

Response of a Molecule to Adding or Removing an Electron

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Abstract

The *ab initio* calculation of molecular electron affinities (EA) and ionization potentials (IP) is a difficult task because the energy of interest is a very small fraction of the total electronic energy of the parent species. For example, EAs typically lie in the 0.01–10 eV range, but the total electronic energy of even a small molecule, radical, or ion is usually several orders of magnitude larger. Moreover, the EA or IP is an intensive quantity but the total energy is an extensive quantity, so the difficulty in evaluating EAs and IPs to within a fixed specified (*e.g.*, ± 0.1 eV) accuracy becomes more and more difficult as the system's size and number of electrons grows. The situation becomes especially problematic when studying extended systems such as solids, polymers, or surfaces for which the EA or IP is an infinitesimal fraction of the total energy. Equations of motion (EOM) methods such as the author developed in the 1970s in collaboration with P. Jørgensen and others offer a route to calculating the intensive EAs and IPs directly as eigenvalues of a set of working equations. A history of the development of EOM theories as applied to EAs and IPs, their numerous practical implementations, and their relations to Greens function or propagator theories are given in this contribution. EOM methods based upon Møller–Plesset, multi-configuration self-consistent field, and coupled-cluster reference wave functions are included in the discussion as is the application of EOM methods to metastable states of anions.

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1. INTRODUCTION

The vertical electron affinity (EA) of a molecule can be estimated by (approximately) solving the Schrödinger equation for the energy $E(0, N)$ of the N -electron neutral molecule and the Schrödinger equation for the energy $E(K, N + 1)$ of the K th state of the $(N + 1)$ -electron anion and subtracting the two energies:

$$EA = E(0, N) - E(K, N + 1). \quad (1)$$

The corresponding vertical ionization potential (IP) is given as

$$IP = E(K, N - 1) - E(0, N). \quad (2)$$

Here, we use K to label the electronic state of the anion or cation that one wishes to study, and 0 to label the state of the neutral (usually but not necessarily the ground state) to which the electron is being attached or from which it is removed.

In using such an approach to obtaining the EA or IP, one is faced with a very difficult numerical challenge because $E(0, N)$, $E(K, N - 1)$, and $E(K, N + 1)$ tend to be extremely large (negative) numbers, whereas EA and IP nearly always lies in the range 0–20 eV. For example, the EA of the $^4S_{3/2}$ state of the carbon atom [1] is 1.262119 ± 0.000020 eV, whereas the total electronic energy of this state of C is -1030.080 eV (relative to a C^{6+} nucleus and six electrons infinitely distant and not moving that defines the zero of energy). Since the EA is *ca.* 0.1% of the total energy of C, one needs to compute the C and C^- electronic energies to accuracies of 0.01% or better to calculate the EA to within 10%.

This observation shows only the “tip of the iceberg”, however as the major problem relates to the fact that $E(0, N)$, $E(K, N - 1)$, and $E(K, N + 1)$ are extensive properties whereas EA and IP are intensive quantities. For example, the EA of C_2 in its $X^2\Sigma_g^+$ ground electronic state is [1] 3.269 ± 0.006 eV near the equilibrium bond length R_e but only 1.2621 eV at $R \rightarrow \infty$ (*i.e.*, the same as the EA of a carbon atom). However, the total electronic energy of C_2 is -2060.160 eV at $R \rightarrow \infty$ and lower by *ca.* 3.6 eV (the dissociation energy [2] of C_2) at R_e , so again EA is a very small fraction of the total energies. For buckyball C_{60} , the EA is [1] 2.666 ± 0.001 eV, but the total electronic energy is sixty times -1030.080 eV minus the atomization energy (*i.e.*, the energy change for $C_{60} \rightarrow 60$ C) of this compound. Clearly, the challenge of evaluating EA (or IP) to within even 50% becomes more and more difficult as the size (*i.e.*, number of electrons) in the molecule grows, and it becomes impossible when the system of interest is an infinite solid, surface, or polymer. This same kind of difficulty (*i.e.*, calculating an intensive quantity as the difference between to extensive energies) plagues the computation of EAs and of ionization potentials (IPs), bond energies, and electronic excitation energies.

The problems discussed in the preceding paragraph do not disappear if one uses a computer with higher numerical precision in its arithmetic (*i.e.*, a longer word length) or algorithms that compute the one- and two-electron integrals needed for any quantum chemistry calculation to more significant figures. No matter how precise the integrals and how long the floating point word length (as long as they are finite), the evaluation of intensive properties such as IPs, EAs, and excitation energies as differences between pairs of extensive total electronic energies is doomed to fail.

