One-Electron Electron−Molecule Potentials Consistent with ab Initio Møller−Plesset Theory[†]

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Ab initio electronic structure methods such as Møller−Plesset (MP) theory can be used to compute electron affinities (EAs) of molecules or clusters of molecules to reasonable accuracy (±a few tenths of an electron volt). For systems in which an electron is bound to a closed-shell neutral in a manner that primarily localizes the excess electron exterior to most of the electron density of the neutral, we investigate how a given level of ab initio description can be accurately described by a one-electron potential governing the excess electron's interaction with the neutral. We show what ingredients such a potential must possess not only to reproduce the ab initio EA but also to have long-range electrostatic, polarization, and other contributions identical to the ab initio potential. In particular, we show that using Hartree−Fock level electrostatic moments and polarizability can produce a one-electron potential consistent with MP2 theory. To be consistent with MP3 theory, MP2-level electrostatics and polarizabilities must be used. The long-range components of the ab initio potential are shown to embody both orbital relaxation induced by the excess electron and the dispersion interactions between the excess electron and the other electrons of the neutral. Even though these individual contributions do not necessarily scale as r^{-4}, they are shown to combine into a total potential that can be represented in the familiar polarization form $-^1/_2\alpha r^{-4}$. These findings suggest that electrostatic potentials combined with polarization potentials scaling as r^{-4} can indeed describe the relaxation (induction) and dispersion energies of an excess electron. Finally, how these observations might assist in constructing new electron−molecule potentials is also discussed.

I. Introduction

A. Goal of this Work. The main goal of this paper is to establish connections between ab initio electronic structure *analytical expressions* for electron affinities (EAs) of molecules (or clusters of molecules) and one-electron *interaction potentials* that can capture this ab initio description. (By analytical expression, we mean that the EA is written, in each order of perturbation theory, in terms of Hartree−Fock orbital energies and two-electron integrals involving the Hartree−Fock spin−orbitals. Of course, the values of these quantities depend upon the atomic orbital basis set employed.) When studying electron−molecule scattering or weak electron binding to closed-shell molecules or clusters, it is common to employ one-electron potentials $V(r,\theta,\phi)$ that contain valence repulsion as well as electrostatic and polarization components. Often, the electrostatic potentials are represented in terms of partial charges, and the polarization potential is taken to be of the $-^1/_2\alpha r^{-4}$ form. This paper attempts to show to what extent such representations are consistent with ab initio descriptions of the electron−molecule interaction. This allows us to suggest how one might then utilize ab initio results on test systems to calibrate or determine parameters when designing new one-electron potentials.

The most commonly used electron−molecule potentials $V(r,\theta,\phi)$ are expressed in terms of: (i) functions of the position (r,θ,ϕ) of the excess electron that contain electrostatic (e.g., dipole and quadrupole moments) and polarization (e.g., dipole polarizability) parameters and that are designed to describe the long-range radial and angular characters of the electron-molecule interaction, and (ii) shorter-range functions (also containing parameters) to represent primarily the repulsion exerted on the excess electron by the valence and inner-shell electrons of the neutral molecule.

Often, one or more parameter in the short-range repulsion potential is adjusted so the EA computed using the model potential agrees with the experimental EA or with the EA obtained at some high level of theory. However, simply requiring the potential $V(r,\theta,\phi)$ to reproduce a known EA is no guarantee that the radial and angular properties of $V(r,\theta,\phi)$ are correct. We suggest here it might be wise to design a potential that has long-range components optimally consistent with a given level of ab initio theory; the short-range potential whose strength is then tuned to generate the correct EA is then more likely to be an accurate and less arbitrary representation.

Toward this goal of concentrating on the long-range character of $V(r,\theta,\phi)$, we focus on species in which one excess electron is bound to a closed-shell molecule in a manner that localizes most of the excess electron density exterior to the molecule or cluster. In so doing, we develop relationships between the ab initio EA expressions and the long-range components of the electrostatic (charge−dipole, charge−quadrupole, etc.) and polarization potentials commonly used to model electron−molecule interactions. (In this paper, we will focus on the charge-induced dipole potential that involves the so-called dipole polarizability although we will show how the analysis can be extended to higher-order polarizabilities.) It is by insisting that the asymptotic radial and angular characters of the ab initio and one-electron model electron−molecule interactions match that we extract the long-range portion of a one-electron potential.

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Following this path, we are able to characterize polarization potentials that achieve EA values and asymptotic forms maximally consistent with MP*n* ab initio theory. At the MP2 level, the Hartree–Fock (HF) level electrostatic moments and polarizabilities of the neutral molecule appear. We also demonstrate how such potentials can be extended to the MP3 level, in which MP2 level electrostatic moments and polarizabilities arise. It is our hope that others can employ and extend this approach to even higher and more robust levels of theory to develop even better electron–molecule interaction potentials. Such advances could have significant impact on how one treats electrons in large molecular clusters, on surfaces, and in electron–molecule scattering.

When electron–molecule interactions are studied, the primary advantage in using a local one-electron potential $V(r,\theta,\phi) = V(\mathbf{r})$ lies in the fact that the associated Schrödinger equation depends only on three coordinates (r,θ,ϕ). In contrast, ab initio approaches involve dealing with many-electron wave functions or complicated density functionals whose utilization is extremely computationally taxing. The approach taken here involves extracting $V(\mathbf{r})$ from an ab initio expression for the molecule's or cluster's EA in a manner that focuses on the large r character of $V(\mathbf{r})$, while expressing the electrostatic and shorter-range repulsive potentials in terms of the electron–nuclei Coulomb attractions and electron–electron Coulomb and exchange repulsions as they appear in the Fock operator. In such a form, applications to small molecules and clusters are quite feasible, but for large molecular clusters, applications would be difficult because of the need to evaluate the Coulomb and exchange integrals appearing in the Fock operator's matrix elements.

B. Model Potentials to Replace the Fock Operator. For the reason just stated, most applications of electron–molecule potentials to larger clusters of molecules involve replacing the valence-repulsion and electrostatic components of the Fock operator by another easily evaluated one-electron effective potential. For example, as mentioned briefly above, these components are often expressed in terms of (i) Coulomb interactions of the excess electron with point partial charges distributed to simulate the molecule's or cluster's dipole and quadrupole moments and (ii) repulsive factors (often depending exponentially with distance) to simulate the excess electron's exclusion from regions of the neutral's occupied valence and inner-shell orbitals.

A significant challenge in combining a one-electron electrostatic-plus-repulsion potential with a one-electron polarization potential is how one cuts off or attenuates the polarization potential $-1/2\alpha/r^4$ and the attractive Coulomb potentials $-q/r$ involving positive partial charges (of magnitude q) as $r \rightarrow 0$. For example, the polarization potential can be multiplied by $(1 - \exp(-br^2))^2$ to overcome its divergence as $r \rightarrow 0$. As noted earlier, the strength and functional form of the short-range repulsion potential must also be carefully chosen (often to guarantee the EA agrees with an accurate value for some test system).

C. Intermolecular Potentials. When dealing with an electron bound to a cluster of closed-shell molecules, it is common to express the interaction between the electron and the cluster as a sum of interaction potentials of the electron with each molecule in the cluster. In such studies, one must also account for the fact that the molecules can polarize one another and that the resulting induced moments alter the interaction potentials among the cluster's constituent molecules. This means that one must employ a molecule–molecule interaction potential (which is necessary for determining the total energies of the neutral and anionic cluster) that can treat the inductive effects of the excess electron and of the other molecules. Moreover, the equations governing the polarization of each molecule by the excess electron and by the other molecules must be solved self-consistently. Needless to say, these considerations add considerable complexity to the study of cluster anions.

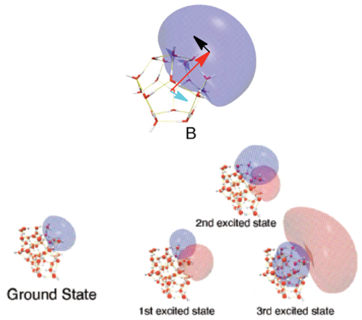

Figure 1. $(H_2O)_{20}^-$ anion and the orbital occupied by the excess electron in its ground state (top). The light blue vector is used to describe the location of an electron localized within the neutral cluster while the red and black vector sum gives the location of the excess electron in the orbital shown. Ground and excited electronic states of $(H_2O)_{45}^-$ anion showing the orbital occupied by the excess electron (bottom) in ground and excited states (adapted from Figures 10 and 12 in ref 11b).

However, it is not the purpose of this paper to address the valence-repulsion components of the electron–molecule potential, how to attenuate the long-range potentials, or how to treat molecule–molecule interactions in clusters. Nor is it our purpose to discuss how to choose parameters (e.g., point partial charges and their placements, exponential damping coefficients in cutoff functions, etc.) used in these aspects of the total one-electron potential. Workers cited later have devoted much effort to these issues with considerable success, and we do not have new insight to offer. Our goals here are to show how to uncover the long-range parts of the electron–molecule *one-electron potential* contained within the ab initio MPn EA expression and to understand what effects they contain. It is toward these goals that we now return.

D. The Kind of Systems To Be Considered. As stated above, we strive to identify the long-range nature of the one-electron potentials that one can use to describe interactions between a single excess electron and a closed-shell neutral molecule or cluster for cases in which it is safe to view the excess electron as primarily occupying a region of space outside that occupied by most of the electron density of the underlying molecule. The kinds of systems we have in mind are represented by the water cluster anion shown in Figure 1.

