

Theoretical Study of Negative Molecular Ions

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Abstract

Although this review provides references to tabulations of molecular electron affinities, primarily it focuses on explaining why theory plays an important role in understanding the behavior of anions, explaining the challenges that anions pose to theory, making connections between the theories used to compute electron affinities and the potentials (e.g., charge-dipole, charge-quadrupole, valence attraction and exchange repulsion, dispersion, and polarization) that govern the electron-molecule interaction, and discussing how species with negative electron affinities may possess metastable anion states and how such states should be treated. In addition to references to published literature, many links are given to websites of practicing theoretical chemists who study molecular anions; these links (which appear in boldface) offer the reader a broad avenue to access much more information about molecular anions than can be covered in a review or even through conventional literature sources.

1. INTRODUCTION

EA: electron affinity

1.1. Why Study Negative Molecular Ions Theoretically?

Molecular anions are interesting and important to study theoretically for a variety of reasons. To begin with, they are constituents in many ionic compounds and materials, so their stability, spectra, sizes, and other chemical properties need to be characterized, and often it is difficult to study them experimentally. For example, the ubiquitous sulfate anion SO_4^{2-} cannot be studied experimentally as an isolated species because it undergoes spontaneous electron loss within a very short time ($<10^{-14}$ s), but it has been studied theoretically (1) using special tools to handle its metastable character. In addition, anions bind their outermost electrons rather weakly [i.e., electron affinities (EAs) are usually considerably smaller than ionization potentials], and hence their valence-range electron densities are diffuse. This causes them to interact strongly with their environment (e.g., in solution or in crystals), making their behavior strongly influenced by the surroundings and causing them to be excellent probes of their environment. Moreover, they usually do not have bound excited electronic states, so many spectroscopic probes cannot be applied to them, which makes theoretical study more important. They also can have bonding and reactivity characters substantially different from those of their parent neutrals when the extra electron occupies a bonding or antibonding molecular orbital. This means that forming an anion by reducing a neutral molecule can offer a route to altering chemical behavior. And they may not even be electronically stable species, in which case they may exist only fleetingly (e.g., for 10^{-14} to 10^{-10} s) although long enough to be involved in important chemical events such as bond breaking or electron transfer. They present special challenges to theory as well, so their study provides opportunities for testing and improving theoretical methods and concepts. Finally, anionic centers can occur in molecules that have overall positive charge or no charge. For example, when an electron binds to an amide π^* orbital in a multiply positively charged polypeptide with protonated side chains, the amide moiety is negatively charged. Knowing the character of such anionic regions is important to understand the behavior of the full polypeptide.

1.2. Other Sources of Information about Anions

In the present review, emphasis is placed on molecular anions because of the author's career-long involvement with them. For information about the study of atomic anions, a recent review (2) by **Prof. David J. Pegg** provides good insight. The author recently provided an extensive review (3) of the experimental and theoretical study of a wide variety of molecular anions. That paper contains a large number of active web links to literature references on anions and links to websites of many researchers who have made important contributions. The latter provide excellent routes to gaining a broad overview of this field. Tabulated values of atomic EAs can be found in the early reviews of Hotop & Lineberger (4, 5) and the more recent review by Andersen et al. (6), whereas those for molecular EAs can be found in several sources (7–11) that span many years, some of which are accessible on the Internet. The author created a **website** that offers much of the same information as in Reference 3, as well as a series of **streaming video lectures** covering electronic structure theory, including material specific to treating molecular anions (see **session 9**). In addition, the author presented lectures at the **2009 Telluride School on Theoretical Chemistry** in which he described special tools needed to handle anions (this information is available in **session 9** of the streaming video lectures mentioned above). For insight into the experimental study of negative molecular ions, the websites of **Prof. W.C. Lineberger** and **John I. Brauman** are useful. These scientists have done much over the past 40 years to contribute to chemists' knowledge about molecular anions. Of course, they stood on the shoulders of earlier masters such as Louis

Branscomb (12), George Schulz (13), and Sir H.S.W. Massey (14). Of the theoretical chemists who have advanced knowledge of molecular anions during this time frame, **Prof. R.S. Berry** (15) was among the earliest, but now there are many theory and experimental groups active in this field.¹

AEA: adiabatic electron affinity

2. MOLECULAR ANIONS AND THEIR SPECIAL CHALLENGES TO THEORY

2.1. What Are Electron Affinities?

The adiabatic electron affinity (AEA) of a molecule (or radical) is the energy difference between the parent molecule in its ground electronic state and its lowest vibration-rotation level and the daughter anion in its ground electronic state and lowest vibration-rotation state. The theoretical evaluation of the AEA requires one to determine the anion-neutral energy gap at the equilibrium geometry of both the anion and the neutral and the vibrational zero-point energies of both. The vertical EA is the energy of the neutral minus the energy of the anion (both in their ground electronic states) at the equilibrium geometry of the neutral. The vertical detachment energy is the energy of the neutral minus the energy of the anion (both in their ground electronic states) at the equilibrium geometry of the anion.

If a molecule has a positive EA, we refer to the anion as electronically stable because it requires energy input to remove an electron from the anion. A molecule can have a positive AEA but can have vertical EAs that are positive at some geometries and negative at other geometries; O₂ is an example (see figure 4 in 16). For some molecules that do not have positive EAs, the anion can survive long enough to be subject to experimental detection. In such cases, we speak of an electronically metastable anion because it can eject spontaneously an electron to regenerate its neutral parent plus a free electron. The ²Π state of N₂⁻ is an example of such a species. Because of their fleeting existence, there are special experimental and theoretical tools needed to study this class of anions, as we discuss below.

2.2. Electron Affinities Are Small Fractions of the Total Energies of Molecules

As early as the 1960s, good quantum chemical calculations of molecular EAs (17–26), including many from Profs. **Enrico Clementi**, **Ernest Davidson**, and **Fritz Schaefer**, were carried out using approximate solutions to the Schrödinger equations to obtain the total Born-Oppenheimer electronic energies of the neutral (E_{neu}) and anionic (E_{an}) species and subtracting these two quantities to compute the EA as

$$EA = E_{\text{neu}} - E_{\text{an}}. \quad (1)$$

As we discuss below, such an approach is useful only for species with positive EAs because the most commonly used methods for approximately solving the Schrödinger equation are limited to determining energies of electronically stable states.

¹The following web links offer good routes to much more information about the anion research going on in these groups: **Lenz Cederbaum**, **Vince Ortiz**, **Bob Compton**, **Kit Bowen**, **Dan Neumark**, **Mark Johnson**, **Lai-Sheng Wang**, **Kent Ervin**, **Barney Ellison**, **Will Castleman**, **Paul Kebarle**, **Alex Boldyrev**, **Ken Jordan**, **Piotr Skurski**, **Maciej Gutowski**, **Ludwik Adamowicz**, **Kwang Kim**, **Fritz Schaefer**, **Carl Lineberger**, **John Brauman**, **Paul Schleyer**, **Lars Andersen**, **Steen Brøndsted Nielsen**, **Veronica Bierbaum**, **Benjamin Schwartz**, **Rod Bartlett**, **Andrei Sanov**, **Dan Chipman**, **Liem Dang**, **Pavel Jungwirth**, **Heather Allen**, **Stephen Bradforth**, **Thomas Sommerfeld**, **Peter Rossky**, **John Herbert**, **Michael Allan**, **Vince McKoy**, **Chris Greene**, and **Mathias Weber**.

HF: Hartree-Fock

Electron correlation: difference between the true pair (and higher) spatial probability densities and those described at the mean-field Hartree-Fock level

Because the EA is an intensive property and is a very small fraction of the total (extensive) electronic energies of the neutral and anion, one must determine E_{neu} and E_{an} to high accuracies to obtain EA to a chemically useful accuracy (e.g., a few tenths of an electron volt). EAs typically lie in the 0.01–5-eV range, but the total electronic energy of even a small molecule is usually orders of magnitude larger. For example, the EA of the $^4S_{3/2}$ state of the carbon atom is 1.262119 ± 0.000020 eV (11), whereas the total electronic energy of this state of C is -1030.080 eV (this total energy is defined relative to a C^{6+} nucleus and six electrons infinitely distant and not moving). Because the EA is approximately 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%. Moreover, the difficulty in evaluating EAs to within a fixed specified (e.g., ± 0.1 eV) accuracy based on subtracting total energies increases as the size and number of electrons in the molecule grow. For example, the EA of C_2 in its $X^2\Sigma_g^+$ ground electronic state is 3.269 ± 0.006 eV near the equilibrium bond length 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 approximately 3.6 eV [the dissociation energy (27) of C_2] at R_e . This situation becomes especially problematic when studying extended systems such as solids, polymers, or surfaces for which the EA is an infinitesimal fraction of the total energy.

