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### Anions

There are several very useful literature sources for values of atomic or molecular electron affinities (EAs).

(i) For atoms, the early reviews of Hotop and Lineberger (1), and the more recent review by Andersen *et al.* (2) remain excellent sources.

(ii) For molecules, there are several sources (3-7) that span many years, some of which are accessible on the web.

In this Chapter, we denote electron charge by -q, with its magnitude being  $q = 4.802 \times 10^{-10}$ 

## Theory (Energies and Potential Energy Surfaces)

 $(erg cm)^{1/2}$  in cgs units. This definition allows us to not include the  $(4\pi\epsilon_0)^{-1}$  factor in our interaction potential expressions. Now, let us start this journey designed to provide you with an understanding of why negative ions are "special" and why they require special tools.

# 1. Why Anions are Different From Neutrals and Cations

The physical and chemical properties of anions are very different from those of neutral molecules or of cations. Obviously, their negative charge causes them to interact with their surroundings differently than do cations or neutrals. For example, when hydrated, the anions are surrounded by H<sub>2</sub>O molecules whose H atoms are directed toward them. For cations, the H atoms are directed away. In addition, the electrons residing in their outermost (i.e., valence) orbitals experience an attractive potential that is qualitatively different than in neutrals and cations. Specifically, such an electron in an anion experiences no Coulomb attraction in its asymptotic (i.e., large-r) regions, but corresponding electrons in neutrals and cations do experience such  $-Zq^2/r$  attractions (here, Zq is the charge of the nucleus). In fact, the longest-range attractive potentials appropriate to such an electron in singly charged anions are the charge-dipole  $(-\mu \bullet rq/r^3)$ , charge-quadrupole  $(-Q \bullet \bullet (3rr - r^2 1)q/3r^5)$ , and charge-induced-dipole  $(-\alpha \bullet rrq^2/2r^6)$  potentials. Here,  $\mu$ , Q, and  $\alpha$  are the neutral's dipole moment vector, quadrupole moment tensor, and polarizability tensor, respectively; r is the position vector of the electron, the • symbols indicate dot products with the vectors or tensors, and 1 is the unit tensor. For multiply charged anions, the asymptotic potential is repulsive and has the Coulomb form  $(Z-1)q^2/r$ , where Z is the magnitude of the charge of the anion. Such potentials are illustrated in Fig. 1 where it is also suggested how the shorter-range repulsive potentials (resulting from the remaining electrons' Coulomb and exchange interactions) eventually "cut off" these long-range behaviors.

In addition to these differences in long-range potentials, there are also qualitative differences in the valence-range potentials appropriate to anions, neutrals, and cations. Specifically, an electron in any molecule or ion experiences Coulomb attractions  $(-\Sigma_a Z_a q^2/|r-R_a|)$  to each nucleus (having charge  $qZ_a$ ); the total of such attractive charges is  $Z_{tot} = \Sigma_a Z_a$ . This same electron experiences repulsive Coulomb and exchange interactions with a total of N-1 other electrons. However the balance between these  $Z_{tot}$  attractions and N-1 repulsions is very different among neutrals, singly charged anions, multiply charged anions, and cations.

For a singly charged anion,  $Z_{tot} = N-1$ , so there is no net Coulomb attraction or repulsion in regions of space where the electron-electron Coulomb and



### Figure 1

Qualitative plots of potentials experienced by outermost electron in neutrals and cations, in singly charged anions, and in multiply charged anions.



Figure 2 Doubly occupied orbital in the  $H_3C^-$  anion.

exchange terms cancel the nuclear attraction terms (e.g., for large r) as noted above. However, in regions of space where this cancellation is not fully realized (e.g., within the lone-pair orbital of  $H_3C^-$  (see Fig. 2) where the "extra" electron is not entirely shielded from the carbon nucleus by the other electron occupying this same orbital), a net attraction can occur. It is this net attractive potential and the fact that it has no long-range Coulomb character that ultimately determines the orbital shape and radial extent as well as the binding energy for the singly charged anion's "extra" electron.

In contrast, for a neutral molecule or cation,  $Z_{tot}$  is larger than N-1, so there exists a net Coulomb attraction at long range, as well as valence-range net attractive potentials, and repulsive potentials at even

shorter range (resulting from repulsion with innershell electrons). The fact that the same kind of valence attractive potentials as in the anion case are augmented by a long-range Coulomb attractive potential gives rise to stronger electron binding and smaller radial extent in such cases. It is for this reason that ionization energies (IEs) of neutrals or of cations (8) usually exceed electron binding energies in anions (alternatively, electron affinities (EAs) of the corresponding neutrals (9)). This difference in the typical magnitudes of EAs and IEs is one of the most troubling facts for the theoretical study of anions. Specifically, any theoretical method that is able to produce electronic energy differences to an accuracy of 0.5 eV can prove valuable for studying IEs, which are usually significantly greater than 0.5 eV. However, many EAs are comparable to or less than 0.5 eV, so such theoretical predictions are of much less value in such cases. In other words, one must use more accurate theoretical tools for anions.

For multiply charged anions, yet another situation arises because  $Z_{tot}$  is smaller than N-1. At long range, a repulsive Coulomb potential is operative. In the valence region, however, nuclear attractive potentials may be strong enough to overcome electron-electron repulsive potentials in certain regions of space. In those regions, an "extra" electron experiences a net attractive potential that may be strong enough to bind the electron, in which case the net potential will have the form shown in the lower plot in Fig. 3. Alternatively, if the valence attractive potential is substantial but not strong enough to overcome the Coulomb repulsion, a potential such as in the top of Fig. 3 can result. In this latter case, a



### Figure 3

Effective potentials experienced by an excess electron when a stable (bottom) or metastable (top) multiply charged anion is formed. metastable state of the multiply charged anion may result; in such a state, an "extra" electron can undergo autodetachment by tunneling through the repulsive Coulomb barrier (RCB).