In these water cluster anions, one excess electron is bound in an orbital that is spatially localized rather distant from the other electrons in the neutral cluster. The excess electron occupies an orbital that might be classified as dipole bound[1] because the electron is bound primarily by the local dipole potentials generated by the surface water molecules in the upper right where we see that at least one of the water molecules has two of its O–H bonds directed outward, thus generating a large dipole potential that attracts the excess electron.

Of course, even for this kind of electron–molecule complex, some of the excess electron's density extends into regions of space occupied by the other electrons. Nice examples of such penetration effects, especially as they relate to hyperfine interactions between the excess electrons and nuclei within the water cluster to which it is bound, can be found in ref 2. However, because we want to focus on the asymptotic (i.e., large r) nature of the electron−molecule interaction potential, we need to (and are permitted to) introduce assumptions and approximations that are valid in such regions even if they are not valid elsewhere. Specifically, analogous to what is done in deriving expressions for van der Waals interactions between two systems,

(i) We will assume that the orbitals of the electron-molecule complex are sufficiently localized that we can identify (a) one set of orbitals localized primarily around the centroid of the excess electron's ground state charge density (these are expected to look like those shown in Figure 1 and will constitute the occupied and virtual orbital space "belonging" to the excess electron) and (b) the remaining orbitals, which will constitute the occupied and virtual orbital space of the underlying neutral.

(ii) We will carry out an expansion of the Coulomb potential $|\mathbf{r}_2 - \mathbf{r}_1|^{-1}$ in powers of $(r_</r_>)$ to achieve analytical expressions in powers of $(r_>)^{-1}$, and we will retain only terms of low order in $(r_>)^{-1}$.

(iii) We will assume that the important contributions to the correlated wave function of the anion are those in which only one electron occupies an orbital belonging to the excess electron; configurations in which zero or two or more electrons occupy these orbitals represent charge-transfer configurations that we will ignore.

With the above decomposition of the orbital space in mind, we can divide the spin−orbitals of the electron−molecule complex into four categories.

(i) The *upper case* index X will be used to label the singly occupied HF spin−orbital holding the excess electron in its ground state, and (ii) *upper case* $P = X + 1, X + 2$, etc., will label the excess electron's virtual spin−orbitals.

(iii) The *lower case* indices a and b will label occupied HF spin−orbitals ($\phi_1, \phi_2, ..., \phi_N$) of the underlying molecule, while (vi) *lower case* m and n will be used to label the corresponding virtual spin−orbitals.

The indices i, j, and k will be used to label arbitrary HF spin−orbitals belonging either to the neutral molecule or the excess electron.

The remainder of this paper is organized as follows. In section II, we describe the electron−molecule interaction energies that are present in the Koopmans' theorem and MP2-level expressions for the EA. In section III, we demonstrate how to use this information to define a one-electron potential that gives, when used in a one-electron Schrödinger equation, an eigenvalue equal to the MP2 EA and has large r character consistent with MP2 theory. In section IV, we summarize our findings, show how to extend to MP3, and discuss how our analysis relates to a very promising recent approach that has been used to treat the correlation components of electron−molecule interactions.

II. Ab Initio Expressions for Electron Affinities and Underlying Potentials

A. Koopmans' Theorem and Its Electrostatic Potential. In the simplest description of electron−molecule interactions, one uses the Fock operator of the neutral molecule to describe the behavior of the excess electron. In this way, one obtains, as an eigenvalue of this Fock operator, the Koopmans' theorem estimate of the EA. When used to describe the behavior of an excess electron that is not bound but whose energy lies in the continuum, this is called the static-exchange approach to electron−molecule scattering.[3,4] The N-electron Fock operator belonging to the underlying molecule can be written as a sum of N one-electron Fock operators $F_N(r_i)$ for a state in which N spin−orbitals (labeled a) are occupied

$$F_N = \sum_{i=1}^{N}\left\{-1/2\nabla_i^2 - \sum_{c=1}^{M}\frac{Z_c}{|r_i - R_c|} + \sum_{a=1}^{N}[J_a - K_a](r_i)\right\} = \sum_{i=1}^{N}F_N(r_i) \qquad (1)$$

Here, Z_c and R_c are the charge and position of the cth nucleus, and J_a and K_a are the Coulomb and exchange operators involving the ath occupied HF spin−orbital of the molecule whose action on a spin−orbital ϕ_j is

$$J_a\phi_j(r_i) = \int \phi_a{}^*(r')\phi_a(r')\frac{1}{|r_i - r'|}\,\mathrm{d}r'\phi_j(r_i) \qquad (2)$$

$$K_a\phi_j(r_i) = \int \phi_a{}^*(r')\phi_j(r')\frac{1}{|r_i - r'|}\,\mathrm{d}r'\phi_a(r_i) \qquad (3)$$

1. There Is No Net Coulomb Potential. To illustrate what electron−molecule potentials are contained in the Fock operators, let us consider various contributions to the $\langle\phi_X(r)|F_N(r)|\phi_X(r)\rangle$ matrix element for a system in which an excess electron in the spin−orbital ϕ_X can be assumed to be localized away from the electrons in the underlying neutral molecule. The first thing to note is that there is no net Coulomb contribution because the Coulomb components of the sum of all the electron−nuclei attractive potentials

$$\int \phi_X{}^*\left[-\sum_{a=1}^{M}\frac{Z_a}{|r - R_a|}\right]\phi_X\,\mathrm{d}r \qquad (4)$$

are *exactly* canceled by the Coulomb components of the sum of all the repulsive potentials generated by the N other electrons

$$\int \phi_X{}^*\sum_{a=1}^{N}J_a\phi_X\,\mathrm{d}r \qquad (5)$$

since the sum of all the nuclear charges $\Sigma_a Z_a$ is equal to the total number of electrons N in the molecule. (This can be proven by expanding $1/(|r - R_a|)$ and $1/(|r - r'|)$ for $r > R_a$ and $r > r'$, respectively, in powers of $|R_a|/|r|$ or $|r'|/|r|$ and keeping the lowest-order terms, which are $1/|r|$ in both cases. Other terms in these expansions varying as $|R_a|^L/|r|^{L+1}$ and $|r'|^L/|r|^{L+1}$ give the dipole ($L = 1$), quadrupole ($L = 2$), etc. electrostatic potentials.) The exchange terms $-\int\phi_X{}^*\sum_{a=1}^{N}K_a\phi_X\,\mathrm{d}r$ vanish at large r (i.e., when the excess electron is far from the molecule) because $K_a\phi_X$ decays exponentially with this distance. (Throughout this paper, exchange interactions between an orbital localized on the molecule and an orbital holding the excess electron will be neglected for this reason, which is consistent with the assumption of spatial septaration introduced earlier and upon which our analysis is based.) It is important to note that the N occupied spin−orbitals $\{\phi_a\}$ were obtained in a HF calculation on the neutral molecule. Thus, they contain no information about the presence of the excess electron in ϕ_X; in particular, they are not polarized by the excess electron.

2. The Dipole and Quadrupole Electrostatic Potentials. The electron−nuclear and electron−electron Coulomb potentials combine as in

$$\int \phi_X{}^*\left[-\sum_{a=1}^{M}\frac{Z_a}{|r - R_a|}\right]\phi_X\,\mathrm{d}r + \int \phi_X{}^*\sum_{a=1}^{N} J_a\phi_X\,\mathrm{d}r \tag{6}$$

to give rise to large r contributions from electron−dipole, electron−quadrupole, and higher electron−multipole potentials. (This can be proven by expanding $1/(|r - R_a|)$ and $1/(|r - r'|)$ for $r > R_a$ and $r > r'$, respectively, in powers of $|R_a|/|r|$ or $|r'|/|r|$ and keeping the lowest-order terms, which are $1/|r|$ in both cases. Other terms in these expansions varying as $|R_a|^L/|r|^{L+1}$ and $|r'|^L/|r|^{L+1}$ give the dipole ($L = 1$), quadrupole ($L = 2$), etc. electrostatic potentials. It is by examining how these potential look at large r that one creates the asymptotic form of a one-electron potential to use in studying electron−molecule interactions.) The first two are often written as

$$V_{\text{dipole}} = -\frac{\boldsymbol{\mu}\cdot\hat{r}e}{r^2} \tag{7}$$

and

$$V_{\text{quadrupole}} = -\frac{e(3\hat{r}\cdot\mathbf{Q}\cdot\hat{r} - \mathbf{I}\cdot\mathbf{Q}\cdot\mathbf{I}}{3r^3} \tag{8}$$

where, $\boldsymbol{\mu}$ and $\mathbf{Q}$ are the dipole moment vector and quadrupole moment tensor of the neutral molecule, $\mathbf{I}$ is the unit tensor, and $\hat{r}$ is a unit vector pointing from the molecule to the excess electron. We note that $\boldsymbol{\mu}$ and $\mathbf{Q}$ are the *permanent* dipole and quadrupole moments of the molecule; they have nothing to do with how the excess electron polarizes the molecule.