2.3. Components of the Special Theoretical Tools Needed for Anions

The above analysis is meant to suggest that an EA, being small, requires that one employ theoretical tools of high accuracy and that one count on there being considerable cancellation of errors made in evaluating $E_{\text{neu}} - E_{\text{an}}$. Within essentially all electronic structure methods for computing E_{neu} or E_{an} , there are three components that contribute to the overall accuracy of the resultant EA. First, an atomic orbital basis set must be chosen. For anion calculations, diffuse basis functions must be included, but it is also important to employ basis sets that are capable of describing the other valence electrons to high accuracy, and carrying out complete basis extrapolations can be of considerable help. **Session 5** of the author's streaming video lectures discusses these issues. Second, the first estimate of an EA is obtained usually within an approximation [often the Hartree-Fock (HF) framework; see **session 4** of the video lectures] that describes the anion's extra electron's interaction with the neutral molecule in terms of its electrostatic interaction with the molecule's nuclei and frozen electron density (i.e., one that does not respond to the presence of the extra electron) constructed from the neutral molecule's N occupied mean-field (i.e., HF) spin-orbitals. This produces the Koopmans' theorem estimate for an EA (see **session 2** of the video lectures). Third, the electrons in the neutral and anion actually interact via mutual instantaneous Coulomb potentials, not in the mean-field manner used in the HF approximation. Therefore, one must account for the difference between the Coulomb and mean-field interactions, which gives rise to correlations among the electrons' motions. The tools used to treat electron correlation are covered in **sessions 6, 7, 8, and 11** of the video lectures, and the physical picture of dynamical electron correlation is explained in **session 3**.

2.4. The Electron Affinity Can Be Determined Directly as an Intensive Quantity

Sections 2.2 and 2.3 discuss why computing the EA of a molecule from the total energies of its neutral and anion can be difficult. How do most experiments determine molecular EAs? The most direct technique involves the use of a photon source of energy $h\nu$ to detach an electron from a molecular anion A^- . By determining the minimum photon energy needed to detach an electron, one determines the EA. The most direct technique for determining negative EAs is to use

electron transmission spectroscopy in which a beam of electrons having kinetic energy impinges on a neutral molecule (for details, see Prof. Paul D. Burrow's **website**). If the negative kinetic energy matches the (negative) EA of the molecule, one of the beam's electrons can be captured into an empty orbital of the neutral to form the metastable anion, which can be detected either by measuring attenuation of the incident electron beam or by probing the electron ejected at right angles to this beam. Nowhere in these experiments is the total energy of either the anion or the neutral measured.

So, it would appear natural to seek a theoretical approach to determining EAs that follows the experimental example, which is what the author and his coworkers did in the early 1970s (28) when they developed the equations-of-motion (EOM) method for computing EAs. At about this same time, Prof. **Lenz Cederbaum** (31) and other groups (29, 30) were developing what turned out to be an equivalent method (the so-called Green's function methods) and applying it to directly calculate ionization potentials. In several of the author's subsequent publications (see the **complete publication list**), the EOM method was refined and applied to a variety of molecular anions. Others (32–38), especially Profs. **Rodney Bartlett**, **John Stanton**, and **Anna Krylov**, have greatly extended the EOM method beyond the Møller-Plesset (MP) framework used in the author's early efforts to allow more powerful coupled-cluster, multiconfiguration, and other wave-function classes to be employed. The implementation of Prof. **Vince Ortiz** (38) is even contained within the widely used Gaussian suite of programs (<http://www.gaussian.com/>).

Nevertheless, to date, most calculations of EAs are still performed by computing E_{neu} and E_{an} because wave-function optimization methods remain more developed and widely known than EOM or Green's function methods. However, the author believes it is informative to discuss the working equations of EOM-type methods because they provide a framework for understanding the various electron-molecule interaction potentials that contribute most to determining the EA. They achieve this by expressing their working equations in terms of a one-electron effective Hamiltonian whose eigenvalues give the EA directly. By analyzing the EOM Hamiltonian, one can make connections with electron-molecule interaction potentials with which one is familiar (e.g., charge-dipole, charge-quadrupole, dispersion, and polarization).

3. ELECTRON-MOLECULE INTERACTION POTENTIALS

3.1. The Effective Hamiltonian of Equations-of-Motion Theory

EOM theory introduces an effective Hamiltonian, H , to describe how an excess electron interacts with a molecule containing N other electrons that occupy spin-orbitals $\{\phi_a; a = 1, \dots, N\}$ in the single-determinant HF approximation. Reference 28 shows that matrix elements $\{H_{i,j}\}$ of this effective Hamiltonian within the space spanned by the occupied $\{\phi_a; a = 1, \dots, N\}$ and unoccupied $\{\phi_n; n = N + 1, \dots, \infty\}$ HF spin-orbitals can be written (in atomic units where e , m_e , and \hbar are absent; lengths are measured in Bohr units $a_0 = 0.529 \text{ \AA}$; and energies are in Hartrees, 27.21 eV) as

$$H_{i,j} = \int \phi_i \left[-1/2 \nabla^2 - \sum_{a=1}^M \frac{Z_a}{|r - R_a|} \right] \phi_j dr + \int \phi_i \sum_{k=1}^N [J_k - K_k] \phi_j dr + \Sigma_{i,j} \quad (2)$$

or

$$H_{i,j} = F_{i,j} + \Sigma_{i,j}. \quad (3)$$

Here $F_{i,j}$ is an element of the Fock matrix (containing the kinetic, electron-nuclear Coulomb, and electron-electron mean-field Coulomb and exchange energies), and the so-called self-energy

EOM: equations of motion

MP: Møller-Plesset
Fock matrix: matrix elements of the one-electron Hamiltonian containing Hartree-Fock-level electrostatic potentials

Self-energy matrix: matrix elements of the one-electron Hamiltonian containing all correlation contributions

matrix $\Sigma_{i,j}$ has elements given through second order (in the usual MP sense) as follows:

$$\Sigma_{i,j} = \sum_{a=1}^N \sum_{m < n = N+1}^{\infty} \frac{\langle mm | ai \rangle \langle aj | mm \rangle}{\varepsilon_a + E - \varepsilon_n - \varepsilon_m} + \sum_{a < b}^N \sum_{m = N+1}^{\infty} \frac{\langle ab | mi \rangle \langle mj | ab \rangle}{\varepsilon_m + E - \varepsilon_a - \varepsilon_b}. \quad (4)$$

In the expression for the Fock matrix elements, R_a and Z_a are the position and charge of the a -th nucleus, and J_k and K_k are the Coulomb and exchange operators, respectively, whose effects on the spin-orbital ϕ_j are

$$J_k \phi_j = \int \phi_k^*(r') \phi_k(r') \frac{1}{|r - r'|} dr' \phi_j(r), \quad (5)$$

$$K_k \phi_j = \int \phi_k^*(r') \phi_j(r') \frac{1}{|r - r'|} dr' \phi_k(r). \quad (6)$$

In Equation 4, ε_j is the HF orbital energy of spin-orbital ϕ_j , and the two-electron integrals are defined as

$$\langle ij | kl \rangle = \int \phi_i^*(r) \phi_j^*(r') \frac{1}{|r - r'|} \phi_k(r) \phi_l(r') dr dr' - \int \phi_i^*(r) \phi_j^*(r') \frac{1}{|r - r'|} \phi_l(r) \phi_k(r') dr dr'. \quad (7)$$

In the author's 1970s papers (listed in the **complete publication list**), the elements of $\Sigma_{i,j}$ were given through third order (because experience showed that second-order estimates of EA were not accurate enough), but here we show them only through second order because this is sufficient to illustrate the important physical meaning of the various terms in the effective Hamiltonian.

In the EOM theory, the eigenvalue problem

$$\sum_{j=1}^{\infty} [H_{i,j}(E_\lambda) - E_\lambda \delta_{i,j}] V_j^\lambda = 0 \quad \text{for } i = 1, \dots, \infty \quad (8)$$

is solved for the eigenvalues E_λ and the associated eigenvector elements V_j^λ . At the lowest order, in which $\Sigma_{i,j}$ is ignored, the eigenvalues are those of the Fock matrix, the HF orbital energies $\{\varepsilon_a; a = 1, \dots, N; \text{ and } \varepsilon_m; m = N + 1, \dots, \infty\}$, so EOM theory reduces to Koopmans' theorem in lowest order (discussed in **session 2** of the video lectures).

