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NEGATIVE MOLECULAR IONS

Final Report

Dr. John P. Simons

August 17, 1977

U. S. ARMY RESEARCH OFFICE

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Salt Lake City, Utah

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Abstract

Having been successful in our studies of isolated (gas-phase) OH^-, NH_2^-, BeH^-, CN^-, BO^-, Li_2^-, and NO_2^-, we are now in a good position to further develop this area by 1) extending our calculations to chemically related molecules, e.g., SH^-, PH_2^-, MgH^-, etc., and 2) beginning to look into the hydration (or other solvation) of the species whose gas-phase properties we already know. Both of these avenues of research are feasible. We now have more powerful computer programs (MOLECULE) which should permit us to study the heavier analogs mentioned above. Moreover, we have also recently gained the experience needed to include solvation effects in our studies of those anions which we earlier studied as isolated systems. The hydration may be described either in terms of "model" H_2O molecules which are simply point charges distributed to represent the dipole moments of the surrounding solvents, or in terms of real ab initio H_2O molecules. The ab initio solvent studies will probably be restricted (by cost) to cases in which only one, two, or three solvent molecules surround the anion. The "model" solvent calculations might not be sufficient; we can only answer these questions by trying the computation, although some existing work on hydration by Morokuma and by ourselves has been encouraging.

Because we have successfully carried out many calculations on anions using the method described here in, a critical evaluation of the theory is available, and therefore, calculations on many other chemically important species can now be undertaken with some confidence. In addition to the above two extensions of our work, we are specifically interested in pushing on toward obtaining accurate electron detachment energies, geometries, and charge densities for the following interesting ions: O_4^-, CO_3^-, NO_3^- and other anions which play important roles in atmospheric chemistry. (O_3^- and NO_2^- have already been characterized). Now that we have more powerful computer programs available,

such studies are within our range (with the MOLECULE program a calculation on NO_2^- with 30 contracted Gaussian orbitals costs less than $50). Of course, the time and computer costs needed to perform a complete investigation of all the species listed above may well exceed the time interval of this proposal and the funds presently available to us. However, the mere fact that the geometry and stability of O_4^- remain as unsettled problems is sufficient to justify a concentration of work on this problem.

We also plan to expand our research into novel new anions whose properties have not been determined experimentally. Our work on the binding of electrons to (closed-shell) highly polar molecules (LiH, LiF, BeO, LiCℓ, NaH, etc.) will be extended to include model studies in which the potential energy field of the polar molecule is replaced (e.g. for a diatomic) by that of two point charges ($\pm q$) separated by the experimental bond length (with $Rq = \mu_{\text{exptl}}$) plus a "core" (e.g., $1s^2$ for Li, $1s^2\ 2s^2\ 2p^6$ for Na) on the electropositive atom. In this manner we hope to extend our investigation to systems containing several (a cluster) such polar molecules. Our initial results from this kind of a model calculation are very encouraging.

I. Historical Perspective

In 1968 Berry[1] reviewed the experimental and theoretical progress which had been made toward understanding the stabilities and bonding characteristics of small isolated (gas-phase) negative ions. In this review Berry commented as follows:

> "For the theorist, electron affinities and other properties of negative ions pose greater difficulties than do properties of neutrals or positives, insofar as electron correlation plays a relatively larger part in determining the properties of a negative ion than it does in other species. In fact, electron affinities are frequently about the same size as the differences between correlation energies in atoms and in the corresponding negative ions."

As an example of the magnitudes of electron correlation effects, one need only consider the results of our calculations on the vertical (R = 1.718 au) electron detachment energy $(X^1\Sigma^+ \; OH^- \rightarrow X^2\pi_i \; OH)$ of OH^-. Using an atomic orbital basis consisting of twenty Slater-type orbitals (STO's), we obtained a Koopmans' theorem approximation to the detachment energy equal to 3.06 eV. The energy difference between two separate SCF calculations (ΔSCF), one on OH^- and one on OH, carried out within the same basis was equal to - 0.20 eV; the difference between Koopmans' theorem and ΔSCF represents the effects of allowing the orbitals to relax upon removal of the π electron. Finally, our best computed energy difference[2], which contains effects of electron correlation through third order, was 1.76 eV which is in good agreement with both Branscomb's early experiments[3] and Lineberger's more recent laser detachment results.[4] The difference between 1.76 eV and the ΔSCF value of -0.2 eV represents the effects of electron correlation. These effects are indeed as large as the entire electron affinity of OH; moreover, this result is not atypical.

Because the treatment of both orbital relaxation and electron correlation effects in a sufficiently rigorous manner is an absolute necessity in any reliable scheme for computing properties of anions, theoretical progress toward understanding negative ions has been made rather slowly. Quite simply put, it is difficult to include correlation effects to a high enough order to guarantee precision ± 0.2 eV in computed ion-neutral energy differences. In Berry's review article, his assessment of the state of quantum chemical research on anions involved briefly mentioning the works of Pekeris[5] on H^-, Weiss[6] on Li^-, Na^-, and K^-, Clementi and co-workers[7] on several atomic ions, Sinanoglu[8] on C^-, O^-, and F^-, Taylor and Harris[9] on H_2^-, Wahl and Gilbert[10] on halogen diatomics, and Cade[11] on OH^-, CH^-, SiH^-, SH^-, and PH^-. Therefore, in 1968 it would have been fair to say that negative molecular ions were not yet within the class of species which could be conveniently studied by existing quantum chemical methods. On the other hand, the development of modern laser technology was making available to the experimentalist new tools to use in carrying out high precision photodetachment and photoelectron spectroscopy studies of gas-phase anions. Thus, even in 1968 a great deal of experimental progress was beginning to be made. These experimental developments made a parallel development of theoretical methods and models aimed at better understanding negative ions a necessary and quite natural step in the scientific progress in this area.