These differences in long-range and valence-range potentials experienced by the electrons produce some of the most important profound differences in the physical and chemical properties of singly charged anions, multiply charged anions, and neutrals or cations. On a qualitative level, the fact that a Coulomb attractive potential, even with Z = 1, is "stronger" than charge-dipole, charge-quadrupole, or charge-induced-dipole potentials for values of  $\mu$ . Q, and  $\alpha$  found in typical molecules causes IEs to be larger than EAs. This also causes the "sizes" (i.e., radial extent of the outermost valence orbitals) of anions to be larger than those of neutrals or cations of the same parent species. The Coulomb repulsive potential that occurs in multiply charged anions causes many such species to be metastable with respect to electron detachment or with respect to bond rupture (which subsequently produces Coulomb explosion). For example, gas-phase (i.e., isolated)  $SO_4^{2-}$ ,  $CO_3^{2-}$ , and  $PO_4^{3-}$  are not stable with respect to loss of an electron; these multiply charged anions undergo rapid autodetachment. Only when strongly solvated or in an ionic crystal environment (e.g., in aqueous solution, in the presence of several solvent molecules, or surrounded by counter-ions) are such multiply charged anions stable with respect to electron loss. In contrast, dicarboxylate dianions  $^{-}O_2C_{-}(CH_2)_n - CO_2^{-}$  in which three or more methylene units separate the two anion centers are both electronically stable (i.e., neither excess charge spontaneously departs) and stable with respect to bond rupture and Coulomb explosion.

Finally, it is worth mentioning how the differences in large-*r* potentials and subsequent differences in radial extent and electron binding energies can provide special challenges to the theoretical study of singly and multiply charged anions. In particular, it is important to utilize a theoretical approach that

(i) properly describes the large-*r* functional form of the potential;

(ii) is accurate enough to produce EAs of sufficient accuracy; and

(iii) is capable of treating electronic metastability when the anion is not electronically stable.

For singly charged anions in which the excess electron is bound tightly in a valence orbital (e.g.,  $F^-$ , RO<sup>-</sup>, RNH<sup>-</sup>, RCOO<sup>-</sup> anions, where R represents an alkyl or more complex organic group), such considerations are often not essential because the large-*r* amplitude of the anion's wavefunction is small. That is, most of the excess electron's density exists in the valence-orbital region. Such anions can be handled with the same kind of theoretical tools that have proven most useful in treating neutrals and cations, some of which are discussed elsewhere (see *Theory*  (Energies and Potential Energy Surfaces): Organics; Theory (Energy and Potential Energy Surfaces): Theoretical Methods).

However, when treating anions with very small binding energies, and thus large radial extent (e.g., dipole-bound anions such as NC-CH<sub>3</sub><sup>-</sup>, (HF)<sub>n</sub><sup>-</sup>, NCH<sup>-</sup> which have electron binding energies in the  $0.1-1.0 \text{ kJ mol}^{-1}$  range), using an accurate method (because the EA is so small) and one that is proper at large r is important. In addition, using accurate methods that are correct at large r and that can handle metastable states is important when dealing with multiply charged anions. As discussed later, not all theoretical methods fulfill the criteria detailed above for use on weakly bound anions or multiply charged anions.

# 2. Anions Experience Strong Environmental Effects

When an anion is surrounded by other molecules, as it is in solution or in a solid matrix, it experiences very strong intermolecular potentials. For example, a typical energy with which a single H<sub>2</sub>O or NH<sub>3</sub> molecule is bound to a small anion such as F<sup>-</sup>, Cl<sup>-</sup>, or OH<sup>-</sup> is in the 80–120 kJ mol<sup>-1</sup> range. In contrast, the energy of attraction between a pair of H<sub>2</sub>O or NH<sub>3</sub> molecules is in the 10-30 kJ mol<sup>-1</sup> range, and these hydrogen bonds are among the stronger attractive potentials that act between pairs of neutrals. One of the most important influences of the large solvation energies that anions experience occurs in the electron binding energies of such solvated anions. Because the anion M<sup>-</sup> is more strongly solvated than its associated neutral M, the  $M^- \rightarrow M$  energy gap is significantly larger for the solvated species than for the gas-phase counterparts. As a result, the photoelectron spectra of solvated anions have their peaks blue-shifted (i.e., moved to higher detachment energies) compared to their gas-phase counterparts.

When anions are stabilized by surrounding solvent molecules, not only do their electron binding energies increase, but the radial extent of the orbitals that contain the excess electron(s) is also reduced. Of course, the two effects an increase in binding energy and shrinkage in orbital size go hand-in-hand, as they do for neutrals and cations. In fact, the functional form of the exponential decay that governs the radial extent of any orbital is related to the binding energy of that orbital as  $\exp[-(2DE)^{1/2} r]$ , where DE is the electron binding energy for removing an electron from that orbital.

# 3. Anions Present Special Challenges to Theoretical Study

There are several sources that one can access to read about how the theoretical study of anions has evolved over the past few decades. These include reviews by Gutsev and Boldyrev (10), Baker et al. (11), Simons and Jordan (12), Kalcher and Sax (13) and Berry (14), as well as "classic" earlier texts and overviews by Massey (15) and Branscomb (16) as well as the author's home web page, http://simons.hec.utah.edu from which one can access the author's textbooks on quantum mechanics and his web books on theoretical chemistry. The present contribution addresses those theoretical details that are special to performing calculations on the electronic states of anions. These details arise in two distinct ways: the atomic orbital basis sets that one uses and the effects of correlations among the motions of the electrons.

### 3.1 Special Atomic Basis Sets Must be Used

Because of the diffuse character of the outermost electron densities of most anions, one must employ atomic orbital (AO) basis sets that decay slowly with radial distance r. Electron binding energies are small quantities, so one must compute both the anion's and neutral's electronic energies with high absolute accuracy to achieve acceptable errors in the energy difference. This requires that the AO basis set be flexible enough to describe accurately the spatial distributions of the electrons as well as their so-called dynamical correlation (we discuss this later). The basis sets that must be used consist of a good quality basis such as described in Theory (Energies and Potential Energy Surfaces): Theoretical Methods, but augmented with additional diffuse basis functions as we now address.

