Theoretical study of stable negative ions of polar molecules: NaH^-, LiH^-, LiF^-, BeO^-

K. D. Jordan

Department of Engineering and Applied Science, Mason Laboratory, Yale University, New Haven, Connecticut 06520

K. M. Griffing, J. Kenney,* E. L. Andersen,* and J. Simons†

Chemistry Department, University of Utah, Salt Lake City, Utah 84112
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In order to investigate the nature of the binding of electrons to polar molecules, we have performed *ab initio* calculations on LiH, LiF, NaH, BeO, and their anions. The anions are predicted to be stable and our calculated vertical electron affinities of the parent molecules are 0.30, 0.46, 0.36, and 1.77 eV for LiH, LiF, NaH, and BeO, respectively. It is demonstrated that electron correlation effects are small in the binding of electrons to these polar molecules since the extra electron occupies a predominantly nonbonding orbital on the electropositive atom.

I. INTRODUCTION

In a preliminary publication[1] we communicated theoretical predictions of stable negative ions of LiH and NaH. The present paper describes the research which led us to the prediction of the existence of these stable anions. We present new results which indicate that the BeO^- and LiF^- anions are stable with respect to dissociation and autodetachment. We also re-examine the HF^- anion, concluding that it is unstable at the equilibrium configuration of HF.

It has been demonstrated by several researchers[2–7] that an electron in the field of a fixed finite dipole greater than 1.625 D possesses an infinity of bound states. Although LiH, NaH, BeO, and LiF all have dipole moments in excess of this value, stable negative ions of these species have not been predicted from *ab initio* calculations prior to our investigations. Stable LiH^-, NaH^-, and BeO^- anions have not been detected experimentally; LiF^- has been detected but a reliable electron affinity is not available.

A stable negative ion of LiCl has been detected by Carlsten, Peterson, and Lineberger,[8] and the Hartree–Fock predictions on $LiCl^-$ of Jordan and Luken[9] are in good agreement with the experimental results. In view of the nonbonding nature of the orbital occupied by the extra electron demonstrated by this theoretical study, inclusion of electron correlation would be expected to result in only a small correction to the description of the binding of an electron to LiCl. This expectation is confirmed by the good agreement between the Hartree–Fock calculations and the experimental results. The success of the Hartree–Fock method in describing the binding of an electron to LiCl suggests the possibility of similar results with other highly polar molecules.

The experimental and theoretical studies on $LiCl^-$ indicated that the simple fixed finite dipole model provides an inadequate description of the binding of an electron to LiCl. One of the motivations of the present paper is to provide a more extensive evaluation of the validity of the dipole model.

In the following sections of the paper we present Hartree–Fock calculations demonstrating the nonbonding nature of the lowest unoccupied molecular orbitals (LUMO) of LiH, LiF, NaH, and BeO. For purposes of comparison we include some of the results of the $LiCl^-$ calculations. Since experimental results presently do not exist for LiH^-, NaH^-, BeO^-, and LiF^-, we employ the equation-of-motion (EOM) method[10–12] (see Appendix) to estimate orbital relaxation and correlation corrections to the predictions obtained from application of Koopmans' theorem (KT).[13] Portions of the potential curves of the anions and the parent neutral species are presented. We then demonstrate that the simple fixed finite dipole model inadequately describes the binding of electrons to highly polar molecules, and discuss some of the causes of the discrepancies between our *ab initio* results and the predictions of the dipole model. We conclude by pointing out the possible significance of the negative ions of highly polar molecules as intermediates in chemical reactions.

II. DIPOLE MODEL

We will find it useful to review the fixed finite dipole model. The Schrödinger equation of an electron moving in the field of two fixed point charges, $+q$ and $-q$, separated by a distance R, is

$$\left[-\nabla^2 - \frac{2q}{r_a} + \frac{2q}{r_b} - \frac{2q^2}{R}\right]\psi = E_T\psi, \tag{1}$$

where r_a and r_b are the distances of the electron from the positive and negative charges, respectively, and distance and charge are in units of bohrs and energy in rydbergs. This equation can be separated in elliptical coordinates: $\lambda = (r_a + r_b)/R$, $\alpha = (r_a - r_b)/R$, ϕ is the azimuthal angle about the dipole axis. The resulting ordinary differential equations are

$$d^2\Phi/d\Phi^2 + m^2\Phi = 0, \tag{2}$$

$$\frac{d}{d\alpha}\left[(1-\alpha^2)\frac{dM}{d\alpha}\right] + \left[p^2\alpha^2 - 2\mu\alpha - A - \frac{m^2}{1-\alpha^2}\right]M = 0, \tag{3}$$

$$\frac{d}{d\lambda}\left[(\lambda^2-1)\frac{dL}{d\lambda}\right] + \left[-p^2\lambda^2 + A - \frac{m^2}{\lambda^2-1}\right]L = 0, \tag{4}$$

and the wavefunction is

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$$\psi = L(\lambda)\, M(\alpha)\, \Phi(\phi)\,. \tag{5}$$