In 1973 Simons and Smith[12] published an article in which they attempted to use equations of motion (EOM) techniques[13] to express the vertical electron affinity (EA) or detachment energy (DE) of a closed-shell species in a manner which treated orbital relaxation and electron correlation through third order in perturbation theory (the difference between the coulombic interaction and the Hartree-Fock interaction being the perturbation). This developmental paper was followed by other formal papers by Simons, Jørgensen, Jordan, and Chen[14-15] in which small deficiencies in the original theory were corrected and connection made with the recent Green's function developments of Cederbaum[16], Pickup and Goscinski[17], Purvis and Öhrn[18], and Freed[19]. The result of these papers was a method which permits the direct calculations of EA's and DE's, of closed-shell species, which are accurate through third order.

In succeeding publications[2,20-26] the third order EOM theory was applied to studies of the stability and bonding characteristics of several molecular anions (and cations). Calculations of the electron affinities of OH, BeH, NH_2, CN, and BH provided theoretical support (to within ± 0.2 eV) for existing experimental measurements. Studies of the EA's of BO and Li_2 resulted in theoretical predictions for species where good experimental data is not available. Calculations of the EA's of LiF, LiCℓ, LiH, NaH, and BeO have led to predictions to both the existence and the stabilities (with respect to electron loss) of the anions of these species. Jordan[92] has also examined the dimer anion $(LiH)_2^-$; Simons and Jordan[93] have recently found Be_2^- to be stable even though Be_2 is unbound. Very recently, the ion $LiCℓ^-$ was observed by Lineberger[27] thereby verifying the theoretical prediction of Jordan _et al_[77]. The precise nature of some of the above calculations together with the principal conclusions of these works are treated later in this proposal.

In the time since Berry's 1968 review article was completed and for a few years prior to that date, several _ab initio_ calculations, in addition to those mentioned above, were performed on molecular anions which are of chemical interest. These studies include the following works: Clementi[28] (N_3^-), Lipscomb[29] (PO^-), Krauss[30] (BH_4^-, O_2^-) Kaufman[31] (O_3^-), Csmizmadia[32] (CH_3^-, NH_2^-), Pfeiffer[33] (NO_s^-), Popkie[34] (C_2^-), McLean[35] (OCN^-, SCN^-), Wahl[36] (Cl_2^-, F_2^-), Fink[37] (OH^-, NH_2^-, CH_3^-, BH_4^-), Geller[38] (BH_2^-), Thulstrup[39] (NO^-), Peyerimhoff[40] (BeH_3^-), Heaton[41] (NH_2^-), Schaefer[42] (NO_2^-), Thulstrup[84] (C_2^-), O'Hare[85] (NF^-, NS^-, PF^-, SF^-). This list is by no means a complete tabulation of all work done on negative molecular ions; it is simply meant to indicate the kinds of systems which have been studied as well as approximately the number of calculations which have been performed to date. Although it is true that a reasonably large number of _ab initio_ calculations have been carried out for diatomic and small polyatomic species, very few of the studies referenced above include any electron correlation effects. Most of these calculations have been done at the SCF-level within small-to-moderate size bases. Therefore, the EA's which have been obtained in this manner are probably not reliable. On the other hand the equilibrium geometries and charge densities obtained in the above SCF-level works may not be any less accurate than the results of analogous calculations on neutral species; electron correlation effects are not as dominant as in determining EA's. Nevertheless, it is our feeling that most of the reliable work on negative ions has been, and will continue to be, characterized by a careful treatment of electron correlation and charge relaxation. For this reason, the remainder of this proposal will be restricted to discussion of results and proposals for studies which treat correlation in an *ab initio* manner, except in those cases where simple chemical models are introduced to permit a qualitative understanding of more complex systems.

With this brief survey of the developments made since 1968 as a background, let us now turn to a more detailed discussion both of the most recently utilized methods and the results which have been obtained with these methods. In Sec. II we review the foundation of the direct-calculation approach of refs. 12-19. Sec. III contains a survey of results on OH^-, NH_2^-, BeH^-, CN^-, BO^-, LiF^-, $LiC\ell^-$, LiH^-, NaH^-, BeO^-, NO_2^- in which the effects of orbital relaxation and correlation have been included. Specific attention is paid to stabilities (EA or DE), geometries (Re, θ_e), vibrational frequencies, dissociation energies, and charge densities of these anions. In Sec. IV we review the conclusions which have been reached thus far and we make concrete proposals for research in areas which seem to show special promise for future development.

II. Review of the Theoretical Methods[15] Employed

The electron propagator or the one-electron Green's function has been used for some time[16,18,20-26,43-46] in the study of electron spectroscopy. The advantages of using the electron propagator arise because the transition energies and the transition strengths are obtained directly as poles and residues of the propagator, respectively. Several alternative procedures for decoupling the Equation-of-Motion for the electron propagator have been developed. In this analysis we use the superoperator formalism of Goscinski and Lukman[47] as the framework for our development of an electron propagator which is consistent through third order. In an alternative derivation using the Equation-of-Motion formalism of Rowe[48], Simons and Smith[12] attempted to obtain an Equation-of-Motion which was consistent through third order. Purvis and Öhrn[49] pointed out some deficiencies in the theory of Simons and Smith; these deficiencies are mentioned again in this section. We show further how the electron propagator can be obtained consistent through third order. The consistency is made more transparent by demonstrating that all second and third order self energy diagrams of Cederbaum[16] are included in our formalism.

