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# A Survey of Some Theoretical Studies of Negative Ions

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### Abstracts

The quantum chemical methods employed by us to investigate the stabilities, charge densities, and bonding characteristics of atomic and molecular anions are briefly reviewed. The results of our work on chemically interesting species are surveyed, as are our initial results on the treatment of solvation effects in anionic systems. Finally, a simple-minded approach to the problem of finding shape resonances for electron-atom scattering processes is outlined.

Nous présentons une revue des méthodes quanto-chimiques que nous avons utilisées pour étudier les stabilités, les densités de charge et les caractéristiques des liaisons d'anions atomiques et moléculaires. Les résultats pour des cas d'intérêt chimique et les premiers résultats sur le traitement des effets de solvation sont donnés. Une esquisse est présentée d'un procédé pour trouver des "résonances de forme" pour des processus de diffusion électron-atome.

Die von uns verwendeten quantenchemischen Methoden fur die Untersuchungen von Stabilitäten, Ladungsdichten und Bindungskennzeichen von atomaren und molekularen Anionen werden kurz besprochen. Die Resultate für Fälle von chemischem Interesse und die ersten Resultate über Lösungseffekte in Anionsystemen werden angegeben. Ein einfaches Verfahren für die Beschreibung von "Formresonanzen" in Elektron-Atom-Streuungsprozessen wird skizziert.

### **1. Introduction**

In surveying the research on negative ions carried out in our research group at Utah, I have decided to attempt to give an overview of several projects, rather than to cover one of them in great detail. In this way, I hope to give the reader a good understanding of how these projects fit together as a single unit whose ultimate goal is the understanding of the physical properties and chemical behavior of stable and metastable anions both in the gas phase and in solution. To provide the reader with access to more detailed treatments of the topics covered, I have given references to the recent literature.

In Section 2, I review the electron propagator theory used to compute electron affinities, which include orbital relaxation and electron correlation effects, and I demonstrate the accuracy of our approach by comparing several of our results to those of accurate experimental determination. Section 3 contains an overview of both our recent work on the binding of electrons to highly polar closed-shell molecules and our model studies of electron-molecule and anionsolvent interactions. In Section 4 I describe an easily implemented procedure for

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identifying electron-atom shape resonances within a conventional squareintegrable basis calculation. Section 5 contains my concluding remarks.

# 2. Propagator Calculation of Molecular Electron Affinities

The electron propagator [1]  $\mathbf{G}(E)$  is defined in terms of the set of spin-orbital creation operators  $\{C_i\}$ , the superoperator Hamiltonian  $\hat{H}$  ( $\hat{H}A \equiv [A, H]$ ), and the reference state  $|g\rangle$  as follows:

$$\mathbf{G}(E) \equiv (C^{\dagger} | E \hat{1} - \hat{H})^{-1} C^{\dagger}) \tag{1}$$

where  $\hat{1}$  is the identity superoperator  $(\hat{1}A \equiv A)$  and the scalar product [2] is defined by

$$(A|B) \equiv \langle g|A^{\dagger}B + BA^{\dagger}|g\rangle \tag{2}$$

The poles of G(E) yield the (vertical) electron affinities and ionization potentials of the parent. By first making an inner-projection [3] representation to the superoperator resolvent  $(E\hat{1}-\hat{H})^{-1} = |h\rangle(h|E\hat{1}-\hat{H}|h)^{-1}(h|)$ , with the projection operator space  $|h\rangle$  chosen to consist of the  $C^{\dagger}$  operator plus higher order fermion operators represented by  $q^{\dagger}$ , and then partitioning [3] the result of substituting this into Eq. (1), one can easily obtain

$$\mathbf{G}^{-1}(E) = (C^{\dagger}|E\hat{1} - \hat{H}|C^{\dagger}) - (C^{\dagger}|E\hat{1} - \hat{H}|q^{\dagger})(q^{\dagger}|E\hat{1} - \hat{H}|q^{\dagger})^{-1}$$

$$(q^{\dagger}|E\hat{1} - \hat{H}|C^{\dagger})$$
(3)

To make use of the propagator given by Eq. (3), one must truncate the inner projection space  $|q^{\dagger}\rangle$  and one must choose some approximation to the reference state  $|g\rangle$ . We have chosen [4] to represent  $|g\rangle$ , for closed-shell parent molecules,\* in terms of the Hartree-Fock wave function plus all first and second order Rayleigh-Schrödinger corrections. We truncate the  $|q^{\dagger}\rangle$  operators at the following level:

$$q^{\dagger} \cong \{ C_{l}^{\dagger} C_{k}^{\dagger} C_{l} + C_{k}^{\dagger} < g | C_{l}^{\dagger} C_{l} | g > - C_{l}^{\dagger} < g | C_{k}^{\dagger} C_{l} | g > \}$$
(4)

where the second and third terms serve to make  $q^{\dagger}$  strictly orthogonal to the  $C^{\dagger}$ .

