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Ab Initio Electronic Structure of Anions

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I. Introduction

A. Characteristics of Negative Ions

In characterizing anion states either experimentally or theoretically different techniques are required for bound and temporary or metastable anions. Anions that lie energetically above the ground state of the neutral molecule (or atom) are called temporary anions since they are unstable with respect to electron detachment. Temporary anions generally have lifetimes in the range of 10^{-13}–10^{-16} s and thus are difficult to study by using optical spectroscopic methods. Various types of electron-impact spectroscopy have proven particularly valuable for characterizing temporary anions.[1,2] Some of these experimental methods are discussed in the accompanying paper[3] of Jordan and Burrow. Because temporary anion states lie in the continuum of the neutral species plus free electron, they cannot be treated in general by means of a straightforward variational calculation. Techniques designed for their study are discussed later in this paper. Bound or stable anions lie energetically below the ground state of their parent neutral and can be studied by a variety of experimental methods including photodetachment spectroscopy[4] and laser photoelectron spectroscopy.[5] The contribution by Wetzel and Brauman in this issue covers many of these experimental techniques. Theoretically they can be characterized by using traditional quantum chemical methods such as the self-consistent field (SCF), configuration interaction (CI), multiconfiguration self-consistent field (MCSCF), and many-body techniques, although extra care must be exercised for reasons outlined below.

The ab initio theoretical study of *stable* atomic and molecular negative ions involves complications not encountered in analogous studies of neutral or cationic species. In particular, the diffuse spatial extent of the outermost orbitals of anions places additional requirements on any quantum chemical calculation. Within the conventional LCAO-MO finite atomic basis approach, adequate description of diffuse charge densities requires that diffuse atomic orbitals be added to the core-and-valence atomic basis sets. Because computational expense varies as a high power of the size of the atomic orbital basis set, this greatly increases the computer-time requirements for negative ion calculations. Diffuse charge densities correspond to weak binding energies and low average values of kinetic energy. The weak binding energies imply that any method used to compute the electron affinities (EA) must be very reliable. The low classical kinetic energies suggest that energy transfer from vibrational and rotational degrees of freedom to the electronic degrees of freedom may be more facile than in neutral or cationic species where the more rapidly moving electrons readily "track" the motion of the underlying nuclei. Thus, the neglect of nonadiabatic interactions, which is the cornerstone upon which the concept of the potential energy surface is predicated, is less likely to be reasonable for anions.

For most classes of molecules, the calculation of accurate EA's requires that the molecular orbital picture be corrected by including so-called electron correlation effects. In the self-consistent field (SCF) Hartree–Fock molecular orbital model of electronic structure, each electron is allowed to "feel" the other electrons only via an *average* interaction potential. This potential consists of the averaged Coulomb and exchange interaction

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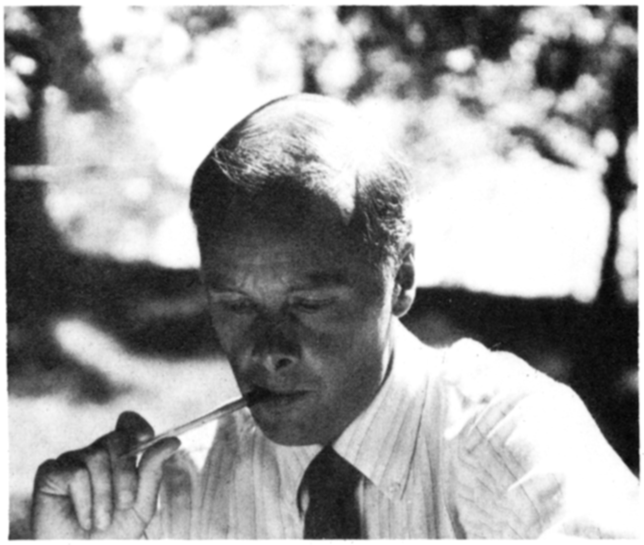
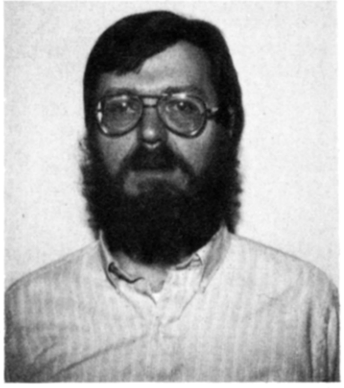


Jack Simons was born in Youngstown, OH, in 1945. He earned his B.S. degree from Case Institute of Technology in 1967 and his Ph.D. degree in theoretical chemistry from the University of Wisconsin in 1970. After one year as an NSF Postdoctoral Fellow at MIT, he joined the University of Utah Chemistry faculty where he is now Professor and Chairman of Chemistry. He has held A. P. Sloan, Camille and Henry Dreyfus, and Guggenheim Fellowships, and he won the 1983 Medal of the International Academy of Quantum Molecular Sciences. His research interests involve quantum chemistry, dynamics, and statistical mechanics, especially as applied to negative molecular ions.



Kenneth D. Jordan was born in Norwood, MA, in 1948, and received his B.A. degree in chemistry from Northeastern University in 1970. He received his Ph.D. in physical chemistry from the Massachusetts Institute of Technology in 1974, working with Professor Robert Silbey. He then joined the faculty at Yale University as a J. Willard Gibbs Instructor of Engineering and Applied Science. In 1978 he moved to the Chemistry Department at the University of Pittsburgh, where he is currently Professor of Chemistry. His research interests include theoretical studies of the electronic structure of neutral and charged molecules and clusters, reaction mechanisms, and properties of electronically excited species. His research group is also applying the techniques of electron transmission spectroscopy and electron energy loss spectroscopy to characterize temporary anions of polyatomic molecules.

energy with the charge densities of the other molecular orbitals of the molecule. The need for a self-consistent solution arises because the Fock operator itself depends on the occupied molecular orbitals for which one is trying to solve. Inclusion of the true electron–electron interaction potential, which the SCF model does not treat properly, is essential for highly accurate calculations. To better appreciate some of the difficulties that occur specifically in anion calculations, let us examine the physical content of the orbital picture and the Koopmans' theorem[6] which relates orbital energies to EA's and ionization potentials (IP's) and which has proven very useful computationally and conceptually in chemistry.

1. Koopmans' Theorem and the Orbital Picture

The need for highly accurate quantum chemical methods when anions in particular are considered can be made clear by considering how we usually formulate the electron affinity of an atom or molecule and contrasting this formulation to that of the ionization potential. In the most commonly used expression, we assume that we have carried out a single-configuration self-consistent field (SCF) calculation on the neutral molecule and obtained an energy $E_N(\text{SCF})$. If we then use the SCF molecular orbitals thus obtained to compute the energy of the cation $E_+(\text{KT})$ or anion $E_-(\text{KT})$ *without* allowing these orbitals to relax (i.e., be reoptimized), we obtain the Koopmans' theorem (KT) approximations to the EA and ionization potential (IP)

$$\text{IP}_{\text{KT}} = E_+(\text{KT}) - E_N(\text{SCF}) = -\epsilon_i$$

and

$$\text{EA}_{\text{KT}} = E_N(\text{SCF}) - E_-(\text{KT}) = -\epsilon_\alpha$$

where ϵ_i and ϵ_α are respectively the energies of the appropriate occupied and unoccupied orbitals of the neutral molecule. (These expressions are appropriate for closed-shell molecules treated within the restricted Hartree–Fock (RHF) approximation and to those open-shell species that can be described by a single configurational spin-unrestricted Hartree–Fock (UHF) wave function.) The exact nonrelativistic expressions for the EA's and IP's can be written in terms of the KT-level estimates together with corrections for "relaxation" and correlation energies. By relaxation we mean the changes in the molecular orbitals needed to make them appropriate SCF orbitals of the cation or anion. The difference between the energy of the ion using the relaxed orbitals and the frozen neutral-molecule orbitals is called the relaxation energy and is denoted $E_+(\text{R})$ and $E_-(\text{R})$ for the cation and anion, respectively. This gives rise to the expressions

$$\text{IP}_{\alpha\text{SCF}} = E_+(\text{SCF}) - E_N(\text{SCF}) = -\epsilon_i + E_+(\text{R})$$

$$\text{EA}_{\alpha\text{SCF}} = E_N(\text{SCF}) - E_-(\text{SCF}) = -\epsilon_\alpha - E_-(\text{R})$$

where $E_+(\text{SCF})$ and $E_-(\text{SCF})$ are the SCF energies of the cation and anion, respectively. (Actually, there is an ambiguity in the definition of E_R and in the correlation corrections to be discussed subsequently. This may be seen as follows: Consider the case of a closed-shell neutral molecule. The open-shell anions or cations of this system can then be described in either the RHF or UHF approximations. Depending on whether the UHF or RHF descriptions are used, the magnitude of the relaxation and correlation corrections will differ. In the RHF picture, the magnitude of the electron correlation corrections to the IP's and EA's are generally greater than those in a UHF picture.)

Even after the orbitals are allowed to relax, one does not yet have fully correct descriptions of the neutral and ion energies. The so-called correlation energies must be brought into the picture. The correlation energy of a given species is defined as the difference between the exact nonrelativistic energy and the fully relaxed SCF energy and is denoted $E_N(\text{C})$, $E_+(\text{C})$, and $E_-(\text{C})$ for the neutral, cationic, and anionic species, respectively. The expressions for the exact nonrelativistic EA and IP are given as

$$\mathrm{IP} = -\epsilon_i + E_+(\mathrm{R}) + \mathrm{XE}_{\mathrm{IP}}(\mathrm{corr})$$

and

$$\mathrm{EA} = -\epsilon_\alpha - E_-(\mathrm{R}) + \mathrm{XE}_{\mathrm{EA}}(\mathrm{corr})$$

where $\mathrm{XE}_{\mathrm{IP}}(\mathrm{corr}) = E_+(\mathrm{corr}) - E_{\mathrm{N}}(\mathrm{corr})$ and $\mathrm{XE}_{\mathrm{EA}}(\mathrm{corr}) = E_{\mathrm{N}}(\mathrm{corr}) - E_-(\mathrm{corr})$ are the correlation corrections to the IP and EA, respectively. For the IP's a fortuitous cancellation often occurs that makes the $\mathrm{IP}_{\mathrm{KT}}$ values more accurate than one might expect. The correlation energy difference $E_{\mathrm{IP}}(\mathrm{corr})$ is usually positive because correlation energy generally increases in magnitude with the number of electrons (correlation energies are inherently negative quantities), whereas the relaxation energy of the cation $E_+(\mathrm{R})$ is negative (i.e., relaxing the orbitals necessarily lowers the cation's energy). As a result, the correlation and the relaxation corrections tend to cancel in the calculation of IP's. The anion case is different. Again the correlation energy difference $E_{\mathrm{EA}}(\mathrm{corr})$ is usually positive but now the relaxation correction enters as a positive quantity $-E_-(\mathrm{R})$. The result is that the correlation and relaxation corrections tend to reinforce in the EA case. For these reasons Koopmans' theorem tends to yield considerably more reliable estimates for IP's than EA's.