To illustrate the physical meaning of corrections to the Koopmans' theorem, let us consider forming an anion by adding an electron to the neutral molecule's lowest unoccupied spin-orbital (LUMO) ϕ_{N+1} . The Koopmans' estimate to the eigenvalue is $E \approx \varepsilon_{N+1}$. In this case, a correction can be obtained by substituting this Koopmans' estimate into $\Sigma_{i,j}$ and adding the diagonal element² of the self-energy:

$$\begin{aligned} \Sigma_{N+1,N+1}(E = \varepsilon_{N+1}) &= \sum_{a=1}^N \sum_{N+1 < n}^{\infty} \frac{\langle N+1, n | a, N+1 \rangle \langle a, N+1 | N+1, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_{N+1}} \\ &+ \sum_{a=1}^N \sum_{m < n = N+2}^{\infty} \frac{\langle m, n | a, N+1 \rangle \langle a, N+1 | m, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_m} + \sum_{a < b}^N \sum_{m = N+1}^{\infty} \frac{\langle a, b | m, N+1 \rangle \langle m, N+1 | a, b \rangle}{\varepsilon_m + \varepsilon_{N+1} - \varepsilon_a - \varepsilon_b}. \end{aligned} \quad (9)$$

²Examining the $i = j = N + 1$ diagonal element of this matrix allows us to identify potential energy factors acting on the excess electron. Forming the full $H_{i,j}$ matrix and finding the eigenvalue corresponding to the EA allow the orbital occupied by the excess electron to be improved beyond the Koopmans' theorem description ϕ_X . The eigenvector $\{V_j\}$ of the $H_{i,j}$ matrix gives the expansion coefficients for describing the improved orbital (known as the Dyson orbital) in terms of the HF orbitals $\{\phi_i\}$: $\phi_{Dyson} = \Sigma_j V_j \phi_j$.

As explained in further detail below, the second sum in $\Sigma_{N+1,N+1}$ gives the second-order approximation to the correlation energy of the extra electron (occupying ϕ_{N+1}) interacting with the N other electrons (occupying $\{\phi_a\}$; $a = 1, \dots, N$). The third sum describes the loss of correlation energies among electron pairs (in ϕ_a and ϕ_b) that occurs once the extra electron occupies the spin-orbital ϕ_{N+1} . The first sum is the change in the HF energy (beyond the Koopmans' value) induced by the addition of the extra electron to ϕ_{N+1} ; this term is often called the orbital relaxation energy.

The EOM theory thus offers a framework in which one can understand an EA in terms of an effective Hamiltonian that acts on the extra electron. It expresses the EA as a Koopmans' theorem estimate (containing all the HF-level electrostatic potentials and the valence repulsion potential generated by the N other electrons), an orbital relaxation component (allowing the N other electrons' orbitals to adjust in a mean-field manner to the extra electron), a component involving the correlation energy of the extra electron, and terms describing changes in the correlation energies of the original N electrons induced by the presence of the extra electron. It is useful now to consider how the potential energy terms appearing in the Hamiltonian elements $H_{i,j}$ relate to various electrostatic and induced potentials that one frequently encounters when thinking of a negative charge (i.e., the extra electron) interacting with a molecule. We do this by examining the potential energy terms in $H_{i,j}$ when the extra electron is far from the nuclei of the parent molecule (i.e., for large $|r - R_a|$).

3.2. Relation to Electrostatic and Polarization Potentials

The extra electron experiences not only the static potential of the underlying molecule, but also the changes in these potentials that it induces within the molecule.

3.2.1. Electrostatics. When dealing with an electron added to a neutral molecule, there is no net Coulomb contribution to $H_{i,j}$ because the Coulomb components of the sum of all the electron-nuclei attractive potentials

$$\int \phi_i \left[- \sum_{a=1}^M \frac{Z_a}{|r - R_a|} \right] \phi_j dr$$

are exactly cancelled by the sum of all the repulsive Coulomb potentials generated by the N other electrons³

$$\int \phi_i^* \sum_{k=1}^N J_k \phi_j dr.$$

The exchange terms $-\int \phi_i^* \sum_{k=1}^N K_k \phi_j dr$ vanish at large r because $K_k \phi_j$ decays exponentially with this distance. So, when adding an electron to a neutral molecule, the extra electron will experience no potential varying as $1/r$ at large r . However, when adding an electron to a singly charged anion to generate a dianion, the above cancellation does not occur, and $H_{i,j}$ contains terms that, at large r , display a net Coulomb repulsion.

³This can be proven by expanding $\frac{1}{|r-R_a|}$ and $\frac{1}{|r-r'|}$ for $r > R_a$ and $r > r'$, respectively, in powers of $\frac{|R_a|}{|r|}$ or $\frac{|r'|}{|r|}$ and keeping the lowest-order terms, which are $\frac{1}{|r|}$ in both cases. Other terms in these expansions varying as $\frac{|R_a|^L}{|r|^{L+1}}$ and $\frac{|r'|^L}{|r|^{L+1}}$ give the dipole ($L = 1$), quadrupole ($L = 2$), etc., electrostatic potentials.

Orbital relaxation: change in the Hartree-Fock orbitals caused by addition of the excess electron

Electrostatic potential: interaction potential between the excess electron and all permanent moments (i.e., dipole, quadrupole) of the molecule

The electron-nuclear and electron-electron Coulomb potentials also combine,

$$\int \phi_i \left[- \sum_{a=1}^M \frac{Z_a}{|r - R_a|} \right] \phi_j dr + \int \phi_i^* \sum_{k=1}^N J_k \phi_j dr,$$

to give rise, at large r , to electron-dipole, electron-quadrupole, and higher electron-multipole potentials. The first two can be written as

$$V_{dipole} = - \frac{\boldsymbol{\mu} \cdot \hat{r} e}{r^2} \quad (10)$$

and

$$V_{quadrupole} = - \frac{\epsilon(3\hat{r} \cdot \mathbf{Q} \cdot \hat{r} - \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I})}{3r^3}. \quad (11)$$

Here, $\boldsymbol{\mu}$ and \mathbf{Q} are the HF-level permanent dipole moment vector and quadrupole moment tensor of the neutral molecule (they are permanent moments of the molecule; they have nothing to do with how the excess electron polarizes the molecule), \mathbf{I} is the unit tensor, and \hat{r} is a unit vector pointing to the extra electron.

In addition, $F_{i,j}$ contains shorter-range valence potentials that are both attractive and repulsive. For example, in the oxygen atom ($1s^2 2s^2 2p^4$; 3P), the nitrogen atom ($1s^2 2s^2 2p^3$; 4S), or the methoxy radical $\text{H}_3\text{C-O}$ (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 $1s^2 2s^2 2p^4$, 7 N $1s^2 2s^2 2p^3$, or 17 $\text{H}_3\text{C-O}$ 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.

In summary, the Fock operator, which produces the Koopmans' estimate to the EA, contains exchange-repulsion and HF-level electrostatic (i.e., Coulomb, which vanishes for a mono-anion, electron-dipole, electron-quadrupole, and other electron-multipole) potentials. What it does not contain are (a) the change in the mean-field interaction of the extra electron with the N other electrons associated with orbital relaxation, (b) the effects of electron correlation among the $N + 1$ electrons, and (c) corrections to the HF-level electrostatic moments and polarizabilities. It is in the $\Sigma_{i,j}$ component of the EOM Hamiltonian that these effects appear. It turns out that, even when a large and flexible basis set is used, Koopmans' EAs are often in error by approximately 1 eV, whereas EAs computed including orbital relaxation are often only within approximately 0.5 eV of the correct values. The differential electron correlation contribution to the EA is thus often approximately 0.5 eV and thus important to consider.