Of course, much progress can be made in computing EAs and IPs as differences between anion and neutral or cation and neutral total energies [3] because of large systematic cancellation in energy errors [4]. For example, the pair correlation energies of the two 1s electron

pairs in C_2 is quite large, but is very nearly the same as in C_2^- , so even a large percent error made in computing these contributions to the total energy may not greatly affect the EA computed by subtracting $E(K, N + 1)$ from $E(0, N)$. Some of the earliest high quality *ab initio* calculations of EAs were carried out using wave function techniques and calculating separate neutral and anion energies. Nevertheless, in the late 1960s and early 1970s, workers were motivated to develop methods that would allow intensive energy differences such as EAs [5], ionization potentials (IPs) and excitation energies (ΔE s) “directly” rather than as differences in two very large numbers. This point of view is what led to the development of so-called equations of motion (EOM) methods as well as Greens function methods [6] pioneered by the Linderberg and Öhrn groups and, more recently, response function approaches [7] of Jørgensen, Olsen, and co-workers. In all of these theories, one performs a derivation in which the two total energies (*i.e.*, ion and neutral or ground and excited state) are subtracted analytically (rather than numerically) thereby achieving an analytical expression for the desired intensive energy difference. It is by thus dealing with equations that involve only intensive energies that one can overcome the problems detailed earlier.

Among the earliest practitioners of EOM methods in the chemistry community were McKoy [8] and his group at Cal Tech. They imported many ideas and mathematical tools from the nuclear physics literature [9], where EOM theories had been used to study excited states of nuclei, and they focused their efforts on electronic excitation energies ΔE , not IPs or EAs. In 1973, the author used the framework of EOM theory [10] as expressed by the McKoy group to develop a systematic (*i.e.*, order-by-order in the Møller–Plesset perturbation theory sense) approach for directly computing molecular EAs and IPs as eigenvalues of the EOM working equations. It is this development and its subsequent improvement, to several of which Prof. Poul Jørgensen contributed, and extensions [11] by our group and others that we now describe.

2. BASICS OF EOM THEORY

2.1. The EA equations of motion

The fundamental working equations of any EOM theory can be derived by writing the Schrödinger equations for the neutral and anion (or neutral or cation or ground and excited) states of interest and subtracting the two equations as a first step toward obtaining a single equation that will yield the EA or IP or ΔE . That is, the EOM theory produces the intensive energy difference directly as an eigenvalue of the working equation. As above, we use $|0, N\rangle$ to denote the 0th electronic state of the N -electron neutral and $|K, N + 1\rangle$ to denote the K th state of the $(N + 1)$ -electron anion and write the two Schrödinger equations as

$$H|0, N\rangle = E(0, N)|0, N\rangle, \quad (3)$$

$$H|K, N + 1\rangle = E(K, N + 1)|K, N + 1\rangle. \quad (4)$$

Because $|0, N\rangle$ and $|0, N + 1\rangle$ contain different numbers of electrons, it is convenient in developing EOM theories of EAs to express the electronic Hamiltonian H in second-

quantized form [12]:

$$H = \sum_{i,j} h(i, j) i^+ j + \frac{1}{2} \sum_{i,j,k,l} \langle i, j | k, l \rangle i^+ j^+ i k \quad (5)$$

where $h(i, j)$ represents a matrix element of the one-electron operators (*i.e.*, kinetic energy, electron-nuclear Coulomb attraction, *etc.*) within the orthonormal molecular spin-orbital basis $\{\phi_j\}$, $\langle i, j | k, l \rangle$ is a matrix element of the two-electron operators (*i.e.*, electron-electron repulsion), and the set of Fermion creation operators $\{i^+\}$ create an electron in the $\{\phi_i\}$ spin-orbitals, whereas the $\{i\}$ operators destroy such an electron. Writing H in such a form allows us to use the same H in equations (3) and (4) even though these two Schrödinger equations relate to N and $N + 1$ electrons, respectively.

The next step in developing an EOM equation is to assume that the anion state $|K, N + 1\rangle$ can be related to the neutral state $|0, N\rangle$ through an operator $Q^+(K)$:

$$|K, N + 1\rangle = Q^+(K)|0, N\rangle \quad (6)$$

that maps the neutral molecule wave function into the desired anion wave function.

For the EA case at hand, the operator $Q^+(K)$ is usually written in terms of scalar coefficients $t(K, l)$ multiplied by operators $T^+(l)$, also expressed in second-quantization language, each of which involves adding an electron

$$Q^+(K) = \sum_l t(K, l) T^+(l). \quad (7)$$

Manne showed [13] that a complete set of such $T^+(l)$ operators consists of the union of sets of operators $\{p^+\}$ that add an electron to a spin-orbital ϕ_p , operators $\{p^+q^+a\}$ that add an electron to ϕ_p and excite another electron from ϕ_a to ϕ_q , operators $\{p^+q^+r^+ab\}$ that add an electron to ϕ_p excite an electron from ϕ_a to ϕ_r and excite another electron from ϕ_b to ϕ_q as well as higher-level electron addition and excitation operators up to the highest-level operators that add an electron and induce N excitations. In labeling these operators, the indices $a, b, c, d, \text{etc.}$, are used to denote spin-orbitals occupied in a so-called reference Slater determinant within $|0, N\rangle$ and $p, q, r, s, \text{etc.}$, are used to denote unoccupied (*i.e.*, virtual) spin-orbitals. The reference determinant, which is what defines the concept of occupied and unoccupied spin-orbitals, is usually chosen to be the determinant $|0\rangle$ within the neutral-molecule wave function

$$|0, N\rangle = \sum_{J=0, M} C(0, J) |J\rangle \quad (8)$$

with the largest amplitude $C(0, 0)$, but it has been shown [13] that $|0\rangle$ can actually be taken to be any determinant within $|0, N\rangle$ that possesses non-zero amplitude. Later we will deal with how one determines the $C(0, J)$ amplitudes in the wave function $|0, N\rangle$; for now, suffice it to say these amplitudes can, for example, be taken from Møller-Plesset (MP) perturbation theory, from multiconfiguration self-consistent field (MCSCF) theory, from configuration interaction (CI) theory or from coupled-cluster (CC) theory.