2. *Need for Accurate Tools*

Not only is the quantum chemical calculation of EA's complicated by the additive nature of the relaxation and correlation corrections but the small magnitudes of most EA's (typical atomic and molecular EA's range from 0.1 to 3 eV) make it imperative that procedures capable of high accuracy be employed. We and others have found that, for most species, accurate computation of EA's requires large atomic orbital basis sets and state-of-the-art treatment of electron correlation. In fact, even with the best efforts that can presently be made, it is extremely difficult to reliably calculate EA's to within an accuracy of better than 0.2 eV for most classes of atoms and molecules.

In a pioneering study of atomic EA's, Sasaki and Yoshimine[7] found that even with Slater-type orbital (STO) basis sets as large as 8s7p6d5f4g3h2i and with electron correlation treated through CI calculations (including all single and double excitations together with a limited number of triple and quadruple excitations) the resulting EA's of O and F were too small by 0.3–0.4 eV. Given the size of the basis sets employed, these results were particularly discouraging. Recent investigations by Feller and Davidson[8] and by Raghavachari[9] are more encouraging. These authors have been able to obtain results superior to those of Sasaki and Yoshimine while using considerably smaller basis sets, 8s5p4d2f1g in the case of Feller and Davidson and 7s6p4d2f in the case of Raghavachari. The success of these recent calculations derives from the facts that care was taken to include those diffuse s, p, and d functions needed to describe the anions and a significant fraction of the valence-space electron correlation was recovered.

The difficulty of achieving reliable estimates of atomic and molecular EA's even for such seemingly simple species has been and continues to be strong motivation for exploring the development of new theoretical models and computational tools.

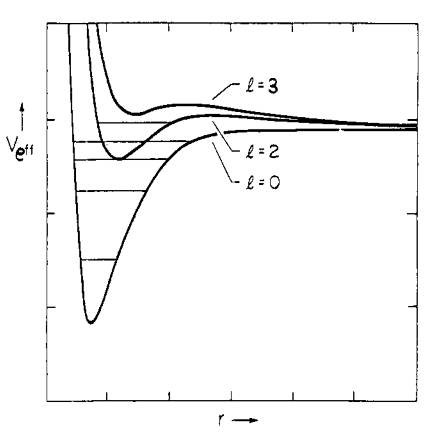


Figure 1. Effective potential energy of interaction between a "target" atom, at the origin, and an electron at a distance *r* for various values of angular momentum *l*.

3. *Other Attributes of Negative Ions*

Relatively few atomic or molecular anions possess bound (with respect to electron detachment) excited electronic states. The weak forces that bind the "extra" electron to the neutral molecule to form the ground-state anion are often too weak to support bound excited states. There are, of course, exceptions, which will be discussed later. Nevertheless, such anions can display spectroscopic characteristics similar to those of species with bound excited states because they often possess metastable excited electronic states whose lifetimes are long enough to yield resolved spectral structure. Moreover, it should be noted that for many molecules, including H_2, N_2, CO, ethylene, and benzene, even the ground-state anion may be metastable; that is, there may exist no bound anion states.

The metastable states of anions are usually classified as either "shape" or "core-excited" resonances.[10] In the former the attractive forces due to the interaction of the "extra" electron's charge with the permanent and induced moments of the ground state of the underlying neutral molecule (or atom) combine with the repulsive centrifugal force caused by the electron's nonzero angular momentum to produce an effective potential for the electron that has an attractive well and a centrifugal barrier (see Figure 1). A shape resonance arises as a result of the electron being trapped behind the barrier. The energy of this state relative to the neutral molecule (or atom) to which it eventually decays via electron loss is called the "position" of the resonance. The lifetimes of shape resonances typically lie in the 10^{-14}–10^{-16}-s range. The ^{2}P anion state of Mg and the π^* states of N_2, CO, and the olefins are examples of shape resonances.

Core-excited resonances may be viewed as arising from the attachment of an "extra" electron to an excited state of the neutral molecule. These may be further divided into Feshbach and core-excited shape resonances.[10] The former lie energetically just *below* the excited "parent" state of the neutral. They tend to be appreciably longer lived than shape resonances because they can decay to the ground state of the neutral only by a two-electron transition in which one electron is ejected and another is "de-excited". An example is the $\pi(3s)^2$ resonance of ethylene (see Figure 2). Lifetimes

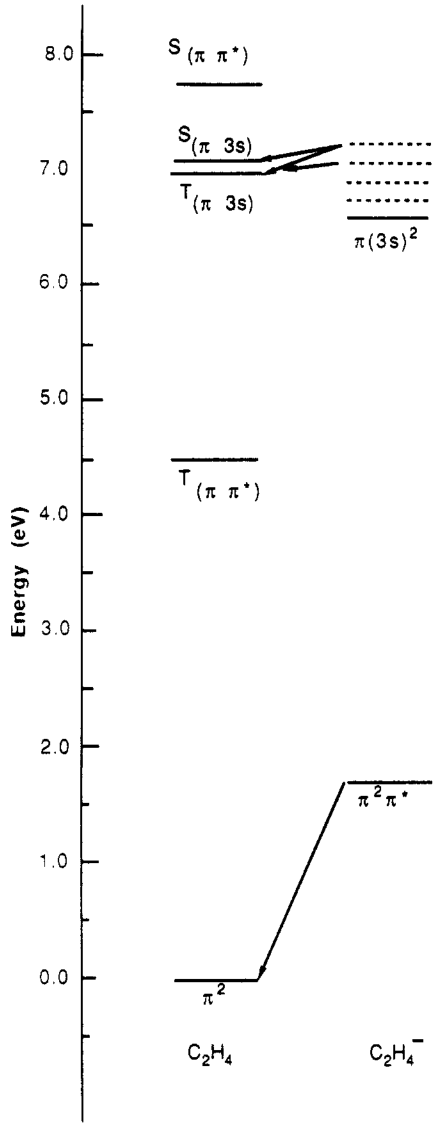


Figure 2. Correlation diagram showing the relative energies of the electronic states of ethylene and its anion. The one-electron-allowed autodetachment channels are indicated by the diagonal lines. For the $\pi(3s)^2$ Feshbach resonance, the horizontal dashed lines indicate the vibrational levels associated with the C–C stretch mode. The $v = 0$–2 levels of the Feshbach resonance cannot decay by a one-electron process, whereas for $v \geq 3$ one-electron decay to the $\pi 3s$ Rydberg states is possible.

of such Feshbach resonances typically lie in the 10^{-12}–10^{-14}-s range. Core-excited shape resonances, on the other hand, lie energetically above the parent excited state of the neutral molecule and thus tend to have significantly shorter lifetimes since they can decay by one-electron detachment to yield their neutral "parents". The $\pi\pi^{*2}$ states of olefins fall into this category of metastable anions.

In addition to their energies or positions, resonances are also characterized by the angular distributions of the resonantly scattered electrons. These, in turn, are determined by the symmetry and shape of the orbital(s) involved in the electron capture process. For example, the $1\sigma_g{}^2 1\sigma_u\ {}^2\Sigma_u$ resonance of H_2 and the ^2P resonance of Mg are said to be p wave, while the π^* resonances of N_2 and ethylene are d wave.

4. Need for New Tools

The theoretical study of metastable shape and core-excited states cannot be performed by using conventional quantum chemical tools because these states lie buried in a continuum of states. This continuum of states corresponds to the neutral molecule plus a free electron whose kinetic energy can have any value (i.e., is not quantized). New theoretical approaches have had to be developed for dealing with the difficulties of metastable anions. Taylor in particular pioneered the development of new techniques for locating these metastable states.[11] He and others[12,13] have extended these methods to permit more accurate determination of the positions of such resonances and for the calculation of their lifetimes. Specific examples of the applications of these new methods will be covered later in this paper.

Here we note that the different types of resonances are often treated with different approaches theoretically. For example, it is often possible to treat Feshbach resonances using standard variational techniques by intentionally excluding electronic configurations that permit decay to energetically accessible states of the neutral molecule. A rigorous procedure for performing such calculations can be formulated by using projection operators.[14]

Single-particle shape resonances pose a particularly challenging theoretical problem since even the single configurational SCF wave function is not stable variationally for these species. A wide range of methods have been developed and applied to the characterization of such shape resonances. For comparison with experiment, it would of course be desirable to utilize scattering procedures capable of giving the scattering cross sections as a function of energy and scattering angle. However, the application of fully ab initio scattering calculations to polyatomic molecules is a very computationally demanding task[15] and unlikely to be useful for characterizing resonances in polyatomic molecules in the near future. This has generated considerable interest in the use of square-integrable (L^2) methods for treating shape resonances.[11-13,16] These methods have the advantage that they utilize standard quantum chemistry codes (suitably modified). They have the disadvantages that they do not yield complete cross sections and that they require very large basis sets (when used with discrete basis sets as is usually the case).