The valence and polarization functions described do not provide enough radial flexibility adequately to describe an anion's charge distribution or the correlation of its outermost orbitals. The PNNL web site (http://www.emsl.pnl.gov:2080/forms/basisform.html) offers a good source for obtaining diffuse functions appropriate to a variety of atoms. These tabulated diffuse functions are appropriate if the anion under study has its excess electron in a valence-type orbital (e.g., as in F<sup>-</sup>, OH<sup>-</sup>, carboxylates, etc.).

However, if the excess electron resides in a Rydberg orbital, in an orbital centered on the positive site of a zwitterion species, or in a so-called dipolebound orbital (17) (all three such orbitals are illustrated in Fig. 4), one must add to the above bases yet another set of functions that are extra diffuse. The exponents of this extra diffuse basis set should be small enough to describe the diffuse charge distribution of the excess electron. Not only *s* but also *p* and sometimes *d* symmetry functions are required. Moreover, this diffuse set should be flexible enough to describe dispersion stabilization between the excess electron and the electrons of the neutral species. Finally, for anions such as shown in Fig. 4, it may not



### Figure 4

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Diffuse orbitals in Rydberg orbital of protonated methylamine (left), in zwitterion orbitals of urea and arginine tenter two), and in the dipole-bound orbital of acetonitrile (right).

be clear exactly where to center such extra diffuse bases. For the Rydberg and zwitterion cases, it has been found that centering them on an atom at or near the center of positive charge is optimal. For dipolebound cases, it is found that centering them on an atom at the positive end of the molecule's dipole is best. Such extra diffuse basis sets have been developed (18) and are currently experiencing wide use in the electronic structure community.

# **3.2** Electron Correlation Involving the Excess **Electron** Must be Treated

To achieve reasonable chemical accuracy (e.g.,  $\pm 20 \text{ kJ mol}^{-1}$ ) in electronic structure calculations, one cannot describe the wave function  $\Psi$  in terms of a single determinant. The reason such a wave function is inadequate is because the spatial probability density functions are not correlated. This means the probability of finding one electron at position r is independent of where the other electrons are, which is absurd because the electrons' mutual Coulomb repulsion causes them to "avoid" one another. This mutual avoidance is called electron correlation because the electrons' motions, as reflected in their spatial probability densities, are correlated (i.e., interrelated). Let us consider a simple example to illustrate this problem with single determinant functions. The  $|1s\alpha(\mathbf{r}) | 1s\beta(\mathbf{r}')|$  determinant appropriate, for example to a He atom, when written as 

$$|1s\alpha(\mathbf{r}) \ 1s\beta(\mathbf{r}')| = 2^{-1/2} \{1s\alpha(\mathbf{r}) \ 1s\beta(\mathbf{r}') - 1s\alpha(\mathbf{r}') \ 1s\beta(\mathbf{r})\}$$
(1)

can be multiplied by itself to produce the twoelectron probability density:

$$P(\mathbf{r}, \mathbf{r}') = 1/2\{[1s\alpha(\mathbf{r}) \ 1s\beta(\mathbf{r}')]^2 + [1s\alpha(\mathbf{r}') \ 1s\beta(\mathbf{r})]^2 - 1s\alpha(\mathbf{r}) \ 1s\beta(\mathbf{r}') \ 1s\alpha(\mathbf{r}') \ 1s\beta(\mathbf{r}) - 1s\alpha(\mathbf{r}') \ 1s\beta(\mathbf{r}) \ 1s\alpha(\mathbf{r}) \ 1s\beta(\mathbf{r}')\}.$$
(2)

If we integrate over the spins of the two electrons and make use of their orthogonality

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$
, and  $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$ , (3)

we obtain the spatial (i.e., with spin absent) probability density:

$$P(\mathbf{r}, \mathbf{r}') = |1s(\mathbf{r})|^2 |1s(\mathbf{r}')|^2.$$
(4)

This probability, being a product of the probability density for finding one electron at r times the density of finding another electron at r', clearly has no correlation in it. That is, the probability of finding one electron at r does not depend on where (r') the other electron is. This product form for P(r, r') is a direct result of the single-determinant form for  $\Psi$ , so this form must be wrong if electron correlation is to be accounted for.

Now, we need to ask how  $\Psi$  should be written if such correlation effects are to be taken into account. It turns out that one can account for electron avoidance by taking  $\Psi$  to be a combination of two or more determinants that differ by the promotion of two electrons from one orbital to another orbital. This approach of combining determinants is called configuration interaction (CI). For example, in describing the  $\pi^2$  bonding electron pair of an olefin or the ns<sup>2</sup> electron pair in alkaline earth atoms, one mixes in doubly excited determinants of the form  $(\pi^*)^2$  and np<sup>2</sup>, respectively.

Briefly, the physical importance of such doubly excited determinants can be made clear by using the following identity involving any pair of determinants:

$$C_{1}|..\phi\alpha\phi\beta..| - C_{2}|..\phi'\alpha\phi'\beta..|$$
  
=  $C_{1}/2\{|..(\phi - x\phi')\alpha(\phi + x\phi')\beta..|$   
 $- |..(\phi - x\phi')\beta(\phi + x\phi')\alpha..|\},$  (5)

where  $x = (C_2/C_1)^{1/2}$ . This identity allows one to interpret the combination of two determinants that differ from one another by a double promotion from one orbital ( $\phi$ ) to another ( $\phi'$ ) as equivalent to a

## Theory (Energies and Potential Energy Surfaces)



Figure 5 Polarized  $\pi$  orbital pairs.

singlet coupling (i.e., having  $\alpha\beta-\beta\alpha$  spin function) of two different orbitals  $(\phi-x\phi')$  and  $(\phi+x\phi')$ .