3.2.2. Correlation, polarization, and relaxation. Through second order, the orbital-relaxation component of the EA is contained in the following component of the self-energy matrix element,

$$\sum_{a=1}^N \sum_{N+1 < n}^{\infty} \frac{\langle N + 1, n | a, N + 1 \rangle \langle a, N + 1 | N + 1, n \rangle}{\epsilon_a + \epsilon_{N+1} - \epsilon_n - \epsilon_{N+1}},$$

and the electron correlation component is

$$\sum_{a=1}^N \sum_{m < n = N+2}^{\infty} \frac{\langle m, n | a, N + 1 \rangle \langle a, N + 1 | m, n \rangle}{\epsilon_a + \epsilon_{N+1} - \epsilon_n - \epsilon_m} + \sum_{a < b}^N \sum_{m = N+1}^{\infty} \frac{\langle a, b | m, N + 1 \rangle \langle m, N + 1 | a, b \rangle}{\epsilon_m + \epsilon_{N+1} - \epsilon_a - \epsilon_b}.$$

To further clarify the physical meaning of these two factors, let us recall how electronic structure theory, in its most common frameworks, describes electron correlation and orbital relaxation.

Orbital relaxation. Let us take a mean-field single-determinant anion wave function as the starting point:

$$\psi(1, 2, \dots, N, N + 1) = |\phi_1(1)\phi_2(2) \dots \phi_a(a) \dots \phi_N(N)\phi_{N+1}(N + 1)|. \quad (12)$$

Now, let us consider any determinant $|\phi_1(1)\phi_2(2) \dots \phi_m(a) \dots \phi_N(N)\phi_{N+1}(N + 1)|$ in which one occupied spin-orbital ϕ_a of the original wave function is replaced by an unoccupied spin-orbital ϕ_m . Any combination of these two determinants

$$\begin{aligned} \psi_{combination}(1, 2, \dots, N, N + 1) = & C_0|\phi_1(1)\phi_2(2) \dots \phi_a(a) \dots \phi_N(N)\phi_{N+1}(N + 1)| \\ & + C_1|\phi_1(1)\phi_2(2) \dots \phi_m(a) \dots \phi_N(N)\phi_{N+1}(N + 1)| \end{aligned} \quad (13)$$

is equivalent to a new single determinant

$$|\phi_1(1)\phi_2(2) \dots [C_0\phi_a(a) + C_1\phi_m(a)] \dots \phi_N(N)\phi_{N+1}(N + 1)|$$

in which the original spin-orbital ϕ_a has been changed into $[C_0\phi_a(a) + C_1\phi_m(a)]$. In other words, such singly excited determinants serve to modify (i.e., relax) the occupied spin-orbitals while retaining the single-determinant nature of the wave function.

This analysis allows us to see in the orbital-relaxation contribution to EA a sum over all occupied spin-orbitals of a coefficient

$$C_a^n = \frac{\langle a, N + 1 | N + 1, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_{N+1}} = \frac{\langle \phi_a | J_{N+1} - K_{N+1} | \phi_n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_{N+1}} \quad (14)$$

that is the first-order perturbation theory amplitude for the change in spin-orbital ϕ_a induced by the Coulomb and exchange interactions with the extra electron in ϕ_{N+1} . This amplitude then multiplies the virtual spin-orbital ϕ_n ($J_{N+1} - K_{N+1}$ is the perturbation) to form a relaxed spin-orbital $\phi_{a,relaxed}$:

$$\phi_{a,relaxed} = \phi_a + \sum_{n=N+2}^{\infty} C_a^n \phi_n. \quad (15)$$

In turn, the second-order relaxation energy for ϕ_a is given by the matrix element of the perturbation ($J_{N+1} - K_{N+1}$) coupling ϕ_a to $\phi_{a,relaxed}$:

$$\sum_{N+1 < n}^{\infty} C_a^n \langle \phi_n | J_{N+1} - K_{N+1} | \phi_a \rangle = \sum_{N+1 < n}^{\infty} \frac{\langle \phi_a | J_{N+1} - K_{N+1} | \phi_n \rangle \langle \phi_n | J_{N+1} - K_{N+1} | \phi_a \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_{N+1}}. \quad (16)$$

Thus, the orbital relaxation energy is the perturbative estimate (with $J_{N+1} - K_{N+1}$ treated as the perturbation) of the change in the mean-field energy induced by the presence of the extra electron.

Electron correlation. To interpret the contributions to the correlation contribution to EA shown above, it is useful to make use of another identity involving Slater determinants. In particular, a combination of two determinants

$$C_0|\phi_1(1)\phi_2(2) \dots \phi_a\alpha(a) \dots \phi_a\beta(a + 1) \dots \phi_N(N)\phi_{N+1}(N + 1)|$$

and

$$-C_1|\phi_1(1)\phi_2(2) \dots \phi_n\alpha(a) \dots \phi_n\beta(a + 1) \dots \phi_N(N)\phi_{N+1}(N + 1)|$$

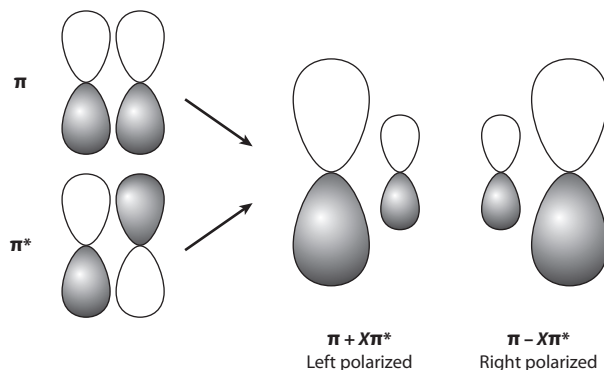


Figure 1

Left and right polarized orbital pairs formed by combining π and π^* orbitals.

differing from one another by the promotion of two electrons (one of α and one β spin) from orbital ϕ_a to ϕ_n is equivalent to the following:

$$\frac{C_0}{2} \{ |\phi_1(1)\phi_2(2) \dots [\phi_a(a) - x\phi_n(a)]\alpha(a)[\phi_a(a+1) + x\phi_n(a+1)]\beta(a+1) \dots \phi_N(N)\phi_{N+1}(N+1)| - |\phi_1(1)\phi_2(2) \dots [\phi_a(a) - x\phi_n(a)]\beta(a)[\phi_a(a+1) + x\phi_n(a+1)]\alpha(a+1) \dots \phi_N(N)\phi_{N+1}(N+1)| \}$$

with $x = (C_1/C_0)^{1/2}$. This two-determinant wave function describes a singlet coupled ($\alpha\beta\text{-}\beta\alpha$) pair of electrons (a and $a+1$) that occupy two different orbitals; whenever one electron occupies the orbital $\phi_a - x\phi_n$, the other electron occupies $\phi_a + x\phi_n$. These so-called polarized orbital pairs are what allow the two electrons to avoid one another. For example, two electrons occupying in the HF picture a C=C π bonding orbital are described in the mean-field model in terms of the single determinant

$$|\pi\alpha(1)\pi\beta(2)|.$$

By instead using the two-determinant wave function

$$C_0|\pi\alpha(1)\pi\beta(2)| - C_1|\pi^*\alpha(1)\pi^*\beta(2)|,$$

which is equivalent to

$$\frac{C_0}{2} \{ |[\pi - x\pi^*]\alpha(1)[\pi + x\pi^*]\beta(2)| - |[\pi - x\pi^*]\beta(1)[\pi + x\pi^*]\alpha(2)| \},$$

the two electrons are allowed to dynamically occupy different regions of space, as shown in **Figure 1**.

Whenever the α electron is more to the right side of the CC bond, the β electron is more to the left, and vice versa. This is an example of dynamical electron pair correlation, which is not a property of any single electron or orbital, but is characteristic of two electrons having correlated probability distributions.