B. Classification of Anions

For the purposes of this paper, we will subdivide all atomic and molecular anions into four groups: (1) "conventional" anions involving common chemical species and functional groups for which the electron's binding arises largely through the usual valence attractions and repulsions (nuclear attraction and electron-electron repulsion); (2) anions in which the "extra" electron can be viewed as bound to the dipole force field of a highly polar molecule or a cluster of such molecules; (3) cluster anions consisting of (a) a conventional anion clustered by one or a few "solvent" molecules, (b) a cluster of molecules which, alone, could not bind an electron but which, in concert, can form a bound anion, or (c) a cluster of alkali or other metal atoms with an electron attached; and (4) metastable states of anions, which may be excited states of anions whose ground states are bound or they may be the lowest energy anion states of species that do not form bound anions.

This classification scheme simply reflects our own perception of the focal points of theoretical and experimental research in anion chemistry. The conventional anions include species such as $[NO_2]^-$, $[HCO]^-$, $[CH_2]^-$, C_2^-, and Cl^-, which have been widely studied for many years both experimentally and theoretically. Current interest in these species focuses on more accurate determination of their electron detachment energies, examination of their excited states, and consideration of where, in geometry space, the anion's and parent neutral's potential energy surfaces cross (because electron ejection can occur if these regions of space are sampled by vibrations).

Polar-molecule anions such as $[LiF]^-$ and $[(NaCl)_2]^-$ are of interest because they serve as prototypical examples for the binding of an electron to dipole force fields. There have been a number of recent experimental spectroscopic studies aimed at elucidating the nature of such electronic states.[17,89-92] The charge–dipole interaction has a long history in physics and continues to intrigue scientists because of its highly singular $1/r^2$ dependence which gives rise to an unusual collection of bound states. For example, it has been shown that within the Born–Oppenheimer approximation any neutral molecule with a dipole moment greater than 1.625 D supports an infinite number of bound anion states.[18-25] For dipole moments only slightly greater than this critical value, the EA's are *very* small, so the charge density is extremely diffuse, with much of the charge density being located 10 Å or more "behind" the electropositive end of the molecule. Such species are difficult to treat theoretically because of the requirement that the dipole moment be accurately characterized and because of the importance of non Born–Oppenheimer terms.

Cluster anions are of great current experimental and theoretical interest. Species such as $H^-(H_2O)_n$, F^-HF, and NO^-Ar_n typify one class of cluster anions; these systems involve an anion, which itself can exist as a stable species, solvated by one or more atoms or molecules. Experimental study of intramolecular rearrangements, for example, $H^-(H_2O) \rightarrow H_2 + OH^-$, and spectroscopic characterization (i.e., geometries, vibrational frequencies) of these systems are especially important. Metal anion clusters, Li_n^-, Cu_n^-, and Na_n^-, are receiving much attention because of the advent of gas-phase nozzle beam techniques for studying neutral and ionic clusters.[26] For these species one is especially interested in the variation of electron affinity with cluster size, the possible role of Jahn–Teller instabilities, and the existence of bound excited-state anions. Anions such as $(H_2O)_n^-$ and Be_4^- are examples of systems whose constituents (i.e., H_2O or Be) alone cannot bind an electron but which can form stable anions in clusters.

The family of anions that are metastable with respect to electron loss has only in recent years become amenable to experimental and theoretical study. The technique of electron transmission spectroscopy, developed by Schulz and co-workers,[27] has proven particularly important for characterizing the unoccupied molecular orbitals of atoms and molecules. The use of ETS in studies of hydrocarbons is reviewed in a companion paper in this issue. Temporary or metastable states of anions arise in a wide variety of atoms and molecules. We chose to discuss these anions as a separate family because the experimental and theoretical methods used to study them are somewhat unique. Moreover, due to their short lifetimes, they exhibit a range of interesting dynamical behavior.

II. Specific Anion Studies

A. "Conventional" Anions

1. Atomic Species

a. Benchmark Studies on First-Row Atoms. Among the numerous articles on EA's of atomic species that have appeared during the 5-year period covered by this paper, we mention only a few which are particularly noteworthy because of the insight they have provided into the types of basis functions and correlation effects important for describing negative ions and calculating EA's. Botch and Dunning,[28] Feller and Davidson,[8] Roos and Sadlej,[29] and Raghavachari[9] all carried out in-depth studies of the EA's of first-row atoms in which the effects of choices of basis sets and electronic configurations on calculated EA's were extensively examined.

Using a multireference SDCI procedure, Feller and Davidson[8] obtained an EA of 1.26 eV for the O atom, 0.20 eV smaller than the experimental value. The inclusion of a Davidson-like correction[30] for higher order excitations reduced the discrepancy with experiment to 0.14 eV. (These authors did not report results for fluorine.) Raghavachari[9] utilized many-body perturbation theory and the coupled cluster method to determine the EA's of boron through fluorine. With the largest basis set utilized (7s6p4d2f), formed by adding two sets of diffuse s and p functions, four d functions, and two f functions to Dunning's 5s4p basis set,[31] the CCD + ST(CCD) method gave EA's within 0.10 eV of the experimental values for all elements considered. The energies in the CCD + ST(CCD) approximation are obtained by adding to the traditional coupled-cluster doubles (CCD) energy a ST(CCD) term which includes the contributions of single and triple excitations evaluated by using the fourth-order perturbation theory expression for these terms but using the CCD doubles wave function rather than the first-order doubles wave function in this expression.

The convergence of the oxygen and fluorine EA's with expansion of the basis set is slow. For example, Feller and Davidson's multireference singles and doubles configuration interaction (MRSDCI) calculations on O revealed that on going from a 2d to a 3d basis set the EA increased by 0.06 eV, while the addition of the first f function contributed 0.06 eV to the EA, the second 0.03 eV, and the g function 0.03 eV. Raghavachari found that the use of a 6-311+G(3df) (5s4p3d1f) basis set gave EA's of O and F 0.12–0.14 eV smaller than those obtained with the 7s6p4d2f basis set. A significant fraction of these energy differences is due to inadequate flexibility of the 5s4p3d1f basis set in the s and p space.

From the results obtained for the atoms it appears that it is necessary to use basis sets of at least 7s5p3d2f quality on elements from the first row of the periodic table (F, O, C, etc.) and probably of at least 4s3p1d quality on the hydrogen atoms to be able to consistently predict EA's to within 0.1 eV of their experimental values. (As will be discussed later, for certain classes of molecules considerably smaller basis sets will suffice.) With basis sets of this size, calculations are feasible for first-row diatomics and triatomics, but would not be feasible on much larger molecules.

It is interesting to compare Raghavachari's CCD results for the EA of F with the corresponding results of Adamowicz and Bartlett,[32] who utilized numerical orbitals. The calculations of the latter authors should be relatively free of basis-set errors. The overall agreement between these two sets of calculations is quite satisfactory, indicating that the basis set used by Raghavachari is indeed adequate.

All three of the studies discussed in this section show that triple and quadruple excitations with respect to the Hartree–Fock reference configurations are very important, particularly for O and F for which they contribute over 0.2 eV to the EA's.

i. Electron Pair Correlations. It is natural to wonder why it is so difficult to achieve accurate EA's for simple atomic species and what physical roles the high angular basis functions and the numerous configurations play in describing the electronic motions in these species. To better appreciate these factors, it helps to review the physical content of various electron correlation contributions and to conceptualize how these factors contribute to the EA. For the sake of clarity, let us focus on one particular atom, fluorine, and its anion, F^-. It is not surprising to any chemist that, because of the additional interelectron repulsions operative in F^-, the 2p SCF orbitals of F^- are more diffuse than those of atomic F. It is precisely this orbital difference that is referred to as "relaxation" and which accounts for a major (>1 eV) correction to the Koopmans' theorem estimate of the EA of F. To allow for this relaxation, one must include basis functions capable of describing both the "normal" valence orbitals and diffuse basis orbitals.

Electron correlation effects are the other major corrections to the simple KT picture. Intrapair correlations are handled by introducing electronic configurations in which the two electrons are "promoted" from an orbital which they occupy in the Hartree–Fock reference configuration to unoccupied orbitals. For example, electronic configurations of the form $1s^22s^22p^43p^2$, $1s^22s^22p^43s^2$, and $1s^22s^22p^43d^2$ (which are denoted $2p^2 \rightarrow 3p^2$, $2p^2 \rightarrow 3s^2$, and $2p^2 \rightarrow 3d^2$ for convenience) are particularly important for correlating a pair of electrons in the 2p orbitals. This interpretation can best be explained by using the following identity among Slater determinants:

$$|...a\alpha a\beta...| - x^2|...b\alpha b\beta...| = \tfrac{1}{2}\{|...(a + xb)\alpha(a - xb)\beta...| + |...(a - xb)\alpha(a + xb)\beta...|\}$$

Here α and β are used to denote the one-electron spin functions and a and b represent molecular orbitals. The quantity x^2 represents the mixing coefficient of the doubly excited determinant. The mixing of two electronic configurations that are related to one another by an electron pair "promotion" of the form $a^2 \rightarrow b^2$ can be viewed alternatively as a single configuration (comprised of two determinants in order to construct a singlet spin eigenfunction) in which one electron resides in one "polarized orbital" (of the form $a + xb$) while the other electron resides in its partner polarized orbital ($a - xb$). The result is that the pair of electrons, which in the single configuration SCF picture occupy the same orbital, can now "avoid one another" by occupying *different* regions of space thereby lowering the energy of the system. This energy lowering is referred to as the electron pair correlation energy. These polarized orbital pairs are analogous to generalized valence bond orbitals with orbitals a and b corresponding to bonding and antibonding orbitals, respectively.