B. The Electrostatic Moments Appear at the HF Level. It is important to note that the Fock operator's dipole, quadrupole, and other electrostatic potentials (i.e., as embodied in eq 6) involve the corresponding moments evaluated at the HF level. Of course, there are corrections to $\boldsymbol{\mu}$ and $\mathbf{Q}$ caused by electron correlation, but these corrections do not alter the electron−molecule interaction energy until third order. To understand why correlation corrections to $\boldsymbol{\mu}$ and $\mathbf{Q}$ contribute first at third order, we first note that the dipole and quadrupole operators are one-electron operators that depend on the positions of the electrons and the positions and charges of the nuclei. Thus, because the first-order MP wave function contains only doubly excited Slater determinants, there are no first-order corrections to $\boldsymbol{\mu}$ and $\mathbf{Q}$. The second-order MP contributions to $\boldsymbol{\mu}$ and $\mathbf{Q}$ arise from the doubly excited determinants in the first-order MP wave function as well as from the singly excited determinants in the second-order MP wave function. However, even these second-order changes in $\boldsymbol{\mu}$ and $\mathbf{Q}$ do not contribute to the EA until third order because (i) it is by altering the molecule's electronic charge distribution that the interaction energy between the molecule and the excess electron is changed and (ii) the dipole and quadrupole components of this interaction energy are contained in Coulomb integrals of the form

$$\int \phi_X{}^*(r')\rho(r)\frac{1}{|r'-r|}\phi_X(r')\,\mathrm{d}r\,\mathrm{d}r' = \int \phi_X{}^*(r')\{\rho^0(r) + \delta\rho^2(r)\}\frac{1}{|r'-r|}\phi_X(r')\,\mathrm{d}r\,\mathrm{d}r' \tag{9}$$

where $\rho(\mathbf{r}')$ is the molecule's electron density, $\rho^0(\mathbf{r}')$ is its HF value, and $\delta\rho^2(\mathbf{r}')$ is the MP2 correction to this density (arising from both first-order double excitations and second-order single excitations). So, although there are second-order corrections to $\rho(\mathbf{r}')$, they induce third-order changes[5] in the electron−molecule interaction energy. These observations are important for the present work because they tell us what level of theory to use in the electrostatic moments (and, as we show later, in the polarizabilities) if one desires to match EAs computed at a specified level of ab initio theory. In particular, they tell us not to go beyond HF-level moments (i.e., the neutral's Fock operator) if our goal is to match MP2-quality EAs.

The above discussion raises the question of whether one should attempt to duplicate MP2-level EAs or whether a higher-level theory is essential. In some cases, the correlation changes to the electrostatic moments can be substantial; for example, for H_2O, the HF-level dipole moment is 2.2 D, while it is 1.85 D at the MP2 level. One might then expect that an MP2-level calculation of the EAs of water clusters would not be highly accurate because the exaggerated HF-level dipole moment might give rise to exaggerated EAs. Thus, one should probably employ a theory (ab initio or one-electron potential based) that is more accurate than MP2 in such cases. For example, one could employ MP3 theory, which would allow for the correlation-derived renormalization of the electrostatic moments as discussed earlier, or one could employ a one-electron model potential that is consistent with MP3.

C. Short-Range Potentials. In addition to the above large r potentials, $\langle\phi_X(r)|F_N(r)|\phi_X(r)\rangle$ contains contributions from shorter-range valence potentials that are both attractive and repulsive. For example, in the oxygen atom ($1s^22s^22p^4$; ^3P), the nitrogen atom ($1s^22s^22p^3$; ^4S), or the methoxy radical $H_3C{-}O$ (^2E), there are regions of space (e.g., in the half-filled 2p orbitals of the former two and in the oxygen-localized e-symmetry orbital of the latter) where there are valence-range attractive potentials. The strength of these potentials depends on the electronegativity of the atom(s) where the orbital is localized (e.g., it is stronger for O than for N). The valence repulsive potentials arise from the 8 O $1s^22s^22p^4$, 7 N $1s^22s^22p^3$, or 17 $H_3C{-}O$ electrons' Coulomb and exchange interactions with the extra electron when the latter tries to occupy the half-filled orbital. The latter potentials are often called exchange-repulsion potentials. As discussed earlier, they are not the focus of the present paper; it is the large r potentials that we want to characterize.

In summary, the N-electron Fock operator, when acting on the excess electron, contains short-range exchange-repulsion, short-range valence potentials, as well as all long-range electrostatic (i.e., charge-dipole, charge-quadrupole, etc.) potentials within the HF level of theory. Therefore, Koopmans' theorem EA includes contributions from all of these terms, but not more.

To gain an appreciation for how large the various electrostatic (HF and beyond), orbital relaxation, and correlation (discussed later) contributions to the EA are for the kind of species considered here, one can look at Tables 1, 3, and 4 in ref 1. The numerical results shown there illustrate that orbital relaxation and electron correlation effects can play important roles in determining the EA, which suggests that using an electron−molecule potential that is capable of representing such effects is important.

Before moving on to discuss orbital relaxation (i.e., induction) and correlation, we want to point out that there are situations in which the approach underlying the developments we offer here will not be fruitful. In particular, if the Koopmans' theorem-level description of the electron-molecule interaction is qualitatively inaccurate, it is probably foolish to pursue a path such as Møller−Plesset theory that assumes its corrections to *KT* are small. For example, if the excess electron is not even bound at the *KT* level (i.e., if the orbital energy ε_X for the lowest virtual orbital of the neutral is positive), the approach offered here cannot be expected to be useful.

D. Beyond Koopmans' Theorem: Relaxation and Correlation. ***1. Equations of Motion Theory.*** It has long been known that it is possible to develop a computational approach in which a one-electron operator, analogous to the Fock operator, has eigenvalues that correspond to EAs (and ionization potentials (IPs)) whose accuracy goes beyond Koopmans' theorem. In the 1970s, the author and his co-workers developed[6] (through third order in Møller−Plesset (MP) perturbation theory) what is called the *equations of motion* (EOM) theory for EAs. Within this theory, the EA of a molecule is obtained as an eigenvalue of a matrix

$$H_{i,j} = F_{i,j} + \Sigma_{i,j} \tag{10}$$

given in terms of the matrix elements $F_{i,j}$ of the neutral molecule's Fock matrix plus those of the so-called self-energy matrix $\Sigma_{i,j}$. Explicit expressions for $\Sigma_{i,j}$ are given in ref 6 through third order in MP theory and discussed further in a recent review[7] by the author within second order.

It might appear that by forming the $i = j = X$ element[8] of $F_{i,j} + \Sigma_{i,j}$, one would have in hand exactly what this paper strives to achieve, a one-electron electron−molecule interaction potential capable of generating EAs in agreement with ab initio theory through second or third order (depending on the order to which the self-energy is written). However, this is not quite the case; the self-energy matrix elements must be subjected to further analysis and approximation before one can extract the kind of local, long-range, one-electron potential that is desired. This additional analysis is how we obtain expressions involving the dipole polarizability and higher polarizabilities, and it is precisely this analysis that we now undertake.

Using EOM theory, the author showed[6] that the neutral-anion energy difference (i.e., the vertical EA) can be expressed at the MP2 level as follows (Recall that the lower case indices *a*, *b*, *m*, and *n* and the upper case indices *X* and *P* run over distinct sets of spin−orbitals. The indices *a* and *b* run over the *N* HF-occupied spin−orbitals f1, f2, ..., f*N*; *m* and *n* run over the corresponding virtual spin−orbitals. *X* labels the HF-occupied orbital f*X* holding the excess electron and *P* labels virtual orbitals for this electron.):

$$\begin{aligned}-\mathrm{EA} = \varepsilon_X + &\sum_{a=1}^{N}\sum_{n}^{\infty}\frac{\langle X,n|X,a\rangle\langle X,a|X,n\rangle}{\varepsilon_a+\varepsilon_X-\varepsilon_n-\varepsilon_X} + \\ &\sum_{a=1}^{N}\sum_{n,P}^{\infty}\frac{\langle P,n|X,a\rangle\langle X,a|P,n\rangle}{\varepsilon_a+\varepsilon_X-\varepsilon_P-\varepsilon_n} + \\ &\sum_{a<b}^{N}\sum_{n}^{\infty}\frac{\langle a,b|n,X\rangle\langle n,X|a,b\rangle}{\varepsilon_n+\varepsilon_X-\varepsilon_a-\varepsilon_b}\end{aligned} \tag{11}$$

where ε_X is the Koopmans' theorem estimate obtained as an eigenvalue of the *N*-electron Fock operator $F_N(r)$ of the neutral molecule.

In the numerators of the three sums in eq 11, which come from the self-energy matrix, the two-electron integrals are defined as

$$\begin{aligned}\langle ij|kl\rangle = &\int \phi_i^*(r)\phi_j^*(r')\frac{1}{|r-r'|}\phi_k(r)\phi_l(r')\,\mathrm{d}r\,\mathrm{d}r' - \\ &\int \phi_i^*(r)\phi_j^*(r')\frac{1}{|r-r'|}\phi_l(r)\phi_k(r')\,\mathrm{d}r\,\mathrm{d}r'\end{aligned} \tag{12}$$

and, in the denominators the ε_a, ε_m, ε_X, and ε_P are HF orbital energies of occupied and virtual molecule-localized and occupied and virtual excess-electron spin−orbitals, respectively.