In the olefin example mentioned above, the two nonorthogonal "polarized orbital pairs" involve mixing the  $\pi$  and  $\pi^*$  orbitals to produce two left-right polarized orbitals as depicted in Fig. 5. In this case, the  $\pi^2$  electron pair undergoes leftright correlation when the  $(\pi^*)^2$  determinant is mixed into the CI wavefunction. Physically, one can view this CI function as allowing one electron to be in the left-polarized orbital while the other electron is in the right-polarized orbital and to thus "avoid" one another.

In the alkaline earth atom case, the polarized orbital pairs are formed by mixing the ns and np orbitals (actually, one must mix in equal amounts of  $p_x$ ,  $p_y$ , and  $p_z$  orbitals to preserve overall <sup>1</sup>S symmetry in this case), and give rise to angular correlation of the electron pair. Such a pair of polarized orbitals is shown in Fig. 6. More specifically, the following four determinants are found to have the largest amplitudes in  $\Psi$ :

$$\Psi \cong C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|].$$
(6)

The fact that the latter three terms possess the same amplitude  $C_2$  is a result of the requirement that a state of <sup>1</sup>S symmetry is desired. It can be shown that this function is equivalent to:

$$\Psi \cong 1/6C_1 |1s\alpha 1s\beta \{ [(2s - a2p_x)\alpha(2s + a2p_x)\beta - (2s - a2p_x)\beta(2s + a2p_x)\alpha] + [(2s - a2p_y)\alpha(2s + a2p_y)\beta - (2s - a2p_y)\beta(2s + a2p_y)\alpha] + [(2s - a2p_z)\alpha(2s + a2p_z)\beta - (2s - a2p_z)\beta(2s + a2p_z)\alpha] ],$$
(7)

where  $a = (3C_2/C_1)^{1/2}$ .



Figure 6 Polarized s, p orbital pairs.

Here two electrons occupy the 1s orbital (with opposite,  $\alpha$  and  $\beta$  spins) while the other pair resides in 2s-2p polarized orbitals in a manner that instantaneously correlates their motions. These *polarized* orbital pairs  $(2s \pm a2p_{x,y, \text{ or } z})$  are formed by combining the 2s orbital with the  $2p_{x,y, \text{ or } z}$  orbital in a ratio determined by  $C_2/C_1$ .

It is also possible to include so-called in-out or radial correlations by including doubly excited configurations in which an occupied orbital is replaced by an orbital of the same symmetry but greater different radial extent. For example, in the alkaline earth atom case, including determinants of the form  $|1s^23s^2|$  allows the dominant  $|1s^22s^2|$ determinant to combine to form in-out polarized orbital pairs  $2s \pm a3s$ . In such a case, one electron is closer to the nucleus while the other is further away.

The ratio  $C_2/C_1$  can be shown to be proportional to the magnitude of the coupling  $\langle 1s^22s^2|H|1s^22p^2\rangle$ between the two configurations involved and inversely proportional to the energy difference  $[\langle 1s^22s^2H|1s^22s^2\rangle - \langle 1s^22p^2|H|1s^22p^2\rangle]$  between these configurations. In general, configurations that have similar Hamiltonian expectation values and that are coupled strongly give rise to strongly mixed (i.e., with large  $|C_2/C_1|$  ratios) polarized orbital pairs.

In each of the three equivalent terms in the above wave function, one of the valence electrons moves in a 2s + a2p orbital polarized in one direction while the other valence electron moves in the 2s-a2p orbital polarized in the opposite direction. For example, the first term  $[(2s-a2p_x)\alpha(2s+a2p_x)-(2s-a2p_x)\beta(2s+a2p_x)\alpha]$  describes one electron occupying a  $2s-a2p_x$  polarized orbital while the other electron occupies the  $2s + a2p_x$  orbital. The electrons thus reduce their Coulomb repulsion by occupying different regions of space; in the self-consistent-field (SCF) picture,  $1s^22s^2$ , both electrons reside in the same 2s region of space. In this particular example, the electrons undergo angular correlation to "avoid" one another.

The use of doubly excited determinants is thus seen as a mechanism by which  $\Psi$  can place electron *pairs*, hich in the single-configuration picture occupy the ame orbital, into different regions of space (i.e., each one into a different member of the polarized orbital pair) thereby lowering their mutual Coulomb repulion. Such electron correlation effects are referred to as *dynamical electron correlation*"; they are extremely important to include if one expects to achieve chemically meaningful accuracy (i.e.,  $\pm 20 \text{ kJ mol}^{-1}$ ) and are especially important when one is studying anions. In practical quantum chemistry calculations on nions, one must compute the  $C_2/C_1$  ratios (more ppropriately, all of the  $C_1$  coefficients in the CI apansion of  $\Psi$ 

$$\Psi = \Sigma_{\rm J} C_{\rm J} \Phi_{\rm J}, \qquad (8)$$

where the  $\Phi_J$  are spin- and spatial symmetry-adapted configuration state functions (i.e., combinations of Slater determinants). There are a variety of approaches that can be used to compute the  $C_I$ coefficients as well as the energy E. The most commonly employed methods are the configuration interaction (CI), Møller–Plesset (MP) perturbation, and coupled-cluster (CC) methods, which have been discussed in *Theory (Energies and Potential Energy Surfaces): Theoretical Methods*.

# **3.3** Tools that Allow One to Compute Electron **Affinities** Directly

In addition to the methods discussed in *Theory* (*Energies and Potential Energy Surfaces*): *Theoretical Methods*, there exists a family of tools that allow one to compute energy differences "directly" rather than by first finding the energies of pairs of states and subsequently subtracting them. Various energy differences can be so computed: differences between two electronic states of the same molecule (i.e., electronic excitation energies  $\Delta E$ ), differences between energy states of a molecule and the cation or anion formed by removing or adding an electron (i.e., ionization energies (IEs) and electron affinities (EAs)).

