

Theory of electron affinities of small molecules

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In this paper, the equations-of-motion method, which has been successfully applied to the prediction of electronic excitation energies, is used to derive a physically clear and computationally tractable theory of molecular electron affinities. The contributions to the calculated electron affinities made by the ion-neutral correlation energy difference and by the Hartree-Fock energy change can be computed separately in this theory. In addition, the change in the correlation energy of the parent molecule's electrons, which is caused by adding an "extra" electron, can be quantitatively assessed. The physical content of this theory is discussed in considerable detail, and a connection is made with the many-body Green Function theory. The technique is shown to have important advantages over the variational wavefunction approach, the most attractive feature being the small size of the matrices occurring in computational applications.

I. INTRODUCTION

The electron affinity of an atom is the decrease in electronic energy which is attained by adding an electron to the atom. For a molecule, there are two electron affinities: thermodynamic and vertical. The thermodynamic electron affinity of a diatomic molecule is defined as the difference between the electronic energy of the molecule AB at its equilibrium bond length R_e , and the electronic energy of the negative ion AB^- at its equilibrium bond length R_e^- :

$$(E.A.)_{\text{thermo}} = E(R_e) - E^-(R_e^-). \quad (1)$$

The vertical electron affinity of AB is the energy difference at R_e :

$$(E.A.)_{\text{vertical}} = E(R_e) - E^-(R_e), \quad (2)$$

and the expression $E(R_e^-) - E^-(R_e^-)$ is known as the vertical ionization potential of AB^- . Analogous definitions can be made for polyatomic species by including in the definition enough bond lengths and angles to specify the nuclear configuration of the molecule.

Knowledge of electron affinities is an important ingredient of quantitative investigations in many areas of science and technology. Electron affinities are helpful for understanding the energetics of ion-molecule reactions of the upper atmosphere, and they are useful in determining the interstellar concentrations of certain molecules and ions. Born-Haber cycle lattice energies can be calculated when electron affinities are known. Inductive effects in the chemical bonding of organic compounds, and electron-donating properties of ligands in coordination compounds are related to electron affinity. The energy changes occurring in oxidation-reduction reactions and in charge-transfer reactions are influenced by the electron affinities of the species involved. In addition, electron affinities play important roles in radiation damage and light detection technology, as well as in determining the electronegativities of atoms and molecules.

Although important experimental progress has been made in recent years, the determination of accurate (± 0.10 eV, or less) molecular electron affinities remains a rather formidable task. The photodetachment method, which was pioneered by Branscomb¹ and later by Berry,² and the surface ionization technique, which was developed by Mayer³ and refined by Page,⁴ have yielded much of the currently available experimental data² on molecular electron affinities. Electron impact fragmentation,² molecular photo-dissociation,² equilibrium sublimation,⁵ radiative electron attachment,⁵ lattice energy measurements,⁵ charge-transfer reactions,⁶ and photosensitized ionization² are other experimental methods which have also contributed significantly to our knowledge in this area. This wide array of independent techniques has led to reliable and accurate values for atomic electron affinities, but has often given inconsistent and confusing results for molecular electron affinities. For example, experimental electron affinities for NO_2 are scattered between 1.6 and 4.0 eV with one measurement claiming $E.A. (\text{NO}_2) > 3.613$ eV and another asserting $E.A. (\text{NO}_2) < 3.063$ eV.⁶

Several review articles on negative ions^{1,2,5,7} make it clear that theoretical research aimed either at helping the experimentalist to resolve some of this confusion, or at predicting the electron affinities of interesting molecules which have resisted experimental investigation is scarce, especially when compared to the theoretical development of molecular electronic spectroscopy. Clementi and co-workers,⁸ Pekeris,^{8(a)} Sinanoğlu and Öksüz,^{8(b)} Glockler,^{8(c)} and Weiss⁹ have done excellent work on atomic electron affinities. Mulliken,¹⁰ Cade,¹¹ Eyring,¹² Dalgarno,¹³ Taylor and Harris,¹⁴ Wahl,¹⁵ and Schaefer¹⁶ have made some progress toward predicting molecular electron affinities. While these studies represent significant achievement, they give information on only eight molecules (all diatomic). Fortunately, recent advances in molecular quantum chemistry

have opened the door to greatly increased theoretical contributions to this important area of research.

In this paper, we put forth a theory for calculating molecular electron affinities, which we believe to be both physically reasonable and computationally tractable. The starting point for the derivation of our method is the equations-of-motion (EOM) idea which McKoy¹⁷⁻²⁰ and others²¹⁻⁴² have cleverly applied to the calculation of electronic excitation energies and oscillator strengths of atoms and molecules.

In the following section, we briefly discuss some previous calculations of molecular electron affinities. Sections III and IV contain a review of the EOM theory, as applied to electronic excitation energy calculations, and as extended to permit the treatment of electron affinities. In Section V, we present the derivation of our final working equations, and in Sections VI and VII, we discuss the physical content of these equations and their relation to the equations of many-body Green's function theory. Finally, Section VIII contains an outline of our computational scheme.

II. EVALUATION OF PREVIOUS MOLECULAR ELECTRON AFFINITY CALCULATIONS

The majority of previous theoretical research on molecular electron affinities consists of variational wavefunction calculations at either the Hartree-Fock or configuration interaction (CI) level of accuracy. In such investigations, two separate variational calculations are performed, one on the neutral parent molecule to obtain $E(R)$ and another on the negative ion to give $E^-(R)$. The thermodynamic and vertical electron affinities are then computed from Eqs. (1) and (2).