The degree of polarization within the orbital pair $\phi_a - x\phi_n$ and $\phi_a + x\phi_n$ is contained in the parameter x ; if x is small, the two electrons' spatial distributions are quite similar, but if x is close to unity, the two electrons strongly avoid one another. A perturbation estimate (with the fluctuation potential as the perturbation and using the Slater-Condon rules; see **session 2** of the video lectures) of the coupling between the two determinants

$$\psi_0 = |\phi_1(1)\phi_2(2) \dots \phi_a\alpha(a) \dots \phi_a\beta(a+1) \dots \phi_N(N)\phi_{N+1}(N+1)| \quad (17)$$

Slater-Condon rules: expressions for the matrix elements of arbitrary one- or two-electron operators between pairs of single Slater determinant functions

and

$$\psi_1 = |\phi_1(1)\phi_2(2) \dots \phi_n\alpha(a) \dots \phi_n\beta(a+1) \dots \phi_N(N)\phi_{N+1}(N+1)| \quad (18)$$

gives x in terms of the two-electron integrals

$$\langle \psi_0 | H | \psi_1 \rangle = \langle \phi_a^*(1)\phi_a^*(2) | \phi_n(1)\phi_n(2) \rangle \quad (19)$$

coupling the two determinants and the corresponding orbital energy denominator

$$x = \frac{\langle \phi_a^*(1)\phi_a^*(2) | \phi_n(1)\phi_n(2) \rangle}{\varepsilon_a + \varepsilon_a - \varepsilon_n - \varepsilon_n}. \quad (20)$$

The correlation energy associated with these two electrons is given by

$$E_{\text{correlation}} = \frac{|\langle \psi_1 | H | \psi_0 \rangle|^2}{\varepsilon_a + \varepsilon_a - \varepsilon_n - \varepsilon_n} = \frac{|\langle \phi_a^*(1)\phi_a^*(2) | \phi_n(1)\phi_n(2) \rangle|^2}{\varepsilon_a + \varepsilon_a - \varepsilon_n - \varepsilon_n}. \quad (21)$$

The take-home lesson is that a determinant in which a pair of electrons is promoted⁴ (relative to the HF determinant) from two occupied spin-orbitals into two unoccupied spin-orbitals (a) allows these two electrons to correlate their spatial distributions (by forming polarized orbital pairs), thereby (b) lowering the energy of the wave function by a certain amount ($E_{\text{correlation}}$).

In the correlation contribution to the EOM's EA expression, we see two sums. Using the above explanation of correlation energies, the terms in the first sum

$$E_{\text{new correlation}} = \sum_{a=1}^N \sum_{m < n = N+2}^{\infty} \frac{\langle m, n | a, N+1 \rangle \langle a, N+1 | m, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_m} \quad (22)$$

represent the dynamical correlation energy of the extra electron in ϕ_{N+1} and another electron in ϕ_a as they form polarized orbital pairs $\phi_{N+1} \pm x\phi_n$ and $\phi_a \mp x\phi_m$ by mixing in doubly excited determinants with the two electrons promoted to ϕ_n and ϕ_m . This sum is the gain in correlation energy that exists in the anion (because it has an extra electron) but not in the neutral.

The second sum

$$\sum_{a < b}^N \sum_{m=N+1}^{\infty} \frac{\langle a, b | m, N+1 \rangle \langle m, N+1 | a, b \rangle}{\varepsilon_m + \varepsilon_{N+1} - \varepsilon_a - \varepsilon_b}$$

represents the loss in the correlation energy for the two electrons in ϕ_a and ϕ_b caused by the occupancy of ϕ_{N+1} in the anion. In the neutral, doubly promoted determinants in which ϕ_a and ϕ_b are promoted to ϕ_m and ϕ_{N+1} do contribute to the correlation energy. However, in the anion, promotions of ϕ_a and ϕ_b to ϕ_m and ϕ_{N+1} cannot occur because the spin-orbital ϕ_{N+1} is occupied already. So, the occupancy of ϕ_{N+1} in the anion blocks certain double excitations of the other N electrons and thus modifies the correlation energy of these N electrons.

Polarization and dispersion. For certain cases, the correlation energy contributions to EA involving dispersion interactions between the extra electron and the N other electrons (39, 40) can be embodied in a polarization potential (41) experienced by the extra electron

$$V_{\text{polarization}} = -\frac{\alpha e^2}{2r^4} \quad (23)$$

interacting with a molecule having polarizability α , with r being the distance from the molecule to the particle.

⁴In the example presented above, the discussion is limited to the promotion of two electrons from the same occupied orbital into the same virtual orbital, but with different spins, but the idea is more general and applies to correlations between electrons in different orbitals with like or different spins.

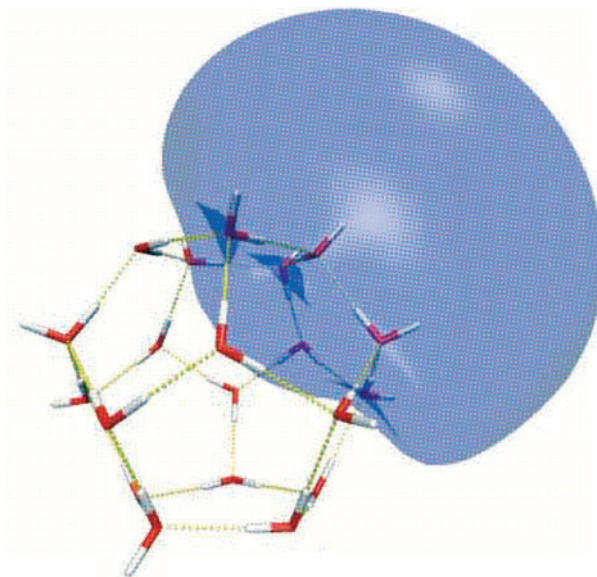


Figure 2

Dipole-bound orbital of $(\text{H}_2\text{O})_{20}^-$. Extracted from figure 7 in Reference 41.

Reference 39 shows that for so-called dipole-bound anions, such as that shown in **Figure 2**, a subset of terms in

$$\sum_{a=1}^N \sum_{m < n = N+2}^{\infty} \frac{\langle m, n | a, N+1 \rangle \langle a, N+1 | m, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_m}$$

represents the dispersion (i.e., van der Waals) interaction energy between the electron occupying the dipole-bound orbital ϕ_{N+1} and the N electrons of the underlying neutral $(\text{H}_2\text{O})_{20}$ cluster whose large dipole potential ($\mu = 18$ D from Reference 41) dominates in binding the extra electron. (Dipole-bound anions are discussed in detail in section 4 of Reference 3.)

Specifically, those terms

$$\sum_{a_{\text{molecule}}=1}^N \sum_{m_{\text{molecule}}, n_{\text{dipole}}}^{\infty} \frac{\langle m, n | a, N+1 \rangle \langle a, N+1 | m, n \rangle}{\varepsilon_a + \varepsilon_{N+1} - \varepsilon_n - \varepsilon_m}$$

involving promotion of (*a*) one electron from an occupied (ϕ_a) to a virtual (ϕ_m) spin-orbital on the underlying neutral cluster and (*b*) a second electron from the occupied dipole-bound (ϕ_{N+1}) to a virtual dipole-bound (ϕ_n) spin-orbital give the dispersion interaction between the dipole-bound electron and the neutral cluster's electrons. For species such as the water cluster shown above, as well as for other strongly polar molecules like HCN and $\text{H}_3\text{C-CN}$, the dipole potential, which is treated at the HF level in the electrostatics of the Fock Hamiltonian, plays the dominant role in binding the extra electron. This is why the anions of such molecules are called dipole-bound. However, it has been shown (39, 41, 42) that the dispersion interactions discussed above can also contribute significantly to binding the electron, in which case it is essential to include correlation when computing EAs for dipole-bound species if one wishes to obtain decent accuracy. It should be mentioned that especially diffuse atomic orbital basis sets (see **session 5** of the video lectures) also must be employed when treating species such as the water-cluster anions; the diffuse functions contained in commonly used **tabulated basis sets** will not be adequate.

Dispersion energy:

correlation energy varying as R^{-6} between two electrons, one in an orbital on one molecule or fragment and another in an orbital on a different molecule or fragment

Reference 41 makes another connection between correlation contributions and polarization contributions to EA by introducing a Drude model (43–45) to replace the self-energy’s representation of the correlated response of the underlying neutral’s electrons to the motions of the dipole-bound electron. In this model, the Hamiltonian H_D for the coupled molecule–electron system is written as

$$H_D = F(r) + b_{osc}(R) + V_{e,osc}(r, R). \quad (24)$$

Based on the earlier discussion, it is natural to take $F(r)$ as the Fock operator containing the kinetic and electrostatic potentials (i.e., electron–nuclear attraction and Coulomb and exchange repulsion) pertinent to the extra electron (whose position is r) in the presence of the neutral molecule. However, to make the method applicable to large water clusters, in Reference 41 and in earlier work (43) from Prof. **Ken Jordan**, $F(r)$ was taken to contain a much simpler potential in which the extra electron’s interaction with each water molecule is modeled in terms of its interaction with three point charges (on the two H atoms and near the O atom) and three polarizable sites (on the H and O atoms) that allow the water molecules to polarize one another. The one parameter of this model, cutting off the electron’s attraction to the point charges, was chosen to make the EA computed with this model agree with the Koopmans’ EA obtained in an HF calculation on the water dimer.