It is important to stress that:

(i) These so-called Greens function or propagator methods (19) utilize essentially the same input information (e.g., atomic orbital basis sets) and perform many of the same computational steps (e.g., evaluation of one- and two-electron integrals, formation of a set of mean-field molecular orbitals, transformation of integrals to the MO basis, etc.) as do the other techniques.

(ii) These methods are now rather routinely used when  $\Delta E$ , IE, or EA information is sought. In fact, the 1998 version of the Gaussian program includes an electron propagator option.

The basic ideas underlying most if not all of the energy-difference methods are:

(i) One forms a reference wave function  $\Psi$  (this can be of the SCF or correlated variety); the energy

differences are computed relative to the energy of this function.

(ii) One expresses the final-state wave function  $\Psi'$  (i.e., that describing the excited, cation, or anion state) in terms of an operator  $\Omega$  acting on the reference  $\Psi:\Psi' = \Omega\Psi$ . The  $\Omega$  operator must be one that removes or adds an electron when one is attempting to compute IEs or EAs, respectively, so it is common to express  $\Omega$  in terms of electron creation and destruction operators in such cases.

(iii) One writes equations that  $\Psi$  and  $\Psi'$  are expected to obey. For example, in the early development of these so-called equations of motion (EOM) methods (20), the Schrödinger equation itself was assumed to be obeyed, so  $H\Psi = E\Psi$  and  $H\Psi' = E'\Psi'$  are the two equations.

(iv) One combines  $\Omega \Psi = \Psi'$  with the equations that  $\Psi$  and  $\Psi'$  obey to obtain an equation that  $\Omega$ must obey. In the above example, one (a) uses  $\Omega \Psi = \Psi'$  in the Schrödinger equation for  $\Psi'$ , (b) allows  $\Omega$  to act from the left on the Schrödinger equation for  $\Psi$ , and (c) subtracts the resulting two equations to achieve  $(H\Omega - \Omega H)\Psi = (E' - E)\Omega\Psi$ , or in commutator form  $[H,\Omega]\Psi = \Delta E\Omega\Psi$ .

(v) One can, for example, express  $\Psi$  in terms of a superposition of configurations  $\Psi = \sum_J C_J \Phi_J$ , whose amplitudes  $C_J$  have been determined from a CC, CI, or MP calculation and express  $\Omega$  in terms of operators  $\{O_K\}$  that cause single-, double-, etc., level excitations. For the IE (EA) cases,  $\Omega$  is given in terms of operators that remove (add), remove and singly excite (add and singly excite, etc.) electrons:  $\Omega = \sum_K D_K O_K$ .

(vi) Substituting the expansions for  $\Psi$  and for  $\Omega$  into the EOM  $[H,\Omega]\Psi = \Delta E\Omega\Psi$ , and then projecting the resulting equation on the left against a set of functions (e.g.,  $\{O_{K'}|\Psi\rangle\}$  or  $\{O_{K'}|\Phi_0\rangle\}$ , where  $\Phi_0$  is the dominant component of  $\Psi$ ), gives a matrix eigenvalue-eigenvector equation

$$\Sigma_{\mathbf{K}} \langle O_{\mathbf{K}} \cdot \Psi | [H, O_{\mathbf{K}}] \Psi \rangle D_{\mathbf{K}}$$
  
=  $\Delta E \Sigma_{\mathbf{K}} \langle O_{\mathbf{K}} \cdot \Psi | O_{\mathbf{K}} \Psi \rangle D_{\mathbf{K}}$  (9)

to be solved for the  $D_{\rm K}$  operator coefficients and the excitation energies  $\Delta E$ . Such are the working equations of the EOM (or Greens function or propagator) methods.

In recent years, these methods have been greatly expanded and have reached a degree of reliability where they now offer some of the most accurate tools for studying excited and ionized states. In particular, the use of time-dependent variational principles have allowed a much more rigorous development of equations for energy differences and nonlinear response properties (21). In addition, the extension of the EOM theory to include coupled-cluster reference functions (22) now allows one to compute excitation and ionization energies using some of the most accurate *ab initio* tools.

### 4. Selected Classes of Molecular Anions

### 4.1 Conventional Valence-bound Anions

Let us begin by considering anions that bind their excess electron(s) in valence orbitals and have electron binding energies from less than 0.1 eV (e.g., for  $H_3C^-$ ) through 3.9 eV (e.g., for NC<sup>-</sup>). Several books and reviews provide the reader with a good overview of such anions (15), (16) dating from 1969 (14) (see 7, 12, 13, 23, 24).

Returning to the issue of conventional molecular anions, we first note that the same kind of atomic orbital basis sets (i.e., conventional core and valence, polarization, and conventional diffuse) can be used within Hartree-Fock, DFT, or correlated treatments of their electronic structure. Because they hold their "excess" electron(s) in valence orbitals, the extremely diffuse basis sets (18) used, for example, on Rydberg and dipole-bound anions need not be used.

However, there are issues that one must be aware of in studying all anions, including conventional valence-type anions. For example, the EAs of such species are typically smaller than the bond strengths connecting the anion's constituent atoms. As a result, one must be prepared to consider electron detachment processes in addition to bond fragmentation whenever a significant amount of excess energy is present. This situation is not typical of neutrals and cations for which electron removal involves an energy considerably in excess of bond dissociation energies.

An example is provided by the NH<sup>-</sup>(X<sup>2</sup>\Pi)  $\rightarrow$ e<sup>-</sup> + NH(X,<sup>3</sup> $\Sigma$ ) process in which an electron is ejected from the anion once it has enough vibrational energy  $\varepsilon_i$  to place it above the lowest vibrational level  $\varepsilon_f$  of neutral NH. The pertinent potential energy curves and state energies are illustrated in Fig. 7. In this case, the electron binding energy is less than 0.5 eV,



Figure 7

Anion and neutral potential energy surfaces illustrative of  $NH^-$  and NH.

which is much smaller than the NH bond strength Thus, as vibrational energy is deposited into NH<sup>-</sup> the electron-detachment channel opens far before the bond-fragmentation channel does.