As an illustration of the accuracy of this method, we examine the excellent work of Cade¹¹ on the vertical electron affinities of OH and SH. Cade used three approaches to calculate these electron affinities. From the ion-neutral Hartree-Fock energy differences, he obtained -0.10 and 1.21 eV for the electron affinities of OH and SH, respectively, whereas Koopmans' theorem⁴³ gave 2.90 and 2.42 eV. By adding estimates⁴⁴ of the negative ion-neutral molecule correlation energy differences to the Hartree-Fock energies, Cade arrived at his final results of 1.91 and 2.25 eV, which compare favorably with the experimental values⁴⁵ of 1.83 and 2.3 eV.

It is clear from these calculations that neither the Koopmans' theorem estimate, nor the ion-neutral Hartree-Fock energy difference give satisfactory values for the electron affinities. The fact that Koopmans' theorem fails implies that the charge density of the negative ion cannot be adequately described by simply adding an electron to the lowest

unoccupied spin orbital of the neutral parent. Apparently, the addition of that electron causes a significant amount of charge redistribution which is reflected in the expanded valence spin orbitals of the ion. The inaccuracy of the Hartree-Fock energy differences suggests that consideration must also be given to the difference in correlation energy between the negative ion and its neutral parent. Indeed, Cade's inclusion of approximate correlation energy improved the accuracy of his results to within 4%.

Another example of the effects of electron correlation is provided by theoretical work on HF. Since $E^-(R)$ for the ion HF^- decreases monotonically^{46a,b} with increasing R , $E^-(R_e^-)$ becomes the energy of the separated species (H and F^-). Thus, the electron affinity of HF is the difference between the dissociation energy of HF and the electron affinity of F. From Cade and Huo's⁴⁶ Hartree-Fock dissociation energy, and Clementi's⁸ SCF atomic electron affinity, one obtains -3.02 eV for the electron affinity of HF. However, using the correlated first-order wavefunction results of Bondybey, Pearson, and Schaefer¹⁶ together with Clementi's correlated electron affinity for fluorine, one calculates -2.51 eV, which is within 5% of the "experimental" result of -2.65 eV obtained by subtracting the photodetachment fluorine electron affinity^{46(a)} from the measured HF dissociation energy.^{46(b)}

Correlated wavefunctions were also used in the important CI calculations of Dalgarno and McDowell,¹³ and of Taylor and Harris⁴⁴ on H_2^- . From their works, the thermodynamic and vertical electron affinities of H_2 can be computed, but there seems to be no direct experimental measurements with which to compare these results.

In reporting their experimental value on the halogens, Chupka *et al.*¹⁵ reference Wahl's CI treatment of the F_2 and Cl_2 electron affinities. Their experimental value for F_2 falls well within the error limits that Wahl estimated for his calculations, and the experimental and theoretical results for Cl_2 are nearly identical.

Molecular electron affinities have been estimated in other ways. Mulliken¹⁰ suggested that for homonuclear diatomic molecules X_2 , the electron affinity $E.A.(X_2)$ is related to the atomic electron affinity $E.A.(X)$ and the molecular dissociation energy $D_e(X_2)$ by the approximate formula,

$$E.A.(X_2) \approx E.A.(X) - \frac{1}{2}D_e(X_2). \quad (3)$$

Values so estimated often come fairly close to the experimental results.⁶ Eyring, Hirschfelder, and Taylor¹² used early valence bond methods to approximate the electron affinity of H_2 with some success. Finally, several interesting semiempirical studies of organic molecules and their negative ions have been carried out by Hush and Pople,⁴⁷ Matsen,⁴⁸ Hall,⁴⁹ Parr and Pariser,⁵⁰ and Hoyland and Goodman.⁵¹

Since the most successful of these previous studies have been those which have properly treated both charge redistribution and changes in electron correlation energy, it is reasonable to conclude that any successful theoretical method of predicting molecular electron affinities must correctly incorporate both of these physical effects.

III. THE EQUATIONS-OF-MOTION THEORY

In the equations-of-motion method,^{52,53} one attempts to find excitation operators O_{λ}^{+} which relate the wavefunctions $|\lambda\rangle$ of the excited electronic states of the molecule to the ground-state wavefunction⁵⁴ $|g\rangle$:

$$|\lambda\rangle = O_{\lambda}^{+} |g\rangle. \quad (4)$$

Using the fact that both $|\lambda\rangle$ and $|g\rangle$ are eigenfunctions of the (Born–Oppenheimer) Hamiltonian H ,

$$H |g\rangle = E_g |g\rangle, \quad (5)$$

$$H |\lambda\rangle = E_{\lambda} |\lambda\rangle, \quad (6)$$

one can easily derive the equations of motion:

$$[H, O_{\lambda}^{+}] |g\rangle = \Delta E_{\lambda} O_{\lambda}^{+} |g\rangle, \quad (7)$$

where the excitation energy ΔE_{λ} is $E_{\lambda} - E_g$. Thus, to apply this method one seeks a set of operators $\{O_{\lambda}^{+}\}$ whose commutators with a given electronic Hamiltonian operate on $|g\rangle$ to give constant multiples of $O_{\lambda}^{+} |g\rangle$. Once this is accomplished, the resulting operators are the excitation operators, and the constants multiples are the excitation energies $\{\Delta E_{\lambda}\}$.

Since it has not proved possible to solve Eq. (7) exactly for any molecule containing more than one electron, reasonable approximate solutions are used in practice. In his pioneering research efforts, McKoy^{17–20} has developed and implemented a useful theory of electronic excitation energies and oscillator strengths⁵⁵ in which the operators O_{λ}^{+} and the ground-state wavefunctions $|g\rangle$ are calculated self-consistently.