In the remainder of the Drude Hamiltonian H_D , $b_{osc}(R)$ is a Hamiltonian,

$$b_{osc}(R) = -\frac{\hbar^2}{2m_D} \nabla_R^2 + \frac{1}{2} k_D (X^2 + Y^2 + Z^2), \quad (25)$$

designed to represent the motion of the underlying molecule’s electrons in terms of simple three-dimensional harmonic motion of a dipole consisting of two oppositely charged particles of mass m_D and charge q_D separated by a distance R . The coupling between the extra electron and the oscillating dipole is taken to be of the charge–dipole form

$$V_{e,osc}(r, R) = q_D \frac{R \cdot \hat{r}}{r^2} f(r). \quad (26)$$

Here \hat{r} is a unit vector pointing to the extra electron, $q_D \mathbf{R}$ is the dipole vector of the Drude oscillator, and $f(r)$ is a cut-off function that attenuates the attractive charge–dipole potential at small r (see 41 for details).

Then Reference 41 introduced an adiabatic approximation in which the Drude oscillator is assumed to respond quickly to the motion of the extra electron. [This assumption is probably valid for dipole-bound electrons because they reside in very diffuse orbitals, and they have very low electron binding energies (often below 0.1 eV) and thus have low kinetic energy compared with the kinetic energies of the neutral molecule’s valence and core electrons.] This suggests the use of the eigenfunctions $\{|\mathbf{n}\rangle = |n_x, n_y, n_z\rangle\}$ and eigenvalues $\{\varepsilon_{\mathbf{n}}\}$ of b_{osc} to form a matrix representation of the Hamiltonian

$$H_F = b_{osc}(\mathbf{R}) + V_{e,osc}(r, \mathbf{R}) \quad (27)$$

describing the motion of the Drude oscillator in the presence of a stationary (at r) extra electron:

$$\langle n_x n_y n_z | H_F | m_x m_y m_z \rangle = \varepsilon_n \delta_{n,m} + f(r) \frac{q_D}{r^3} [x \langle n | X | m \rangle + y \langle n | Y | m \rangle + z \langle n | Z | m \rangle]. \quad (28)$$

Here, $\delta_{n,m}$ means $\delta_{n_x, m_x} \delta_{n_y, m_y} \delta_{n_z, m_z}$, x , y , and z are the Cartesian coordinates of the extra electron, and the X , Y , and Z matrix elements are given by the harmonic oscillator expressions

$$\langle n_x n_y n_z | X | m_x m_y m_z \rangle = \delta_{n_y, m_y} \delta_{n_z, m_z} \sqrt{\frac{n_x + 1}{2m_D \omega_D}} \text{ when } n_x = m_x - 1, \quad (29)$$

Drude model:
electron–molecule interaction potential in which all but one electron are modeled in terms of a single harmonic oscillator and with a coupling to the excess electron given in the charge–dipole form

$$\langle n_x n_y n_z | X | m_x m_y m_z \rangle = \delta_{n_y, m_y} \delta_{n_z, m_z} \sqrt{\frac{n_x}{2m_D \omega_D}} \text{ when } n_x = m_x + 1, \quad (30)$$

$$\langle n_x n_y n_z | X | m_x m_y m_z \rangle = 0, \text{ otherwise,} \quad (31)$$

with analogous formulas for the Y and Z matrix elements. The eigenvalues are given by

$$\varepsilon_{n_x, n_y, n_z} = (n_x + n_y + n_z + 3/2) \hbar \omega_D \quad (32)$$

with the Drude frequency given by

$$\omega_D = \sqrt{\frac{k_D}{m_D}}. \quad (33)$$

Using only the lowest four Drude oscillator states $\{|n_x, n_y, n_z\rangle = |0, 0, 0\rangle, |1, 0, 0\rangle, |0, 1, 0\rangle \text{ and } |0, 0, 1\rangle\}$, the matrix representation of H_F reduces to

$$H_F = \begin{bmatrix} 3/2 \hbar \omega_D & xv(r) & yv(r) & zv(r) \\ xv(r) & 5/2 \hbar \omega_D & 0 & 0 \\ yv(r) & 0 & 5/2 \hbar \omega_D & 0 \\ zv(r) & 0 & 0 & 5/2 \hbar \omega_D \end{bmatrix}, \quad (34)$$

where

$$v(r) = \frac{q_D}{r^3} f(r) \sqrt{\frac{\hbar}{2\omega_D m_D}}. \quad (35)$$

As in the Born-Oppenheimer approximation, the slow-moving dipole-bound electron then is assumed to move under the influence of a Hamiltonian $H_{adiabatic}$ consisting of $F(r)$ plus the lowest eigenvalue $[U(r)]$ of the above H_F matrix

$$H_{adiabatic} = F(r) + U(r), \quad (36)$$

where

$$U(r) = 2\hbar\omega_D - \sqrt{(1/2\hbar\omega_D)^2 + \frac{\hbar q_D^2}{2\omega_D m_D r^4} f^2(r)}. \quad (37)$$

Using the definition of the polarizability⁵ α_D of the Drude oscillator

$$\alpha_D = \frac{q_D^2}{k_D} = \frac{q_D^2}{\omega_D^2 m_D}, \quad (38)$$

the expression for $U(r)$ can be written in terms of the zero-point energy of the oscillator ($3/2\hbar\omega_D$) and a factor written (by expanding the square root) as

$$\begin{aligned} U(r) &= 3/2\hbar\omega_D + 1/2\hbar\omega_D - \sqrt{(1/2\hbar\omega_D)^2 + \frac{\alpha_D(1/2\hbar\omega_D)}{r^4} f^2(r)} \\ &= 3/2\hbar\omega_D - \frac{\alpha_D}{2r^4} f^2(r) + \dots \end{aligned} \quad (39)$$

The final result is that the Hamiltonian $H_{adiabatic}$ governing the excess electron,

$$H_{adiabatic} = F(r) + 3/2\hbar\omega_D - \frac{\alpha_D}{2r^4} f^2(r) + \dots, \quad (40)$$

⁵In Reference 41, α_D was chosen to be $9.745 a_0^3$, that of a water molecule; the Drude mass m_D was taken to be the electron mass m_e ; and the magnitude of the Drude charge q_D was taken equal to the charge of an electron. These choices then determine k_D and the excitation energy $\hbar\omega$ of the Drude oscillator, which turns out to be 8.7 eV, not unreasonable for a water molecule.

reduces to $F(r)$, which contains the electrostatic potentials, the zero-point energy of the Drude oscillator, and a series of terms, the first of which is of the charge-polarization form varying as r^{-4} . Jordan and coworkers have shown that appropriate choices for the parameters in $F(r)$ allow this model to reproduce well Koopmans' estimates of electron binding energies. Importantly, they also have demonstrated that the Drude model shown above is capable of duplicating to high accuracy the correlation energies obtained on small $(\text{H}_2\text{O})_n^-$ clusters using CCSD(T)-level calculations at much lower computational effort. Recently, the author offered a more in-depth analysis (46) of how the Drude model and other one-electron electron-molecule potentials connect to various electrostatic, relaxation, polarization, and dispersion terms contained in the Fock and second- and third-order self-energy potentials.

By using simple electrostatic model potentials in $F(r)$, employing widely used water-water intermolecular potentials, and making use of the Drude model outlined above to include the correlation interaction between the extra electron and the electrons of the underlying water molecules, the Jordan group has been able to study $(\text{H}_2\text{O})_n^-$ cluster anions ranging from small ($n = 3, 4, 5, 6, \dots$) to large ($n = 25, 30, 200$). Moreover, because of the low computational cost involved in evaluating the water-water and electron-water potentials, they have been able to do so even within parallel tempering Monte-Carlo and molecular dynamics studies of such clusters.

4. TREATING ELECTRONICALLY METASTABLE ANIONS

4.1. What Is the Problem?

For anions that are electronically stable, theoretical methods based on variational theory [e.g., methods such as HF (see **session 2** of the video lectures), density functional⁶ (see **session 11**), configuration interaction (see **session 7**), and **multiconfiguration self-consistent field** theory (see **session 7**) that are derived by making an energy functional stationary] can be used much as one would when treating a neutral molecule or a cation. For an anion that has a positive EA (**Figure 3a**), as long as one employs an atomic orbital basis set capable of describing the diffuse nature of the anion's charge density, one usually finds (a) a Koopmans' theorem estimate EA_{KT} that is positive but smaller than the true EA (because Koopmans' theorem includes neither orbital relaxation, which lowers the HF energy of the anion, nor electron correlation, which usually differentially stabilizes the anion); (b) a so-called Δ -HF $\text{EA}_{\Delta\text{HF}}$ that is also positive, larger than EA_{KT} but smaller than the true EA; and (c) the need to compute the EA at a correlated level $\text{EA}_{\text{correlated}}$ to achieve good accuracy (e.g., ± 0.3 eV). Most if not all of the theoretical results reported, for example, in the excellent recent review (11) from Profs. **Schaefer** and **Ellison's** groups were carried out following the above prescription.