The definition of the spectral electron propagator[44] can be written within the superoperator formalism as

$$\underline{\underline{G}}\,(E) = (\underline{a}|(E\hat{I} - \hat{H})^{-1}|\underline{a}) \tag{1}$$

where $\hat{I}$ and $\hat{H}$ are the superoperator identity and hamiltonian respectively and the $\underline{a}$ are a set of annihilation operators $\underline{a} = \{a_i\}$, which are arranged in a super row vector. The superoperator scalar product is defined in the conventional fashion[47]. The superoperator resolvent $(E\hat{I} - \hat{H})^{-1}$ can be approximated via the inner projection technique and the propagator then takes the form

$$\underline{\underline{G}}\,(E) = (\underline{a}|\underline{h})\,(\underline{h}|E\hat{I} - \hat{H}|\underline{h})^{-1}(\underline{h}|\underline{a}) \tag{2}$$

where $\underline{h}$ is a projection manifold which, if chosen to be complete and orthonormal, makes Eqs. (1) and (2) identical. The operator space

$$\{h_1, h_3, h_5 \ldots\} = \{a_i, a_i^{+}a_k a_l, a_i^{+}a_j^{+}a_k a_l a_r \ldots\},\ k>l,\ i>j,\ k>l>r \ldots \tag{3}$$

spans the manifold $\underline{h}$. We now discuss appropriate selections of $\underline{h}$ which, in conjunction with our choice of the reference state, ensure that the electron propagator is calculated correctly through third order in the electronic interaction.

It is well known[17,45] that the projection manifold $\underline{h}_1$, $\underline{h}_3$ in connection with the Hartree-Fock (HF) ground state is able to give the electron propagator correct through second order in the electronic interaction. Our experience[2,20,26] tells us that second order calculation of EA's are not sufficiently precise to be useful. (except in well-understood special cases which are discussed below). We demonstrate how, using a correlated ground state and the same projection manifold, we are able to get the electron propagator correct through third order in the electron interaction.

The effect of including $\underline{h}_5$ in the projection manifold, where the HF ground state is used as reference state, has been discussed by Tyner et al[50], and from their analysis it is clear that $\underline{h}_5$ introduces terms which are at least fourth order in the electronic interaction, independent of the choice of reference state. We therfore concentrate on using $\underline{h}_1, \underline{h}_3$ as our projection manifold in our search for a theory which is consistent through third order.

As the reference state in our analysis we use a correlated wavefunction given by

$$|0> = N^{-\frac{1}{2}}\{1 + \sum_{p\delta} (K^{p}_{\delta}\, a^{+}_{p} a_{\delta}) + \sum_{\substack{m>n \\ \alpha>\beta}} (K^{mn}_{\alpha\beta}\, a^{+}_{m} a^{+}_{n} a_{\beta} a_{\alpha})$$

$$+ \sum_{\substack{m>n>p \\ \alpha>\beta>\delta}} (K^{mnp}_{\alpha\beta\delta}\, a^{+}_{m} a^{+}_{n} a^{+}_{p} a_{\alpha} a_{\beta} a_{\delta}) + \ldots\} \, |HF> \qquad (4)$$

where the $\underline{a}^{+}$ are a set of HF creation operators and where indices m,n,p,q (α,β,δ,γ) refer to unoccupied (occupied) spin orbitals in the HF ground state and i,j,k,l,r are unspecified spin orbitals. We take the correlation coefficients from Rayleigh-Schrödinger perturbation theory

$$K^{p}_{\delta} = \sum_{\substack{m>n \\ \alpha>\beta}} \{<p\alpha||mn>\, \delta_{\delta\beta} - <p\beta||\, mn>\, \delta_{\alpha\delta} + <\beta\alpha||\, \delta m>\, \delta_{np} - <\beta\alpha||\delta n>\, \delta_{pm}\}$$

$$\times \frac{<mn||\alpha\beta>}{(\varepsilon_{\delta} - \varepsilon_{p})\, (\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{n} - \varepsilon_{m})} + \text{higher order terms in the electronic interaction} = K^{p}_{\delta}\, (2,3\ldots) \qquad (5)$$

$$K^{mn}_{\alpha\beta} = \frac{\langle mn||\alpha\beta\rangle}{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_m - \varepsilon_n} + \begin{array}{l}\text{higher order terms}\\ \text{in the electronic}\\ \text{interaction}\end{array} = K^{mn}_{\alpha\beta}\,(1,2\ldots) \tag{6}$$

$$K^{mnp}_{\alpha\beta\delta} = K^{mnp}_{\alpha\beta\delta}\,(2,3\ldots) \tag{7}$$

where the first number in the bracket indicates the lowest order in the electronic interaction. The ε_i indicate HF orbital energies and the two electron integral $\langle mn|\alpha\beta\rangle$ refers to the charge densities $m\alpha$ and $n\beta$ and

$$\langle mn||\alpha\beta\rangle = \langle mn|\alpha\beta\rangle - \langle mn|\beta\alpha\rangle \tag{8}$$

in our analysis we consider the projection manifold $\{\underline{h}_1, \underline{h}_3\}$ where the $\underline{h}_3$ space for convenience has been redefined as

$$\underline{h}_3 = \{a^+_i a_k a_l + \langle a^+_i a_l\rangle a_k - \langle a^+_i a_k\rangle a_l\} \tag{9}$$

The choice of the subspace $\underline{h}_3$ ensures that this space is orthogonal to $\underline{h}_1$

$$(\underline{h}_1|\,\underline{h}_3) = \underline{0} \tag{10}$$

even for a correlated reference state. We also have the following orthogonality relations

$$(\underline{h}_1|\underline{h}_1) = \underline{\underline{1}},\ (\underline{h}_3|\underline{h}_3) = \underline{\underline{S}}\,(0,2,3\ldots) \tag{11}$$