2. Orbital Relaxation (Induction) and New Correlation (Dispersion-like) Energies. The three sums in eq 11 were earlier shown by the author (see ref 6) to be the MP2-level contributions to EA due to (i) changes (called induction or relaxation) in the occupied HF spin−orbitals (labeled a) induced by the presence of the excess electron in the spin−orbital ϕ_X (These relaxations generate the perturbative corrections to EA that attempt to replicate the so-called ΔSCF approximation to EA.), (ii) the pair correlation energy between the excess electron in the spin−orbital ϕ_X and the *N* other electrons in spin−orbitals labeled *a*, and (iii) the loss in pair correlation energies for electron pairs in spin−orbitals labeled *a* and *b* due to the presence of the excess electron in the spin−orbital ϕ_X, respectively. The first two contributions act to differentially stabilize the anion, while the third differentially destabilizes the anion.

E. Relaxation Contains Mean-Field Polarization. Let us further examine the electron−molecule potentials contained within the orbital-relaxation contribution to EA. The first summation in eq 11 consists of terms summed over all of the molecule's occupied spin−orbitals (labeled *a*). Each term contains a coefficient

$$C_a^{\,n} = \frac{\langle X,a|X,n\rangle}{\varepsilon_a+\varepsilon_X-\varepsilon_n-\varepsilon_X} = \frac{\langle\phi_a|J_X-K_X|\phi_n\rangle}{\varepsilon_a-\varepsilon_n} \tag{13}$$

that is the first-order perturbation theory amplitude for the change in spin−orbital ϕ_a induced by its Coulomb and exchange interactions with the excess electron in ϕ_X. This amplitude then multiplies the virtual spin−orbital ϕ_n to form the relaxed spin−orbital $\phi_{a,\mathrm{relexed}}$

$$\phi_{a,\mathrm{relaxed}} = \phi_a + \sum_{n}^{\infty} C_a^{\,n}\phi_n \tag{14}$$

It is by inducing such changes in the neutral's occupied spin−orbitals that the excess electron causes the neutral's electron density to become that of the anion.

The corresponding second-order relaxation energy $\Delta E^a{}_{\mathrm{relaxation}}$ of the spin−orbital ϕ_a is given by the matrix element of the perturbation $(J_X - K_X)$ coupling ϕ_a to $\phi_{a,\mathrm{relaxed}}$

$$\begin{aligned}\Delta E^a\mathrm{relaxation} &= \sum_{n}^{\infty} C_a^{\,n}\langle\phi_n|J_X-K_X|\phi_a\rangle \\ &= \sum_{n}^{\infty}\frac{\langle\phi_a|J_X-K_X|\phi_n\rangle\langle\phi_n|J_X-K_X|\phi_a\rangle}{\varepsilon_a-\varepsilon_n}\end{aligned} \tag{15}$$

The sum (over *a*) of such contribution is what we see in the first summation in eq 11.

The sum over n runs only over the unoccupied spin−orbitals of the underlying neutral molecule, not over any of the spin−orbitals (ϕ_X or ϕ_P) of the excess electron. Terms in which, for example, $n = P$ (a spin−orbital of the excess electron) represent charge-transfer configurations in which two excess electrons (one in ϕ_X another in ϕ_P) are bound to a cationic molecular core. (All such charge-transfer configurations are neglected throughout this paper.) Such terms can be neglected here because their amplitudes would involve (see eq 13) integrals of the form $\langle X,a|X,P\rangle$, which exponentially vanish because ϕ_P is a spin−orbital localized exterior to the neutral molecule while ϕ_a is localized on the molecule.

F. Focus on Large *r* Forms of the Potentials. To further interpret these relaxation energies, and later when examining the correlation energies, we use the following expression for the electron−electron Coulomb interaction potential to separate the integrals appearing in eq 15 into factors depending on the coordinates of the N electrons in the neutral molecule and the coordinate of the one excess electron

$$\frac{1}{|r_< - r_>|} = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\frac{4\pi}{2L+1}Y_{L,M}{}^*(\theta_<,\phi_<)Y_{L,M}(\theta_>,\phi_>)\frac{r_<^{\,L}}{r_>^{\,L+1}} = \sum_{L=0}^{\infty}P_L(\cos\omega_{<,>})\frac{r_<^{\,L}}{r_>^{\,L+1}} \qquad (16)$$

Here $\mathbf{r}_<$ and $\mathbf{r}_>$ label the coordinates of the electrons closest to and furthest from the origin, respectively, and $\omega_{<,>}$ is the angle between the two vectors $\mathbf{r}_<$ and $\mathbf{r}_>$. (The coordinate $\mathbf{r}_>$ will be taken as equivalent to r_{N+1}, the coordinate of the excess electron, throughout this paper.) It is by using this expansion that we are able, throughout this paper, to develop expressions for electron−molecule interaction potentials in powers of $(\mathbf{r}_>)^{-1}$, as one desires for writing the long-range form of such potentials.

To illustrate, for the water cluster anion shown in Figure 1, where we choose the origin of our coordinate system to be within the molecular cluster, the light blue vector gives the location $\mathbf{r}_<$ of an electron of the neutral cluster. The location $\mathbf{r}_>$ of the excess electron is the vector sum of the red vector (giving the centroid of the orbital holding the excess electron) and the black vector (giving the instantaneous location of the excess electron relative to the ϕ_X orbital centroid). Expressing $\mathbf{r}_>$ in this manner allows us later to determine how various contributions to EA scale with the distance (the length of the red vector) between the molecule and the centroid of the excess electron's charge density.

Inserting the expansion in eq 16 into the two-electron integral appearing in the numerator of eq 15, we obtain

$$\langle X,a|X,n\rangle = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\frac{4\pi}{2L+1}\left\langle X\middle|Y_{L,M}\frac{1}{r^{L+1}}\middle|X\right\rangle\langle a|Y_{L,M}{}^*r^L|n\rangle \qquad (17)$$

where the integrations over $\mathbf{r}_>$ and $\mathbf{r}_<$ occur in the first and second integrals, respectively. The $L = 0$ contributions in eq 17 vanish because orbitals ϕ_a and ϕ_n are orthogonal. The lowest-order term (We will focus primarily on the lowest-order terms arising in each contribution to EA as a means of determining the electron−molecule potentials of longest range. Of course, considering terms with $L > 1$ would allow one to derive expressions for potentials of shorter range and higher angular anisotropy; it is by pursuing such higher-order terms that one could improve upon the development provided in this paper.), and that having the longest range in the $r_>$ variable, arises from $L = 1$ and is

$$\langle X,a|X,n\rangle_{L=1} = \sum_{M=-1}^{1}\frac{4\pi}{3}\left\langle X\middle|Y_{1,M}\frac{1}{r^2}\middle|X\right\rangle\langle a|Y_{1,M}{}^*r^1|n\rangle \qquad (18)$$

The integral over the $r_>$ variables

$$\left\langle X\middle|Y_{1,M}\frac{1}{r^2}\middle|X\right\rangle = \int_{\text{blackarrow}}|\phi_X(r_{\text{red}}+r_{\text{black}})|^2\frac{Y_{1,M}}{(r_{\text{red}}+r_{\text{black}})^2}\,\mathrm{d}r_{\text{black}} \qquad (19)$$

can be interpreted as the average over the probability density $|\phi_X|^2$ of a quantity that is the $Y_{1,M}$ component of the charge density of the excess electron divided by the square of the distance ($r_{\text{red}} + r_{\text{black}}$). (The variable r_{black} ranges over the volume occupied by the orbital shown in Figure 1.) This integral is expected to scale as $r_{\text{red}}{}^{-2}$ with the distance between the molecule and the centroid of the orbital holding the excess electron; because squares of these integrals appear in $\Delta E^a{}_{\text{relaxation}}$, this energy contribution is expected to scale as $r_{\text{red}}{}^{-4}$. The other integrals $\langle a|Y_{1,M}{}^*r^L|n\rangle$ are the various M-components of the transition dipole matrix element between ϕ_a and ϕ_n.

When eq 18 is inserted into eq 15, we obtain an expression for the $L = 1$ component of the orbital relaxation contribution to EA

$$\Delta E^{L=1}\text{relaxation} = \sum_{a,n}\frac{1}{\varepsilon_a-\varepsilon_n}\left|\sum_{M=-1}^{1}\frac{4\pi}{3}\left\langle X\middle|Y_{1,M}\frac{1}{r^2}\middle|X\right\rangle \times \langle a|Y_{1,M}^*r^1|n\rangle\right|^2 \qquad (20)$$

This result can be seen to contain the components of the polarizability tensor (More precisely, this is the dipole polarizability; there are higher polarizabilities arising from higher-L components in eq 16.) $\alpha_{M,M'}$ of the underlying molecule (evaluated at the HF level)

$$\alpha_{M,M'} = 2\frac{4\pi}{3}\sum_{a,n}\frac{\langle a|rY_{1,M}|n\rangle\langle n|rY_{1,M'}{}^*|a\rangle}{\varepsilon_n-\varepsilon_a} \qquad (21)$$

as well as factors $\langle X|Y_{1,M}{}^*(1/r^2)|X\rangle\langle X|Y_{1,M'}(1/r^2)|X\rangle$ that, according to eq 19, scale as r_{red}^{-4} with the distance r_{red} between the molecule and the centroid of the excess electron's charge distribution, as expected for a polarization-related potential.