However, for anions whose lowest electronic state lies, at a given molecular geometry, above the energy of the lowest state of the corresponding neutral, one should not use variational-based methods (good basis, Koopmans' theorem, ΔHF , $\text{EA}_{\text{correlated}}$). If one does, one will fail because the lowest-energy $N + 1$ -electron state corresponds to the neutral molecule in its N -electron ground state with the extra electron infinitely far away and having zero kinetic energy. It is this state that any variational method will converge toward.

Again let us use **Figure 3** as an illustration. If a small or modest atomic basis set is used to carry out Koopmans', HF, and correlated estimates for a metastable anion, one will find (a) a

⁶Caution must be exercised when using density functional theory to study anions because many of the theory's functionals possess artificial Coulomb potentials at large r . As noted above, an electron attached to a neutral molecule should experience no such potential. So, one should be careful to use functionals that have been corrected to remove this artifact.

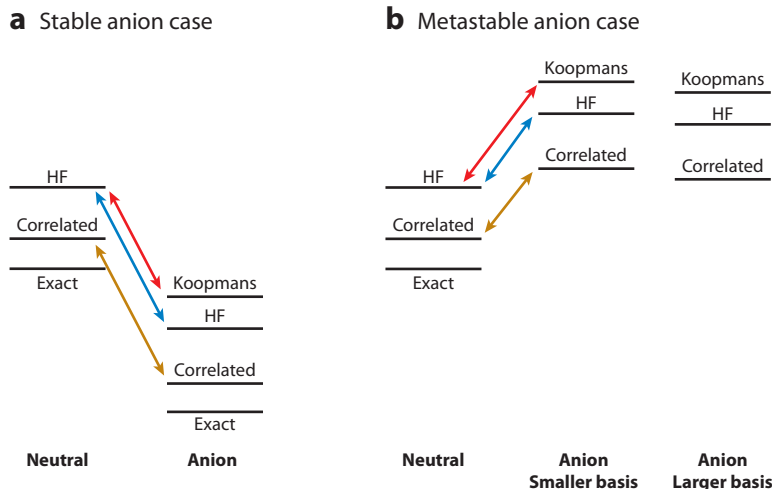


Figure 3

Koopmans, Hartree-Fock (HF), and correlated estimates of electron affinities for electronically stable anions (*a*) and for metastable anions (*b*).

Koopmans' theorem EA that is negative (i.e., the anion has a higher total energy than the neutral), (*b*) a Δ HF EA that is also negative, but smaller than the Koopmans' value because Δ HF includes the (mean-field) orbital relaxation, and (*c*) a correlated EA that is also negative and usually a bit smaller than the Δ HF EA. If the atomic orbital basis is enhanced (e.g., by adding increasingly diffuse functions to accommodate the extra electron's radial extent), the situation will not improve. One will still find Koopmans', Δ HF, and correlated EAs that are negative. In fact, if the basis is enhanced greatly, one will find that the Koopmans' theorem, Δ HF, and correlated EAs approach zero because the HF and correlated energies of the anion approach those of the corresponding neutral. This happens because the anion wave function undergoes variational collapse to a function appropriate for the neutral molecule plus an electron far away and with little kinetic energy. [The radial extent of the atomic basis will determine how far away and how slowly (i.e., governed by the de Broglie wave length that the basis can describe) the extra electron can escape.]

Before describing how one can overcome variational collapse, it is important to emphasize that perturbative (e.g., MPn methods), coupled-cluster, or EOM-type methods will also fail when applied to metastable anions (for more detail on the MPn and coupled-cluster methods, see **session 8** of the video lectures). The former two methods use the HF wave function as a starting point and thus are plagued by its collapse. The EOM approach yields a multitude of solutions to its eigenvalue problem, the lower of which will describe the neutral molecule plus a free electron.

So, what can be done to find a metastable anion state? Above we point out that, when considering a singly charged anion, the extra electron experiences no long-range Coulomb attraction. The charge-dipole, charge-quadrupole, and charge-induced-dipole (i.e., polarization) potentials are expected to dominate at large r , and the valence attraction and exchange repulsion potentials will dominate at smaller r . However, there is also the centrifugal potential

$$V_{\text{centrifugal}} = \frac{L(L+1)}{2r^2} \text{ (in Hartree units)} \quad (41)$$

that contributes to the net radial potential.

Centrifugal potential:

contribution to the electron-molecule radial potential arising from nonzero angular momentum of the excess electron

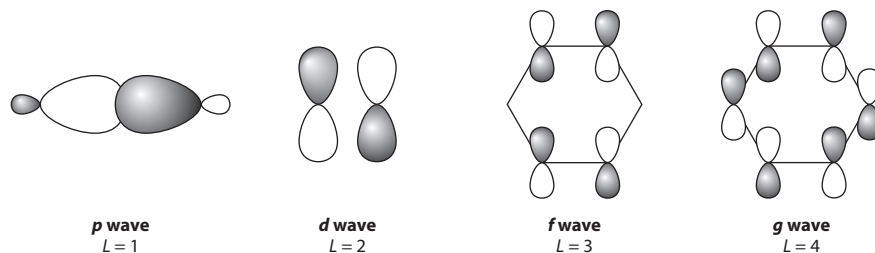


Figure 4

Dominant L values belonging to σ^* , olefin π^* , and aromatic π^* orbitals. For situations in which the orbital does not possess the perfect nodal symmetry shown in the figure (e.g., as in the $SS \sigma^*$ orbital of $H_3C-S-SCH_2CH_3$ or the π^* orbital in $Me_2C = CH_2$ or substituted aromatics), the orbital does not possess only the L character shown, but it is dominated by this L character, so the analysis following still holds reasonably well.

To understand the role and magnitude of this centrifugal potential, let us consider several cases in which an extra electron is placed into an unoccupied orbital ϕ_{N+1} . **Figure 4** shows four examples, and each orbital is labeled with an L value reflecting the number of nodal planes this orbital possesses ($L = 1$ having one nodal plane; $L = 2$, two planes; and so on).

The centrifugal potential is repulsive for all r values. The total radial potential experienced by the extra electron is thus a sum of a repulsive centrifugal⁷ potential, the electrostatic (i.e., charge-dipole, charge-quadrupole), polarization, and valence-range potentials discussed above. **Figure 5** displays three examples of such a total radial potential.

For the red and blue potentials, the sum of the attractive potentials is strong enough to generate a bound state whose radial wave functions are depicted by the localized red and blue functions in **Figure 5**. Because these functions are bound, (a) their energies (the horizontal red and blue lines in **Figure 5**) lie below the asymptote of the potential, and (b) their wave functions decay within the classically forbidden regions and thus do not extend to large r .

In contrast, the black potential does not have sufficiently strong attractive contributions to produce a bound state. However, if its attractive regions are nearly strong enough to bind and its barrier is high and wide enough to inhibit electron tunneling, a metastable anion state will exist that (a) has a wave function with large amplitude in the region inside the barrier and (b) has a lifetime long enough to allow the excess electron to exert influence (e.g., generate forces) on the underlying nuclear framework (e.g., 10^{-14} s or longer).

However, this state also has amplitude beyond the barrier and is not the lowest-energy state of this potential. There are, in principle, a continuum of states having lower energies than the metastable state with wave functions having large amplitude beyond the barrier and longer de Broglie wavelengths (and thus lower kinetic energy) than that of the large- r tail of the metastable state. The problem one faces in such cases is how to uncover the metastable state from the quasi-continuum⁸ of states surrounding it.

Metastable state: an electronic state that is not bound but that has a lifetime (often determined by tunneling through a centrifugal barrier) long enough to make it experimentally detected

⁷When considering forming a multiply charged anion from one of lower charge, there is also the long-range Coulomb repulsion that must be added to the other potentials. In such cases, the repulsive potential at large r contains contributions from both the Coulomb and centrifugal terms.

⁸In any finite basis set, there will be a discrete set of states in close energy proximity; only in the complete-basis limit will a true continuum occur.