Using Eqs. (10) and (11), Eq. (2) can be partitioned into the form

$$\begin{aligned}\underline{\underline{G}}^{-1}\,(E) &= (\underline{h}_1|E\hat{I} - \hat{H}|\underline{h}_1) - (h_1|\hat{H}|\underline{h}_3)(\underline{h}_3|E\hat{I} - \hat{H}|\underline{h}_3)^{-1}\,(\underline{h}_3|\hat{H}|\underline{h}_1)\\ &= E\underline{\underline{1}} - \underline{\underline{A}} - \underline{\underline{B}}\,\underline{\underline{D}}^{-1}\,\underline{\underline{C}}\end{aligned} \tag{12}$$

where the matrices $\underline{\underline{A}}$ $\underline{\underline{B}}$ $\underline{\underline{C}}$ and $\underline{\underline{D}}$ are defined as

$$\underline{\underline{A}} = (\underline{h}_1|\hat{H}|\underline{h}_1)$$

$$\underline{\underline{B}} = (\underline{h}_1|\hat{H}|\underline{h}_3)$$

$$\underline{\underline{D}} = (\underline{h}_3|E\hat{I} - \hat{H}|\underline{h}_3)$$

$$\underline{\underline{C}} = (\underline{h}_3|\hat{H}|\underline{h}_1) \tag{13}$$

We will now make an order by order analysis of Eq. (12) in which we retain only those terms which are zeroth, first, second, or third order in the electronic interaction. Since the $\underline{\underline{B}}$ and $\underline{\underline{C}}$ matrices are at least of first order[12], we need to consider only that part of the $\underline{\underline{D}}$ matrix which is zeroth and first order. This constrains the indices in the projection manifold $\underline{h}_3$ to be of the form $a^+_m a_\alpha a_\beta$ $\alpha>\beta$ or $a^+_\alpha a_m a_n$ $m>n$ since operators such as $a^+_m a_n a_\alpha$ lead to matrix elements in the $\underline{\underline{D}}$ matrix which are at least of second order. The resulting subspace $\underline{h}_3$ is thus identical to that used in calculating the electron propagator correct through second order. To calculate the electron propagator through third order in the electron repulsions, we thus need to obtain the $\underline{\underline{B}}$ and $\underline{\underline{C}}$ matrices through second order, the $\underline{\underline{D}}$ matrix through first order, and the $\underline{\underline{A}}$ matrix through third order.

Previous attempts[12] to obtain the electron propagator correct through third order have used as reference state

$$0 = N_0^{-\frac{1}{2}} (1 + \sum_{\substack{m>n \\ \alpha>\beta}} K^{mn}_{\alpha\beta}\, a^+_m a^+_n a_\alpha a_\beta)|HF> \tag{14}$$

theory. In calculating the $\underline{\underline{B}}$ ($\underline{\underline{C}}$) and $\underline{\underline{D}}$ matrix elements correct through second and first order, respectively, no changes are obtained from considering the higher correlated ground state in Eq. (4). The matrix elements of $\underline{\underline{B}}$, $\underline{\underline{C}}$, and $\underline{\underline{D}}$ are given by

$$B_{i,\alpha m\beta} = -\langle im|\alpha\beta\rangle - \tfrac{1}{2}\sum_{p,q} \langle im|pq\rangle K^{pq}_{\alpha\beta} + \sum_{\gamma,p}\left[\langle i\gamma|p\alpha\rangle K^{mp}_{\beta\gamma} - \langle i\gamma|p\beta\rangle K^{mp}_{\alpha\gamma}\right] \tag{15}$$

$$B_{i,n\alpha m} = \langle i\alpha|mn\rangle + \tfrac{1}{2}\sum_{\gamma\delta} \langle i\alpha|\delta\gamma\rangle K^{mn}_{\delta\gamma} + \sum_{\gamma p}\left[\langle ip|\gamma n\rangle K^{mp}_{\alpha\gamma} - \langle ip|\gamma m\rangle K^{np}_{\alpha\gamma}\right] \tag{16}$$

$$\underline{\underline{C}}^{+} = \underline{\underline{B}} \text{ (through second order)} \tag{17}$$

$$D_{n\alpha m,\delta p\gamma} = 0, \tag{18}$$

$$\begin{aligned} D_{n\alpha m,q\beta p} = {} & \delta_{nq}\delta_{\alpha\beta}\delta_{mp}\,(\varepsilon_m + \varepsilon_n - \varepsilon_\alpha) - \delta_{qn}\langle m\beta||p\alpha\rangle - \delta_{pm}\langle n\beta||q\alpha\rangle \\ & + \delta_{qm}\langle n\beta||p\alpha\rangle + \delta_{\alpha\beta}\langle mn||pq\rangle + \delta_{pn}\langle m\beta||q\alpha\rangle, \end{aligned} \tag{19}$$

$$\begin{aligned} D_{\delta p\gamma,\alpha q\beta} = {} & -\{\delta_{\delta\alpha}\delta_{pq}\delta_{\gamma\beta}\,(\varepsilon_p - \varepsilon_\delta - \varepsilon_\gamma) - \delta_{\gamma\beta}\langle\delta q||\alpha p\rangle - \delta_{\delta\alpha}\langle\gamma q||\beta p\rangle \\ & + \delta_{\gamma\alpha}\langle\delta q||\beta p\rangle - \delta_{pq}\langle\delta\gamma||\beta\alpha\rangle + \delta_{\delta\beta}\langle\gamma q||\alpha p\rangle \end{aligned} \tag{20}$$