The importance of various excited configurations (i.e., the magnitude of the mixing coefficients, x^2) depends upon the "promotion energy" (i.e., the energy difference $\epsilon_b - \epsilon_a$) between the occupied orbital a and the unoccupied orbital b) and the strength of interaction between the orbitals a and b as measured by their integral $\int a(1)b(1)(1/r_{12})a(2)b(2)\,d\tau$. The magnitude of this interaction is small whenever orbitals a and b are localized in different regions of space. For this reason, "promotions" involving unoccupied orbitals b which are of very different radial size or radically different directional character than the occupied orbital are expected to contribute little to the intrapair correlation of orbital a even if the $a \rightarrow b$ excitation energy is low.

ii. Intrapair Correlations. Returning to the specific F and F^- case at hand, it is now possible to give interpretations to the major electron correlation effects operative in this and other atomic anion systems that contain both ns and np valence electrons. The $2p^2 \rightarrow 3s^2$ and $2p^2 \rightarrow 3d^2$ configurations allow for angular correlation and permit the two electrons to "avoid" one another by forming hybrid orbitals localized in different regions of space. Excitations of the form $2p^2 \rightarrow 3p^2$ give rise to polarized orbitals that differ in their *radial* extent and hence give rise to radial or inner–outer correlations. Examples of other types of promotions that allow for intrapair correlation are $2p^2 \rightarrow 3p4p$, $2p^2 \rightarrow 3s4s$, $3p^23d4d$, and $2p^2 \rightarrow 3s3d$.

iii. Interorbital Correlations. Another physically distinct type of electron pair correlation effect is accounted for by introducing configurations in which two electrons from different orbitals are promoted to unoccupied orbitals, for example, $2s2p \rightarrow 3p3d$ or $2p_x2p_y \rightarrow 3p_x3p_y$. These configurations give rise to interorbital electron correlation effects. For electron pairs that reside in orbitals localized on different atomic centers, the singlet-coupled components of these interorbital correlations result in van der Waals or dispersion interactions. For example, the He_2 $1s^21s^2 \rightarrow {}^1(1s_A2p_A)^1(1s_B2p_B)$ doubly excited configuration mixes with the $1s^21s^2$ configuration to yield polarized orbital pairs, one on each He atom, of the form $1s + x2p$ and $1s - x2p$. Here A and B label the two He atoms. These polarized orbitals are said to possess instantaneous dipole moments because their charge distribution is not spherically symmetric. The interaction of the electrons that occupy such polarized orbitals causes the dispersion interaction between the two He atoms. Within an atom or molecule, similar interorbital electron pair correlations arise. Their contributions to the total energy of the atom or anion can be viewed as interorbital dispersion energies arising from orbitals in the same atom.

iv. Need for Different Polarization Functions for Anions and Neutrals. Having now clarified the role of electron pair correlation, it still remains to examine why correlation effects in EA's of atoms should be so difficult to compute accurately and why high angular momentum orbitals should be as important as they are. It should be noted that because the 2p orbitals are of rather different radial extent in F and F^- the 3s and 3d orbitals needed to correlate F are quite different from those needed to correlate F^-. As a result, it is essential to employ very flexible basis sets to describe the correlation energy difference between F and F^-. Higher angular momentum functions (specifically f functions) become involved via either of two mechanisms: *direct* $p^2 \rightarrow f^2$ mixing or *indirect* $p^2 \rightarrow d^2 \rightarrow f^2$ mixing. The latter arises since f functions are needed to provide angular correlation to the $p^2 \rightarrow d^2$ terms in the wave function.

v. Effects of High Degeneracy in Atoms. Orbital degeneracies and near degeneracies occur in atomic systems (e.g., the 2s and 2p orbitals of first-row atoms are close in energy), and the corresponding electron pair interactions are either equal or comparable in magnitude. This makes the electron correlation problems in atoms especially difficult because these degeneracies tend to make pair–pair correlations and higher order (i.e., triple and quadruple) excitations important.

It should now be clearer why atomic anions are so difficult to study accurately. The spherical symmetry gives rise to degeneracies in the occupied orbitals and to near degeneracies in the "correlation orbitals" (i.e., the 3s, 3p, and 3d correlation orbitals of F^- are not very different in energy). These near or absolute degeneracies then give rise to a large number of electron pair promotions and hence a large number of polarized orbital pairs whose mixing strengths are approximately equal. Less important but still significant are excitations into empty 4f orbitals. The recent theoretical calculations also underscore the importance of triple and quadrupole excitations in determining accurate atomic EA's. The importance of such terms indicates that a "simple" pair correlation approach is not adequate for treating these species.

The benchmark studies of first-row atoms and their anions cited above provided important insight into the difficulties that arise when one attempts to treat electron correlation in systems with a large number of excited configurations which contribute nearly equally. As one progresses from atomic to diatomic to less symmetrical polyatomic molecules, these degeneracies are lifted and the electron correlation problem may actually become less complicated.

b. Other Atomic Anion Studies. In addition to the above benchmark calculations aimed at determining the EA's of first-row atoms accurately, several other works merit mention here. Barnett, Reynolds, and Lester[33] used the quantum Monte Carlo method, which is free from basis set limitations, to examine F^- and to determine the EA of F. McDowell and Doll[34] used this same technique to examine the H^- ion. The anions of heavier elements have also been examined by using ab initio methods.[35-38]

It has even become possible to incorporate relativistic effects into atomic EA studies.[39,40] The electronic spectra[41] and physical properties[42-49] of atomic anions have also come under study. Perturbation treatments[50,51] of electron pair correlation have been applied to atomic anions, and new basis sets[52,53] specifically designed for anion calculations have been developed. All of these advances are cataloged in the Bibliography, where titles, authors, and journal references are given for all articles covered in this review.

2. Molecular Species

The status of ab initio calculations on conventional bound molecular anions has very recently been reviewed by Baker, Nobes, and Radom[54] and by Nobes, Poppinger, Li, and Radom.[55] These excellent overviews, together with a corresponding review of atomic electron affinity calculations by Bunge and Bunge,[56] make it unnecessary for us to consider, in depth, the numerous molecular anion calculations that have been carried out since 1980. Instead, we choose to provide a bibliography that includes molecular anion calculations and to focus our review on especially novel classes of anions, which we treat in sections II.B–II.D.

B. Polar Molecules and Their Clusters

1. Polar Molecules

The binding of electrons to polar molecules has been addressed in several theoretical and experimental studies. Much of the interest in these systems derives from the fact that, assuming validity of the Born–Oppenheimer (BO) approximation, there is a critical dipole moment of 1.625 D beyond which electron binding is assured.[18-25] Moreover, in the BO approximation, molecules with dipole moments in excess of the critical value will have an infinity of bound anion states. However, correction terms to the BO approximation alter the critical moment and reduce the number of bound states to a finite number.[57,58] This may be seen qualitatively as follows: for molecules with dipole moments only slightly greater than the critical moment, the electron binding energy in the BO approximation will be less than the rotational energy level spacings. In such cases the loosely bound electron will not be able to "follow" the rotating dipole and then the rotational-to-electronic energy transfer will cause the electron to detach. (The same problem exists for the weakly bound excited states of molecules with larger dipole moments.) Even in the low-temperature limit, in which only the lowest rotational levels are populated, BO corrections cause the critical moment and the number of bound states to depend on the moments of inertia of the molecule.[57,58] Thus molecules such as HF and H_2O, which have dipole moments in the range of 1.8–1.9 D, are believed not to have stable anions at geometries near their equilibrium structures. Evidence exists that molecules such as CH_3CN with dipole moments in the 3-D range do bind electrons to yield stable anions.[59-61]

For highly polar molecules with dipole moments in excess of 4 D, the ground-state anions are sufficiently strongly bound that BO corrections are relatively unimportant. However, even for molecules with dipole moments as large as 4 D, the BO corrections may be so important that there are not bound excited states of the electron in the dipole field.[58] Garrett has provided the rough rule of thumb that, for the ground state, a dipole moment in excess of 2 D is required for binding of one millivolt (or greater) and that dipole moments in excess of 5 and 10 D are required to have millivolt binding in the first and second excited states, respectively.[58] The most extensively studied dipole-bound anions are those of the alkali halides and alkali hydrides. Both pseudopotential[58] and ab initio[61–88] methods have been utilized to characterize theoretically the anions of these species. The ground-state anions of the alkali halides have also been studied experimentally by laser photodetachment spectroscopy,[89] photoelectron spectroscopy,[90,91] and halogen anion–alkali atom scattering measurements.[92]

We will not attempt to comprehensively review the work in the area of anions of polar ionic molecules since these species have been treated in other recent reviews.[87,88] Here we will only summarize the most important findings of the earlier studies and will discuss in greater detail the more recent work examining the dipole-bound excited states of these systems.

The theoretical investigations have shown that in calculations using finite basis sets and the LCAO approach the most important requirement in describing the ground-state anions of these species is the inclusion of diffuse functions capable of describing the lowest unoccupied molecular orbital (LUMO) which localizes most of its charge "behind" the positive end of the molecule, hybridized away from the electronegative group.[61–86] In terms of atom-centered basis functions this most naturally translates into the inclusion of diffuse s and p functions on the electropositive atom(s). In fact, the ground-state anions of the alkali halides and hydrides are perhaps best described as neutral alkali atoms polarized by the negatively charged halide or hydride group.[64,91]

Because most of the charge associated with the extra electron is located in a region of space where the density due to the other electrons is low, the relaxation and correlation corrections to the EA prove to be relatively unimportant, and the Koopmans' theorem (KT) approximation gives fairly accurate EA's. However, it should be noted that the small corrections to the EA's due to the inclusion of correlation effects is due in part to the fact that electron correlation affects the EA's in two distinct ways which generally tend to oppose one another.[61,67,84,85] First, electron correlation tends to decrease the dipole moment and hence to decrease the EA. Second, assuming that the dipole moment is not affected by electron correlation, there are "true" correlation effects which would generally lower the energy of the anion more than the neutral molecule, hence tending to increase the EA.