Using equation (6) in equation (4) and subtracting equation (3) from (4) gives a single equation whose eigenvalue gives the desired EA:

$$(H Q^+(K) - Q^+(K) H) |0, N\rangle = (E(K, N + 1) - E(0, N)) Q^+(K) |0, N\rangle \quad (9)$$

or, in terms of the commutator $[H, Q^+(K)]$

$$[H, Q^+(K)]|0, N\rangle = EQ^+(K)|0, N\rangle \quad (10)$$

where the eigenvalue E is the negative of the EA. The key point is that one now has a single equation to be solved that produces the intensive EA as its eigenvalue. This equation appears to be of the conventional eigenvalue-eigenfunction form, but it is somewhat different because the operator that acts on the eigenfunction $Q^+(K)|0, N\rangle$ is not the Hamiltonian but a commutator involving the Hamiltonian. The fact that the commutator appears is what causes the eigenvalue to be an intensive energy difference.

To progress further toward practical implementation, specific choices must be made for how one is going to approximate the neutral-molecule wave function $|0, N\rangle$ and at what level one is going to truncate the expansion of the operator $Q^+(K)$ given in equation (7). It is also conventional to reduce equation (10) to a matrix eigenvalue equation by projecting this equation onto an appropriately chosen space of $(N+1)$ -electron functions. Let us first deal with the latter issue.

Once the number of $T^+(l)$ operators used to construct $Q^+(K)$ has been chosen (we discuss this choice later), the total number l^{\max} of $t(K, l)$ amplitudes has been determined. Multiplying equation (10) on the left by the adjoint $T(j)$ of any one of the T^+ operators, and then projecting the resultant equation against $\langle 0, N|$ gives one form of the working EOM EA equations:

$$\sum_l \langle 0, N|T(j)[H, T^+(l)]|0, N\rangle t(K, l) = E \sum_l \langle 0, N|T(j)T^+(l)|0, N\rangle t(K, l). \quad (11)$$

To make use of this equation, the $\langle 0, N|T(j)[H, T^+(l)]|0, N\rangle$ and $\langle 0, N|T(j)T^+(l)|0, N\rangle$ matrices of dimension $l^{\max} \times l^{\max}$ must first be evaluated in terms of one- and two-electron integrals (appearing in H) and one-, two-, and higher-body density matrices (depending upon the level at which the $\{T^+(l)\}$ operator expansion is truncated). Subsequently, the EA values (*i.e.*, EAs for the various anion states, K , relative to the $|0, N\rangle$ state of the neutral) are computed as minus the eigenvalues E of equation (11).

2.2. The analogous equations of motion for ionization potentials

It is useful to explore how this same framework has been used to compute molecular ionization potentials (IPs). It is fairly straightforward to show that an equation analogous to equation (10) but reading

$$\langle 0, N|(HQ^+(K) - Q^+(K)H) = (E(0, N) - E(K, N-1))\langle 0, N|Q^+(K) \quad (12)$$

is valid if the operators $\{Q^+(K)\}$ are as given in equation (7) but with the $\{T^+(l)\}$ defined to include operators of the form $\{a^+, a^+b^+p, a^+b^+c^+qr, \text{etc.}\}$. Of course, in equation (12), the operators within $Q^+(K)$ act to the left on $\langle 0, N|$ to generate cationic states. As a result, neutral-cation energy differences appear in equation (12) and thus this offers a route to computing IPs. Multiplying this equation on the right by any one of the $T(j)$ operators and then projecting against $|0, N\rangle$ gives

$$\sum_l \langle 0, N|[H, T^+(l)]T(j)|0, N\rangle t(K, l) = E \sum_l \langle 0, N|T^+(l)T(j)|0, N\rangle t(K, l) \quad (13)$$

but now the eigenvalues E denote values of $(E(0, N) - E(K, N - 1))$, which are the negatives of the IPs.

Thus far, we see that EOMs can be written that allow EAs or IPs to be computed. The fundamental constructs within these equations are as follows:

- (i) For the EA case, matrix elements $\langle 0, N | T(j) [H, T^+(l)] | 0, N \rangle$ involving the commutator of H with the $T^+(l)$ operators then multiplied on the left by a $T(j)$ operator, as well as an analogous overlap matrix element $\langle 0, N | T(j) T^+(l) | 0, N \rangle$;
- (ii) for the IP case, matrix elements $\langle 0, N | [H, T^+(l)] T(j) | 0, N \rangle$ of the same commutator but with the $T(j)$ operator on the right, as well as the corresponding overlap matrix element $\langle 0, N | T^+(l) T(j) | 0, N \rangle$;
- (iii) the neutral-molecule wave function $|0, N\rangle$ with respect to which the EA or IP is to be evaluated.

