rangle\, (\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_m)^{-1} \\ &\quad \times \left[1 - \frac{\langle \alpha m|\alpha m\rangle + \langle \beta m|\beta m\rangle - \langle \alpha\beta|\alpha\beta\rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_m}\right] \\ &\quad + B_{p,\alpha m\beta}^{(2)} (\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_p)^{-1} \,, \end{aligned} \qquad (13)$$

and

$$K_\alpha^p = \sum_{m<n} \sum_\beta \frac{\langle mn|\alpha\beta\rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n} \, \frac{\langle p\beta|mn\rangle}{\epsilon_m + \epsilon_n - \epsilon_\beta - \epsilon_p} . \qquad (14)$$

In eq. (13), $B_{p,\alpha m\beta}^{(2)}$ is the second-order component of $B_{p,\alpha m\beta}$ which is defined in eq. (1-31e).

$$\begin{aligned} B_{p,\alpha m\beta}^{(2)} &= \tfrac{1}{2} \sum_{t,q} \frac{\langle pm|tq\rangle \langle tq|\alpha\beta\rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_t - \epsilon_q} \\ &\quad - \sum_{\gamma,t} \left[\frac{\langle p\gamma|t\alpha\rangle \langle mt|\beta\gamma\rangle}{\epsilon_\beta + \epsilon_\gamma - \epsilon_m - \epsilon_t} - \frac{\langle p\gamma|t\beta\rangle \langle mt|\alpha\gamma\rangle}{\epsilon_\alpha + \epsilon_\gamma - \epsilon_m - \epsilon_t}\right] . \end{aligned} \qquad (15)$$

These final working expressions for K_α^p and $K_{\alpha\beta}^{pq}$ provide all the information needed to carry out a self-consistent calculation of Ω_λ^+ and $|g_C\rangle$. The expansion coefficients given in eqs. (13) and (14) can be used to construct a new $H_{ij}(\Delta E_\lambda)$ matrix which will yield new excitation energies ΔE_λ and new coefficients $X_i(\lambda)$, $Y_{\alpha m\beta}(\lambda)$, $Y_{n\alpha m}(\lambda)$.

Because the iterative calculation outlined above introduces additional complexities into our present scheme for obtaining molecular electron affinities and ionization potentials, it is important to investigate both the rate of convergence of the calculation and the contributions of the second-order terms in $K_{\alpha\beta}^{pq}$ and K_α^p to the computed quantities. As was stated earlier, to obtain $H_{ij}(\Delta E_\lambda)$ through third order requires that K_α^p and $K_{\alpha\beta}^{pq}$ be computed through second order only. Therefore, eqs. (11) and (12) need not be used in any calculation; the approximate results given in eqs. (13) and (14) are sufficient. Because the quantities appearing on the right sides of eqs. (13) and (14) would not vary from one iteration to the next, i.e., they are given in terms of the (unchanging) orbital energies and two-electron integrals only, it follows that the above iterative procedure will converge (through the order treated here) after one iteration to a self-consistent Ω_g^+ and $|g_C\rangle$. That is, neither the $H_{ij}(\Delta E_\lambda)$ matrix nor the resulting $X_i(\lambda)$, which determine the consistent $|g_C\rangle$, will change after the first iteration in which the second-order $|g_C\rangle$ is used. This result implies that the self-consistent calculation described here does not complicate our original theory to such an extent as to render it computationally intractable. Quite to the contrary, the additional difficulties introduced by this modification are minor since only a single iteration is needed.

In addition to this rapid convergence of the iterative scheme, another equally important characteristic of our method should be pointed out. Although the first-order RS approximation to $|g\rangle$ is not consistent with the excitation operator Ω_λ^+ used in our theory, it can be shown that the second-order components of the consistent $|g_C\rangle$ do not contribute to the calculated electron affinities and ionization potentials through third order. This conclusion is based on the observation that both $|g_{RS}\rangle$ and $\Omega_g^+|g_{RS}\rangle$ agree with the RS expansions of the neutral-molecule and negative-ion wavefunctions through first order ‡. Thus, by a well-known theorem of perturbation theory [11], the expectation values

$$\langle g_{RS}|H|g_{RS}\rangle \{\langle g_{RS}|g_{RS}\rangle\}^{-1} = E \qquad (16)$$

and

$$\langle g_{RS}|\Omega_g H \Omega_g^+|g_{RS}\rangle \{\langle g_{RS}|\Omega_g \Omega_g^+|g_{RS}\rangle\}^{-1} = E_g^- \qquad (17)$$

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‡ That $\Omega_g^+|g_{RS}\rangle$ is identical to the first-order RS wavefunction of the negative ion can easily be shown by applying the excitation operator of eq. (2) to the $|g_{RS}\rangle$ of eq. (5).

are correct through third order. Because the quantity ΔE_g, which is directly calculated in our method, can be shown to be identical to the difference of these two expectation values through third order[‡]

$$\Delta E_g \equiv \frac{\langle g_{\mathrm{RS}}|\{\Omega_g, [H, \Omega_g^+]\}|g_{\mathrm{RS}}\rangle}{\langle g_{\mathrm{RS}}|\{\Omega_g, \Omega_g^+\}|g_{\mathrm{RS}}\rangle}$$

$$= E_g^- - E + \text{fourth-order terms}\,, \tag{18}$$

it follows that our electron affinities are also correct through third order. That is, the second-order components of $|g_C\rangle$ and $|g_-\rangle$, which can be obtained through the iterative procedure discussed earlier, are not needed to compute ΔE_g through third order; only the first-order wavefunctions $|g_{\mathrm{RS}}\rangle$ and $\Omega_g^+|g_{\mathrm{RS}}\rangle$ are required. Our final conclusion, therefore, is that our original theory which employs the first-order RS approximation $|g_{\mathrm{RS}}\rangle$ is sufficient to guarantee that ΔE_g is given through third order, even though $|g_{\mathrm{RS}}\rangle$ is not consistent with Ω_g^+.