Equations for the elements of  $\mathbf{G}^{-1}$  in terms of Hartree-Fock orbital energies and two-electron integrals are given in Ref. [4]. We have shown [4] that the above choices of  $q^{\dagger}$  and  $|g\rangle$  are sufficient to guarantee that the  $\mathbf{G}^{-1}(E)$  obtained through Eq. (3) will be correct through third order in the electron interaction. From our experience [5-13] and that of others [14-16], we know that electron affinities which contain correlation corrections through second order are not sufficiently accurate to be useful in studies of negative ions. Because electron affinities are often less than 1 eV in magnitude, any successful procedure must have an accuracy of  $\pm 0.2 \text{ eV}$ . We have found that the third order electron propagator approach seems to possess this required accuracy. The result shown in Table I support this statement. As can be seen from this data, the effects of orbital

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<sup>\*</sup> At present our approach is limited to systems for which either the neutral or the anion is closed-shell.

### SURVEY NEGATIVE ION STUDIES

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.36 (vertical)	
.29 (Koopmans)	
.76 (vertical	
.41 (Koopmans)	
.42 (adiabatic)	0.74 <sup>e</sup>
.60 (adiabatic)	2.8 <sup>f</sup>
.38 (vertical)	
	<ul> <li>.36 (vertical)</li> <li>.29 (Koopmans)</li> <li>.76 (vertical</li> <li>.41 (Koopmans)</li> <li>.42 (adiabatic)</li> <li>.60 (adiabatic)</li> <li>.38 (vertical)</li> </ul>

<sup>a</sup> H. Hotop, T. A. Patterson, and W. C. Lineberger, J. Chem. Phys. 60, 1806, (1974).

<sup>b</sup> D. Feldman, private communication.

<sup>c</sup> J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969). <sup>d</sup> D. E. Jensen, J. Chem. Phys. **52**, 330 (1970); R. D. Srivastava, O. M. Uy, and M. Farber, Trans. Faraday Soc. 67, 2491 (1971).

<sup>e</sup>K. C. Smyth and J. I. Brauman, J. Chem. Phys. 56, 4620 (1972); R. J. Celotta, R. A. Bennett, and J. L. Hall, ibid. 60, 1740-5 (1974).

<sup>f</sup> J. H. Richardson, L. M. Stephenson, and J. I. Brauman, Chem. Phys. Lett. 25, 318 (1974).

relaxation and electron correlation are often of the same size as the magnitude of the molecular electron affinity. In the next section, examples are considered for which these effects are especially small and for which Koopmans' theorem or  $\Delta$ (scf) calculations suffice.

## 3. Binding of Electrons to Highly Polar Molecules

The question of binding an electron to the potential energy field of either a point dipole or a fixed finite dipole consisting of two charges (+q and -q)separated by a fixed distance (R) has been studied by many people [17]. It is well known that an electron will bind to either of the above potentials if the dipole moment (D) is greater than 1.625 debyes. Jordan [18] and the author [10, 11] have carried out several ab initio third order correlated calculations on systems in which an electron has been added to a neutral molecule whose dipole moment is greater than 1.625 debyes. In Table I a summary of some of our results on LiH<sup>-</sup>, LiF<sup>-</sup>, NaH<sup>-</sup>, and BeO<sup>-</sup> is given. We find that the electron binds to the polar molecule in a region of space which lies primarily on the electropositive atom, the charge density being polarized away from the more electronegative atom. Moreover, we found that inclusion of the effects of electron correlation and relaxation on the electron's binding energy was not essential to obtain accurate estimates of these properties. This result is consistent with a description of the electron attachment as addition of the electron to a previously unoccupied region of space (orbital) whose primary amplitude is spatially well separated from the parent's electrons. Thus, one can adequately describe the binding of an electron to such highly polar closed shell molecules at the Koopmans' theorem or  $\Delta(s_{CF})$ level.