This shows clearly that orbital relaxation contains, in its $L = 1$ component, the *mean-field polarization* of the neutral molecule's electron density resulting from its interaction with an electron density given by $Y_{1,M}\,|\phi_X|^2$. It is a mean-field polarization because the molecule is polarized not by the instantaneous Coulomb potential of the excess electron but by the spatially averaged charge density $Y_{1,M}\,|\phi_X|^2$. The higher-order (i.e., $L = 2, 3, ...$) terms of eq 16 contribute factors scaling as r_{red}^{-6}, r_{red}^{-8}, etc., and represent contributions to mean-field quadrupole and higher polarizations.

G. Large *r* Analysis of the New Correlation and Correlation Loss Energies. In the correlation contribution to the EOM's EA expression, we see two sums. The terms in the second sum

$$\Delta E_{\text{newcorrelation}} = \sum_{a=1}^{N} \sum_{n,P}^{\infty} \frac{\langle P, n|X, a\rangle\langle X, a|P, n\rangle}{\varepsilon_a + \varepsilon_X - \varepsilon_n - \varepsilon_P} \tag{22}$$

represent the dynamical correlation energy between the excess electron in ϕ_X and another electron in ϕ_a. (Recall that n and P run over the unoccupied spin–orbitals of the molecule and excess electron, respectively.) These contributions have a form that has been described[9] in terms of a dispersion or van der Waals-like interaction between the excess electron and the electrons of the neutral molecule. One might expect such factors to scale as r_{red}^{-6} in analogy with how van der Waals potentials scale, but as we show below, this is not the case; instead, their contributions scale as r_{red}^{-4} and thus contribute to the electron–molecule polarization potential.

The third sum

$$\Delta E_{\text{correlationloss}} = \sum_{a<b}^{N} \sum_{n}^{\infty} \frac{\langle a, b|n, X\rangle\langle n, X|a, b\rangle}{\varepsilon_n + \varepsilon_X - \varepsilon_a - \varepsilon_b} \tag{23}$$

represents the *loss* in the correlation energy between the two electrons in ϕ_a and ϕ_b caused by the occupancy of ϕ_X in the anion. In the neutral, doubly excited determinants in which ϕ_a and ϕ_b are promoted to ϕ_n and ϕ_X *do contribute* to the correlation energy. However, in the anion, promotions of ϕ_a and ϕ_b to ϕ_n and ϕ_X cannot occur because the spin–orbital ϕ_X is already occupied. So, the occupancy of ϕ_X in the anion "blocks" certain double excitations of the other N electrons and thus modifies the correlation energy of these N electrons.

In carrying out an analysis of the asymptotic r dependence of the *new correlation* and *correlation loss* contributions to EA, we use a strategy similar to that employed above for the relaxation energy. For example, in the numerator of eq 22 there appear products of integrals that can be written using the expansion in eq 16 as follows

$$\langle X, a|P, n\rangle = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \frac{4\pi}{2L+1} \left\langle X \middle| Y_{L,M} \frac{1}{r^{L+1}} \middle| P \right\rangle \langle a|Y_{L,M}{}^{*} r^{L}|n\rangle \tag{24}$$

Again focusing on the $L = 1$ components, we obtain

$$\langle X, a|P, n\rangle_{L=1} = \sum_{M=-1}^{1} \frac{4\pi}{3} \left\langle X \middle| Y_{1,M} \frac{1}{r^{2}} \middle| P \right\rangle \langle a|Y_{1,M}{}^{*} r^{1}|n\rangle \tag{25}$$

Unlike the orbital-relaxation case, these integrals now contain products of two transition moments—one involving the $\mathbf{r}_<$ variable and the other involving the $\mathbf{r}_>$ variable. (Unlike in eq 20 where the diagonal matrix element $\langle X|Y_{1,M}(1/r^2)|X\rangle$ appears and can be shown to scale as $r_{\text{red}>}{}^{-2}$, here we have the transition element $\langle X|Y_{1,M}(1/r^2)|P\rangle$, which cannot be assumed to scale as r_{red}^{-2}. So, at this point, it remains to be shown (which we do later) that the correlation energy contributions indeed scale as r_{red}^{-4} not as r_{red}^{-6} as dispersion energies do.)

$$\left\langle X \middle| Y_{1,M} \frac{1}{r^{2}} \middle| P \right\rangle = \int_{\text{blackarrow}} \phi_X{}^{*}(r_{\text{red}} + r_{\text{black}}) \frac{Y_{1,M}}{(r_{\text{red}} + r_{\text{black}})^{2}} \phi_P(r_{\text{red}} + r_{\text{black}})\, \mathrm{d}r_{\text{black}} \tag{26}$$

Later, we will make use of this and analogous treatments when decomposing the correlation components of the EA expression given in eq 11, but first we need to discuss how people often go about defining a polarization potential. We then return to compare the polarization potentials thus obtained with the large r decompositions of the MP2-level EAs introduced above to see if the two approaches reconcile.

III. A Polarization Potential Consistent with MP2

Earlier, we showed that the orbital relaxation contribution to EA involved the mean-field polarization of the underlying molecule by the excess electron. However, one might desire to introduce a different kind of polarization interaction, as has been shown to be of much utility in many electron–molecule and electron–cluster studies,[10,11] that goes beyond the mean-field approximation, which is what we explore in this section.

The total Born–Oppenheimer Hamiltonian for the N-electron neutral molecule can be written as a sum of the N-electron Fock operator and the N-electron fluctuation potential

$$H_N = F_N + \sum_{i<j=1}^{N} \frac{1}{|r_i - r_j|} - \sum_{i=1}^{N}\sum_{a=1}^{N} [J_a - K_a](r_i) \tag{27}$$

The fluctuation potential appearing in eq 27 is the difference between the true Coulomb interactions among the N electrons and the mean-field ($J_a - K_a$) potentials experienced by each of the N electrons. The corresponding Hamiltonian for the $N + 1$ electron anion is given by

$$H_{N+1} = H_N - 1/2\nabla_{N+1}{}^2 - \sum_{c=1}^{M} \frac{Z_c}{|r_{N+1} - R_c|} + \sum_{a=1}^{N} [J_a - K_a](r_{N+1}) + \sum_{i=1}^{N} \frac{1}{|r_i - r_{N+1}|} - \sum_{a=1}^{N} [J_a - K_a](r_{N+1}) \tag{28}$$

which is equivalent to

$$H_{N+1} = H_N + F_N(r_{N+1}) + \sum_{i=1}^{N} \frac{1}{|r_i - r_{N+1}|} - \sum_{a=1}^{N} [J_a - K_a](r_{N+1}) \tag{29}$$

where $F_N(\mathbf{r}_{N+1})$ is the Fock operator of the N-electron neutral molecule acting on the coordinate of the excess electron $\mathbf{r}_{N+1}$. In eq 29, the $(N + 1)$-electron Hamiltonian is written as the N-electron Hamiltonian plus the N-electron Fock operator acting on $\mathbf{r}_{N+1}$ plus the fluctuation potential of the excess electron.

A. Defining a Polarization Potential. The next step[12] in deriving a polarization potential is to consider a N-electron Hamiltonian that has added to it the Coulomb interactions of its N electrons with the $(N + 1)^{\mathrm{st}}$ electron whose position is held fixed at $\mathbf{r}_{N+1}$

$$H_N^{\mathrm{pol}} = H_N + \sum_{i=1}^{N} \frac{1}{|r_i - r_{N+1}|} \tag{30}$$

The eigenvalues and eigenfunctions of this Hamiltonian will depend parametrically on the location of the excess electron. The introduction of H_N^{pol} and the subsequent developments given below amount to making an *adiabatic treatment* of the $(N + 1)^{\mathrm{st}}$ electron. That is, by initially holding $\mathbf{r}_{N+1}$ fixed, one is taking a step much like in the Born−Oppenheimer approximation where one begins by holding the nuclei fixed. Of course, this then raises the question of how important non-Born−Oppenheimer type corrections will be for the (N + 1)-electron system when such a polarization potential is used to describe it. In Figures 4 and 5 of ref 11b this adiabatic potential, computed at the MP2 level, is plotted for the electron−water system and compared to several one-electron model potentials that have been commonly used. These comparisons show that even though a model potential can reproduce an accurate EA, it may not have radial and angular characters consistent with such an ab initio-derived potential.

Returning to our derivation, we then express H_N as in eq 27, and treat the N-electron Fock operator F_N as a zeroth-order Hamiltonian and both the N-electron fluctuation potential

$$V_N = \sum_{i<j=1}^{N} \frac{1}{|r_i - r_j|} - \sum_{i=1}^{N}\sum_{a=1}^{N} [J_a - K_a](r_i) \tag{31}$$

and the Coulomb potential of the $(N + 1)^{\mathrm{st}}$ electron interacting with the N other electrons

$$\delta V = \sum_{i=1}^{N} \frac{1}{|r_i - r_{N+1}|} \tag{32}$$

as perturbations, both of which are first order in the electron−electron interaction strength. This perturbative approach to determining the energy and wave function of the ground state of the N-electron molecule in the presence of a spatially fixed (N + 1) electron then yields the following zeroth- through second-order energies and zeroth- and first-order wave functions. The zeroth-order wave function

$$\psi^0 = |\phi_1\phi_2 ... \phi_a\phi_N| \tag{33}$$

is the single Slater determinant in which the N occupied HF spin−orbitals of the neutral molecule appear, and the zeroth-order energy

$$E^0 = \sum_{a=1}^{N} \varepsilon_a \tag{34}$$

is the sum of the HF orbital energies of the N-electron Fock operator of the neutral.