The mechanism by which the NH<sup>-</sup> anion's excess electron is ejected involves coupling between the electronic and vibrational motions of the NH<sup>-</sup> anion Specifically, so-called non-Born-Oppenheimer couplings give rise to this energy flow. The rate of such transitions is related to the derivative of the orbital out of which the electron is ejected with respect to the vibrational (or rotational) motion that is inducing the ejection (25, 26). In all such nonadiabatic electronejection processes, the rate of ejection is governed not only by how strongly the HOMO is modulated by the vibration (or rotation), but also by Franck-Condonlike factors (25). These factors do not involve the overlap  $\langle v_i | v_f \rangle$  of the anion and neutral vibrational states. Rather, they involve the overlap of the neutral's vibrational state v<sub>f</sub> with the derivative of the anion's vibrational state with respect to the vibrational coordinate (X) that promotes the detachment  $\langle dv_i/dX | v_f \rangle$ . Because the electron ejection requires energy input, the vibrational mode that promotes the ejection is left with less energy as a result of which it undergoes a change in quantum number.

The above example serves to show that even what we consider chemically conventional anions can display behavior that is not common in neutrals and cations. This behavior is a result of the fact that EAs are usually smaller than bond dissociation energies, so electron detachment can be the first process that becomes possible as the anion's internal vibrational energy increases.

#### 4.2 Dipole-bound Anions

This section will deal with molecular anions in which the "extra" electron is bound to a large extent by the long-range electrostatic potential of the underlying neutral molecule rather than by shorter-range valence potentials. When the dominant such potential is the electron-dipole potential ( $-\mu \cos \theta q/r^2$ ), one speaks of dipole-bound anions such as in the cases of HCN<sup>-</sup>, H<sub>3</sub>C-CN<sup>-</sup> and the others whose dipole-binding orbitals are shown in Fig. 8. Notice that the species binding the excess electron may be an intact molecule such as HCN, but it can also be a complex or cluster of molecules bound to one another by van der Waals forces such as (HF)<sub>2</sub> and (H<sub>2</sub>O)<sub>n</sub>.

Many of the molecules that form these dipolebound anions are closed-shell species that have no low-energy vacant valence orbitals into which the electron can enter. Thus, the lowest energy anion states that can be formed in such cases are the anions in which the electron is bound to a region of space dictated by the electron-dipole potential. However,



*Figure 8* Dipole bound orbitals for a variety of anions.

there are species that have both valence-bound and dipole-bound states. For example,  $H_2C-CN^-$  is an anion in whose ground state the excess electron resides in a  $p_{\pi}$  orbital on the carbon atom of the  $H_2C$ group. As such, this is a valence-bound anion. However, upon excitation of an electron from this valence orbital to the lowest excited state, the  $H_2C$ - $CN^-$  anion holds its excess electron in a dipolebound orbital that is localized to the left of the two hydrogen atoms in  $H_2C-CN$  near the positive end of this molecule's dipole moment.

There have been many theoretical and experimental studies of electrons bound to polar molecules in which the binding is ascribed primarily to the chargedipole attractive potential. Recent reviews (27) offer excellent insight into the current state of affairs of the theoretical studies most of which have been carried out in the laboratories of Drs. Jordan (23, 28-32), Adamowicz (33-36), Chipman (37), Bartlett (38), Gutowski (31, 32, 39-44), Desfrançois (45), and the author (27, 28, 31, 32, 46, 47). Much of the early experimental work on dipole-bound anions was produced in the Brauman (48-51), Lineberger (52, 53), Desfrançois (54-58), Compton (59, 60) and Bowen (61-63) laboratories. More recently, the Johnson group (64, 65) has also generated a substantial body of data on such anions, and many other experimental and theoretical groups are joining these exciting studies.

In nearly all of these studies, there is good reason to believe that the binding is largely a result of the dipole potential, but in no case can it be shown that the resultant anions are purely dipole-bound. In fact, a simple model in which two charges  $+\zeta q$  and  $-\zeta q$ are separated by a distance R with  $\zeta qR$  chosen to duplicate the dipole moment (this is termed the fixedfinite-dipole (FFD) model) is known to poorly represent the potential experienced by an excess electron. In fact, such a potential significantly over binds the excess electron even though the minimum value of  $\zeta qR$  needed to effect any binding is correctly obtained in such a model.

Let us further illustrate the deficiencies in simple electrostatic models by examining a few anions that have been termed dipole-bound. The H<sub>3</sub>C–CN molecule has a dipole moment of 4.34 D and has been shown to form an anion with an electron binding energy of  $108 \text{ cm}^{-1}$  (0.0134 eV). Calculations show that the excess electron occupies an orbital localized on the positive end of this dipole within the H<sub>3</sub>Cgroup's "pocket" and rather distant from the underlying molecule's valence orbitals as shown in Fig. 4.

Clearly, CH<sub>3</sub>CN has no vacant or half-filled valence orbitals that could attach the excess electron (its CN  $\pi^*$  orbital is very high in energy), so it is quite appropriate to call its anion dipole-bound. However, not all molecules having this dipole moment bind an electron to the same extent; for example, H2CCC also has a dipole moment of 4.34 D but binds by 173 cm<sup>-</sup> (0.021 eV) (66). So, the binding energy is determined not only by  $\mu$  but also by the nature of the molecule's other occupied orbitals as reflected in their Coulomb and exchange potentials. Moreover, when one examines the contributions to the electron binding energy of the H<sub>3</sub>C-CN<sup>-</sup> anion, one finds that the electron-dipole attraction (plus other charge-multipole interactions) combined with the Coulomb and exchange interactions do not reproduce the full electron binding energy. In fact, 57 cm<sup>-1</sup> (0.007 eV) or 53% of the binding arises from the dispersion interaction (31) between the excess electron and the other electrons. Such dispersion contributions have been found to be substantial in many dipole-bound anions. Hence, it is not entirely correct to think of these species as being entirely dipole-bound although the charge-dipole potential is the effect that attracts the excess electron at the longest range.