In the $\underline{\underline{A}}$ matrix we need to include all terms up to third order. The $\underline{\underline{A}}$ matrix elements obtained by using Eq. (14) as a reference state need to be modified by third order terms which result from interaction between the singly excited states and the HF ground state. The triply excited states which also result from a second order Rayleigh-Schrödinger perturbation calculation do not introduce third order terms. We thus have to add to the $\underline{\underline{A}}$ matrix elements given in ref. [12] the terms δA_{ij}

$$\delta A_{ij} = \sum_{\substack{\delta\beta \\ pmn}} \frac{\langle jp||i\delta\rangle\langle\delta\beta||mn\rangle\langle mn||p\beta\rangle}{(\varepsilon_\delta-\varepsilon_p)(\varepsilon_\delta+\varepsilon_\beta-\varepsilon_m-\varepsilon_n)} \tag{A3}$$

$$+ \sum_{\substack{\delta\beta \\ pmn}} \frac{\langle j\delta||ip\rangle\langle p\beta||mn\rangle\langle mn||\delta\beta\rangle}{(\varepsilon_\delta-\varepsilon_p)(\varepsilon_\delta+\varepsilon_\beta-\varepsilon_m-\varepsilon_n)} \tag{A4}$$

$$+ \sum_{\substack{\delta\alpha\beta \\ pn}} \frac{\langle jp||i\delta\rangle\langle\delta n||\beta\alpha\rangle\langle\alpha\beta||pn\rangle}{(\varepsilon_\delta-\varepsilon_p)(\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_p-\varepsilon_n)} \tag{A5}$$

$$+ \sum_{\substack{\delta\alpha\beta \\ pn}} \frac{\langle j\delta||ip\rangle\langle\beta\alpha||\delta n\rangle\langle pn||\alpha\beta\rangle}{(\varepsilon_\delta-\varepsilon_p)(\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_p-\varepsilon_n)} \tag{A6}$$

The $\underline{\underline{A}}$ matrix of ref. [12] is

$$A_{ij} = \delta_{ij}\varepsilon_i + \sum_{k,l} \langle ik|jl\rangle F_{kl} \tag{21}$$

$$F_{kl} = \sum_{\alpha>\beta,p} K^{pk}_{\alpha\beta} K^{pl}_{\alpha\beta} - \sum_{p<q,\alpha} K^{pq}_{\alpha l} K^{pq}_{\alpha k} \tag{22}$$

We thereby have calculated the electron propagator consistently through third order.

A comparison with a diagrammatic perturbation expansion of the self-energy[86] makes it further transparent that we have really included all terms through third order in our analysis of the electron propagator. In Fig. 1 we have displayed the terms A3 - A6 as diagrams using the rules of Brandow[51] which combine the Goldstone diagrams with the antisymmetrized vertices of Hugenholtz. The diagrams labelled A3 - A6 are identical to the third order diagrams given by Cederbaum[16], in which dots refer to antisymmetrized vertices. The diagrams A3 - A6 were shown by Purvis and Öhrn[49] to be the only missing third order

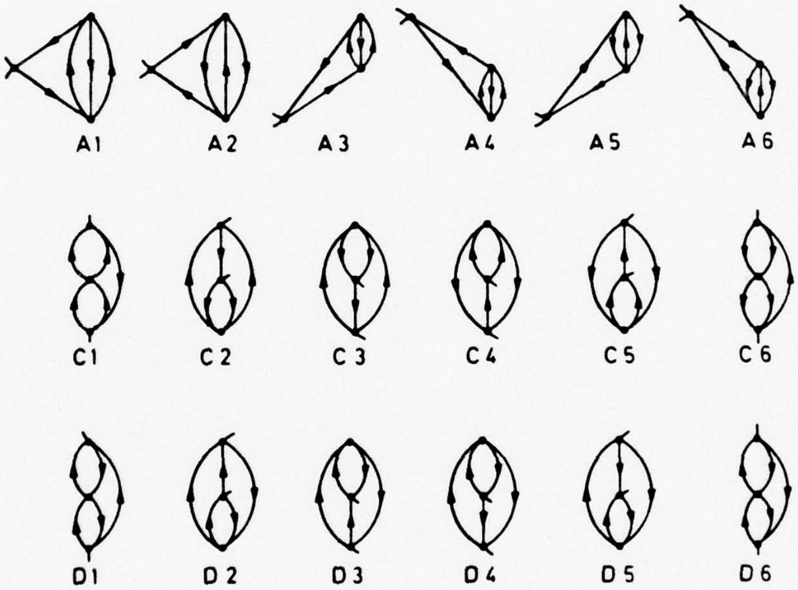

Fig. 1

diagrams which evolve from a theory where the reference state is given by Eq. (14). The analysis of Purvis and Öhrn considered $(\underline{h}_3|E\hat{I} - \hat{H}|\underline{h}_3)$ as two matrices; $\underline{\underline{u}}$ which contains E and orbital energies (zeroth order terms) and $\underline{\underline{M}}$ which contains the two electron integrals (first order terms). Making use of the identity $(\underline{\underline{u}} + \underline{\underline{M}})^{-1} = \underline{\underline{u}}^{-1} - \underline{\underline{u}}^{-1}\,\underline{\underline{M}}(\underline{\underline{u}} + \underline{\underline{M}})^{-1}$ to expand the inverse, Purvis and Öhrn identified the diagrams C1 - C6 and D1 - D6 of Cederbaum[16] to originate from the $\underline{\underline{B}}\,\underline{\underline{D}}^{-1}\underline{\underline{C}}$ term while the diagrams A1 - A2 were found to arise from the $\underline{\underline{A}}$ matrix previously given in ref. [12]. We thus have accounted for all third order diagrams which arise from an expansion of the self energy. The electron propagator calculation thus needs to use the second-order correlated ground state given in Eq. (4) as a reference state and the subspace $\{\underline{h}_1, \underline{h}_3\}$ given by Eq. (3) as the projection manifold to be correct through third order.

We have shown how the electron propagator can be obtained correctly through third order. Our development stresses the fact that a complete treatment of the inverse of the $\underline{\underline{D}}$ matrix is needed to guarantee that all desired terms are included. Computational applications have so far only been carried out using a diagonal approximation to the D matrix. This situation is unsatisfactory and should be improved. A unitary transformation which brings the $\underline{\underline{D}}$ matrix closer to diagonal form is related to the theory of linear response as discussed by Jørgensen and Purvis[52]. Using this kind of procedure we would expect to get an approximation to the propagator which would be nearly complete through third order. The energy shifted denominators which result from evaluating the $\underline{\underline{D}}$ matrix, correspond to the result of summing certain classes of diagrams to infinite order, which implies that the electron propagator treatment has the computational advantage of expressing these summations in closed form. In a diagrammatic summation of self-energy diagrams one has to explicitly account for each energy shifted denominator through each order. We finally note that the side shifted diagrams given in Fig. 1 do not appear in the original third order theory of Simons and Smith[12] for calculating ionization potentials and electron affinities. These diagrams result from using a more highly correlated wavefunction than the one considered by Simons and Smith as the reference state.