Instead of using Eq. (7), McKoy begins with an equivalent expression derived by Rowe⁵²:

$$\langle g | [\delta O_{\lambda}, H, O_{\lambda}^{+}] |g\rangle = \Delta E_{\lambda} \langle g | [\delta O_{\lambda}, O_{\lambda}^{+}] |g\rangle. \quad (8)$$

Here, δO_{λ} is an arbitrary operator, and the double commutator is defined as

$$[A, H, B] = \frac{1}{2}[A, [H, B]] + \frac{1}{2}[[A, H], B]. \quad (9)$$

McKoy then assumes that the correlated ground-state wavefunction $|g\rangle$ can be approximated by the CI expansion,

$$|g\rangle = N_0^{-1/2} (1 + \sum_{\alpha < \beta, m < n} K_{\alpha\beta}{}^{mn} C_m^{+} C_n^{+} C_{\beta} C_{\alpha}) |0\rangle, \quad (10)$$

where $|0\rangle$ is a Hartree–Fock single-determinant⁵⁶ wavefunction, and where N_0 is the normalization

constant,

$$N_0 = 1 + \sum_{\alpha < \beta, m < n} |K_{\alpha\beta}{}^{mn}|^2. \quad (11)$$

The indices α, β, γ , and $\delta (m, n, p, q)$ are used to label Hartree–Fock spin orbitals which are occupied (unoccupied) in $|0\rangle$. The double particle–hole operators $C_m^{+} C_n^{+} C_{\beta} C_{\alpha}$, which are products of fermion creation and annihilation operators, operate on $|0\rangle$ to give doubly excited configurations $|_{\alpha\beta}^{mn}\rangle$, in which spin orbitals ϕ_{α} and ϕ_{β} are replaced by spin orbitals ϕ_m and ϕ_n . The expansion coefficients $K_{\alpha\beta}{}^{mn}$ can be found either by carrying out a variational calculation or, as McKoy suggests,¹⁷ by solving the equation

$$O_{\lambda} |g\rangle = 0, \quad (12)$$

provided O_{λ}^{+} is known.

In order to obtain approximations to the excitation operators O_{λ}^{+} , McKoy expands them in the truncated space of single and double excitations,⁵⁷ that is, as linear combinations of single and double particle–hole and hole–particle operators only:

$$O_{\lambda}^{+} = \sum_{m, \gamma} [g_{m\gamma}(\lambda) C_m^{+} C_{\gamma} - h_{m\gamma}(\lambda) C_{\gamma}^{+} C_m] \\ + \sum_{m < n, \gamma < \delta} [g_{m\gamma, n\delta}(\lambda) C_m^{+} C_n^{+} C_{\delta} C_{\gamma} \\ - h_{m\gamma, n\delta}(\lambda) C_{\gamma}^{+} C_{\delta}^{+} C_n C_m], \quad (13)$$

where the expansion coefficients $\{g, h\}$ are to be determined. By substituting Eq. (13) into Eq. (8) and successively choosing δO_{λ} as $C_p^{+} C_{\alpha}$, $C_{\alpha}^{+} C_p$, $C_p^{+} C_q^{+} C_{\beta} C_{\alpha}$, and $C_{\alpha}^{+} C_{\beta}^{+} C_q C_p$, McKoy obtains a matrix eigenvalue equation for $\{g, h\}$ and ΔE_{λ} . This equation, known as the Higher Random Phase Approximation (HRPA) equation, is not computationally tractable because of the large dimensions of the matrices involved. To alleviate this difficulty, McKoy rewrites the HRP equation by formally solving for the double particle–hole coefficients $g_{m\gamma, n\delta}(\lambda)$ and $h_{m\gamma, n\delta}(\lambda)$ in terms of ΔE_{λ} and the single particle–hole coefficients. This partitioning leads to a renormalized matrix equation for $g_{m\gamma}(\lambda)$ and $h_{m\gamma}(\lambda)$ which is no longer an eigenvalue equation since ΔE_{λ} now appears both in the modified HRP equation and as an eigenvalue.⁵⁸ However, by expanding the matrix elements of this new pseudoeigenvalue problem through second order in the electronic interactions, McKoy is able to express all the elements in terms of the Hartree–Fock orbital energies $\{\epsilon_{\alpha}, \epsilon_p\}$, the expansion coefficients $K_{\alpha\beta}{}^{mn}$ in Eq. (10), and certain two-electron integrals

$$\langle ij | kl \rangle = \int \phi_i^{*}(1) \phi_j^{*}(2) r_{12}^{-1} [\phi_k(1) \phi_l(2) \\ - \phi_l(1) \phi_k(2)] d\tau. \quad (14)$$

Thus, to calculate O_{λ}^{+} and ΔE_{λ} by solving the renormalized HRP pseudoeigenvalue equation one needs to know the $K_{\alpha\beta}{}^{mn}$. On the other hand, the solution of Eq. (12) for $K_{\alpha\beta}{}^{mn}$ depends on knowledge

of O_λ^+ . Hence, the excitation energies cannot be calculated directly in a one-step process; however, McKoy suggests the following iterative procedure to compute self-consistent values of $K_{\alpha\beta}{}^{mn}$, O_λ^+ , and ΔE_λ : (a) Approximate $K_{\alpha\beta}{}^{mn}$ by Rayleigh–Schrödinger perturbation theory,

$$K_{\alpha\beta}{}^{mn} = \langle mn | \alpha\beta \rangle [\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n]^{-1}. \quad (15)$$

(b) Use an approximate ΔE_λ and the calculated $K_{\alpha\beta}{}^{mn}$ to form the renormalized HRP matrix elements. (c) Solve the HRP eigenvalue problem to obtain the single particle-hole components of the excitation operators O_λ^+ and new excitation energies ΔE_λ . (d) Use the O_λ^+ in Eq. (12) to calculate a new set of $K_{\alpha\beta}{}^{mn}$. (e) Return to step 2, and continue to iterate until the resulting ΔE_λ , $\{g, h\}$, and $K_{\alpha\beta}{}^{mn}$ converge.