A more extreme example of the roles played by shorter-range potentials is offered when one considers anion states of alkali halides or alkali hydrides such as LiF<sup>-</sup>, NaH<sup>-</sup>, or the alkaline earth analogues such as BeO<sup>-</sup> or MgO<sup>-</sup>. For example, in neutral LiF, the bonding at the equilibrium internuclear distance is very ionic. Hence, one can view the neutral as a closed-shell  $F^-$  anion sitting next to a closed-shell  $Li^+$  cation. Undoubtedly, at very long range, the excess electron is attracted primarily by its dipole interaction with the  $Li^+F^-$ . However, in regions of space closer to the Li and F centers, the excess electron experiences both the repulsive Coulomb and exchange interactions mentioned earlier as well as attractive interactions when it is near the  $Li^+$  center, which has an empty 2s orbital. As a result, the excess electron feels the dipole potential at long range but a potential more like that experienced by a Li 2s electron polarized by a nearby  $F^-$  charge. So, in such cases, shorter-range valence potential to bind the excess electron.

The "bottom line" in terms of our understanding of binding an excess electron to polar molecules is that:

(i) Dipole moments considerably in excess of the predictions of the FFD model (1.625 D) are needed before binding exceeds 0.001 eV. Experience shows that at least 2.5 D is necessary.

(ii) The FFD model overestimates binding energies, but, when Coulomb and exchange potentials of inner shell electrons are included, the model is reasonable but not reliably accurate.

(iii) Dispersion interaction of the excess electron with the remaining electrons is usually important to include if one wants accurate results.

(iv) Relaxation of the neutral's orbitals caused by attaching an excess electron is usually small. As a result, a Koopmans' theorem treatment of the excess electron using specially designed basis sets (18, 67) followed by inclusion of the dispersion interactions (31, 68) between the excess electron and the others is often adequate.

(v) When electron binding energies exceed the spacings between rotational levels of the molecule, it is safe (69) to neglect non-Born-Oppenheimer (non-BO) couplings that can induce electron ejection. Likewise, when the binding energy exceeds vibrational level spacings, it is usually safe to neglect vibrational non-BO couplings that can lead to electron loss.

(vi) Even species that form valence-bound anions may also form dipole-bound states if their dipole moments are large enough.

(vii) The range of molecules that have been determined to form dipole-bound states is large and growing. In addition to those mentioned above, such states are formed in clusters such as  $(H_2O)_n^-$  and  $(HF)_n^-$  (70) and in nucleic acid bases such as uracil and thymine.

### 4.3 Multiply Charged Anions

Not surprisingly, to bind two electrons to a single molecule in the absence of stabilizing solvation effects, one must either:

(i) have an electron binding site of unusual intrinsic strength; or

(ii) have two distinct binding sites that are far enough apart to reduce their mutual Coulomb repulsion.

In either case, the primary obstacle to forming dianions is the Coulomb repulsion between the two excess electrons. Nevertheless, dianions do exist in the absence of solvation, but they often present special challenges to experimental and theoretical study.

When considering the possibility of binding two electrons to two distinct sites in a molecule, one must consider the mutual Coulomb repulsion energy between the two anion sites. An excellent illustration of this effect is presented in the photoelectron spectra of dicarboxylate dianions (71) taken in the Wang laboratory as shown in Fig. 9. In these spectra, massselected dianions are exposed to radiation having more than enough energy to detach one electron.

The binding energies are determined for dicarboxylate dianions  $^{-}O_2C-(CH_2)_n-CO_2^-$  having varying numbers of -CH<sub>2</sub>- units. In Fig. 9, the detachment energies of dianions  $^{-}O_2C-(CH_2)_n-CO_2^-$  of varying length are plotted as a function of the inverse of the distance  $r_n$  between the two carboxylate centers. The linear slope is interpreted in terms of the intrinsic binding energy of a R-CO<sub>2</sub><sup>-</sup> anion (the  $\nu$ -axis



#### Figure 9

Measured detachment energies of dicarboxylates having various (n)  $CH_2$ - units (from reference 71).

intercept of ca. 3 eV) being lowered by the Coulomb repulsion  $q^2/r_n$ . This Coulomb model has proven to be very useful both in interpreting experimental data on such nonproximate dianions (71) and in theoretically predicting binding energies of dianions (72).

One might wonder if it is possible to form dianions in molecules where the two excess electrons reside in more proximate orbitals. Such systems include many ubiquitous species (e.g.,  $SO_4^{-2}$  and  $CO_3^{-2}$  (72, 73) as well as more exotic systems (74, 75) (e.g.,  $TeF_8^{-2}$  (76) and  $MgF_4^{-2}$  (77, 78)). Of course, if the two sites are too close, as they are in  $O_2^{-2}$ , the Coulomb repulsion is too large to be offset by the intrinsic binding of each site. However, for the systems listed above and many others, the intrinsic bindings and Coulomb repulsions are close enough to balancing to make such species fascinating to study. Let us consider a few examples.

For tetrahedral MgF<sub>4</sub><sup>-2</sup> and square antiprism D<sub>4d</sub> TeF<sub>8</sub><sup>-2</sup>, the intrinsic binding of the fluorine ligands as well as the delocalization of the two excess electrons over four or eight equivalent sites, respectively, more than offsets the Coulomb repulsion  $q^2/R_{FF}$  ( $R_{FF}$  is the ligand-ligand distance). As a result, these dianions are electronically stable by ca. 3 eV and 5 eV, respectively. In contrast, for SO<sub>4</sub><sup>-2</sup> and CO<sub>3</sub><sup>-2</sup>, which were briefly discussed earlier, the Coulomb repulsion more than offsets the intrinsic binding strengths of the oxygen ligands, so these dianions turn out to be unstable with respect to electron loss. However, there is more to this interesting competition between Coulomb repulsion and intrinsic valence-range attraction that needs to be discussed.