Along a series of MX compounds, where M is a particular alkali atom and X is a halogen atom or other electronegative group, the EA's are found to increase nearly linearly with the dipole moment (at least over the range of 4–8 D).[63,88] However, when the results for different alkali atoms are included, the correlation between EA and dipole moment is not very good. From electrostatic (Rittner-type[93,94]) models one can derive the following expression (in atomic units) for the EA's of the alkali halides

$$\mathrm{EA(MX)} = \mathrm{IP(M)} + C_{\mathrm{N}}e - B_{\mathrm{N}}R - C_{\mathrm{A}}e - B_{\mathrm{A}} - R - 1/R + (\alpha_{\mathrm{M}} - \alpha_{\mathrm{M}^+} - \alpha_{\mathrm{X}^-})/2R^4$$

where α_{M}, α_{M^+}, and α_{X^-} are the polarizabilities of the alkali atom, alkali positive ion, and halide negative ions, respectively, and the exponential terms are due to the "short-range" repulsive interactions. The corresponding expression

$$\mathrm{IP(MS)} = -\mathrm{EA(X)} + 1/R + (\alpha_{\mathrm{M}^+} + \alpha_{\mathrm{X}^-} - \alpha_{\mathrm{X}})/2R^4$$

was found by Potts[95] to adequately describe the trends in the IP's in the alkali halides. In this latter equation the exponential terms have been omitted because it has been assumed that they are of comparable importance in the neutral and cationic species near the equilibrium bond lengths of the neutral molecules. However, because of the much larger size of the alkali atoms compared to their cations, the exponential terms cannot be neglected in the expression for the EA's. Further, because of the large distortions of the valence s electrons of the alkali atoms in the presence of the halogen anions, the Rittner-type electrostatic expansion fares poorly for describing the molecular anions and hence for calculating the EA's. This has been recognized by Lineberger and co-workers,[91] who have developed an electrostatic model in which they explicitly account for the displacement of the charge on the alkali atom due to polarization. Using this model they are able to predict the EA's of the various alkali halides to within 0.2 eV, and they demonstrate that the EA's of the various alkali halides depend approximately linearly on the quantity $\alpha_{\mathrm{M}}/(R_{\mathrm{MX}})^2$.

TABLE I. Binding Energies (eV) of the Anion States of LiH and LiF[a]

method/state	ground	1st excited	2nd excited
		LiH	
KT	0.213	0.23×10^{-2}	
HF	0.247	–	
CCSD	0.293	0.28×10^{-2}	
RD	0.32	0.26×10^{-2}	
		LiF	
KT	0.283	0.39×10^{-2}	0.55×10^{-4}
HF	0.29	–	–
CCSD	0.312	0.38×10^{-2}	0.43×10^{-4}
RD	0.38	0.46×10^{-2}	0.12×10^{-4}

[a] The ab initio results (other than the HF EA for LiF) are from Adamowicz and Bartlett (ref 84 and 85). The HF values for LiF is obtained by adding the relaxation correction of Seeger and Jordan (ref 65) to the KT value of Adamowicz and Bartlett. The rotating dipole (RD) results are from Garrett (ref 58).

In the simple dipole model the critical moment does not depend separately on the charges or their separation; however, the actual binding energies do depend on these quantities. Thus divalent compounds with dipole moments comparable to the alkali halides are expected to have much larger EA's than the alkali halides. This is confirmed by comparing the theoretical predictions for LiF and BeO, both of which have dipole moments near 6.3 D. BeO is predicted to have an EA of 1.98 eV, while that of LiF is 0.3 eV.[67]

Detailed theoretical studies of the properties of the excited-state dipole anions have been carried out by Adamowicz and McCullough,[82,83] Adamowicz and Bartlett,[84,85] and Garrett.[57,58] Whereas Adamowicz and co-workers employed ab initio methods and invoked the BO approximation, Garrett utilized a pseudopotential method and allowed for non-BO corrections. Table I summarizes the Koopmans' theorem and coupled-cluster (CCSD) results of Adamowicz and Bartlett for LiH and LiF. These calculations show that the binding energies of the first excited states of LiF$^-$ are in good agreement with the earlier calculations.[65,74,82,83] There is nearly another 2 orders of magnitude difference between the binding energies of the first and second excited states of these anions in the BO approximation. Although the binding energies of the first two excited states obtained from the ab initio calculations are in fairly good agreement with the rotating dipole (RD) calculations of Garrett, the ab initio result for the third anion state of LiF is found to be about 4 times greater than the RD value, indicating the importance of the BO corrections for this anion state. The breakdown of the BO approximation is even more severe for the third anion state of LiH: The ab initio calculations predict a binding energy of the order of 2×10^{-5} eV, while the RD calculations indicate that this state is unbound (i.e., lies in the continuum for electron–molecule scattering).

Electron correlation is found[84,85] to increase the binding energies of the first two anion states of LiH by 37% and 20%, respectively. On the other hand, electron correlation effects increase the binding energy of the ground-state anion of LiF by 10% and decrease the binding energies of the first and second excited anion states by 3% and 21%, respectively. These results reflect the interplay between the two effects on the EA's of correlating the wave functions. Electron correlation decreases the dipole moment of LiF and, as a result, the binding energies of the excited-state anions, for which the correlation effects involving the electron in the diffuse dipole-field orbitals are relatively unimportant, also decrease. For the ground-state anion, however, the correlation effects involving the dipole-bound orbital are sufficiently important that they more than compensate for the decrease in the binding energy caused by the reduction in the dipole moment. For LiH electron correlation causes a small increase in the dipole moment, which, in turn, leads to an increase of the binding energies of all the dipole-bound anion states.

One of the most exciting developments in the area of dipole-bound anion states is the detection of narrow resonances in the photodetachment spectra of certain molecular anions.[96,97] For example, Mead et al. in their ultrahigh-resolution photodetachment spectrum of the acetaldehyde enolate anion observed about 50 sharp resonances which they attributed to excited rotational levels of a weakly dipole-bound excited anion state.[97] This spectrum is discussed nicely in the paper by Wetzel and Brauman in this issue. This system has been addressed theoretically by Wetmore et al.,[96] who found that the ground-state anion of this system is a "conventional" anion, i.e., nondipolar in nature, with the "extra" electron being added to the half-filled 2a″ MO of the neutral radical. However, the excited state formed by 2a″ → 11a′ promotion has a charge distribution consistent with that of the free molecule together with an electron weakly bound in the dipole field of the neutral. Although the excited-state anion was predicted to be slightly unbound in these calculations, the 3.5-D value of the dipole moment of the neutral radical would seem to assure that the anion should, in fact, be weakly bound. (Wetmore et al. estimate that it may be bound by 0.01 eV.) Even though the anion is expected to be bound when vibrationally and rotationally unexcited, those vibrational and rotational levels with energy in excess of the purely electronic binding energy will autodetach. Excited rotational levels are responsible for the sharp resonances in the spectrum of Mead et al.[97] These authors estimated that the mean radius of the orbital occupied by the extra electron in the excited-state anion is of the order of 125 Å.

2. *Cyclic and Linear Dimers of Highly Polar Molecules*

The problem of the binding of an electron in a dipole field is now fairly well understood. However, the situation with regard to electron binding in quadrupole and higher moment fields is not well understood. Critical moments do not exist for the quadrupole or higher multipole fields; that is, given the quadrupole moment alone, one cannot say whether electron binding will occur. Model calculations[98] on a system consisting of an electron in the field of four point charges (two with charges of $+q$ and two with $-q$) located at the corners of a square (so that there is no net dipole moment) demonstrate electron binding for physically reasonable values of q. Although ab initio calculations on the cyclic structures of $(LiH)_2$ and $(NaCl)_2$ failed to give any bound anion states,[66,99] the cyclic $(BeO)_2$ species was found to have an EA of 0.40 and 0.53 eV in the KT and ΔSCF approximations, respectively.[98] The charge distribution of the LUMO of $(BeO)_2$ is similar to that found for the corresponding point charge model (i.e., the charge is hybridized behind the two Be atoms away from the O atoms). The optimized structure for $(BeO)_2^-$ is found to be close to that of $(BeO)_2$, namely, rhombic with an OBeO angle of 105°.

The linear MXMX forms of these molecules have EA's, consistent with their large dipole moments. For example, the calculated EA's of LiH and LiHLiH are 0.3 and 1.0 eV, respectively.[66] It has also been suggested that the dimers of weakly polar molecules such as HF and H_2O, whose dipole moments are too small to support bound anion states (when BO corrections are included), may have dipole-bound anions.[61,100,101]

3. *Electron Trapping*

In the above discussion we have considered electron attachment to the stable forms of the neutral dimers. A more intriguing possibility is that polar molecules can "arrange around an electron" so as to trap it. For the dimer such a structure could be described as XMe^-MX or, more conveniently, $[XMMX]^-$. If the MX species itself has a sufficiently large dipole moment that it has a dipole-bound anion, then the stability with respect to both electron detachment and dissociation to MX and $[MX]^-$) of the $[XMMX]^-$ form of the dimer anion is assured. These conclusions follow from the fact that one can always localize the odd electron on one of the MX molecules and choose a distance between the two MX molecules sufficiently great that the only important interaction is that between the $[MX]^-$ and the dipole moment of the neutral MX molecule. Actual calculations are required to determine whether the binding (relative to MX + $[MX]^-$) is appreciable, whether the odd electron is localized or delocalized, and whether the $[XMMX]^-$ species is stable with respect to rearrangement to $[MXMX]^-$.

Recent calculations on $[NaCl]_2^-$ have shown that the $X^2\Sigma_g^+$ $[ClNaNaCl]^-$ species is 1.3 eV more stable than the isolated NaCl + $[NaCl]^-$ species.[99] At the equilibrium bond length (3.68 Å) of the anion, the electron is bound by 2.6 eV, more than compensating for the 0.7-eV repulsion between the two NaCl molecules. The calculations also give a bound $^2\Pi_u$ species, lying 2.3 eV above the ground-state anion but only 0.2 eV below the neutral molecule at the same geometry. The linear $[ClNaNaCl]^-$ species is predicted to lie 0.5 eV above the $[NaClNaCl]^-$ species; however, there is a barrier to rearrangement.

Larger NaCl clusters, with the neutral molecules arranged so that there is no net dipole moment, also yield stable negative ions, with the stability of the cluster ions increasing as the number of molecules in the cluster increases from two to three to four. The systems investigated include equilateral triangular $(NaCl)_3$ and the square and tetrahedral forms of $(NaCl)_4$. For these species, several weakly bound excited-state anions were found.

The importance of the trapped structures for the NaCl clusters suggests that other less polar molecules may also be able to bind electrons via this mechanism. Of particular interest are species such as $(H_2O)_n^-$ and $(HCN)_n^-$. Several of the $(H_2O)_n^-$ ions, including $(H_2O)_2^-$ have been observed mass spectroscopically.[102] The $(H_2O)_n^-$ species will be considered in more detail in section II.C.2.