The above observation led us to consider the possibility of modeling this kind of electron-highly polar molecule interaction by a simple effective potential. A point dipole approximation is improper because it gives an infinite binding energy [17]. By examining the binding of an electron to a fixed finite dipole, with Rchosen equal to the bond length of the species under study and the charge magnitude (q) chosen such that qR gave the experimental dipole moment, we are able to conclude [11] that neither the ground state (which correlates [18] with the 1s state of the +q charge as  $R \rightarrow \infty$ ) nor the lowest excited state (which correlates [18] with the 2s state) gave reasonable predictions for the electron binding energies. However, a model which replaces the electronegative atom by a -qpoint charge and the electro-positive atom by a  $Z_c + q$  charge plus  $Z_c$  electrons in the lowest  $Z_c/2$  Hartree-Fock orbitals, where Z<sub>c</sub> equals the number of "core" electrons (2 for Li, 10 for Na), did yield reasonably accurate (±0.2 eV) binding energies [19] and charge densities. Clearly, the inclusion of the core electrons of the electropositive atoms seems to be an important ingredient in a successful model potential. We feel that a fixed finite dipole with the core of the electropositive atom presents a reasonably effective potential which merits further investigation.

Having achieved some degree of success with the above model potential for the case of an electron binding to a polar molecule, we decided to look into the use of such models for describing anion-solvent interactions and the hydration energy of solvated electrons. We have been able to demonstrate [20], by actual quantum chemical calculations within Gaussian basis sets, that the use of point dipoles to simulate solvent H<sub>2</sub>O molecules (with D > 1.625 debyes) is, as expected, entirely hopeless. The fact that the point dipole potential has an infinite binding energy in this case allows one to achieve any hydration energy (for anions, cations, and electrons) desired by simply modifying the orbital basis.

We have also begun to consider the fixed finite dipole model to describe the solvent effects. In these studies, 2+q charges replace the two hydrogen atoms of H<sub>2</sub>0 and one -2q charge replaces the oxygen. Again *q* is chosen to duplicate the experimental dipole moment of water. Our initial results [20] indicate that such a model is not really capable of giving a quantitatively accurate description of the properties (hydration energy, cage size, spectral absorptions) of the hydrated electron. We are now considering other electron-solvent potentials which include Coulomb, exchange, and polarization effects as candidates for our studies of solvated electrons. We are also performing ab initio calculations which are designed to yield the hydration energies of molecular anions. In these studies we are presently considering the use of the fixed finite dipole model for the solvent H<sub>2</sub>O molecules. Noell and Morokuma's success [21] in employing this model for solvation effects is encouraging, although their results on  $F^{-}(aq)$  and ours<sup>22</sup> on OH<sup>-</sup>(aq) lead us to be quite cautious about concluding that the model is capable of adequately describing hydration effects for anions. We must perform considerably more numerical calculations before the accuracy of the model can be objectively assessed. Such calculations are now in progress at Utah.

# 4. Searching for Shape Resonance in Electron-Atom Collisions

The radial Schrödinger equation for an electron moving in a spherically symmetrical potential can be written (in atomic units) as

$$=\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\psi\right) + \frac{l(l+1)}{2r^2}\psi + V(r)\psi = E\psi$$
(5)

If, as is the case for an electron interacting with a spherically symmetric atom, V(r) has a long range attractive part, such as the charge-induced dipole potential, plus a shorter range repulsive part, then the "effective potential"  $V_l(r) \equiv l(l+1)/2r^2 + V(r)$  can have bound, resonance, and scattering states. Resonances which are caused by tunneling through the repulsive centrifugal barrier  $(l(l+1)/2r^2)$  are called shape resonances. The bound states have  $E < V_l(r \to \infty)$ . The resonance states, which are not square integrable states, have large amplitude for regions of r where  $V_l(r)$  is attractive and smaller amplitude for "large" r (where  $V_l(r)$  is attractive; their major amplitudes are for large values of r. Although resonance states belong to the continuum, they are somewhat localized because they have large amplitude for small values of r.