In using this procedure to calculate the excitation energies and oscillator strengths of C_2H_4 , CO, and N_2 , McKoy found¹⁹ that the process⁵⁹ converged rapidly to yield accurate results. Significantly, the values for ΔE_λ from the first iteration (with $K_{\alpha\beta}{}^{mn}$ given by Rayleigh–Schrödinger perturbation theory) were within a few percent of the converged results.

IV. EXTENSION OF THE EQUATIONS-OF-MOTION THEORY

The energy differences $\Delta E_\lambda = E_\lambda - E_g$ in Eq. (7) are associated with the vertical excitation energies of a molecule because McKoy's excitation operators O_λ^+ [Eq. (13)] preserve the total number of electrons. However, in addition to these electron-conserving operators, there exist other operators, Ω_λ^+ and Ξ_μ^+ , which satisfy Eq. (7), and which add and subtract an electron from the neutral molecule, respectively. Thus, for the ground state $|g^N\rangle$ of an N -electron molecule, Eq. (7) can be rewritten for these new operators as

$$[H, \Omega_\lambda^+] |g^N\rangle = (E_\lambda^{N+1} - E_g^N) \Omega_\lambda^+ |g^N\rangle, \quad (16a)$$

or as

$$[H, \Xi_\mu^+] |g^N\rangle = (E_\mu^{N-1} - E_g^N) \Xi_\mu^+ |g^N\rangle, \quad (16b)$$

where E_λ^{N+1} is the electronic energy of the λ th state of the negative ion, and E_μ^{N-1} is the energy of the μ th state of the positive ion. The energy differences here have new interpretations. The quantities $E_\mu^{N-1} - E_g^N$ are vertical ionization potentials, and the differences $E_\lambda^{N+1} - E_g^N$ are, except for sign, vertical electron affinities [cf. Eq. (2)].

In this paper, we make use of the generalized excitation operators Ω_λ^+ to develop a technique, analogous to McKoy's powerful HRP method, by which molecular electron affinities can be calculated. Our goal is to obtain the quantity $(E.A.)_{\text{vertical}} = -(E_g^{N+1} - E_g^N)$ from an approximate solution of Eq. (16a); hence,

to begin we need adequate approximations for $|g^N\rangle$ and Ω_λ^+ .

A. Approximation for $|g^N\rangle$

Following McKoy's reasonable assumption, we approximate the ground state $|g^N\rangle$ by the CI wavefunction of Eq. (10), which consists of a Hartree–Fock single determinant plus double excitations into virtual Hartree–Fock orbitals.

The expansion coefficients $K_{\alpha\beta}{}^{mn}$ will be taken from Rayleigh–Schrödinger perturbation theory⁶⁰ and are given by Eq. (15). Our choice of this form for $K_{\alpha\beta}{}^{mn}$ is prompted by McKoy's success¹⁹ with it, and by our desire to avoid the major computational effort involved in the self-consistent determination of Ω_λ^+ and $|g^N\rangle$.

The spin orbitals $\{\phi_i\}$ used in constructing $|g^N\rangle$ are taken to be restricted canonical Hartree–Fock spin orbitals of the neutral molecule, and all single, triple, and higher excitations into virtual orbitals are neglected in $|g^N\rangle$. These Hartree–Fock orbitals are appropriate basis functions for use in our electron affinity theory for the following reasons: (a) CI wavefunctions, as given in Eq. (10), are well-studied and are considered to be reasonably accurate.⁶¹ (b) Hartree–Fock virtual orbitals of the neutral molecule are plausible first approximations to the orbitals of its negative ion since they describe the motion of an electron in the average field of all the parent's N electrons. For this reason, the Hartree–Fock orbitals fit our purposes better than the V^{N-1} orbitals of Kelly,⁶² Huzinaga,⁶³ and Silverstone and Yin,⁶⁴ which are more appropriate for describing excited states of the neutral molecule. (c) Use of the parent's Hartree–Fock orbitals aids in identifying the contribution of charge redistribution to calculated electron affinities.⁶⁵

B. Approximation for Ω_λ^+

To describe the change in $|g^N\rangle$ which accompanies the addition of an electron to the neutral molecule, we propose the generalized excitation operator Ω_λ^+ :

$$\Omega_\lambda^+ = \sum_i X_i(\lambda) C_i^+ + \sum_{m < n, \alpha} Y_{nam}(\lambda) C_n^+ C_\alpha C_m^+ + \sum_{\alpha < \beta, m} Y_{\alpha m \beta}(\lambda) C_\alpha^+ C_m C_\beta^+, \quad (17)$$

where the index i runs over all occupied and unoccupied Hartree–Fock spin orbitals.

The significance of each term in Eq. (17) can be made clear by considering the approximate negative ion wavefunctions generated by applying Ω_λ^+ to $|g^N\rangle$. To illustrate, we restrict our attention to the specific function $\Omega_g^+ |0\rangle$, which is the ground-state wavefunction of the negative ion in which we temporarily neglect the double excitations in $|g^N\rangle$.