C. Cluster Anions

1. Conventional Anions with Solvent Attached

The theoretical study of anions consisting of clusters of two or more chemically distinct species has been encouraged by great advances in the experimental preparation and spectroscopic probes of such species. The first class of cluster anions to be reviewed here involves a conventional anion that is "solvated" by one or more solvent molecules. In fact, even such seemingly simple systems are quite complex because they often can undergo chemical rearrangements that lead to more exotic fragments. For example, $F^-(CH_4)$ can rearrange to yield $FH(CH_3^-)$; that is, the very stable F^- species can (with substantial activation energy) give rise to the marginally stable (EA = 0.05 eV) $[CH_3]^-$ anion. The theoretical modeling of these systems must therefore carefully include enough flexibility in atomic basis functions and in electronic configurations to adequately describe all possible rearrangement products of the cluster (and the transition states connecting them).

Among the works aimed at elucidating the structures and energetics of solvent-clustered anions, several contributions stand out as representing either long-term projects involving several publications with a coherent direction or especially novel studies. The works of Sapse et al.[103-105] on hydrate-clustered and CO_2-clustered atmospheric anions and of Hirao et al.[106-110] on Cl^- clustered by various solvents characterize the first class of research efforts, as do the works of Dacre et al.[111,112] on the interaction of various anions with H_2O. The work of Curtiss, Melendres, Reed, and Weinhold[113] on $O_2^-(H_2O)_n$ clusters and of Bounds and Bounds[114] on $Cl^-(H_2O)_n$ also meet this criterion. Especially nice overviews of the interactions of various anions with H_2O are given by Gowda and Benson[115] and by Gao, Garner, and Jorgensen.[116] The emphasis of most of these works has been on obtaining ion–solvent interaction energies because of interest in solvent effects on ion behavior.

Theoretical studies on H_n^- (i.e., $H^-(H_2)_m$) have been reported by Rayez, Rayez-Meaume, and Massa,[117] Hirao,[118] and Sapse;[119] Szczesniak and Scheiner[120] studied $OH^-(H_2O)$, and Cremer and Kraka[121] have reported structures and energies for $H^-(H_2O)$. Other H^--based clusters have been examined by Nguyen, Hegarty, Sana, and Leroy[122] (H^-HCN), by Boldyrev, Sukhanov, and Charkin[123] (H^-BeH_2), and by Cremer and Kraka[121] ($[FH_2]^-$, $[OH_3]^-$, $[NH_4]^-$, and $[CH_5]^-$).

Interactions of F^- with HCl, HF, He, and ClF have been examined by Sannigrahi and Peyerimhoff,[124,125] by Frisch, Del Bene, Binkley, and Schaefer,[126] and by Diercksen and Sadle.[127] These studies utilize very sophisticated treatments of electron correlation as well as detailed analyses of the physical origin of the various contributions to the ion–neutral interaction energy (e.g., charge dipole, charge-induced dipole, etc.). Their directions were strongly affected by experimental interest in van der Waals complexes involving neutral or ions bound to one or a few molecules such as HF, HCl, or He.

In our opinion, some of the most thorough and novel studies of anion clusters were carried out by Kalcher, Rosmus, and Quack[128] on $[NH_4]^-$, by Cremer and Kraka[121] on $[FH_2]^-$, $[OH_3]^-$, $[NH_4]^-$, and $[CH_5]^-$, and by Cardy, Lanieu, and Dargelos[129] on $[NH_4]^-$, all of which can be viewed as H^- interacting with a solvent molecule. In these works, the equilibrium structures (there are several possible minima corresponding to various arrangements of the H^- relative to the bond orientations in the solvent) and vibrational frequencies at these structures were examined.

Quite recently, Chalasinski, Kendall, and Simons[130] examined $H^-(H_2O)_n$ (n = 1,2), $H^-HF \rightarrow H_2+F^-$, and $OH^-H_2 \rightarrow OH_2+H^-$ using analytical energy derivative methods and including electron correlation effects. Both stable structures and transition states were located and characterized through their local vibrational frequencies. These studies demonstrate that one must use highly accurate methods which include electron correlation, which are size consistent, and which consider basis set superposition effects to achieve reliable predictions of the "shapes" and energies of such weakly bound complexes.

All of the above theoretical studies on clustered anions are especially timely because of the breakthroughs that have recently been made in the experimental probes of such systems. They represent the following special challenges to the theoretical community:

1. The calculation of the anion–solvent interaction energy requires that so-called size-consistent methods be employed. Only such methods guarantee that the total energy calculated for fragments A + B^- will equal the sum of the energies calculated separately for A and for B^-. Without such methods, one cannot be certain that large portions of the interaction energies are not artifacts of the computational method.

2. Because the local minima and transition states on the anion–solvent potential energy hypersurface often differ by only a few kilocalories per mole in energy, highly accurate methods must be used.

3. Because these clusters are very "floppy" (i.e., they involve several low-frequency degrees of freedom), the comparison of experimentally observed features (e.g., vibrational frequencies, moments of inertia), which are averaged over the cluster's motion, with the theoretically computed features (geometries and energies of local minima, local vibrational frequencies in a har-

monic approximation) is difficult.

2. Anions Which Require Clustering To Be Stable with Respect to Electron Detachment

Numerous theoretical studies have appeared addressing the question as to whether an electron can bind to small water clusters.[131-134] Originally, much of this work was motivated by interest in the properties of excess electrons in liquid water. More recently, $(H_2O)_n^-$ clusters have been observed in the gas phase by Haberland et al.[102,135] and Bowen and co-workers.[136] The former set of authors have observed $(H_2O)_n^-$ ($n \geq 10$) mass spectroscopically following a supersonic expansion of H_2O in the presence of low-energy (1 eV) electrons generated from a hot filament located about 2–3 mm from the nozzle. Smaller cluster anions were also observed when the water was seeded with inert gas atoms, presumably due to the effective lowering of the temperature of the clusters. With 2% Ar in H_2O, $(H_2O)_2^-$, $(H_2O)_6^-$, and $(H_2O)_7^-$ were seen as well as $(H_2O)_n^-$ ($n \geq 10$). At very low partial pressures of H_2O in Ar, only $(H_2O)_2^-$ was observed, while at high pressures of H_2O only the larger ($n \geq 10$) cluster anions were observed. When the seeding was done with Xe, $(H_2O)_3^-$, $(H_2O)_5^-$, $(H_2O)_8^-$, and $(H_2O)_9^-$ were also observed. H_2O^- and $(H_2O)_4^-$ were not observed under any of the experimental conditions employed.

Chipman[101] utilized ab initio electronic structure methods to study electron binding to the water dimer. He observed that the dipole moment of the dimer is sufficient to bind an electron, and he estimated that the binding energy is 0.2–9 meV. Consistent with the very diffuse nature of the orbital occupied by the extra electron, the geometry of the dimer anion was found to be very close to that of the neutral dimer. More recently, Wallquist, Thirumulai, and Berne[137] have studied electron localization in water clusters using the path integral Monte Carlo method in the interaction of the extra electron with the water molecules, and the water–water interactions are modeled by means of empirical potentials. These authors predict electron binding energies of 2–3 meV for $(H_2O)_2^-$ and 4–9 meV for one of the structures of the water trimer. They also note that at a temperature of 20 K the dimer is predicted to no longer bind an electron, consistent with the experimental finding that $(H_2O)_2^-$ is observed only when the beam is seeded. Several of the cluster calculations[131-134] have shown that $(H_2O)_6^-$ is stable with respect to $e^- + 6H_2O$. However, the hexamer anion is predicted to be unstable with respect to $e^- + (H_2O)_6$, implying that the adiabatic EA is negative.

Bowen and co-workers,[136] using a source similar to that employed by Haberland and co-workers, have obtained photodetachment spectra of $(H_2O)_{11}^-$–$(H_2O)_{19}^-$, determining the detachment energies of 0.75–1.12 eV for these species. Recent path integral Monte Carlo calculations of Landman et al.[138] indicate that $(H_2O)_{16}$ has an adiabatic EA of about 0.6 eV and a vertical detachment energy of 1.3 eV, in good agreement with the experimental value. Results for the clusters with $n = 11$–15 are not available.

Clusters of alkaline earth metals form another family of species that require clustering to give anions which are stable. The lowest ^2P states of Be^-, Mg^-, etc. lie energetically above the ^1S ground states of the respective atoms; thus the lowest anion states are shape resonances having lifetimes in the 10^{-14}-s range. Bauschlicher and Partridge[139] and Jordan and Simons[140] have examined the small clusters of Be atoms at a correlated level and have found even the Be_2 molecule is able to bind an electron. The origin of the extra stability of the dimer and higher cluster anions can be understood in terms of the stabilization of the valence p orbitals that results when two or more of these orbitals overlap. For example, the two 2p orbitals in Be_2 combine to form bonding $2p\sigma_g$ and $2p\pi_u$ molecular orbitals. In the neutral Be_2 molecule both of these MO's are empty in the simple SCF-level picture. However, placing an extra electron into either of these bonding orbitals yields a stable Be_2^-. The most accurate calculations appear to be those of Bauschlicher and Partridge, who report vertical detachment energies of 0.61 eV ($^2\Pi_u$) and 0.44 eV ($^2\Sigma_g^+$). Previous SCF-level calculations[141] had indicated that the $^2\Sigma_g^+$ anion is considerably more stable than the $^2\Pi_u$ anion. The new studies, which include correlation effects, reverse the order of the two anion states. To date, analogous calculations on Mg_2^- have indicated that the potential minima in the $^2\Pi_u$ and $^2\Sigma_g^+$ states of this species lie energetically above the $X^1\Sigma_g^+$ ground-state curve of the neutral molecule. However, calculations on Mg_3^- and Mg_4^- indicate that these species are bound relative to Mg_3 and Mg_4.[142]

The $(CO_2)_n^-$ species have been the subject of several experimental studies. These cluster ions were first observed mass spectroscopically by Compton and coworkers[143,144] and subsequently by several other researchers.[145-150] Whereas Compton et al. studied the formation of the negative ions formed by impact of 3–4-eV electrons on CO_2 clusters, Stamatovich et al.[145] examined the anions formed upon impact of low-energy (around 0.5 eV) electrons. Herschbach and co-workers[146,151] have studied the formation of $(CO_2)_n^-$ and a variety of other anions (e.g., $SO_2^-(CO_2)_n$) formed in charge-transfer reactions with alkali atoms. The $(CO_2)_n$ ions have been studied via laser photodetachment spectroscopy by Lineberger and co-workers[152] and Bowen et al.[150] Lineberger and co-workers have also examined the process: $(CO_2)_n^- + h\nu \rightarrow (CO_2)_m^- + (n - m)CO_2$. For clusters with $n < 12$ they find that only electron detachment is important, while for $n \geq 13$ sequential evaporation of CO_2 monomers dominates.