To add support to the foundations of this result, it is helpful to point out the connection between the equations of motion which resulted in eq. (4) and the variational determination of $|g_-\rangle$. If the operators Ω_λ^+ depend upon a set of parameters (the X_i, $Y_{n\alpha m}$, and $Y_{\alpha m \beta}$ in our case) which we shall collectively label as $\{a_i\}$, the result of extremizing ΔE_g [see eq. (18)] with respect to these parameters can easily be stated as follows:

$$\partial \Delta E_g/\partial a_i = \langle g_{\mathrm{RS}}|\{\partial\Omega_g/\partial a_i, [H, \Omega_g^+]\}|g_{\mathrm{RS}}\rangle$$

$$- \langle g_{\mathrm{RS}}|\{\partial\Omega_g/\partial a_i, \Omega_g^+\}|g_{\mathrm{RS}}\rangle = 0\,. \tag{19}$$

By substituting the expression given in eq. (2) for Ω_g^+ and successively choosing $\partial\Omega_g/\partial a_i$ equal to C_i, $C_m C_\alpha^+ C_n$, and $C_\beta C_m^+ C_\alpha$, we arrive at the same starting equations as were obtained in ref. [1]. Thus, we see that our final working equations [eq. (4)] can also be based on a stationary principle. Recalling the connections between perturbation theory and the variational principle, which are stressed in ref. [11], it is therefore not surprising that $\Omega_g^+|g_{\mathrm{RS}}\rangle$ agrees with the first-order RS negative-ion wavefunction.

Furthermore, if one considers the negative-ion state $|g_-\rangle$ to be related to $|g\rangle$ by the transformation Ω_g^+,

$$|g_-\rangle = \Omega_g^+|g\rangle\,, \tag{20}$$

it can be seen that the basic equation of our theory

$$(E_g^- - E)\,\langle g|\{\Omega_g, \Omega_g^+\}|g\rangle = \langle g|\{\Omega_g, [H, \Omega_g^+]\}|g\rangle \tag{21}$$

is an example of a hypervirial relation [13]. There are several interesting and potentially useful theorems which make connections between the first-order perturbation theory approximations to $|g_-\rangle$ and $|g\rangle$, the variational extremization of the functional ΔE_g, and these hypervirial relations. Thus it is also not surprising that the first-order approximations $\Omega_g^+|g_{\mathrm{RS}}\rangle$ and $|g_{\mathrm{RS}}\rangle$ should obey the above eq. (21). It is clear that there exists a very close connection between the EOM techniques used in the present work and the elegant work cited in ref. [13] involving perturbation theory, variational principles, and hypervirials. We believe that a great deal of new progress can be made in the applications of EOM theories to chemical problems if we are able to make use of the numerous results which are now available in the areas discussed above.

3. Concluding remarks

For the sake of clarity and organization, let us briefly review the principal results which have been obtained in this paper. After briefly reviewing the notation and philosophy of the EOM theory of molecular electron affinities developed in ref. [1], we showed that the first-order RS approximation to $|g\rangle$, which is *not* consistent with our excitation operator Ω_λ^+, could be replaced by a consistent ground-state wavefunction of second order by carrying out an iterative calculation involving both $\Omega_\lambda|g\rangle = 0$ and eq. (4). This self-consistent determination of $|g_C\rangle$ and Ω_λ^+ was shown to converge after only one iteration *if* one is satisfied with computing all of the elements of $H_{ij}(\Delta E_\lambda)$ through third order in the electron repulsions. In this case, closed expressions for the contributions of both single- and double-excitations to $|g_C\rangle$ were given in eqs. (13) and (14). Finally, by pointing out that

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[‡] Because the proof of eq. (18) is rather involved, it will not be presented here. Suffice it to say that, by using the specific forms of Ω_g^+ and $|g_{\mathrm{RS}}\rangle$, it can be shown that the quantity $\langle g_{\mathrm{RS}}|\{\Omega_g, [H, \Omega_g^+]\}|g_{\mathrm{RS}}\rangle/\langle g_{\mathrm{RS}}|\{\Omega_g, \Omega_g^+\}|g_{\mathrm{RS}}\rangle$, which is shown in ref. [1] to equal ΔE_g, is identical to $E_g^- - E$ through third order.

$\Omega_g^+|g_{\mathrm{RS}}\rangle$ is identical to the RS wavefunction of the negative ion through first order, we were able to demonstrate that the electron affinities calculated in our original EOM theory using only the first-order $|g_{\mathrm{RS}}\rangle$ are correct through third order in r_{ij}^{-1}. The most important, and final, conclusion is that the electron affinities and ionization potentials which result from the application of the theory of ref. [1] *are correct*; the second-order components of $|g_{\mathrm{C}}\rangle$ and the iterative solution of eqs. (4) and (7) are *not* needed to develop a third-order theory of molecular electron affinities.

Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The author also thanks Professor J.O. Hirschfelder for helpful remarks.

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