With this derivation of the needed third order equation accomplished, let us now turn to a more detailed description of selected results which have been obtained by making use of the propagator approach. Recall that we are limiting the discussion to studies which have treated electron correlation effects in an ab initio manner. The anions which we have chosen to discuss in some detail can be divided into several classes. NH_2^-, OH^-, BeH^-, are hydrides whose parents have a half-filled orbital to which the "extra" electron is added. CN^-, BO^-, and NO_2^- are ions whose parents also have half-filled orbitals. All of the above ions are closed-shell species. Li_2^- and Be_2^- are open-shell ions which are formed by adding an electron either to an antibonding (Li_2^-) or bonding (Be_2^-) molecular orbital of the closed-shell parent. LiF^-, $LiC\ell^-$, LiH^-, NaH^-, and BeO^- are each formed by adding an electron to an essentially nonbonding orbital of the very polar neutral parent; in these ions correlation and relaxation are not very important because the "extra" electron resides in an orbital which is localized on the "back" end of the electropositive atom where it encounters little dynamic interaction with the other electrons. It is clear that our studies of anions have covered a wide range of chemically quite different species in which the factor (or factors) governing the binding of the electron to the parent include dipole forces, valence attraction of a half-filled orbital, polarization of charge, and formation of new bonding orbitals (Be_2^-).

III. Brief Survey of Some Results

A. OH^-: Our First Comparison With Experiment

In carrying out the calculations on OH^- described here[2], we employed an atomic orbital basis consisting of Slater-type functions whose orbital exponents were taken from the bases of Cade[53] for HO^-, and of Cade and Huo[54] for $\cdot OH$. Information describing our basis and the essential results of the SCF calculation on the parent $X^1\Sigma^+ OH^-$ for this basis are given in table A1. Note that the basis used in this work is not very large.

As shown in table A2, the vertical detachment energies computed using the basis of table A1 are within 0.10 eV of the experimental result quoted by Lineberger *et al*[4]. An important observation which should be made here is that the basis given in table A1 is capable of yielding a very accurate detachment energy. Our results show that the theory of molecular electron affinities and ionization potentials in ref. (12) is capable of yielding the vertical electron detachment energy of $X^1\Sigma^+ OH^-$ to within 0.1 eV. It has also been demonstrated that a highly accurate description of the core orbital of OH^- is not essential to an accurate calculation of the $^2\Pi_i$ valence electron detachment energy. Finally, an investigation of the roles of orbital relaxation and correlation energy change in determining the ion-molecule energy difference has led to the conclusion[2] that both of these effects must be treated properly in any study of negative molecular ions unless one knows that the "extra" electron is essentially uncorrelated (perhaps by spatial localization) with the other electrons. As discussed in part E of this section, such is the case for the family of anions formed by adding an electron to a highly polar closed-shell molecule.

Table A1

20-Function Hartree-Fock Wavefunction for OH^-. R = 1.781 au, E = -75.3801 au,

$\epsilon_{1_\sigma} = -20.22091$, $\epsilon_{2_\sigma} = -.94178$, $\epsilon_{3_\sigma} = -.27867$, $\epsilon_{1_\pi} = -.12616$

σ atomic orbitals	1σ	2σ	3σ	π atomic orbitals	1π
O1s (7.0168)	.9721	-.1645	.1213	O2p (2.0624)	.5857
O2s (2.8646)	.1268	.8711	-.0336	O2p' (3.7529)	.1949
O2p (2.1172)	-.0349	.0490	.3761	O2p" (0.7128)	.3246
O1s' (12.3850)	.0961	-.0081	-.0111	O3d (1.2500)	.0133
O2s' (1.5729)	.0141	.3714	-.3687	H2p (0.9250)	.0958
O2p' (1.0227)	.0067	-.0065	.2047		
O2p" (3.7596)	-.0053	.0074	.1777		
H1s (1.1986)	-.0027	.1507	.4723		
H2s (2.3003)	-.1816	-.3336	-.1403		
H1s' (2.4385)	-.0014	.0494	.0024		

Table A2

Summary of Detachment Energies for OH^-

Detachment Energy (eV)	Source
1.773	EOM[2]
1.825 ± 0.002	Hotop, Patterson, Lineberger[a]
1.83	Branscomb[b]

a. Hotop, Patterson, Lineberger, J. Chem. Phys., <u>60</u>, 1806 (1974).

b. L. M. Branscomb, Phys. Rev., <u>148</u>, 11 (1966).

B. BeH^-: An Experimentally Understudied Anion

An initial basis set for the closed-shell ($^1\Sigma^+$) BeH^- consisting of 20 Slater-type orbitals (STO's) was adapted from the optimized BeH basis set reported by Cade and Huo.[54] To accomodate the extra electron correlation, $2p_\pi$ functions and diffuse s and $2p_\sigma$ functions were added to the "sigma only" BeH basis set to replace functions contributing nominally to the description of the occupied BeH molecular orbitals.