The first-order energy contains contributions from the interaction of the neutral's N electrons with the $(N+1)^{\mathrm{st}}$ electron as well as the usual sum of Coulomb minus exchange integrals $(J_{a,b}-K_{a,b})$ that correct for the double counting of the electron−electron interactions that occurs in E^0

$$E^1 = \left\langle \psi^0 \middle| V_N + \delta V \middle| \psi^0 \right\rangle = \sum_{a=1}^{N} \int \phi_a{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< - \frac{1}{2} \sum_{a,b=1}^{N} (J_{a,b} - K_{a,b}) \tag{35}$$

where $P_{>,<}$ is the operator that interchanges $\mathbf{r}_>$ and $\mathbf{r}_<$ to generate the exchange contribution. The first-order wave function contains both singly $|(n)/(a)\rangle$ and doubly $|(n,m)/(a,b)\rangle$ excited Slater determinants

$$\psi^1 = \sum_{a=1}^{N} \sum_{n}^{\infty} \frac{\left\langle \frac{n}{a} \middle| V_N + \delta V \middle| \psi^0 \right\rangle \left| \frac{n}{a} \right\rangle}{\varepsilon_a - \varepsilon_n} + \sum_{a<b=1}^{N} \sum_{n<m}^{\infty} \frac{\left\langle \frac{n,m}{a,b} \middle| V_N + \delta V \middle| \psi^0 \right\rangle \left| \frac{n,m}{a,b} \right\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_n - \varepsilon_b} = \sum_{a=1}^{N} \sum_{n}^{\infty} \frac{\int \phi_n{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_<}{\varepsilon_a - \varepsilon_n} \left| \frac{n}{a} \right\rangle + \sum_{a<b=1}^{N} \sum_{n<m}^{\infty} \frac{\left\langle n, m \middle| a, b \right\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_n - \varepsilon_b} \left| \frac{n,m}{a,b} \right\rangle \tag{36}$$

in which one electron is promoted from ϕ_a to ϕ_n or two electrons are promoted from ϕ_a and ϕ_b to ϕ_n and ϕ_m, respectively. ($\langle (n/a)|V_N|\psi^0\rangle$ vanishes by the Brillouin condition, and $\langle (n,m/a,b)|\delta V|\psi^0\rangle$ vanishes because δV is a one-electron operator in the space of the N electrons.). Finally, the second-order energy

$$E^2 = \sum_{a=1}^{N} \sum_{n}^{\infty} \frac{\left| \int \phi_n{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< \right|^2}{\varepsilon_a - \varepsilon_n} + \sum_{a<b=1}^{N} \sum_{n<m}^{\infty} \frac{\left| \left\langle n, m \middle| a, b \right\rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_n - \varepsilon_b} \tag{37}$$

has contributions from these singly and doubly excited determinants when E^2 is evaluated as $\langle \psi^0 | V_N + \delta V | \psi^1 \rangle$.

Some of the contributions to $E^0 + E^1 + E^2$ do not depend on the location $\mathbf{r}_>$ of the excess electron. These include all of E^0, the second terms on the right-hand side of eq 35, and the second sums in eq 37, and add up to yield the HF energy of the neutral plus its second-order correlation energy E_N(HF+MP2). In contrast, the first terms in eqs 35 and 37 are functions of the $(N+1)^{\mathrm{st}}$ electron's coordinate; it is these terms (defined as $U(\mathbf{r}_>)$)

$$U(r_>) = \sum_{a=1}^{N} \int \phi_a{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< + \sum_{a=1}^{N} \sum_{n}^{\infty} \frac{\left| \int \phi_n{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< \right|^2}{\varepsilon_a - \varepsilon_n} \equiv \sum_{a=1}^{N} \int \phi_a{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< + U_{\mathrm{pol}}(r_>) \tag{38}$$

that we now need to analyze further to see how $U(\mathbf{r}_>)$ relates to the desired polarization potential as suggested by the second equality in eq 38.

B. Obtaining a Polarized Orbital and Orbital Energy from $U_{\mathrm{pol}}(r_>)$. The first thing to notice about $U(\mathbf{r}_>)$ is that its first term is nothing but the Coulomb minus exchange contribution to the N-electron Fock operator F_N acting on $r_>$ (which is the same as r_{N+1}, under the assumption that the excess electron is localized far from the molecule)

$$\sum_{a=1}^{N} \int \phi_a{}^*(r_<) \frac{1 - P_{>,<}}{|r_> - r_<|} \phi_a(r_<)\, \mathrm{d}r_< = \sum_{a=1}^{N} (J_a - K_a)(r_>) \tag{39}$$

so, it relates to the HF-level electrostatic potential. This suggests that one could define the second term in eq 38 as a polarization potential $U_{\mathrm{pol}}(\mathbf{r}_>)$ and then use it in the one-electron Schrödinger equation

$$[F_N(r_>) + U_{\mathrm{pol}}(r_>)]\phi_{\mathrm{pol}} = \varepsilon_{\mathrm{pol}} \phi_{\mathrm{pol}} \tag{40}$$

to obtain a polarized orbital ϕ_{pol} and its orbital energy $\varepsilon_{\mathrm{pol}}$. With the energy of the neutral molecule then expressed as E_N(HF+MP2), and the energy of the polarized $(N+1)^{\mathrm{st}}$ electron's orbital as $\varepsilon_{\mathrm{pol}}$, it remains to determine how the energy of the $(N+1)^{\mathrm{st}}$ electron system through second order (as with E_N) can be related to the sum $\varepsilon_{\mathrm{pol}} + E_N$(HF+MP2).

C. Relating $\varepsilon_{\mathrm{pol}}$ to the EA of MP2 Theory. To see whether $\varepsilon_{\mathrm{pol}}$ can reproduce the ab initio expression for −EA given in eq 11, it is instructive to use the $L = 1$ components of the expansion for $|r_> - r_<|^{-1}$, as given in eqs 16 and 18 and in eqs 11 and 38. The results for the relaxation and correlation components to −EA are

$$\Delta E^{L=1}\text{relaxation} = \sum_{a,n}\frac{1}{\varepsilon_a - \varepsilon_n}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|Y_{1,M}\frac{1}{r^2}\middle|X\right\rangle\langle a|Y_{1,M}{}^*r^1|n\rangle\langle n|Y_{1,M'}r^1|a\rangle\left\langle X\middle|Y_{1,M'}{}^*\frac{1}{r^2}\middle|X\right\rangle \tag{41}$$

$$\Delta E^{L=1}\text{newcorrelation} = \sum_{a=1}^{N}\sum_{n,P}^{\infty}\frac{1}{\varepsilon_a + \varepsilon_X - \varepsilon_n - \varepsilon_P}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|\frac{Y_{1,M}}{r^2}\middle|P\right\rangle\left\langle P\middle|\frac{Y_{1,M'}{}^*}{r^2}\middle|X\right\rangle\langle a|rY_{1,M}{}^*|n\rangle\langle n|rY_{1,M'}|a\rangle \tag{42}$$

$$\Delta E^{L=1}\text{correlationloss} = \sum_{a<b1}^{N}\sum_{n}^{\infty}\frac{1}{\varepsilon_n + \varepsilon_X - \varepsilon_b - \varepsilon_a}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|\frac{Y_{1,M}}{r^2}\middle|a\right\rangle\left\langle a\middle|\frac{Y_{1,M'}{}^*}{r^2}\middle|X\right\rangle\langle b|rY_{1,M}{}^*|n\rangle\langle n|rY_{1,M'}|b\rangle \tag{43}$$

To compare these components of −EA to ε_{pol}, we consider solving eq 40 in a perturbative manner realizing the $F_N(\mathbf{r}_>)$ is zeroth order and $U_{\text{pol}}(\mathbf{r}_>)$ is second order in the electron−electron interaction strength. This means that ϕ_X and ε_X, the Koopmans' theorem results, are the zeroth-order approximations to ϕ_{pol} and ε_{pol}, respectively, and that the perturbative corrections are

$$\phi_{\text{pol}} = \phi_X + \text{second order} + ... \tag{44}$$

and

$$\varepsilon_{\text{pol}} = \varepsilon_X + \langle\phi_X|U_{\text{pol}}(r_>)|\phi_X\rangle + \text{fourth order} + ... \tag{45}$$

Substituting the explicit expression for U_{pol} (eq 38) into eq 45 yields (through second order)

$$\begin{aligned}\varepsilon_{\text{pol}} = \varepsilon_X + \left\langle\phi_X\middle|\sum_{a=1}^{N}\sum_{n}^{\infty}\frac{\left|\int\phi_n{}^*(r_<)\frac{1-P_{>,<}}{|r_> - r_<|}\phi_a(r_<)\,\mathrm{d}r_<\right|^2}{\varepsilon_a - \varepsilon_n}\middle|\phi_X\right\rangle = \varepsilon_X + \sum_{a,n}\frac{1}{\varepsilon_a - \varepsilon_n}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|Y_{1,M}\frac{1}{r^2}\langle a|Y_{1,M}{}^*r^1|n\rangle\right.\\ \left.\langle n|Y_{1,M'}r^1|a\rangle Y_{1,M'}{}^*\frac{1}{r^2}\middle|X\right\rangle + ... = \varepsilon_X + \sum_{a,n}\frac{1}{\varepsilon_a - \varepsilon_n}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|Y_{1,M}\frac{1}{r^2}Y_{1,M'}{}^*\frac{1}{r^2}\middle|X\right\rangle\langle a|Y_{1,M}{}^*r|n\rangle\langle n|Y_{1,M'}r|a\rangle + ...\end{aligned} \tag{46}$$