In the first summation in Eq. (17) appears the creation operator C_{N+1}^+ . Its action on $|0\rangle$ produces the Slater determinant $C_{N+1}^+ |0\rangle \equiv |^{N+1}\rangle$ formed by adding

the spin orbital ϕ_{N+1} to $|0\rangle$. This is the first approximation to the ground state of the negative ion. The functions $\{C_p^+ | 0\rangle, p > N+1\}$ are Slater determinants $\{|^p\rangle\}$ which can be viewed as single excitations of $|^{N+1}\rangle$ where the spin orbital ϕ_{N+1} is replaced by ϕ_p :

$$|^p\rangle = C_p^+ C_{N+1} |^{N+1}\rangle. \quad (18)$$

The remaining terms in the first summation $\{C_\alpha^+ | 0\rangle\}$ are zero in our illustration. In general, however, the functions $\{C_\alpha^+ | g^N\rangle\}$ are not zero, and their presence is essential to the self-consistent determination of Ω_λ^+ and $|g^N\rangle$. Were these terms not included, the equation

$$\Omega_\lambda |g^N\rangle = 0, \quad (19)$$

which can be used to calculate $|g^N\rangle$ iteratively, would imply that all the $K_{\alpha\beta mn}$ are zero.

Continuing with our example, we examine the second summation in Eq. (17). The functions $\{C_n^+ C_\alpha C_{N+1}^+ | 0\rangle\}$ are also single excitations of $|^{N+1}\rangle$ in which ϕ_n replaces ϕ_α :

$$|^{\alpha N+1 n}\rangle = C_n^+ C_\alpha |^{N+1}\rangle. \quad (20)$$

These singly-excited contributions to $\Omega_\alpha^+ | 0\rangle$, together with those of Eq. (18), transform the lowest $N+1$ Hartree-Fock spin orbitals of the parent molecule into approximate Hartree-Fock spin orbitals of the negative ion. In our theory, this yields the component of the electron affinity which arises from charge redistribution. The other terms of the second summation are double excitations. The determinants $\{C_n^+ C_\alpha C_m^+ | 0\rangle, m > N+1\}$ have spin orbitals ϕ_m and ϕ_n in the place of ϕ_{N+1} and ϕ_α , respectively:

$$|^{\alpha n m}\rangle = C_n^+ C_\alpha C_m^+ C_{N+1} |^{N+1}\rangle. \quad (21)$$

Such configurations produce the component of the electron affinity which is due to the correlation energy difference between the negative ion and the neutral molecule.

The terms of the third summation $\{C_\alpha^+ C_m C_\beta^+ | 0\rangle\}$ all vanish in this example. However, like the $\{C_\alpha^+\}$, the $\{C_\alpha^+ C_m C_\beta^+\}$ must be included, both to avoid the conclusion that the $K_{\alpha\beta mn}$ vanish and to preserve the possibility that Ω_λ^+ and $|g^N\rangle$ can be determined self-consistently.

V. DERIVATION OF OUR WORKING EQUATIONS

To transform Eq. (16a) into a more computationally manageable form, we multiply it on the left by $\langle g^N | \delta\Omega_\lambda$, where $\delta\Omega_\lambda$ is an arbitrary operator:

$$\langle g^N | \delta\Omega_\lambda [H, \Omega_\lambda^+] | g^N \rangle = (E_\lambda^{N+1} - E_\sigma^N) \langle g^N | \delta\Omega_\lambda \Omega_\lambda^+ | g^N \rangle. \quad (22)$$

As the next step, we employ the conjugate of Eq. (19)

to write zero as

$$0 = \langle g^N | [H, \Omega_\lambda^+] \delta\Omega_\lambda | g^N \rangle = (E_\lambda^{N+1} - E_\sigma^N) \langle g^N | \Omega_\lambda^+ \delta\Omega_\lambda | g^N \rangle. \quad (23)$$

Adding Eq. (23) to Eq. (22), we have

$$\langle g^N | \{\delta\Omega_\lambda, [H, \Omega_\lambda^+]\} | g^N \rangle = (E_\lambda^{N+1} - E_\sigma^N) \times \langle g^N | \{\delta\Omega_\lambda, \Omega_\lambda^+\} | g^N \rangle, \quad (24)$$

where the anticommutator is

$$\{F, G\} \equiv FG + GF. \quad (25)$$

Successively choosing $\delta\Omega_\lambda$ as C_i , $C_m C_\alpha^+ C_n$, and $C_\beta C_m^+ C_\alpha$, we obtain from Eq. (24) a set of equations for the $X_i(\lambda)$, $Y_{nam}(\lambda)$, and $Y_{\alpha m \beta}(\lambda)$ of Eq. (17). In matrix form, these equations become

$$\mathbf{AX}(\lambda) + \mathbf{BY}(\lambda) = \Delta E_\lambda^N \mathbf{X}(\lambda), \quad (26)$$

and

$$\mathbf{B}^+ \mathbf{X}(\lambda) + \mathbf{D}\mathbf{Y}(\lambda) = \Delta E_\lambda^N \mathbf{S}\mathbf{Y}(\lambda). \quad (27)$$

Here ΔE_λ^N is $(E_\lambda^{N+1} - E_\sigma^N)$, and the coefficients $X_i(\lambda)$ and $Y_{nam}(\lambda)$, $Y_{\alpha m \beta}(\lambda)$ appear in column vector form as $\mathbf{X}(\lambda)$ and $\mathbf{Y}(\lambda)$, respectively. Elements of the other matrices in Eqs. (26) and (27) are given by

$$A_{i,j} = \langle g^N | \{C_i, [H, C_j^+]\} | g^N \rangle, \quad (28a)$$

$$B_{i,nam} = \langle g^N | \{C_i, [H, C_n^+ C_\alpha C_m^+]\} | g^N \rangle, \quad (28b)$$

$$B_{i,\alpha m \beta} = \langle g^N | \{C_i, [H, C_\alpha^+ C_m C_\beta^+]\} | g^N \rangle, \quad (28c)$$

$$D_{nam,q\beta p} = \langle g^N | \{C_m C_\alpha^+ C_n, [H, C_q^+ C_\beta C_p^+]\} | g^N \rangle, \quad (28d)$$