2.3. The rank of the operators

It is now useful to analyze the density matrix elements¹ that enter into these equations. Each of the $T^+(j)$ operators contains an odd number of creation or annihilation operators, and the Hamiltonian H contains two (*i.e.*, i^+j) or four (*i.e.*, i^+j^+lk) such operators. It can be seen that the commutator $[H, T^+(l)]$ does not contain four plus the number of creation or annihilation operators in $T^+(l)$, but two fewer operators. For example, the commutator $[i^+j^+lk, p^+q^+a]$ does not yield any terms with four creation and three annihilation operators but only terms with three creation and two annihilation operators. We say that the act of forming the commutator (which is what causes the higher order operators to cancel) gives rise to a reduction in the rank of the operators. As a result, both the operator products $T(j)[H, T^+(l)]$ and $[H, T^+(l)]T(j)$, which appear in the EA and IP equations of motion, respectively, contain terms only involving both creation and annihilation operators equal to the number of creation operators in $T^+(l)$ plus one plus the number of creation operators in $T(j)$. For example, if $T^+(l) = p^+q^+a$ and $T(j) = b^+rs$, then $T(j)[H, T^+(l)]$ and $[H, T^+(l)]T(j)$ will contain terms with no more than four creation and four annihilation operators. This means that the density matrices needed to form $\langle 0, N | T(j) [H, T^+(l)] | 0, N \rangle$ and $\langle 0, N | [H, T^+(l)] T(j) | 0, N \rangle$ will be, at most, fourth order density matrices of the $\langle 0, N | \dots | 0, N \rangle$ density.

2.4. Equations of lower rank for both EAs and IPs

Indeed, in the early years of using EOM methods [14] to compute EAs and IPs, operator manifolds of the form $\{T^+(l)\} = \{p^+; p^+q^+a, p^+q^+r^+ba, \text{etc.}\}$ or $\{T^+(l)\} = \{a^+, a^+b^+p, a^+b^+c^+qr, \text{etc.}\}$ were employed with Møller–Plesset approximations to $|0, N\rangle$ (usually taken through first order) to form the kind of matrix elements appearing in equations (11) and (13) and to then evaluate EAs and IPs from their eigenvalues E . However, it became more common to use a combination of the EA and IP EOMs formed

¹ The first- and second-order density matrices, respectively, have elements given by $\langle 0, N | j^+k | 0, N \rangle$ and $\langle 0, N | j^+k^+lh | 0, N \rangle$.

by adding equations (11) and (13), while expanding the $\{T^+(l)\}$ operator manifold to include both those needed to evaluate EAs $\{p^+; p^+q^+a, p^+q^+r^+ba, \text{ etc.}\}$ and those needed for the IPs $\{a^+, a^+b^+p, a^+b^+c^+qr, \text{ etc.}\}$, to simultaneously compute both such energy differences.

To understand why such a combination has proven beneficial, it suffices to examine the form and rank of the operators whose $\langle 0, N | \dots | 0, N \rangle$ matrix elements must be evaluated

$$\begin{aligned} & \sum_l \langle 0, N | [H, T^+(l)]T(j) + T(j)[H, T^+(l)] | 0, N \rangle t(K, l) \\ & = E \sum_l \langle 0, N | T^+(l)T(j) + T(j)T^+(l) | 0, N \rangle t(K, l). \end{aligned} \quad (14)$$

Recall that the $T^+(j)$ operators contain an odd number of creation or annihilation operators. Each of the products $[H, T^+(l)]T(j)$, $T(j)[H, T^+(l)]$, $T^+(l)T(j)$, and $T(j)T^+(l)$ thus contain an even number of such operators. However, because of the fundamental anti-commutation properties of these operators

$$i^+j + ji^+ = \delta_{i,j}, \quad (15)$$

$$ij + ji = 0, \quad (16)$$

$$i^+j^+ + j^+i^+ = 0 \quad (17)$$

it can easily be shown that the *operator combinations* $T^+(l)T(j) + T(j)T^+(l)$ and $[H, T^+(l)]T(j) + T(j)[H, T^+(l)]$ contain one fewer creation and one fewer annihilation operator than does either of the two terms in the sums. So, by combining the EA and IP EOMs, one effects a rank reduction in the operators appearing in the equations although the dimensions of the matrices one needs to construct are doubled (because the $\{T^+(l)\}$ operator manifold was doubled when both EA and IP operators were included. The rank reduction is important because it means that the density matrices that need to be evaluated to compute the $\langle 0, N | \dots | 0, N \rangle$ matrix elements are of lower rank in equation (14) than in either equation (11) or equation (13). As we said, it has become more common to use the combined EA and IP equation (14) because lower-order density matrices are required.