At first glance, it appears that the expressions for ε_{pol} in eq 46 and for −EA in eq 11 as ε_X plus the relaxation, new correlation, and correlation loss energies do not reconcile. However, with one reasonable approximation, they can be shown to be essentially identical. Specifically, if the $(N + 1)^{\text{st}}$ electron is very weakly bound, as it often is when localized exterior to and distant from a closed-shell neutral molecule, the denominators $(\varepsilon_a + \varepsilon_X - \varepsilon_n - \varepsilon_P)$ appearing in the new correlation contribution of eq 42 can be approximated by $(\varepsilon_a - \varepsilon_n)$ because the excitation energies associated with the excess electron $(\varepsilon_X - \varepsilon_P)$ are much smaller than those associated with the valence electrons of the underlying neutral molecule. (Of course, ε_P can extend into the continuum describing states in which the excess electron is detached. However, for continuum orbitals ϕ_P having appreciable kinetic energy, the matrix elements $\langle X|(Y_{1,M}/r^2)|P\rangle$ are expected to be very small because of the oscillatory nature of ϕ_P.) Making this approximation and using the completeness relation

$$1 = |X\rangle\langle X| + \sum_P|P\rangle\langle P| \tag{47}$$

the expression for the $L = 1$ component of the new correlation energy can be rewritten as

$$\begin{aligned}\Delta E^{L=1}\text{newcorrelation} = \sum_{a=1}^{N}\sum_{n,P}^{\infty}\frac{1}{\varepsilon_a - \varepsilon_n}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\langle X\middle|\frac{Y_{1,M}}{r^2}\middle|P\right\rangle\left\langle P\middle|\frac{Y_{1,M'}{}^*}{r^2}\middle|X\right\rangle\langle a|rY_{1,M}{}^*|n\rangle\langle n|rY_{1,M'}|a\rangle =\\ \sum_{a=1}^{N}\sum_{n}^{\infty}\frac{1}{\varepsilon_a - \varepsilon_n}\sum_{M,M'=-1}^{1}\left(\frac{4\pi}{3}\right)^2\left\{\left\langle X\middle|\frac{Y_{1,M}}{r^2}\frac{Y_{1,M'}{}^*}{r^2}\middle|X\right\rangle\langle a|rY_{1,M}{}^*|n\rangle\langle n|rY_{1,M'}|a\rangle - \left\langle X\middle|\frac{Y_{1,M}}{r^2}\middle|X\right\rangle\left\langle X\middle|\frac{Y_{1,M'}{}^*}{r^2}\middle|X\right\rangle\langle a|rY_{1,M}{}^*|n\rangle\langle n|rY_{1,M'}|a\rangle\right\}\end{aligned} \tag{48}$$

In this form and with the approximation to the denominator introduced above, we see that the terms entering with a minus sign in eq 48 exactly cancel the $L = 1$ part of the relaxation energy (eq 41). Moreover, the remaining parts of eq 48 are exactly equal to

$\varepsilon_{\mathrm{pol}} - \varepsilon_X$ as seen in eq 46, and reflecting back on eq 21, one can clearly identify the HF-level polarizability components $\alpha_{M,M'}$ of the neutral molecule within these parts of eq 48. This means that $\varepsilon_{\mathrm{pol}}$ is indeed equal to −EA (at least through second order and at least in their $L = 1$ components), except for the correlation-loss energy given in eq 43. For the kind of systems forming the focus of the present work, the correlation loss is expected to be very small because eq 43 contains terms of the form $\langle X|(Y_{1,M}/r^2)|a\rangle\langle a|(Y_{1,M'}{}^*/r^2)|X\rangle$ that should be very small because the orbital ϕ_a is, by assumption, distant from ϕ_X, so the product $\phi_X\,\phi_a$ should be exponentially small.

Notice that, as expressed in eq 42, the new-correlation energy contained transition matrix elements of the form $\langle X|Y_{1,M}(1/r^2)|P\rangle$, which did not allow it to be expressed in a form scaling as r^{-4}. However, the exact cancellation of parts of the new correlation and relaxation energies noted above produced a total that does indeed scale as r^{-4}. This is important because it means one can employ electron−molecule potentials containing repulsive, electrostatic, and polarization (varying as r^{-4}) functions, but one does not need a factor varying as r^{-6} to treat the dispersion interaction between the excess electron and the electrons of the neutral.

IV. Summary, Extensions to Higher Order, Comparison to Drude Electron−Molecule Theory, and Nonadiabatic Corrections

A. Summary and Extensions. The primary goal of this work was to identify the long-range radial and angular characteristics that an electron−molecule potential should have to be consistent with ab initio descriptions that include electrostatic, orbital relaxation, and dispersive correlation interactions. We have shown how one can define a polarization potential $U_{\mathrm{pol}}(\mathbf{r}_>)$ as in eq 38 that can be used, in combination with the Fock operator F_N of the neutral molecule or cluster, to obtain EAs that are expected to agree well with ab initio MP2-calculated EAs for the class of anions considered here. We also showed that this $U_{\mathrm{pol}}(\mathbf{r}_>)$ scales as r^{-4} at large $\mathbf{r}$ even though it contains the dispersion-like interaction of the excess electron and the electrons of the neutral; one does not need a function scaling as r^{-6} to describe these interactions.

These findings suggest that one-electron potentials containing short-range repulsion, electrostatics and dipole polarization can indeed be employed to describe electron−molecule interactions, that they are capable of embodying both orbital relaxation (induction) and dispersion within the conventional $-{}^1/_2\alpha r^{-4}$ function, and that they can be consistent with MP2 or MP3 theory if appropriate electrostatic moments and polarizabilities are used within their parameters.

To be consistent with MP2-level theory, the polarization potential should contain the HF-level polarizability tensor of the neutral, much like the Fock operator contains HF-level electrostatic moments, and it describes *both* mean-field polarization (i.e., MP2-level *orbital relaxation*) and the *new pair correlation energy* (i.e., that often termed dispersion) involving the excess electron.

The strategy used in this paper to relate MP2-level EAs to a particular form (eq 38) of the dipole polarization potential can be extended in at least two directions:

(i) Going to MP3 and higher levels, one can define polarization potentials that are consistent with this higher level and that incorporate correlation corrections to the dipole, quadrupole and higher electrostatic moments and to the dipole—and higher—polarizabilities of the underlying neutral.

(ii) Including terms from eq 16 involving values of $L > 1$, one can develop quadrupole and higher polarization potentials (i.e., contributions to the one-electron potential varying with higher powers of $r_>^{-1}$).

To achieve an MP3 level potential, one can combine MP2 level electrostatic moments with polarization potentials (dipole and perhaps quadrupole) in which the polarizabilities are also evaluated at the MP2 level The derivation of the third-order self-energy matrix presented in ref 6 can be used to prove this.

(1) In particular, in eq 37 of ref 6a and eqs A3−A6 of ref 6b, the third-order self-energy matrix appears in a form very close to that shown in eq 11 of the present paper.

(2) In particular, we note that the two-electron integrals appearing in the numerators of this paper's eq 11 are replaced by matrix elements (labeled B in ref 6a) that are equal to the (first-order) two-electron integrals of eq 11 plus second-order corrections arising from the first-order doubly excited determinants of the MP2 reference wave function multiplied by other two-electron integrals (see eqs 31e and 31f of ref 6a). As discussed earlier, these wave function corrections alter the electron density and thus the electrostatic moments and polarizabilities of the neutral molecule.

(3) There are also corrections (see eqs A3−A6 of ref 6b) arising from the second-order singly excited determinants to the wave function. These also alter the electron density and thus the moments and polarizabilities.

(4) However, there are no third-order contributions to the self-energy that do not derive from the first-order (double excitations) or second-order (single excitation) corrections to the MP wave function. This thus suggests that by making MP2-level corrections to the moments and polarizabilities, one generate a one-electron electrostatic plus polarization potential consistent with MP3-level EAs.

For workers involved in designing electron−molecule interaction potentials, we suggest that, when deciding what level of theory (i.e., what electrostatic moments and polarizabilities) to use in such a model potential, it would be wise to employ values that are consistent with a specified level of ab initio theory if one wants to use results from the ab initio theory to validate the one-electron model. For example, if ab initio MP2 theory produces EAs of sufficient quality, it may be wise to combine a HF-level polarization potential with the Fock operator (and hence the HF-level electrostatic moments) of the neutral molecule to define a one-electron Hamiltonian. Alternatively, one could use MP2-level electrostatic moments and polarizability if one wanted to reproduce MP3-level EAs. On the other hand, it would be inconsistent, if one desires to obtain MP2-quality EAs, to use an electrostatic potential in which MP2-level dipole, quadrupole, and higher moments appear.