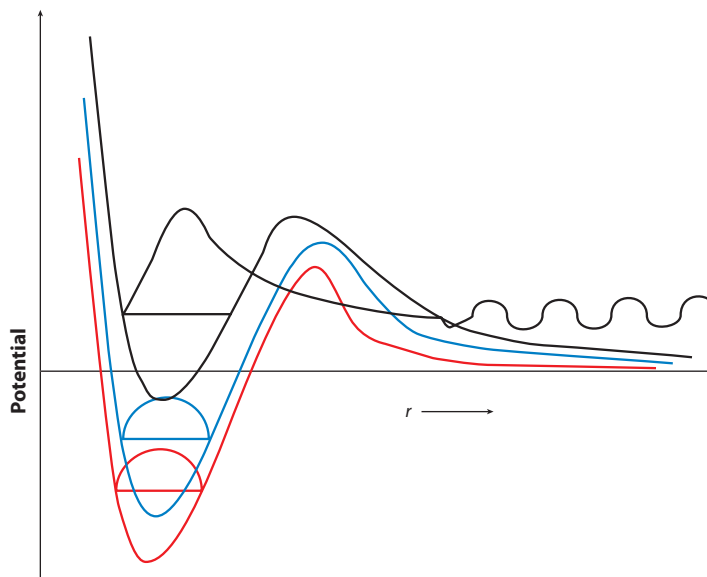


Figure 5

Total radial potentials for a range of strengths in the valence-region part of the potential, with red corresponding to the strongest valence-range attraction, also showing the potential barrier.

4.2. Finding the Metastable State

The most widely used tools for finding metastable states buried in quasi-continua are the stabilization-based methods (47–51). In the approach pioneered by Prof. **Howard Taylor**, the de Broglie wavelengths of the orbitals forming the discrete quasi-continuum are varied (e.g., by varying orbital exponents of diffuse basis functions) until one of the eigenfunctions can match, in amplitude and first derivative, the portion of the metastable state's wave function localized inside the barrier (see **Figure 5**). Under such conditions, the energy of the metastable state becomes relatively stable as a function of further wavelength variation. In this conventional **stabilization method**, a plot of the energy of the metastable state as a function of the parameter used to alter the wavelength of the quasi-continuum states also can be used to obtain an estimate of the lifetime of this state.

Another stabilization method that is more straightforward can be used to estimate the energy of the metastable state but not its lifetime. In this **charge-stabilization approach**, one first decides into which virtual orbital one wants to place the extra electron. One then increases the nuclear charges of the nuclei spanning this orbital by a small amount δq and carries out a series of calculations of the neutral-anion energy separation (e.g., by computing E_{neu} and E_{an} or using EOM theory) for several values of δq . One then plots these energy separations versus δq and extrapolates to $\delta q \rightarrow 0$ to obtain an estimate of the (negative) EA. In this technique the increase in nuclear charges introduces a perturbation potential

$$V = \sum_a \sum_{i=1}^{N+1} \frac{-\delta q}{|r_i - R_a|}, \quad (42)$$

where $|r_i - R_a|$ is the distance of the i -th electron to the a -th nucleus whose charge is incremented by δq . Because this potential is stabilizing in regions of space near the nuclei, it tends to lower the energies of states having high electron density near these nuclei relative to states with high density

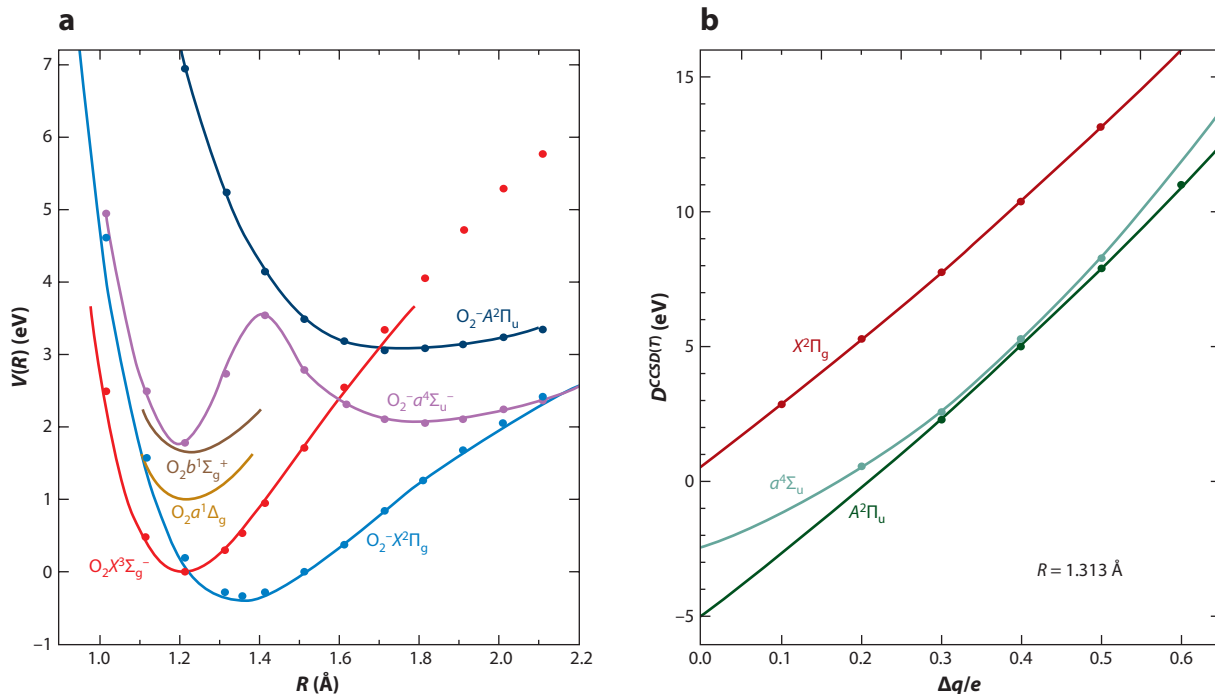


Figure 6

Potential curves (a) for O_2 and O_2^- as well as the charge-stabilization plots (b) used to establish the anion states' energies at one O-O internuclear distance, $R = 1.313$ Å. Figure adapted from Reference 16.

in the large- r region. In effect, this extra potential V causes the black curve in **Figure 5** to be pulled down to the blue curve and, as δq is further increased, to the red curve. This perturbation differentially stabilizes valence-localized electron-attached states and thus renders positive their electron binding energies, allowing them to be treated reliably using variational methods.

An example of a charge-stabilization plot is shown in **Figure 6b**. **Figure 6a** shows the low-energy O_2 and O_2^- potential curves; whenever an anion curve lies above the ground-state energy of the neutral O_2 , the energy of the anion was computed using the charge-stabilization method.

The anion-neutral energy differences plotted in **Figure 6b** are extrapolated to produce estimates of the energies of the $X^2\Pi_g$, $\sigma^4\Sigma_u$, and $A^2\Pi_u$ anion states at $R = 1.313$ Å. Analogous plots associated with different internuclear distances were used to generate the other data point shown in **Figure 6a**.

SUMMARY POINTS

1. Being intensive quantities, EAs become increasingly difficult to evaluate as the number of electrons in the molecule grows if one uses traditional methods that compute separately the extensive total electronic energies of the neutral and anion.
2. The inclusion of special diffuse basis functions and consideration of electron correlation are usually important because EAs are small quantities, so they must be computed to high precision.

3. EOM theory is an efficient tool both for calculating the intensive EAs directly and for deriving electron-molecule interaction potentials.
4. From EOM theory, it is possible to write down electron-molecule interaction potentials that will yield electron binding energies equivalent to those obtained from ab initio MP perturbation theory.
5. A potential constructed from HF-level permanent electrostatic moments (i.e., charge-dipole, charge-quadrupole) and HF-level polarizability (e.g., $-1/2 \alpha r^{-4}$) is consistent with second-order MP theory.
6. To achieve consistency with third-order MP theory, one needs lowest-order corrections to electrostatic moments and polarizability.
7. To obtain proper descriptions of metastable anion states and associated lifetimes, one must employ special tools such as stabilization-type methods.
8. Some familiar multiply charged anions (e.g., SO_4^{2-} , PO_4^{3-}) are not electronically stable as isolated species in the gas phase.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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39. Along with Ref. 40, shows early recognition that dispersion contributions to electron-molecule interactions can be important.

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