$$D_{nam,\delta p \gamma} = \langle g^N | \{C_m C_\alpha^+ C_n, [H, C_\delta^+ C_p C_\gamma^+]\} | g^N \rangle, \quad (28e)$$

$$D_{\delta p \gamma, nam} = D_{nam, \delta p \gamma}^*, \quad (28f)$$

$$D_{\delta p \gamma, \alpha q \beta} = \langle g^N | \{C_\gamma C_p^+ C_\delta, [H, C_\alpha^+ C_q C_\beta^+]\} | g^N \rangle, \quad (28g)$$

$$S_{nam,q\beta p} = \langle g^N | \{C_m C_\alpha^+ C_n, C_q^+ C_\beta C_p^+\} | g^N \rangle, \quad (28h)$$

$$S_{nam,\delta p \gamma} = \langle g^N | \{C_m C_\alpha^+ C_n, C_\delta^+ C_p C_\gamma^+\} | g^N \rangle, \quad (28i)$$

$$S_{\delta p \gamma, nam} = S_{nam, \delta p \gamma}^*, \quad (28j)$$

and

$$S_{\delta p \gamma, \alpha q \beta} = \langle g^N | \{C_\gamma C_p^+ C_\delta, C_\alpha^+ C_q C_\beta^+\} | g^N \rangle. \quad (28k)$$

Using the fact that $|g^N\rangle$ contains double excitations only, one can show that the coefficients of \mathbf{Y} on the right hand side of Eq. (26) and those of \mathbf{X} on the right of Eq. (27) all vanish and, therefore, need not be considered further.

In all of these equations, the subscripts α, β, γ , and $\delta(m, n, p, q)$ run over occupied (unoccupied) spin orbitals, whereas the subscripts i, j, k , and l label either occupied or unoccupied spin orbitals.

Because of the large dimensions of the \mathbf{D} and \mathbf{S} matrices, straightforward solutions of Eqs. (26) and (27) are generally impractical. However, we can consolidate these large matrices by formally solving Eq. (27) for \mathbf{Y} and substituting the result into Eq. (26) to obtain the pseudoeigenvalue equation,

$$[\mathbf{A}-\mathbf{B}(\mathbf{D}-\Delta E_\lambda^N \mathbf{S})^{-1} \mathbf{B}^+] \mathbf{X}(\lambda) = \Delta E_\lambda^N \mathbf{X}. \quad (29)$$

Using the second quantized form of the electronic Hamiltonian,⁶⁶

$$H = \sum_{i,j} \langle i | h | j \rangle C_i^\dagger C_j + 1/4 \sum_{i,j,k,l} \langle ij | kl \rangle C_i^\dagger C_j^\dagger C_l C_k, \quad (30)$$

and the Rayleigh-Schrödinger-CI expansion of $|g^N\rangle$ [Eq. (10)], we order the terms in Eq. (29) with respect to the electronic interaction r_{ij}^{-1} , neglecting all contributions higher than third order. Since \mathbf{B} contains no zeroth-order terms, $(\mathbf{D}-\Delta E_\lambda^N \mathbf{S})^{-1}$ needs to be evaluated only through first order in this approximation. Only the smaller \mathbf{A} matrix is evaluated through third order. With this approximation, the matrix elements in Eqs. (28a) to (28k) simplify to

$$S_{n\alpha m, q\beta p} = \delta_{nq} \delta_{\alpha\beta} \delta_{mp}, \quad (31a)$$

$$S_{\delta p \gamma, \alpha q \beta} = \delta_{\delta\alpha} \delta_{p q} \delta_{\gamma\beta}, \quad (31b)$$

$$S_{\delta p \gamma, n\alpha m} = 0, \quad (31c)$$

$$A_{ij} = \delta_{ij} \epsilon_i + \sum_{k,l} \langle ik | jl \rangle F_{kl}, \quad (31d)$$

$$B_{i, \alpha m \beta} = -\langle im | \alpha \beta \rangle - \frac{1}{2} \sum_{p,q} \langle im | pq \rangle K_{\alpha\beta}^{\overline{pq}}, \\ + \sum_{\gamma,p} [\langle i\gamma | p\alpha \rangle K_{\beta\gamma}^{\overline{mp}} - \langle i\gamma | p\beta \rangle K_{\alpha\gamma}^{\overline{mp}}], \quad (31e)$$

$$B_{i, n\alpha m} = \langle i\alpha | mn \rangle + \frac{1}{2} \sum_{\gamma\delta} \langle i\alpha | \delta\gamma \rangle K_{\delta\gamma}^{\overline{mn}} \\ + \sum_{\gamma p} [\langle ip | \gamma n \rangle K_{\alpha\gamma}^{\overline{mp}} - \langle ip | \gamma m \rangle K_{\alpha\gamma}^{\overline{np}}], \quad (31f)$$

$$D_{n\alpha m, \delta p \gamma} = 0, \quad (31g)$$

$$D_{n\alpha m, q\beta p} = \delta_{nq} \delta_{\alpha\beta} \delta_{mp} E_\alpha^{mn}, \quad (31h)$$

and

$$D_{\delta p \gamma, \alpha q \beta} = -\delta_{\delta\alpha} \delta_{p q} \delta_{\gamma\beta} E_{\delta\gamma}^p, \quad (31i)$$

where

$$F_{ki} \equiv \sum_{\alpha < \beta, p} [K_{\alpha\beta}^{pk} K_{\alpha\beta}^{pl} + K_{\alpha\beta}^{kp} K_{\alpha\beta}^{lp}] \\ - \sum_{p < q, \alpha} [K_{\alpha l}^{pq} K_{\alpha k}^{pq} + K_{l\alpha}^{pq} K_{k\alpha}^{pq}], \quad (32)$$