Perhaps the most fundamental question concerning these cluster anions is whether the odd electron is localized on a single CO_2 molecule, on a $(CO_2)_2$ species, or delocalized over the entire cluster. Also one would like to know whether there is a change from a localized to a delocalized state at a particular cluster size.

Theoretical calculations[153-160] have been carried out on both $[CO_2]^-$ and $[CO_2]_2^-$. We consider first the results for the monomer. The CO_2 and CO_2^- species have linear and bent equilibrium structures, respectively. The CO_2^- molecule has an equilibrium bond angle of 135° and a CO bond length about 0.1 Å longer than that of CO_2.[157] The energy of $[CO_2]^-$ drops rapidly with bending, with the vertical[159] and adiabatic[160] EA's of CO_2 being $-0.6 \div 0.2$ and -3.5 eV, respectively. Since the adiabatic EA of CO_2 is negative, the anion can decay through autodetachment of an electron. However, $[CO_2]^-$ in its equilibrium geometry lies 1.4 eV below CO_2 at the same geometry.[150] This has two important consequences. First, since it is believed that between the classical turning points of the zero-point motion the $[CO_2]^-$ potential energy surface lies below that of CO_2, the electron detachment is expected to be induced by the nuclear kinetic energy operator.[151] As a result, $[CO_2]^-$ in its zero-point level is relatively long-lived, with a lifetime of about 60–90 μs.[160] (This is in contrast to the very short, 10^{-15} s, lifetime of the anion formed by vertical electron attachment to the neutral molecule.) Second, this means that one can perform calculations on $[CO_2]^-$ near its equilibrium structure without the problem of variational collapse due to the detachment of an electron.

Several theoretical calculations of the adiabatic EA of CO_2 have appeared.[153–157] Early studies showed that SCF calculations with flexible sp basis sets give adiabatic EA's within the experimental error limits.[53–55] This suggested that, due to the diffuse nature of the orbital occupied by the extra electron, electron correlation does not play a significantly greater role in the anion than in the neutral molecule. It is now known that the good agreement with experiment obtained by these calculations was fortuitous: In 1976 England[155] showed that the SCF calculations with spd basis sets give an adiabatic EA of –1.2 eV, much smaller than the SCF value with the sp basis set. Subsequently, Yoshioka et al.,[157] using the SDCI procedure, showed that with an spd basis set the electron correlation in the anion is several tenths of an electronvolt greater than in the neutral molecule, with the result that their adiabatic EA was –0.8 eV. Recently Fleischman and Jordan[160] found that third- and fourth-order many-body perturbation theory (MBPT) calculations as well as coupled cluster doubles (CCD) calculations all give an adiabatic EA of –0.75 eV. This value is modified to –0.67 eV, in excellent agreement with the experimental value, when corrections for the zero-point vibrational effects are included. These results show that the MBPT method converges well for CO_2 and $[CO_2]^-$ and that the MP3 level of treatment should suffice for studies of the anions of the dimer and large clusters.

In the original theoretical studies of the $[C_2O_4]^-$ species, the Hartree–Fock procedure with sp basis set was employed.[158,159] Three structures—D_{2d} and D_{2h} symmetrical forms and a C_s $[CO_2{\cdot}CO_2]^-$ type structure—were considered. These calculations indicated that the C_s structure is about 0.2 and 0.4 eV more stable than the D_{2d} and D_{2h} structures, respectively. The most recent calculations of Fleischman and Jordan,[160] employing the 6-31G+* basis set and including electron correlation via the MP3 procedure, indicate that the most stable form is the D_{2d} with the C_s structure lying about 0.2 eV higher in energy. The D_{2h} structure is found to be a saddle point.

In going from CO_2 to the $(CO_2)_2$ van der Waals molecule, the adiabatic EA is predicted in the MP3 approximation to shift from –0.75 to –0.22 eV. Zero-point corrections do not significantly alter the adiabatic EA of the dimer. It is unlikely (but not impossible) that the use of a still more flexible basis set and an even more complete treatment of the electron correlation effects would give rise to a positive EA. However, it is extremely unlikely that the $(CO_2)_2$ species could have an EA as large as the 0.9-eV value deduced by Quitevis.[146]

The MP3 vertical detachment energies shift from 1.2 eV for $[CO_2]^-$ to 2.8 eV for D_{2h} $[C_2O_4]^-$ and 1.7 eV for C_s $[C_2O_4]^-$. Bowen et al.[150] have concluded, on the basis of their photodetachment measurements, that the vertical detachment energies of the monomer and dimer anions are 1.4 and >2.3 eV, respectively. These results indicate that the peak in the photodetachment spectrum of the dimer anion is likely to derive from the D_{2d} structure.

It is expected that the larger CO_2 cluster anions, i.e., $(CO_2)_n^-$ ($n \geq 3$), will be stable with respect to electron detachment, at least in their zero-point levels. Several structures are possible for the $(CO_2)_3^-$ ion. In addition to structures with the odd electron delocalized over the three CO_2 groups, $[(CO_2)_2{\cdot}CO_2]^-$ and $CO_2{\cdot}(C_2O_4^-)$ ion–molecule complexes are also possible. From simple electrostatic considerations, it is expected that the energies of these two ion–molecule complexes will be quite similar in magnitude. For the trimer and larger cluster anions it may turn out to be necessary to consider simultaneously the electronic and nuclear degrees of freedom in determining whether the electron is localized or delocalized.

3. Metal Cluster Anions

The binding of electrons to small clusters of alkali metals has been studied by several groups. These systems are of interest as prototypes for metal cluster catalysis studies. The geometries, binding energies, low-lying excited electronic states, Jahn–Teller distortions, and electron densities are among the interesting aspects of such clusters.

Recent theoretical calculations,[163–166] in agreement with those performed earlier, show that the bonding in the $X^2\Sigma_u^+$ state of Li_2^- and Na_2^- is quite different from that in the corresponding state of H_2^-, the principal difference being that the D_e of the alkali dimer anions is comparable to that in the neutral dimers, whereas $D_e(H_2^-)$ is (in accord with simple MO ideas) much smaller than $D_e(H_2)$. These calculations[164–166] show further that the lowest $(...\sigma_g\ \sigma_u^2)$ $^2\Sigma_g^+$ state of Li_2^- or Na_2^- is also quite different from that in H_2^-. Whereas this state of H_2^- is strongly repulsive, it is attractive in the alkali dimers, being weakly so in Na_2^- and much more strongly attractive in Li_2^-. This is apparently important for the low-energy dissociative attachment process, $e^- + Na_2 \rightarrow Na_2^- \rightarrow Na + Na^-$, investigated experimentally by Ziesel,[167] and the analogous $e^- + Li_2/Li_2^-/Li + Li^-$ process studied theoretically by Michaels and Wadhera.[168] Dixon, Gole, and co-workers[169,170] have examined Li_3^- and found the minimum energy structure of this ion to be linear.

The Al_2 species has been considered by Leleyter and Joyes[171] and more recently by Sunil and Jordan.[172] There are several important electronic configurations for stable Al_2^- species, the possible MO occupancies being $...(3p\sigma_g)^2(3p\pi_u)$, $...3p\sigma_g(3p\pi_u)^2$, and $...(3p\pi_u)^3$. Sunil and Jordan have found that the ground-state anion derives from the second of these, being $^4\Sigma_g^-$, and that there are two bound $^2\Pi_u$ states. It is also possible that there will be bound $^2\Sigma_g^+$ and $^2\Delta_g$ anion states, but they have not yet been investigated.

D. Metastable Anions

The most rigorous theoretical treatments of metastable anion states are formulated in terms of electron–molecule scattering theory.[173,174] Phase-shift or scattering-matrix analyses[175] then yield resonance-state positions and widths. A scattering theory starting point rather than bound-state variational or perturbative approaches is more rigorously appropriate because of the asymptotic boundary conditions obeyed by the continuum-electron wave function. As mentioned earlier, bound-state computational methods have been successfully applied[10–13,15,16] to metastable states but only by suitable modification to overcome the asymptotic boundary condition differences between bound and scattering states.

Regardless of whether scattering or modified bound-state techniques are employed, one is faced with describing the potential energies of interactions among the electrons in the metastable anion system. In the static-exchange (SE) approximation[176] one uses the Coulomb and exchange potentials between the frozen occupied molecular orbitals of the "target" neutral molecule and the "extra" electron. This one-electron-level treatment does not describe any polarization (static or dynamic) of the target's orbitals by the scattering electron. It gives the equivalent of a Koopmans' theorem description of the extra electron's motion in the metastable-state case. Static-exchange predictions of resonance energies and widths are often in error by an electronvolt or more.[176]

More realistic results are obtained when polarization of the target's molecular orbitals is included in the one-electron potential felt by the scattering electron. In the static-exchange-plus-polarization (SEP) approximation,[176] one adds to the SE potential an (empirical) polarization potential which attempts to include the static charge-induced-dipole interactions. The $-\alpha/2r^4$ functional form of the polarization potential must be "cutoff" at small r to avoid unphysical results; the value of r at which the cutoff is made is, in essence, a parameter in the model.