2.5. Summary

Thus far, we have shown how one can obtain eigenvalue equations, in which the energy eigenvalues correspond to the intensive EAs (or IPs), by postulating that the anion (or cation) wave function can be related to the neutral-molecule wave function through an operator. We have also shown how the EA and IP equations of motion can be combined to generate a combined EOM from which both EAs and IPs can be obtained. The advantage to the latter approach is that the operators appearing in the resultant equations are of lower rank and thus lower-order density matrices must be evaluated to carry out the calculations. Let us now move on to address more specific embodiments of such EOM theories that result from different choices of the neutral-molecule wave function and of the operator connecting the neutral and anion wave functions.

3. PRACTICAL IMPLEMENTATIONS OF EOM THEORIES FOR EAS AND IPS

The basic ideas underlying any EOM method for computing EAs or IPs appear above. However, as discussed earlier, in any specific embodiment of such a method, one must commit to

- (i) a specific approximation to the neutral-molecule wave function $|0, N\rangle$,
- (ii) a specific choice of how large an operator manifold $\{T^+(I)\}$ to employ, and
- (iii) how to solve the resultant EOM equations for the eigenvalues E that then produce the EAs or IPs. In the following subsections, we describe the most commonly used choices for these three issues.

3.1. The Møller–Plesset based approximations

In the earliest implementation of EOM approaches to EAs, the author's group [10,14] chose to represent the $|0, N\rangle$ wave function in a Møller–Plesset (MP) expansion

$$|0, N\rangle = \psi^0 + \psi^1 + \psi^2 + \dots \quad (18)$$

with the single-determinant unrestricted Hartree–Fock (HF) function being ψ^0 and the corresponding neutral-molecule HF Hamiltonian being H^0 . This choice was made because there existed substantial evidence that EAs and IPs computed at the Koopmans' theorem level would not meet the desired 0.1 eV accuracy. The evidence on atoms and small molecules also showed that EAs and IPs computed using standard second-order MP theory were much more accurate but not sufficient to approach the 0.1 eV standard. For this reason, the author's group set their sites on the next reasonable level, that of third-order MP theory.

The operator manifold $\{T^+(I)\}$ was taken to consist of $\{p^+; p^+q^+a\}$ and $\{a^+, a^+b^+p\}$. In a close collaboration with P. Jørgensen, this choice of operator manifold was shown to be capable of producing EAs and IPs that were precise through third order² in the MP perturbation, which is why this choice was made.

The resultant variant of equation (14) was not solved by finding the eigenvalues of this matrix eigenvalue equation whose dimension is the sum of the dimensions of the $\{p^+; p^+q^+a\}$ and $\{a^+, a^+b^+p\}$ operator manifolds. Rather, that large matrix eigenvalue problem was partitioned [10] using a primary subspace defined by the $\{p^+, a^+\}$ operators and a secondary subspace defined by the $\{p^+q^+a, a^+b^+p\}$ operators. The partitioned eigenvalue problem

$$\sum_{j=a,p} H_{i,j}(E)X_j = EX_i \quad (19)$$

whose dimension was that of the $\{p^+, a^+\}$ operator space was used to find the eigenvalues E . Of course, the act of partitioning the higher-dimension matrix eigenvalue problem does not change the values of E that represent solutions to the equations. That is, the same E values that fulfill the original equations are also solutions to the partitioned equations. However, once one introduces approximations designed to evaluate elements of the partitioned $H_{i,j}(E)$ matrix to a chosen order in perturbation theory, this equivalence is lost.

² See Ref. [6k].

It is precisely by making such an order analysis (e.g., computing $H_{i,j}(E)$ through second or third order) that EOM theories capable of evaluating EAs or IPs to a given order were obtained.

When the elements of the partitioned matrices were evaluated through second order in the MP series, the following expression was obtained for the matrix elements $H_{i,j}$:

$$H_{i,j}(E) = \varepsilon_i \delta_{i,j} - \sum_{p,q,a} \frac{\langle i, a || p, q \rangle \langle p, q || j, a \rangle}{\varepsilon_p + \varepsilon_q - \varepsilon_a - E} + \sum_{a,b,p} \frac{\langle i, p || a, b \rangle \langle a, b || j, p \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_p - E}. \quad (20)$$

Here, the ε_j denote the UHF spin-orbital energies of the neutral molecule and the $\langle i, j || k, l \rangle$ denote differences in two-electron integrals ($\langle i, j || k, l \rangle = \langle i, j | k, l \rangle - \langle i, j | l, k \rangle$). Such expressions were also obtained by Reinhardt and Doll [17] within the Greens function framework, but they had not extended their efforts to third or higher orders.

The expression for $H_{i,j}(E)$ valid through third order in the MP series is more complicated and is derived in Refs. [10].³ The partitioned matrix eigenvalue equation was written in those works as

$$\mathbf{H}(E)\mathbf{X} = E\mathbf{X} \quad (21)$$

where the elements of the \mathbf{H} matrix were defined as follows:

$$H_{i,j}(E) = A_{i,j} + \sum_{\alpha < \beta, m} \frac{B_{i,\alpha m \beta} B_{j,\alpha m \beta}^*}{E_{\alpha \beta}^m + E} - \sum_{N+1 < n, \alpha} \frac{B_{i,n \alpha N+1 g} B_{j,n \alpha N+1}^*}{E_{\alpha}^{N+1n} - E} - \sum_{N+1 < m < n, \alpha} \frac{B_{i,n \alpha m g} B_{j,n \alpha m}^*}{E_{\alpha}^{mn} - E}. \quad (22)$$