The orbital exponents of the four BeH^- STO's in the original basis set having the largest expansion coefficients in the 3σ highest occupied molecular orbital (HOMO) were optimized at the initially calculated BeH^- equilibrium internuclear distance of 2.660 au. The initial and optimized BeH^- basis sets and expansion coefficients for occupied molecular orbitals are listed in Table B1. Basis functions which were also used in the Cade and Huo BeH basis set have been marked with an asterisk. From this table we observe that optimization of the BeH^- basis set cuased dramatic increases in the importance of the diffuse 2sBe and 1sH basis functions describing the 3σ HOMO. SCF calculations for $E_{BEH^-}(R)$ were executed on the University of Utah Univac 1108 computer using a modified version of the Harris DIATOM program. Execution time for each run was approximately 4.50 minutes. Vertical ionization energies of BeH^-, $IP_{BeH^-}(R)$, were calculated by our third order equations-of-motion program. Execution time for each ionization energy calculation on the Univac 1108 was approximately 25 seconds. BeH energies were calculated by adding the vertical ionization energy of BeH^- to the BeH^- energy,

$$E_{BeH}(R) = E_{BeH^-}(R) + IP_{BeH^-}(R) \qquad (23)$$

Table B1 Original and optimized 20 STO basis sets for BeH$^-$. Original basis set; R_e = 2.660 au, E = -15.12104 au, $\varepsilon_{1\sigma}$ = -4.51210 au, $\varepsilon_{2\sigma}$ = -0.28926 au, $\varepsilon_{3\sigma}$ = -0.02032 au; IP = 0.02751 au. Optimized basis set; R_e = 2.670 au, E = -15.12308 au, $\varepsilon_{1\sigma}$ = -4.50693 au, $\varepsilon_{2\sigma}$ = -0.27730 au, $\varepsilon_{3\sigma}$ = -0.01877 au, IP = 0.02913 au.

BeH Basis	Orbital	ζ(original)	ζ(optimized)	$C_{1\sigma}^{(or.)}$	$C_{1\sigma}^{(op.)}$	$C_{2\sigma}^{(or.)}$	$C_{2\sigma}^{(op.)}$	$C_{3\sigma}^{(or.)}$	$C_{3\sigma}^{(op.)}$
*	1sBe	2.9448		0.84377	0.85361	-0.16987	-0.15081	-0.09822	-0.08297
*	1s'Be	5.7480		0.23092	0.22616	-0.00186	-0.01822	-0.01053	-0.01590
	2sBe	0.4000	0.4250	0.01243	-0.03928	0.01391	-0.09120	0.63441	1.08018
*	2s'Be	0.8925	1.1500	0.07134	0.10249	0.29861	0.39163	0.65860	0.56833
	2s"Be	1.7238		-0.11599	-0.16573	0.12175	-0.02368	0.06845	-0.05473
	$2p_\sigma$Be	0.4000		0.01257	-0.01303	0.03299	-0.03817	-0.13953	-0.01732
*	$2p_\sigma$'Be	0.8030		0.03336	0.01491	0.03954	-0.01068	-0.11016	-0.28577
*	$2p_\sigma$"Be	1.0460		-0.04211	-0.00897	0.12792	0.13522	-0.08124	0.05031
*	$2p_\sigma$'''Be	1.5000		0.01356	0.00198	0.09628	0.08734	-0.10446	-0.12657
	$2p_\pi$Be	0.8080		0.0	0.0	0.0	0.0	0.0	0.0
	$2p_\pi$'Be	1.0460		0.0	0.0	0.0	0.0	0.0	0.0
	$2p_\pi$"Be	1.5000		0.0	0.0	0.0	0.0	0.0	0.0
	1sH	0.4000	0.3000	-0.05489	0.03915	0.03648	0.13939	-0.47443	-0.75778
	1s'H	1.0000	1.0500	0.01772	-0.02409	0.71242	0.64325	-0.19299	-0.19021
*	2sH	2.5000		-0.00019	0.01496	0.01453	-0.01514	0.00898	0.00635
	$2p_\pi$H	1.4500		0.0	0.0	0.0	0.0	0.0	0.0

Approximate vibrational force constants (Table B2) and fundamental vibrational frequencies for the BeH and BeH^- systems were obtained by fitting a least squares quadratic polynomial to each potential energy curve. Agreement of these calculations with the experimental BeH values was quite good. For the original basis set, $\nu_e^{(calc.)} - \nu_e^{(exp.)}$ was +44.6 cm^{-1}, a +2.17% deviation, and for the optimized basis set the deviation was -60.0 cm^{-1} or -2.91%. For comparison, the value for ν_e^{BeH} reported by Cade and Huo deviated from the experimental value by +95.0 cm^{-1} or +4.66%. It is reasonable to assume our calculated fundamental vibrational frequencies for BeH^- are at least this accurate.

In reporting Feldmann's value for IP_{BeH^-}(Thermo.) of 0.74 eV in Table B2, we have subtracted 0.01 eV (zero-point corrections) from the BeH^- photodetachment energy value of 0.75 eV. Calculated thermodynamic ionization potentials for BeH^- deviate from the experimental value by $[-0.01 \text{ eV}, -1.4\%]^{(or.)}$, $[+0.03 \text{ eV}, +4.1\%]^{(op.)}$. Vertical ionization energies and electron affinities differ no more than 7% from the experimental thermodynamic value. These results indicate that for reasonable approximations to the thermodynamic ionization energy of BeH^- our vertical EOM ionization energy calculations at R_e^{BeH} and $R_e^{BeH^-}$ are quite good.

Table B2. Calculated and experimental spectroscopic parameters for BeH and BeH^-

Parameter	Units	$BeH^{(exp.)}$	$BeH^{(HF)}$	$BeH^{(or.)}$	$BeH^{(op.)}$	$BeH^{-(or.)}$	$BeH^{-(op.)}$	$BeH^{-(exp)}$
R_e	au	2.538^a	2.528^c	2.540	2.560	2.660	2.670	
k_e	$dyne/cm \times 10^{-1}$	$2.246^{a,h}$	2.461^c	2.345	2.118	1.903	1.753	
ν_e	cm^{-1}	2058.6^a	$2154.6^{c,h}$	2103.2^h	1998.6^h	1894.9^h	1818.5^h	
D_e	eV	$(2.33)^{a,b}$	2.18^c			2.15^e 2.31^f	$2.20^{d,e}$ $2.35^{d,f}$	
$EA_{BeH}(R_e^{BeH})$	eV			0.7031	0.7560			
$IP_{BeH^-}(R_e^{BeH^-})$	eV					0.7485	0.7926^d	
IP_{BeH^-}(Thermo.)	eV					0.7253	0.7727^d	0.74^g

[a] Herzberg, ref. (55).