If one thinks of "constructing" any of the dianions mentioned above by bringing a second excess electron toward the corresponding monoanion, one can imagine what potential this second electron would experience. Certainly, at long range, it would experience Coulomb repulsion caused by the monoanion's negative charge. This repulsion would depend on the distance of the second excess electron from the site(s) where the monoanion's excess charge is localized. Such long-range repulsive potentials are shown on the right-hand side of Fig. 3.

As the second excess electron approaches closer, it eventually enters the region of space where the attractive valence-range potentials (e.g., near the fluorine or oxygen ligand orbitals) are strong. In such regions, the total potential will be a sum of these short-range attractions and the Coulomb repulsions. If the former are strong enough, a deep attractive "well" will develop as shown in the bottom plot in Fig. 3, and the dianion will be stable with respect to the monoanion plus a free electron. Such is the case for TeF<sub>8</sub><sup>-2</sup> and MgF<sub>4</sub><sup>-2</sup>.

for  $\text{TeF}_8^{-2}$  and  $\text{MgF}_4^{-2}$ . On the other hand, as for  $\text{SO}_4^{-2}$  and  $\text{CO}_3^{-2}$ , if the valence-range attractions are not strong enough, the total potential can display a minimum (as in the upper plot of Fig. 3) that lies above the monoanion plus free electron asymptote. In such cases, the dianion will not be stable, but can be metastable with a substantial lifetime. The lifetimes in such cases are determined by:

(i) the height and thickness of the barrier shown in Fig. 3 (the barriers, in turn, are determined by the maximum Coulomb repulsion); and

(ii) the energy at which the dianion state exists (determined by the intrinsic binding energy minus the Coulomb destabilization).

Such lifetimes of such metastable anions have been estimated by using a simple tunneling model and potentials as shown above. When this kind of model is applied to isolated  $SO_4^{-2}$  and  $CO_3^{-2}$ , the lifetimes turn out to be  $10^{-10}$  s and  $10^{-11}$  s, respectively.

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# Organics

### 1. Intrinsic Reactivity of Organic Molecules

Theoretical methods play an important role in the understanding of the reactivity of organic molecules, particularly if we are interested in gas-phase processes. In the gas-phase low-pressure regime, the molecule manifests its intrinsic reactivity (i.e., the reactivity it has by itself without being perturbed by solvation effects). In this context, the theoretical approach is immediately relevant because theoretical calculations generally refer to isolated species. This means that we can obtain the energy of a system as a function of geometry, and therefore we can calculate energy profiles that show how the energy changes from reactants to products. In other words, we can calculate equilibrium geometries (i.e., stable intermediates (local minima) of the potential energy surface (PES)), the vibrational frequencies of which are all real, or we can calculate the transition states (saddle points) connecting them, which have one imaginary vibrational frequency (1). Another important aspect is that theory can be applied as readily to reactive or to low-stability species as to stable compounds. Furthermore, different ab initio or density functional theory methods, such as the G2 (2), G3 (3), CBS (4), and B3LYP (5, 6) approaches, can reach what is usually called chemical accuracy, i.e., they can provide estimations of many thermodynamic magnitudes with an average deviation from experiment of less than  $8 \text{ kJ mol}^{-1}$ .

### 2. Proton Affinities and Gas-phase Acidities

Different available experimental methods, such as Fourier transform ion cyclotron resonance (FTICR) (7) (see *Instrumentation: Fourier Transform Ion Cyclotron Resonance*), have provided accurate values for the gas-phase basicity of many organic systems. This is achieved by measuring the equilibrium constant, K, associated with the gas-phase process of Eqn. (1) from which the value of  $\Delta G$  (usually called gas-phase basicity, GB) can be obtained as

$$\mathbf{B}_{ref}\mathbf{H}^{+} + \mathbf{B} \rightleftharpoons \mathbf{B}_{ref} + \mathbf{B}\mathbf{H}^{+} \tag{1}$$

$$\Delta G = -RT \ln K \tag{2}$$

The corresponding enthalpy, or proton affinity, is given by

$$\Delta H = \Delta G + T \Delta S \tag{3}$$

From the theoretical viewpoint, the protonation energy is obtained as the difference between two large numbers: the total energies of the protonated and the unprotonated species. Therefore, it is crucial to determine these energies with high accuracy to minimize the error in the calculated proton affinity. But this is not enough, because the zero-point energy (ZPE) correction is also an important factor. In the protonation process, a new covalent bond between the basic site and the proton is formed and, as a consequence, the ZPE correction for the protonated species is larger than for the neutral species. In general, calculated ZPEs significantly overestimate experimental ones, so different scale factors have been proposed in the literature (8). However, the influence of ZPEs on the accuracy of the calculated proton affinities is rather small because of error cancellations. In summary, high-level theoretical schemes usually provide proton affinities (9) that differ from experiment by less than 10 kJ mol<sup>-1</sup>. This high accuracy was actually used to produce a unified proton affinity scale, by anchoring the experimental absolute proton affinity of some reference systems. Density functional theory (DFT) methods also perform very well (9), although they occasionally show large errors. It has been shown (10) that basicities can be reproduced with an average absolute error of 10 kJ mol<sup>-1</sup> if the B3LYP approach and a very large 6-311 + G(3df, 3pd) basis set expansion is used.

It is also worth noting that, in general, the aforementioned experimental techniques provide gas-phase basicities (i.e., free energies, rather than proton affinities, which are enthalpies). The experimental measurement of the entropy term is not a