In turn, the elements of the A and B matrices are shown below:

$$B_{i,\alpha m \beta} = -\langle i m | \alpha \beta \rangle - \frac{1}{2} \sum_{p,q} \langle i m | p q \rangle K_{\alpha \beta}^{(pq)} + \sum_{\gamma, p} [\langle i \gamma | p \alpha \rangle K_{(\beta \gamma)}^{(mp)} - \langle i \gamma | p \beta \rangle K_{(\alpha \gamma)}^{(mp)}], \quad (23)$$

$$B_{i,n \alpha m} = \langle i \alpha | m n \rangle + \frac{1}{2} \sum_{\gamma, \delta} \langle i \alpha | \gamma \delta \rangle K_{(\delta \gamma)}^{mn} + \sum_{\gamma, p} [\langle i p | \gamma n \rangle K_{(\alpha \gamma)}^{(mp)} - \langle i p | \gamma m \rangle K_{(\alpha \gamma)}^{(np)}], \quad (24)$$

$$A_{i,j} = \delta_{i,j} \varepsilon_i + \sum_{k,l} \langle i k | j l \rangle F_{kl} \quad (25)$$

to which one adds the following E -independent terms

$$\delta A_{i,j} = \sum_{\delta, \beta, p, m, n} \frac{\langle j p || i \delta \rangle \langle \delta \beta || m n \rangle \langle m n || p \beta \rangle}{(\varepsilon_{\delta} - \varepsilon_p)(\varepsilon_{\delta} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_n)} + \sum_{\delta, \beta, p, m, n} \frac{\langle j \delta || i p \rangle \langle p \beta || m n \rangle \langle m n || \delta \beta \rangle}{(\varepsilon_{\delta} - \varepsilon_p)(\varepsilon_{\delta} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_n)}$$

³ See Ref. [6k].

$$\begin{aligned}
& + \sum_{\delta, \alpha, \beta, p, n} \frac{\langle jp || i \delta \rangle \langle \delta n || \beta \alpha \rangle \langle \alpha \beta || pn \rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p - \varepsilon_n)} \\
& + \sum_{\delta, \alpha, \beta, p, n} \frac{\langle j \delta || i p \rangle \langle \delta n || \beta \alpha \rangle \langle \alpha \beta || pn \rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p - \varepsilon_n)}.
\end{aligned} \tag{26}$$

The energy denominators appearing in the H_{ij} matrix elements are

$$E_\alpha^{mn} = \varepsilon_m + \varepsilon_n - \varepsilon_\alpha - \langle \alpha m | \alpha m \rangle - \langle \alpha n | \alpha n \rangle + \langle mn | mn \rangle, \tag{27}$$

$$E_{\delta\gamma}^p = \varepsilon_p - \varepsilon_\delta - \varepsilon_\gamma - \langle \delta p | \delta p \rangle - \langle \gamma p | \gamma p \rangle + \langle \delta\gamma | \delta\gamma \rangle. \tag{28}$$

Finally, the F quantities appearing above are given as

$$F_{kl} = \sum_{\alpha < \beta, p} [K_{\alpha\beta}^{pk} K_{\alpha\beta}^{pl} + K_{\alpha\beta}^{kp} K_{\alpha\beta}^{lp}] - \sum_{p < q, \alpha} [K_{\alpha l}^{pq} K_{\alpha k}^{pq} + K_{l\alpha}^{pq} K_{k\alpha}^{pq}] \tag{29}$$

where

$$K_{\alpha\beta}^{(pq)} = K_{\alpha\beta}^{pq} - K_{\alpha\beta}^{qp}, \tag{30}$$

$$K_{(\alpha\beta)}^{pq} = K_{\alpha\beta}^{pq} - K_{\beta\alpha}^{pq}, \tag{31}$$

$$K_{(\alpha\beta)}^{(pq)} = K_{\alpha\beta}^{pq} - K_{\alpha\beta}^{qp} - K_{\beta\alpha}^{pq} + K_{\beta\alpha}^{qp}, \tag{32}$$

and the latter quantities are the MP expansion coefficients of the first-order wave function:

$$K_{\alpha\beta}^{mn} = \frac{\langle mn | \alpha \beta \rangle}{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_m - \varepsilon_n}. \tag{33}$$

Although more complicated than their second-order counterparts, the basic structure of the above expressions for $H_{i,j}(E)$ are the same as those shown earlier.

These third-order equations have been used in many applications in which molecular EAs have been computed for a wide variety of species as illustrated in Refs. [14]. Clearly, all of the quantities needed to form the second- or third-order EOM matrix elements $H_{j,k}$ are ultimately expressed in terms of the orbital energies $\{\varepsilon_k\}$ and two-electron integrals $\langle j, k | l, h \rangle$ evaluated in the basis of the neutral molecule's Hartree-Fock orbitals that form the starting point of the Møller-Plesset theory. However, as with most electronic structure theories, much effort has been devoted to recasting the working EOM equations in a manner that involves the atomic-orbital (AO) two-electron integrals rather than the molecular-orbital based integrals. Because such technical matters of direct AO-driven calculations are outside the scope of this work, we will not delve into them further here although we note that J. Oddershede [15] and our group looked into how to express EOM-type calculations in the AO basis.