By exploiting this localization characteristic of the resonance states, we have developed an easily implemented procedure for finding shape resonances in an atomic system within the framework of conventional Slater or Gaussian basis ( $L^2$  functions) set calculations. We simply add to the effective potential another term of the form  $Ar^s$  with A small ( $\sim 10^{-7}$ ) and S large (e.g., 6, 8, 10). The values of A

and S are chosen so that this term is negligible for values of r where  $V_{\text{eff}}(r)$  is attractive and so that it is large (compared to the low-lying positive eigenenergies of  $V_{\text{eff}}(r)$ ) when r is large. The effect of the added potential on the energies of scattering states, which have large  $\langle r^{s} \rangle$  even as described within the  $L^{2}$  basis, is to greatly increase their eigenenergies. On the other hand the extra potential has little effect on the bound and resonance states for which  $A\langle r^{s} \rangle$  is small. Then by adding  $\sum_{i=1}^{N} Ar_{i}^{s}$  to the one electron part of the Hamiltonian of an atom, one removes the (unwanted) scattering states from the low energy (E > 0) eigenvalue spectrum of H which now contains only bound and resonance states. That is, the potential function  $Ar^{s}$  has the effect of enclosing the system in a "box."

We have successfully applied this procedure [23] to the resonance states of one-dimensional model potentials of the form  $(V(x) = \frac{1}{2}x^2\theta(-x) + [\frac{1}{2}x^2 \exp(-\lambda x^2) - J \exp(-\lambda x^2) + J]\theta(x)$ , where J and  $\lambda$  are parameters and  $\theta(x)$ is the Heaviside step function. We found that, for choices of the potential parameters A and S which yielded significant changes  $(\pm 2\%)$  in the bound and resonance state eigenenergies, the scattering states had indeed been removed from the low energy spectrum of H. Moreover, we found that the effect of the added potential on the desired resonance (and bound) state eigenvalues can be removed using first order perturbation theory. We simply subtract  $A\langle r^S \rangle$  from the eigenenergy obtained with the external potential added, the average value  $\langle r^S \rangle$ being taken over the resonance state wave function computed with  $Ar^S$  in the Hamiltonian.

Recently we have also employed [24] this procedure to look for shape resonances in Li<sup>-</sup>( $1S^2 2S 2p$ ), Be<sup>-</sup>( $1S^2 2S^2 2p$ ), and Mg<sup>-</sup>( $1S^2 2S^2 2p^6 3S^2 3p$ ). These calculations are being carried out both at the scr level (by adding  $\sum_{i=1}^{N} Ar_i^{S}$ to the Fock operator) and at the correlated level (by adding  $Ar^{s}$  as a one electron part of the self-energy or optical potential in the Dyson equation [1]). As expected, our scF-level results do not give accurate positions (eigenenergies) of the resonances because of the total absence of the long-range polarization potential. On the other hand, our initial calculations including polarization and electron correlation effects do seem to yield reasonable values for the atomic resonance positions. We are still in the process of performing these calculations, so it would be premature to give an evaluation of the overall accuracy of our method. Questions concerning lifetimes of the resonance states have not yet been considered in our studies. Even if the positions of resonance states are not obtained more accurately by this approach than by other methods (e.g., the widely used stabilization technique [25]), our method may serve as a useful tool for removing unwanted scattering states from the low-energy spectrum, thereby allowing the researcher to more easily identify those roots of the secular problem which are true resonance states. As stated above, our research in the area has only recently begun; we plan to devote considerably more effort to this problem in the future.

# 5. Concluding Remarks

In this brief survey of some of our past and current contributions to the field of negative ion chemistry, I have attempted to demonstrate how modern quantum chemical tools, when combined with some simple physical models, can be used to study gas-phase anions, solvation effects, and metastable anions. By no means did I intend this survey to be an extensive review of work in each of these areas. For reasons of time and space I chose to limit my perspective to discussing in very little detail a few of our projects on atomic and molecular anions. I have recently written two more extensive reviews of the status of quantum chemical methods for studying anions [26] and of the results [27] obtained using these methods. These reviews, combined with a careful reading of the references given in the present paper should provide the interested reader with the detail which is lacking here.

In concluding, I would like to thank the organizers of the Symposium in Honor of Per-Olov Löwdin both for inviting me to discuss our work at Dalseter and for inviting me to summarize that discussion in the form of this paper.

### Acknowledgments

It is a great pleasure for me to dedicate this survey paper to Professor Per-Olov Löwdin on the occasion of his sixtieth birthday. I was fortunate to be acquiring my early education in theoretical chemistry at a time when Professor Löwdin's educational efforts were available. I consistently found his articles and lectures to be most clearly written, understandable, and inspiring. I hope that the members of our scientific community will follow Professor Löwdin's example and continue in the tradition of high scholarship established by him.

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