$$K_{\alpha\beta}^{\overline{pq}} \equiv K_{\alpha\beta}^{pq} - K_{\alpha\beta}^{qp}, \quad (33a)$$

$$K_{\alpha\beta}^{\overline{pq}} \equiv K_{\alpha\beta}^{pq} - K_{\beta\alpha}^{pq}, \quad (33b)$$

$$K_{\alpha\beta}^{\overline{pq}} \equiv K_{\alpha\beta}^{pq} - K_{\alpha\beta}^{qp} - K_{\beta\alpha}^{pq} + K_{\beta\alpha}^{qp}, \quad (33c)$$

$$E_\alpha^{mn} = \epsilon_m + \epsilon_n - \epsilon_\alpha - \langle \alpha m | \alpha m \rangle - \langle \alpha n | \alpha n \rangle + \langle mn | mn \rangle, \quad (34)$$

and

$$E_{\delta\gamma}^p = \epsilon_p - \epsilon_\delta - \epsilon_\gamma - \langle \delta p | \delta p \rangle - \langle \gamma p | \gamma p \rangle + \langle \delta\gamma | \delta\gamma \rangle. \quad (35)$$

In Eqs. (32)-(33c), the $K_{\alpha\beta}^{pq}$ are nonzero only if $p < q$ and $\alpha < \beta$.

Using the above results, we rewrite Eq. (29) in a computationally tractable form which is valid through third order and which represents our final working equations:

$$\mathbf{H}(\Delta E_\lambda^N) \mathbf{X}(\lambda) = \Delta E_\lambda^N \mathbf{X}(\lambda), \quad (36)$$

where the matrix elements of $H_{ij}(\Delta E_\lambda^N)$ are compactly written, in terms of Hartree-Fock information only, as

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

VI. PHYSICAL CONTENT OF THE WORKING EQUATIONS

Since the lowest root of Eq. (36),

$$\Delta E_\theta^N = E_\theta^{N+1} - E_\theta^N = -(\text{E.A.})_{\text{vertical}}, \quad (38)$$

can be identified with a vertical electron affinity, it is important to describe clearly the physical meaning of each term appearing in the $\mathbf{H}(\Delta E_\lambda^N)$ matrix. To do this, we obtain an approximation $\Delta \tilde{E}_\theta^N$ to the lowest root of Eq. (36) by writing⁴¹

$$\Delta \tilde{E}_\theta^N = A_{N+1, N+1} + \sum_{\alpha < \beta, m} \frac{|B_{N+1, \alpha m \beta}|^2}{E_{\alpha\beta}^m + \epsilon_{N+1}} \\ - \sum_{N+1 < n, \alpha} \frac{|B_{N+1, n\alpha N+1}|^2}{E_\alpha^{N+1n} - \epsilon_{N+1}} - \sum_{N+1 < m < n, \alpha} \frac{|B_{N+1, n\alpha m}|^2}{E_\alpha^{mn} - \epsilon_{N+1}}. \quad (39)$$

By neglecting the expansion coefficients $K_{\alpha\beta}^{mn}$ implicit in Eq. (39), we obtain an even rougher approximation, but one which makes the physical content of Eq. (36) particular clear:

$$\Delta \tilde{E}_\theta^N \cong \epsilon_{N+1} + \sum_{\alpha < \beta, m} \frac{|(N+1m | \alpha\beta)|^2}{E_{\alpha\beta}^m + \epsilon_{N+1}} \\ - \sum_{N+1 < n, \alpha} \frac{|(N+1\alpha | N+1n)|^2}{E_\alpha^{N+1n} - \epsilon_{N+1}} \\ - \sum_{N+1 < m < n, \alpha} \frac{|(N+1\alpha | mn)|^2}{E_\alpha^{mn} - \epsilon_{N+1}}. \quad (40)$$

The second sum in Eq. (40) gives an approximation to the ion-neutral Hartree-Fock energy difference;

therefore, this term contains the effects of charge redistribution on the calculated electron affinities. The third sum approximates the correlation energy of an electron in ϕ_{N+1} interacting with all other electrons, while the first sum gives the approximate change in correlation energy of the parent's N electrons caused by the "extra" electron. Analogous conclusions can be reached concerning each of the sums in Eq. (37). Thus, by separately deleting from Eqs. (36) and (37) each of the above three sums, we can assess the effects of charge redistribution and changes in correlation energy on the molecular electron affinity.

VII. RELATION TO MANY-BODY GREEN'S FUNCTION THEORY

If one sets the $K_{\alpha\beta}{}^{mn}$ coefficients equal to zero and replaces $E_{\alpha\beta}{}^m$ and $E_{\alpha}{}^{mn}$ by $\epsilon_m - \epsilon_\alpha - \epsilon_\beta$ and $\epsilon_m + \epsilon_n - \epsilon_\alpha$, respectively, Eq. (36) becomes equivalent to the second-order Dyson equation of Reinhardt and Doll.⁴¹ From the results of their excellent atomic calculations with the Dyson equation, these authors concluded that highly accurate ionization potentials cannot be obtained from second-order Green's function theory and that higher-order contributions must be included. It is our feeling that these conclusions apply equally to the calculation of electron affinities. Our theory provides a numerically practical and physically reasonable method of going beyond second order with a minimum of additional work. Third-order results from Eq. (36) require only that additional two-electron integrals be transformed to the Hartree-Fock basis. Both methods calculate the ion-neutral energy differences directly, and in both theories only matrices of relatively small dimensions occur.

VIII. COMPUTATIONAL PROCEDURE

We now outline our step-by-step process for calculating vertical and thermodynamic electron affinities for a given molecule.