Both the SE and SEP potentials are one-electron- or orbital-level potentials. To go beyond this treatment and explicitly include electron correlation efforts (both among the target's electrons and with the extra electron), one introduces[177–180] a configuration interaction type wave function consisting of two classes of configurations: (1) open-channel configurations each containing one continuum orbital and included to describe the asymptotic (correlated) target-plus-free-electron situation and (2) closed-channel configurations containing all bound orbitals and describing the "in close" valence portion of the anion wave function. Solution of the CI Schrodinger equation, subject to proper asymptotic boundary conditions, then gives the relative mixing coefficients of the open- and closed-channel components of the wave function. Examination of these open- and closed-channel CI coefficients as functions of total energy E (which can be varied, for example, by varying the energy of the continuum orbital) permits phase shifts and resonance energies and widths to be evaluated.

Modified bound-state methods such as Taylor's stabilization method[10,11] and the complex coordinate technique can be used within either orbital level (SE or SEP) approaches or explicitly correlated (CI or Green's function) calculations. They focus on how to extract resonance positions and widths from the energies obtained in either type of calculation.

1. Atomic Species

Both shape and core-excited metastable states of atomic anions have been the subject of numerous investigations in recent years. Development of new methodology to more accurately estimate the positions and widths (or lifetimes) of these states has also been actively pursued. The works of Donnelly,[181] using Green's function methods on alkaline earth anions, of McNutt and McCurdy[182] on Be^-, of McCurdy, Lauderdale, and Mowrey[183] on Mg^- and Ca^-, and of Kurtz and Jordan[184] on Be^-, Mg^-, and Ca^- stand out in terms of quality among the shape-resonance studies. All of these calculations focused on both the positions and lifetimes of the shape resonances. The ^2P resonance states arising in these systems can be thought of as involving a p-wave electron temporarily bound to a target atom in its ^1S ground state. Kurtz and Jordan also considered the ^2D resonance states arising from electron capture into unoccupied d orbitals.

The most substantial contributions to the study of core-excited metastable states of atomic anions come from two collaborative groups. The Bunge and Bunge team has for many years pioneered the search for long-lived states of atomic anions of the core-excited variety. Their work[185–192] on Li^-, He^-, H^-, and Be^-, which involve the binding of an electron to an excited neutral atom, is widely known and appreciated. The efforts of Beck and of Nicolaides constitute the second major contribution to this area. They have searched for metastable states of Mg^-, Be^-, Li^-, B^-, and He^-, with the emphasis again being on states of the core-excited variety.[193–198] Junker[199] and Lin[200] have, within the time covered by this paper, carried out careful research into several metastable states of He^- and H^-, respectively. Not all of these studies determined both positions and lifetimes of the metastable core-excited states. Those that focused on the positions and ignored the lifetimes included only the closed-channel components of the anion wave function; they did not include any continuum functions to describe the outgoing electron plus the neutral atom.

2. Molecular Anions

$X^2\Sigma_u^+$ H_2^- and $X^2\Pi_g$ N_2^- continue to be the primary test cases for new theoretical methods for treating shape resonances in molecules. These two species are particularly good test cases because of their rather different lifetimes. The H_2^- resonance is so short-lived that it is not even detected via ETS. It does manifest itself, however, through the enhanced cross section for vibrational excitation of $X^1\Sigma_g^+$ H_2. The N_2^- species is appreciably longer lived, being a classic example of a "boomerang" system. The boomerang model of Herzenberg and co-workers[201] assumes that the anion lives sufficiently long that a sizable portion of the wavepacket describing nuclear motion survives one reflection in the potential.

A wide variety of theoretical methods have been applied to N_2^-. In recent years Rescigno and co-workers[202] have carried out complex SCF calculations, and Donnelly[203] has done a coordinate-rotated/propagator calculation on $X^2\Pi_g$ N_2^-. Both of these procedures de-

TABLE II. Resonance Positions and Widths for $X^2\Pi_g$ N_2^-

method	authors	E_R, eV	Γ, eV
static exchange	Schneider (204)	3.70	1.16
complex SCF	Rescigno et al. (201)	3.19	0.44
CI/Stieltjes imaging	Hazi et al. (205)	2.23	0.40
coord.-rot/propagator	Donnelly (203)	2.15	0.2
R-matrix/relaxed core	Schneider et al. (206)	2.15	0.34
experiment	Schulz (207)	2.2	0.57

termine complex energies for the resonance, with the real part of the energy corresponding to the resonance position and the imaginary part of its width (i.e., the reciprocal of the lifetime). A comparison of the resonance parameters of N_2^- obtained via various procedures is given in Table II.

The static-exchange approximation,[204] which is the scattering version of Koopmans' theorem, yields a resonance energy 1.5 eV too high and a width 0.6 eV too large. The complex SCF method gives a width much closer to the value deduced from experiment, but still yields an SCF energy 1 eV too high. The *R*-matrix method of Schneider,[206] the CI/Stieltjes imaging method[205] of Hazi et al., and the propagator/coordinate rotation method[203] of Donnelly all yield very good results[207] for the resonance position and width. These results are most encouraging, and we look forward to the application of these methods to polyatomic molecules.

$X^2\Sigma_u^+$ H_2^- has been studied in the SCF and CI approximations by Sabelli and Gislason and DeRose, Gislason, and Sabelli.[208,209] These authors employed a new variation[208] of the stabilization method. Specifically, stabilization was accomplished by application of a grid of fractional positive charges on a sphere surrounding the H_2^-. This converted the resonance eigenvalue to a bound state, the estimate of the resonance energy being obtained by shifting this result back into the continuum.

One of the most exciting developments in the area of resonances has been the prediction[210] by Berman, Mundel, and Domcke that discrete structure should appear in the cross section for exciting high-lying vibrational levels of H_2 via electron impact (with intermediate formation of $X^2\Sigma_u^+$ H_2^-) and the subsequent experimental confirmation[211] of this by Allan.

Merry and Thomson[212] and Paddon-Row et al.[213] have examined the role of molecular distortion in ethylene and the fluoroethylenes following electron capture. $[C_2H_4]^-$, $[CH_2CF_2]^-$, and $[CF_2CF_2]^-$ are all found to undergo a syn-type distortion away from the planar structure, with the degree of distortion and accompanying energy lowering increasing with the extent of fluorine substitution. These studies showed that the *adiabatic* EA's of the fluoroethylenes increase with the degree of fluorine substitution. The ETS studies,[214,215] on the other hand, show that the *vertical* EA decreases with increasing fluorine substitution.

More than one mechanism may be involved in the detachment from a given anion state; this is illustrated by $[CO_2]^-$ (discussed in section II.C.2). At energies near the zero-point level of $[CO_2]^-$, the bending motion's classical turning points probably[156,157] constrain it to regions of space where the electronic energy of $[CO_2]^-$ lies below that of CO_2. In this case, coupling of vibrational and electronic motion may be the dominant mechanism for electron loss. At even slightly higher vibrational energies, the bending motion of $[CO_2]^-$ samples geometries where the $[CO_2]^-$ electronic surface passes above the CO_2 surface. In such circumstances, electron detachment can be effected by the purely electronic resonance-decay mechanisms discussed earlier. Lauderdale, McCurdy, and Hazi[221] encountered analogous behavior when they examined the general problem of the evolution of bound anion states to metastable states with changing internuclear distance for diatomic species.

Recently, Acharya, Kendall, and Simons[216-218] examined another class of metastable anions that require energy transfer from rotational-vibrational degrees of freedom to the electrons to cause electron loss. In these cases, the potential energy curve of the anion *never* lies above that of the neutral; this, of course, means that the electronic energy of the anion never exceeds the neutral's (i.e., these are not curve-crossing situations). As a result, purely electronic processes cannot operate to cause electron ejection; coupling with the nuclear motion is essential. These workers examined electron loss rates for excited vibrational levels of the ground electronic states[217] of $[LiH]^-$ and $[OH]^-$ and for collisions[218] involving $O^- + H$ to produce OH neutral. Very recently, this same group has extended their studies to include consideration of rotational effects in the autoionization[219] of $^2\Pi$ $[NH]^-$ and to a polyatomic case[220] for which extensive experimental data exists—enolate anions $[HOCCH_2]^-$.

In addition to the above calculations, which were directed toward specific anion systems, several papers appeared which addressed methodological matters. Nestmann and Peyerimhoff[222,223] have developed new CI-based methods for locating resonances and computing their lifetimes. Yabushita and McCurdy[224] and McCurdy, Rescigno, Davidson, and Lauderdale[225] exploited the complex coordinate method within the SCF and CI methods to devise techniques for calculating resonance energies and widths. McCurdy and Turner[226] introduced a novel wavepacket formulation as a means of extending the well-known boomerang model of electron–molecule scattering. Several papers have appeared[12,16] discussing the use of "stabilization graphs" (i.e., how the calculated *real* energies in a resonance problem vary with some "scaling" parameter, for example, the physical extent of the basis set) for determining resonance energies and widths.

III. Conclusions

In general it is necessary to employ flexible basis sets and to carefully treat electron correlation effects in order to obtain accurate electron affinities of molecules. For this reason, there are relatively few molecular species for which calculations of sufficiently high quality as to yield EA's accurate to 0.1 eV have been performed. For other properties such as the determination of structures and vibrational frequencies of bound anions, even SCF calculations and modest-size basis sets frequently suffice. In recent years, there has been a rapidly growing interest in the spectroscopy of molecular anions and cluster anions. This is certain to motivate more high-quality calculations on the properties of molecular anions.

Much of the recent effort (both experimental and theoretical) in the area of molecular anions has focused on those species that are unique, i.e., for which cationic and neutral molecules do not have a counterpart. These include negative ions of highly polar molecules and temporary anion resonances. In the former case, essentially all the theoretical studies have addressed the problem of electron binding in the dipole field of ground-state molecules. Very little is known about the electron "binding" to the dipole fields of electronically excited states.

In recent years, there has been a growing body of evidence that negative states of molecules on metal surfaces are important for a variety of processes such as vibrational excitation. The technique of inverse photoemission spectroscopy has proven useful for characterizing negative ion states of adsorbed molecules located below the Fermi level. The calculation of the shifts in energy of the anion states upon adsorption on the surface and the elucidation of the factors responsible for the line widths of such species are major theoretical problems.

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