3.2. Relationship to Greens functions/propagators

It turns out that in the early 1970s when we were developing and implementing the EOM method for treating EAs and IPs, several groups had taken a different approach to the evaluation of atomic and molecular electronic energy differences using what were called Greens

functions (GF) or propagators. Linderberg and Öhrn pioneered⁴ the use of such methods in quantum chemistry, while Cederbaum and co-workers [16], Reinhardt and Doll [17], Taylor, Yaris, and co-workers [18] and Pickup and Goscinski [19] were among the first to apply the methods to EAs and IPs using an *ab initio* approach. Purvis and Öhrn [20] soon thereafter expanded the range of the theory to include open-shell systems. These workers as well as Jørgensen and Oddershede [21] and others [22] developed Møller–Plesset based GFs for evaluating electronic excitation energies but we will not discuss these developments further here because our emphasis is on IPs and EAs.

The GF EA and IP theories were derived from consideration of the following time-dependent matrix elements:

$$G_{j,k}(t) = (1/i\hbar)\Theta(t)\langle 0, N | \exp(iHt/\hbar)j^+ \exp(-iHt/\hbar)k | 0, N \rangle \\ + (1/i\hbar)\Theta(-t)\langle 0, N | k \exp(iHt/\hbar)j^+ \exp(-iHt/\hbar) | 0, N \rangle. \quad (34)$$

Here, $\Theta(t)$ is the Heaviside step function, which equals unity when t is positive and zero when t is negative, j^+ and k are the same creation and annihilation operators discussed earlier, and $|0, N\rangle$ is the neutral-molecule reference wave function. Introducing complete sets of $N-1$ and $N+1$ electron Hamiltonian eigenfunctions into the first and second terms in equation (34), it is straightforward to see that one observes time dependences varying as $\exp(i[E(0, N) - E(K, N-1)]t/\hbar)$ and $\exp(i[E(K, N+1) - E(0, N)]t/\hbar)$, respectively.

Taking the time derivative of equation (34), one obtains expressions involving commutators of the form $[H, j^+]k$ and $k[H, j^+]$ just as one finds in equation (14). By analyzing the resulting time-derivative equations, workers in this field were able to obtain equations that such $G_{j,k}(t)$ matrix elements obey (n.b., these were called the equations of motion for these quantities). The workers named above were able to express the resulting equations in terms of one- and two-electron integrals and corresponding density matrices much as the author had done within the EOM framework. In fact, it turned out that the final working equations of the so-called one-electron Greens function (GF) or electron propagator defined in equation (34), when Fourier transformed from the time to the energy domain, were exactly the same as the EOM equations given above (*i.e.*, equation (20) and those reproduced from Refs. [10]).⁵ However, only the Cederbaum group achieved the full third-order expressions within the GF framework analogous to what we reproduced above.

Especially in recent years, much of the work aimed at calculating EAs and IPs using these direct-calculation EOM and GF methods has been performed within the notation of Greens functions and has been carried out by Vince Ortiz's group [23] as well as by the Cederbaum group. The workers who pioneered GF theory have also shown that the residues (or eigenvectors, depending on how one solves the equations) also provide a wealth of information other than energy differences. To further illustrate the impact that such advances have had within the quantum chemistry community, we note that the Ortiz group has implemented various (*i.e.*, Møller–Plesset and other) variants of these theories within the highly successful Gaussian [24] suite of computer codes as a result of which many workers worldwide now employ EOM of GF-type methods to evaluate EAs and IPs.

⁴ See Refs. [6l] and [6r].

⁵ See Ref. [6k].

3.3. The natural orbital or extended Koopmans' theorem approach

In the mid 1970s, R.G. Parr and co-workers [25] and, independently, D. Smith and co-workers [26] proposed to use an equation such as equation (13) for computing IPs and they referred to these methods as natural orbital or extended Koopmans' theorem theories. Subsequently, E. Andersen and the author analyzed [27] the working equations of this approach through second and third order in the MP series and noted differences between them and the Greens function and equivalent EOM theories computed through these same orders. Of course, based on the discussion of Section 2. D, these differences relate to the ranks of the operators appearing in the working equations and are not surprising. More recently, Cioslowski and co-workers [28] have shown that these extended Koopmans' theorem approaches indeed offer a very efficient and reasonably accurate route to computing IPs or EAs, so it is likely that these methods will continue to develop. One of the more attractive aspects of the extended Koopmans approaches is that they have been shown [29] to be capable, at least in principle, to be able to yield the correct lowest ionization potential of a neutral molecule because they are capable of generating the proper asymptotic form for the density.