Step (1). We choose a particular molecular geometry. For a diatomic molecule, we specify the internuclear separation. For a polyatomic molecule, we pick enough bond lengths and angles to define precisely its shape.

Step (2). We obtain the Hartree-Fock orbital energies ϵ_i and the necessary two-electron integrals $\langle ij | kl \rangle$.

Step (3). We employ Eq. (15) to obtain approximations to the CI expansion coefficients $K_{\alpha\beta}{}^{mn}$ from Rayleigh-Schrödinger perturbation theory.

Step (4). As a first approximation to ΔE_g^N , we use the $\Delta \tilde{E}_g^N$ of Eq. (39) which incorporates some of the effects of charge redistribution and correlation energy change. Based on the ionization potential results which Reinhardt and Doll⁴¹ have obtained using their analog of Eq. (40), we expect that Eq. (39) will give

a reasonably accurate starting point for the iterative determination of ΔE_g^N .

Step (5). Knowing the orbital energies, two-electron integrals, and CI expansion coefficients, we form the matrix elements of **A** and **B** from Eqs. (31)–(35).

Step (6). We use the approximate energy difference $\Delta \tilde{E}_g^N$ to construct the $\mathbf{H}(\Delta \tilde{E}_g^N)$ matrix in the form given in Eq. (37).

Step (7). We solve the pseudoeigenvalue equation (Eq. (36)) for ΔE_g^N by using either of following numerical methods:

(a). The more rigorous approach is a root-search method which was used by Reinhardt and Doll in their early ionization potential calculations.³⁹ We use it to solve Eq. (36) by first calculating the matrix $[\mathbf{H}(E) - E\mathbf{I}]^{-1}$ for $E = \Delta \tilde{E}_g^N$. By repeating the calculation of this inverse matrix as the parameter E is varied, we locate the smallest E for which this matrix fails to exist and set that value of E equal to ΔE_g^N . In this procedure, $[\mathbf{H}(E) - E\mathbf{I}]^{-1}$ must be computed at many values of the parameter E . Clearly, this method, though rigorous, is probably unrealistically time consuming for all but the smallest molecules, a fact which will limit the systems for which the root-search technique is practical.

(b). When the root-search method proves impractical, we use an iterative procedure which is substantially faster and considerably less expensive. Starting with $H(\Delta \tilde{E}_g^N)$, we solve Eq. (36) for a new approximation to ΔE_g^N , and use this approximation to construct a new $\mathbf{H}(\Delta E_g^N)$ matrix. If this procedure is stable, it will lead to successively better approximations to ΔE_g^N , until convergence is reached. The sensitivity of the convergence to the initial approximation for ΔE_g^N is presently being determined.

In both of these techniques, only the lowest root of Eq. (36) need be calculated. In the root-search method, this limits the numerical search to the neighborhood of $\Delta \tilde{E}_g^N$, and in the iteration scheme, it permits one to stop after computing only the lowest eigenvalue of the $H(\Delta \tilde{E}_g^N)$ matrix. This fact is an attractive feature of our theory.

Step (8). With the result of Step (7a) or (b), we obtain the vertical electron affinity from the identity

$$(\text{E.A.})_{\text{vertical}} = -\Delta E_g^N. \quad (41)$$

Step (9). To determine the effects of charge redistribution and correlation energy change, we return to Step (7) and solve for ΔE_g^N using a truncated $\mathbf{H}(\Delta E_g^N)$ matrix in which specific contributions are neglected. Deleting the second sum of Eq. (73), we calculate the electron affinity without the effects of charge redistribution. We can then attribute the difference between this value and the full electron affinity to the influence of charge redistribution.

Similarly, by omitting just the third sum from Eq. (37), we can assess the change in correlation energy caused by interactions of the extra electron with the other N electrons. Finally, leaving out only the first sum allows us to determine the extent to which the correlation energy of the parent's N electrons is altered by the presence of the extra electron.

Step (10). To obtain the thermodynamic electron affinity from Eq. (36) is a major computational undertaking. It involves the calculation of vertical energy differences between the parent molecule and its negative ion at many molecular geometries. Given this set of energy differences and the energy curve $E(R)$ of the neutral molecule we can calculate the energy curve $E^-(R^-)$ of the negative ion and thereby obtain the thermodynamic electron affinity from Eq. (1). Good energies $E(R)$ of many neutral molecules are presently available⁶¹; for other molecules, we calculate $E(R)$ as the expectation value

$$\langle g^N | H | g^N \rangle, \quad (42)$$

where $|g^N\rangle$ and H are given by Eqs. (10) and (30), respectively.

Step (11). We collect the set of vertical energy differences obtained by repeating Steps (2)–(9) for enough molecular geometries to include the equilibrium internuclear distances of both the molecule and the negative ion.

Step (12). The energy curve $E^-(R)$ is plotted by adding the vertical energy difference at each R to

$E(R)$. The minima of the two curves, $E(R_e)$ and $E^-(R_e^-)$, are then used in Eq. (1) to obtain the thermodynamic electron affinity.

This then concludes the calculation of vertical and thermodynamic electron affinities by our theory. In another article,⁶⁷ we apply this new theory to the minimal-basis hydrogen molecule. This model problem allows us to compare the formal and numerical results of our method with electron affinities obtained from exact configuration interaction calculations on H_2 and H_2^- , within the same basis. Although the outcome of this simple calculation is quite encouraging, a proper assessment of this theory can not be made until many more calculations have been completed. We are presently carrying out *ab initio* calculations on several small molecules of chemical interest within the framework of our theory. These investigations will hopefully shed more light on the potential accuracy and practicality of our theory. Results of the application of our method to conjugated pi electron molecules, within the Pariser–Parr–Pople approximation,^{68,69} will be presented in another article in the near future.

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