[b] Gaydon, ref. (56), reports 2.3 eV with an uncertainty of ±0.3 eV.

[c] Cade and Huo, ref. (54).

[d] Calculated from Cade and Huo HF D_e^{BeH} of 2.18 eV.

[e] Calculated from Herzberg's D_e^{BeH} of 2.33 eV.

[f] Feldmann, ref. (57), photodetachment energy value corrected for zero point vibrational energy difference by Eq. (19).

[g] Calculated from k_e or ν_e assuming $\nu_e = \frac{1}{2}\pi c \sqrt{k_e/\mu}$

C. CN^- and BO^-: A Well-Known Ligand and its Isoelectronic Partner

The starting point for the construction of the double zeta basis sets used in these calculations was Roetti and Clementi's excellent set[58] of double zeta functions for the component atoms. To better describe the charge distribution in the resultant negative molecular ions, the orbital exponents of the functions with large expansion coefficients in the highest occupied molecular orbital (HOMO) of CN^- and of BO^- were varied to maximize the ionization energies. The greatest changes in each case were produced by modifying the exponents of the 2s and 2pσ functions on the less electronegative atom in the ion.

Since little is known about the geometry of BO^-, its basis set was optimized at $R = 2.278$ bohr, which corresponds to the equilibrium separation of the neutral BO molecule. The total energy before optimization was -99.550 hartree and the corresponding $X\ ^1\Sigma^+ \rightarrow X\ ^2\Sigma^+$ ionization potential was 2.16 eV. The final basis gave a slightly lower SCF energy, -99.554 hartree, and a vertical ionization potential of 2.81 eV.

The CN^- basis set optimizations were performed at $R = 2.2$ bohr, the internuclear separation corresponding to the lowest energy found after a few preliminary SCF calculations on CN^- with the starting basis. The initial energy at 2.2 bohr was -92.2634 hartree, and the vertical ionization energy for the starting basis was 3.04 eV. After optimization of 2s and 2pσ functions on carbon and 2s functions on nitrogen, the total energy was -92.2645 hartree and the $X\ ^1\Sigma^+ \rightarrow X\ ^2\Sigma^+$ vertical ionization energy was 3.69 eV. The diffuse 2pπ function on nitrogen was varied slightly in an attempt to obtain a reasonable $^1\Sigma \rightarrow {}^2\pi$ ionization potential. However, the $^2\pi$ state of CN is not expected to be well described in our basis since the optimization of the pi functions was not extensive. The final optimized CN^- and BO^- basis sets shown in Table C1 were used to compute ion-molecule energy differences at several internuclear separations; these differences were added to the total SCF energies at corresponding R values of the negative ions to generate SCF-level potential curves for BO and CN.

Examination of the ground state potential curves for BO, BO^-, CN and CN^- allows us to determine the adiabatic electron affinities of BO and CN, which we can compare with existing experimental data. Our predicted electron affinity for BO, 2.79 ± .2 eV, is within the range of experimental estimates[59] which vary from 2.4 eV to 3.1 ± .1 eV. Experimental studies of CN have yielded more precise results. Chupka, et al[60], have reported an electron affinity of 3.82 ± .02 eV, which was obtained from photodissociation measurements on HCN. Our calculated electron affinity, 3.70 ± .2 eV, is in good agreement with this value.

The results of our EOM calculations and Koopmans' theorem estimates for vertical ionization potentials of CN^- and BO^- are shown in Table C2 for selected internuclear separations. The Koopmans' theorem values deviate considerably from EOM results for the ${}^1\Sigma^+ \rightarrow {}^2\Sigma^+$ ionization of CN^-, less so for the ${}^1\Sigma^+ \rightarrow {}^2\Sigma^+$ BO^- ionization, and are actually very close to EOM results for the ${}^1\Sigma^+ \rightarrow {}^2\pi$ ionization of CN^-.

The large difference between Koopmans' theorem and the equations-of-motion result for the ${}^1\Sigma^+ \rightarrow {}^2\Sigma^+$ ionization of CN^- indicates that orbital relaxation and electron correlation effects are important in the process of removing an electron from the 5σ orbital of CN^-. Analogously, relaxation and correlation effects appear to be less important in the ionization of BO^-.

Table C1-Basis Sets (STO's) for CN^- and BO^-

CN^-						BO^-					
σ orbitals			π orbitals			σ orbitals			π orbitals		
center	nl	ζ	center	nl	ζ	center	nl	ζ	center	nl	ζ
C	1s	5.1231	C	2p	1.2566	B	1s	4.2493	B	2p	.9500
C	1s	7.5223	C	2p	2.7304	B	1s	6.5666	B	2p	2.2173
C	2s	.9750	N	2p	1.3380	B	2s	.8250	O	2p	1.5200
C	2s	1.9400	N	2p	3.2493	B	2s	1.6500	O	2p	3.6944
C	2p	1.2566				B	2p	.8500			
C	2p	2.8700				B	2p	2.2173			
N	1s	5.9864				O	1s	6.8377			
N	1s	8.4960				O	1s	9.4663			
N	2s	2.3500				O	2s	2.8200			
N	2s	1.3750				O	2s	1.6754			
N	2p	1.4992				O	2p	1.6586			
N	2p	3.2493				O	2p	3.6944			

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