Even if one has no interest in generating EAs of a specified MP*n* level of accuracy, the observations made above may still be of use in determining the parameters appearing in the short-range repulsive portion of a model electron−molecule potential. After all, it is the balance between these short-range repulsions and the long-range attractions that determine the EA, and one should be careful not to (fortuitously) reproduce the correct EA by using inaccurate long-range and inaccurate short-range potentials. Clearly, one would prefer to use accurate long-range potentials and then create a short-range repulsive potential that gives the correct EA when balanced against these accurate long-range terms. For example, the results provided here suggest that one could employ HF-level electrostatic moments and polarizabilities and then adjust the parameters in the short-range repulsions to reproduce MP2-level EAs on test systems (e.g., the water dimer anion if one is interested in developing an electron−water potential to use on larger water cluster anions).

Alternatively, one could use MP2-level electrostatic moments and polarizabilities and adjust the repulsive potential's parameters to reproduce MP3-level EAs. It would even make sense if Koopmans' theorem EAs are of sufficient accuracy (this is not likely, be we use this example to make a point), to use HF-level electrostatic moments, to include no polarization potential, and then adjust the parameters in the short-range repulsions to reproduce the Koopmans EAs. In addition, one could plot (as was done in ref 11b) the long-range part of a candidate one-electron potential and compare it to a plot of the MP2- or MP3-level potential obtained as in ref 11b

B. Connections to the Drude Model. We would like to show, as part of this summary, that many of the observations made above concerning orbital relaxation and new correlation (i.e., dispersion effects involving the excess electron) were made, albeit in a different framework, by Professor Ken Jordan's group when treating their Drude model[13] for electron−molecule and electron−cluster interactions. In particular, for dipole-bound and water−cluster anions, they showed the Drude model capable of reproducing high-level ab initio electron binding energies that include dispersion effects, and they showed[11b] that a polarization potential scaling as r^{-4} arises from the Drude model when an adiabatic approximation (much as used here in deriving $U_{\mathrm{pol}}(\mathbf{r}_>)$) is employed.

In the model discussed in refs 11b and 13, the coupling between the N electrons belonging to the underlying molecule or cluster and the excess electron is described by a potential

$$V_{\mathrm{e,osc}}(r,R) = q_D \frac{R\cdot\hat{r}}{r^2} f(r) \tag{49}$$

expressed in terms of the coordinates $\mathbf{r}$ of the excess electron and of the so-called Drude oscillator $\mathbf{R}$. The response of all N of the neutral's electrons to the presence of the excess electron is modeled in terms of a single three-dimensional Drude oscillator, which is characterized (These parameters and the force constant k_{D} are chosen to make the polarizability of the Drude oscillator equal to that of the water molecule.) by a charge q_{D}, a mass m_{D}, and a displacement vector $\mathbf{R}$ that is assumed to undergo harmonic motion according to the Hamiltonian

$$h_{\mathrm{osc}}(R) = -\frac{\hbar^2}{2m_{\mathrm{D}}}\nabla_R^{\ 2} + \frac{1}{2}k_{\mathrm{D}}(X^2 + Y^2 + Z^2) \tag{50}$$

in the absence of coupling to the excess electron. The function $f(r)$ in eq 49 serves to cutoff the coupling at small r.

Using a basis $\{|\alpha, n_x, n_y, n_z\rangle\}$ consisting of products of (i) orbitals $\{\phi_\alpha\}$ for the excess electron (i.e., the orbitals we denoted ϕ_X and ϕ_P) and (ii) harmonic oscillator eigenfunctions for the Hamiltonian of eq 50 and treating the coupling given in eq 49 either by configuration interaction or by perturbation theory, the workers in refs 11b and13 showed that the energy change induced by the coupling can be viewed as a dispersion-like energy arising from correlated excitations of the Drude oscillator and of the excess electron. Such doubly excited contributions are depicted qualitatively in the central part of Figure 2 and correspond, in our eq 23, to the *new-correlation* terms that describe the dispersion interactions between the excess electron and the neutral's electrons.

This Drude model was subjected (see ref 11b) to an adiabatic treatment in which the oscillator Hamiltonian including the coupling to the excess electron was diagonalized for a fixed position of the excess electron. A matrix representation of the Hamiltonian

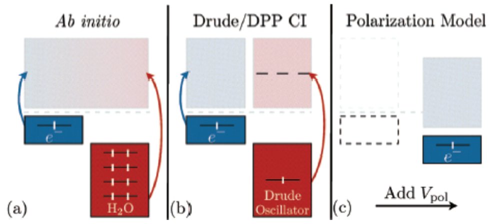

Figure 2. Descriptions of the couplings between electrons of a neutral molecule or cluster (water in this case) and an excess electron described by ab initio MP2 dispersion (a), Drude-model CI or perturbation theory (b), and adiabatic treatment of Drude model (c). Reprinted with permission from ref 11b. Copyright 2008 American Chemical Society.

$$H_F = h_{\mathrm{osc}}(R) + V_{\mathrm{e,osc}}(r,R) \tag{51}$$

is formed within a basis $\{|n_x, n_y, n_z\rangle\}$consisting of products of harmonic oscillator eigenfunctions but constrained to $n_k = 0$ or 1 only ($k = x$, y, or z). The lowest eigenvalue of the resultant 4 × 4 matrix, which depends parametrically on the position $\mathbf{r}$ of the excess electron, was shown to have the form

$$U(r) = 2\hbar\omega_{\mathrm{D}} - \sqrt{(1/2\hbar\omega_{\mathrm{D}})^2 + \frac{\hbar q_{\mathrm{D}}^{\ 2}}{2\omega_{\mathrm{D}} m_{\mathrm{D}} r^4} f^2(r)} \tag{52}$$

where ω_{D} is the frequency of the Drude oscillator. This can be seen (after removing the zero-point energy of the oscillator) to be of the polarization-potential form

$$U(r) = -\frac{\alpha_{\mathrm{D}}}{2r^4} f^2(r) \tag{53}$$

where α_{D} is the polarizability of the Drude oscillator[t]

$$\alpha_{\mathrm{D}} = \frac{q_{\mathrm{D}}^{\ 2}}{k_{\mathrm{D}}} \tag{54}$$

and $f(r)$ is the same cutoff function discussed earlier. This view of the coupling of the excess electron to the underlying molecule is shown in the right side of Figure 2.

It is our view that this derivation and the related observations offered by the Jordan group for their Drude model—that the dynamical coupling between the excess electron and the electrons of the underlying neutral can be viewed either as dispersion-like (Figure 2 in the center) or polarization-derived (Figure 2 on the right)—are consistent with the analysis of MP2 theory offered here. We concluded that the dispersion-like *new-correlation* energy plus the mean-field *orbital relaxation* energy can be combined and expressed in terms of a single polarization-derived energy analogous to the adiabatic Drude model's potential of eq 53. We also showed that the combination of all of these terms indeed scale as r^{-4} even though they contain dispersion contributions that might be expected to scale as r^{-6}.

C. What about Nonadiabatic Corrections? In closing, we note that it is somewhat surprising the degree to which using

$F_N + U_{\mathrm{pol}}(\mathbf{r}_>)$ to evaluate $\varepsilon_{\mathrm{pol}}$ can be trusted to yield EAs consistent with MP2-level calculations. After all (i) in MP2, the orbital relaxation contributions contain only the *mean-field* polarization of the neutral molecule's N electrons, while (ii) in defining $U_{\mathrm{pol}}(\mathbf{r}_>)$, the excess electron is held fixed and the neutral molecule's electrons are allowed to *fully* polarize in the presence of this fixed charge. (iii) In forming $U(\mathbf{r}_>)$, one makes an adiabatic treatment of how the neutral molecule's electrons respond to the presence of the excess electron. One should then subsequently examine, when solving $[F_N + U_{\mathrm{pol}}(\mathbf{r}_>)]\phi_{\mathrm{pol}} = \varepsilon_{\mathrm{pol}}\,\phi_{\mathrm{pol}}$, *nonadiabatic couplings* that arise from the dynamical motion of the excess electron. However, such couplings were not considered[14] in the analysis offered here and they are not often included when polarization potentials are used to study dipole-bound anions or molecule−cluster anions. This suggests that further consideration of the relationships between MP*n*-based expressions for EAs and results derived from one-electron polarization potentials may be warranted, especially if one extends the analysis to higher order where such nonadiabatic couplings may come into play.

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(12) On pp 151−165 of ref 3a, Professor Don Truhlar offers a nice overview of how such approaches lead to defining polarization potentials. We used this strategy because it also allows us to make connections with the polarization potential that arises within the so-called Drude model that we discuss later.

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(14) In using an adiabatic separation approach analogous to that introduced in eq 30, earlier workers have derived polarization potentials to describe, for example, the ns valence electrons of alkali metal atoms. For example, see Callaway, J. Contributions of Core Polarization to the Cohesive Energies of the Alkali Metals. *Phys. Rev.* **1957**, *106*, 868–874. In those studies, it was concluded that the non-Born−Oppenheimer couplings are expected to be small, but this author is not convinced this is necessarily the case for the electron−molecule or electron−cluster systems considered here. In fact, a very nice recent study by Professor B. Schwartz (Glover, W. J.; Larsen, R. E.; Schwartz, B. J. The roles of electronic exchange and correlation in charge-transfer-to-solvent dynamics: Many-electron nonadiabatic mixed quantum/classical simulations of photoexcited sodium anions in the condensed phase. *J. Chem. Phys.* **2008**, *129*, 164508) on alkali anions in solution emphasizes the roles played by such nonadiabatic couplings.

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