3.4. Multi-configuration based approximations

Following on the proof by R. Manne [13] that the operator spaces $\{T^+(l)\} = \{p^+; p^+q^+a, p^+q^+r^+ba, \text{ etc.}\}$ and $\{T^+(l)\} = \{a^+, a^+b^+p, a^+b^+c^+qr, \text{ etc.}\}$ can be used (*i.e.*, is capable of forming complete sets of ion states) even when no single determinant forms a dominant component of the neutral-molecule wave function $|0, N\rangle$, the author's group extended the combined EA and IP EOM theory to the case in which $|0, N\rangle$ is of an arbitrary multi-configuration self-consistent field (MC-SCF) form [30] and the ionization operator manifold $\{T^+(l)\}$ included operators of the form $\{p^+; p^+q^+a\}$ and $\{a^+, a^+b^+p\}$. The resultant working equations were written as in equation (19), with the $H_{j,k}$ matrix elements given in equations (18) of Ref. [30a], which we do not reproduce here because of their complexity. The primary additional difficulty involved in implementing these multi-configuration-based equations is the fact that three-electron density matrices $\langle 0, N | i^+ j^+ k^+ l h n | 0, N \rangle$ taken with respect to the MC-SCF wave function $|0, N\rangle$ are involved. These density matrices arise when the commutators $[H, p^+q^+a]$ and $[H, a^+b^+p]$ are evaluated.

To date, not much use has been made of the MC-SCF based EOM theories as developed in the author's group. Instead, the framework of time-dependent response theory, which can treat essentially any kind of reference wave function $|0, N\rangle$ including the MC-SCF variety, has superseded the EOM-based developments for such cases. It is important to keep in mind, however, that both the EOM and response function theories involve formulating and solving sets of equations whose solution (*i.e.*, the unknown energy) is an intensive energy.

3.5. Coupled-cluster based EOM

The use of coupled-cluster (CC) wave functions within EOM theory for excitation energies, IPs, and EAs has been developed [31,32] upon slightly different lines than outlined in Section 2. The CC wave function ansatz for $|0, N\rangle$ is written as usual in terms of an exponential

operator acting on a single-determinant (*e.g.*, unrestricted HF) “reference function” $|0\rangle$

$$|0, N\rangle = \exp(T)|0\rangle. \quad (35)$$

The so-called cluster operator T is expressed in terms of spin-orbital excitation operators of the form $\{T_1\} = \{p^+a\}$, $\{T_2\} = \{p^+q^+ba\}$, $\{T_4\} = \{p^+q^+r^+cba\}$, *etc.*, with T_k relating to the excitation of k electrons from occupied spin-orbitals (a, b, c , *etc.*) to virtual spin-orbitals (p, q, r , *etc.*). Prior to forming any EA EOM, the neutral-molecule CC equations need to be solved for the amplitudes $\{t_n\}$ that multiply the $\{T_n\}$ operators to form the CC T operator. For completeness, let us briefly review how the conventional CC wave function evaluation is carried out.

We recall the CC equations are formed by manipulating the Schrödinger equation

$$H \exp(T)|0\rangle = E \exp(T)|0\rangle \quad (36)$$

to read

$$\exp(-T)H \exp(T)|0\rangle = E|0\rangle \quad (37)$$

and subsequently projecting this equation against the set of functions $\{0|T_n^+\}$. Because the T operator contains only creation operators for unoccupied spin-orbitals and annihilation operators for occupied spin-orbitals, it turns out that the commutator expansion

$$\begin{aligned} \exp(-T)H \exp(T) &= H - [T, H] + 1/2[T, [T, H]] - 1/3![T, [T, [T, H]]] \\ &+ 1/4![T, [T, [T, [T, H]]]] + \dots \end{aligned} \quad (38)$$

exactly truncates at the fourth order term. So, the final working equations of CC theory can be written as

$$\begin{aligned} \langle 0|T_n^+ \{H - [T, H] + 1/2[T, [T, H]] - 1/3![T, [T, [T, H]]] \\ + 1/4![T, [T, [T, [T, H]]]]\} |0\rangle = 0. \end{aligned} \quad (39)$$

Once the CC amplitudes $\{t_n\}$ are determined by solving these quartic equations, the CC energy is computed as

$$\begin{aligned} \langle 0|H - [T, H] + 1/2[T, [T, H]] - 1/3![T, [T, [T, H]]] \\ + 1/4![T, [T, [T, [T, H]]]] |0\rangle = E. \end{aligned} \quad (40)$$

The operator $Q^+(K)$ that maps the CC wave function $|0, N\rangle$ into an anion or cation state is expressed as in equation (7) with the $\{T^+(l)\}$ operators including, for example, $\{T^+(l)\} = \{p^+; p^+q^+a, p^+q^+r^+ba, \text{etc.}\}$ when EAs are to be computed and the adjoints of $\{a^+, a^+b^+p, a^+b^+c^+qr, \text{etc.}\}$ when IPs are computed. The basic EOM analogous to equation (10) is then written as

$$[H, Q^+(K)] \exp(T)|0\rangle = E Q^+(K) \exp(T)|0\rangle. \quad (41)$$

Multiplying on the left by $\exp(-T)$ and realizing that T and $Q^+(K)$ commute reduces this equation to

$$[H', Q^+(K)]|0\rangle = E Q^+(K)|0\rangle \quad (42)$$

where

$$H' = \exp(-T)H \exp(T), \quad (43)$$