In these equations m and A are separation constants,

$$p^2 = -R^2 E/4\,, \tag{6}$$

and μ is the dipole moment. The total energy E_T and the electronic energy E are related as follows:

$$E = E_T + 2q^2/R\,. \tag{7}$$

The bound states may be labeled by the three integers (n_λ, n_α, m), where n_λ and n_α give the number of nodes in the $L(\lambda)$ and $M(\alpha)$ wavefunctions, respectively. In the limit $R \to \infty$, the energy levels may be expressed in terms of hydrogenic wavefunctions, and the principal quantum number n is related to n_λ, n_α, and m as follows:

$$n = n_\lambda + n_\alpha + m + 1\,. \tag{8}$$

The electron-dipole model described above possesses a critical dipole moment of $\mu_{crit} = 1.625$ D.[3,9] If $\mu < \mu_{crit}$, there are no bound states, while if $\mu > \mu_{crit}$ there is an infinity of bound states; all the states labeled (n, 0, 0), n any interger > 0, are bound for $\mu > \mu_{crit}$. We note that q and R do not separately enter Eqs. (3) and (4) but appear only in terms of their product, the dipole moment. Consequently, p and A, and hence the values of the critical moments, depend only on μ and not on q and R separately.

With this background information in mind, we now turn to discuss the results of our *ab initio* calculations on negative molecular ions and to compare these results with predictions of the above dipole model.

III. CHOICE OF BASIS SETS

The most essential aspect of our investigation of the binding of electrons to polar molecules is the choice of basis sets in which diffuse functions are added to the electropositive atom to permit the "extra" electron to "attach" to the positive end of the polar parent molecule. Most of the calculations in the present paper employ Slater-type orbitals (STO's); the unnormalized STO's are functions of the type $r^{n-1}e^{-\zeta r}$, where n is the principal quantum number and ζ the orbital exponent. In Table I we list the STO basis sets employed in our calculations.

The LiH and NaH basis sets were constructed by adding optimized diffuse s and p_σ orbitals on the more electropositive atom to the dominant orbitals from the appropriate neutral molecules bases of Cade and Huo[14] (CH). In particular, the LiH basis contains ten of the most important CH STO's to which we have added a diffuse $2s$ hydrogen orbital and two sets of lithium $2p_\pi$ functions. In addition we have placed two diffuse $2s$ and two diffuse $2p_\sigma$ orbitals on the lithium nucleus to permit the formation of s–p hybrid orbitals. The exponents of the added functions were optimized at the experimental equilibrium bond length (R_e) of LiH to give maximum binding of LiH^-. The NaH basis was constructed in an analogous fashion from 15 dominant CH orbitals together with a diffuse hydrogen $2s$ function and two diffuse $3s$ and $3p_\sigma$ orbitals centered on sodium. The exponents of the diffuse $3s$ and $3p_\sigma$ sodium orbitals were then optimized to give maximum binding of NaH^-.

TABLE I. STO basis sets for LiH, LiF, NaH, and BeO. LiF: $R_e = 3.015$ a.u.; $E = -7.9866$ a.u.; LiF: $R_e = 2.955$ a.u.; $E = -106.5855$ a.u.; NaH: $R_e = 3.566$ a.u.; $E = -161.9422$ a.u.; BeO: $R_e = 2.51$ a.u.; $E = -89.3432$ a.u.

LiH		LiF		NaH		BeO	
$1s_\sigma$Li	(4.6990)	$1s_\sigma$Li	(4.6925)	$1s_\sigma$Na	(11.1543)	$1s_\sigma$Be	(6.4072)
$1s'_\sigma$Li	(2.5212)	$1s'_\sigma$Li	(2.4739)	$2s_\sigma$Na	(2.0006)	$1s'_\sigma$Be	(3.5297)
*$2s_\sigma$Li	(1.2000)	$2s_\sigma$Li	(1.6350)	$2p_\sigma$Na	(4.1786)	$2s_\sigma$Be	(1.1956)
*$2s'_\sigma$Li	(0.7972)	*$2s'_\sigma$Li	(1.0287)	$2p'_\sigma$Na	(2.2798)	*$2s'_\sigma$Be	(0.8557)
*$2s''_\sigma$Li	(0.6000)	*$2s''_\sigma$Li	(0.5352)	$3s_\sigma$Na	(6.2601)	*$2s''_\sigma$Be	(0.4677)
*$2s'''_\sigma$Li	(0.3000)	*$2s'''_\sigma$Li	(0.3223)	$3s'_\sigma$Na	(0.9106)	$2p_\sigma$Be	(2.0717)
$2p_\sigma$Li	(2.7500)	*$2p_\sigma$Li	(0.4066)	$3s''_\sigma$Na	(0.4000)	*$2p'_\sigma$Be	(0.8557)
$2p'_\sigma$Li	(1.2000)	$2p_\pi$Li	(0.4066)	*$3s'''_\sigma$Na	(0.2000)	*$2p''_\sigma$ Be	(0.4677)
$2p''_\sigma$Li	(0.7369)	$1s_\sigma$F	(14.1095)	$3p_\sigma$Na	(1.2631)	$2p_\pi$Be	(1.0846)
$2p'''_\sigma$ Li	(0.6000)	$1s'_\sigma$F	(7.9437)	$3p'_\sigma$Na	(0.7108)	$1s_\sigma$O	(7.6092)
*$2p''''_\sigma$ Li	(0.3000)	$2s_\sigma$F	(3.2563)	*$3p''_\sigma$ Na	(0.4000)	$2s_\sigma$O	(3.1394)
$2p_\pi$Li	(0.7369)	$2s'_\sigma$F	(1.9346)	$3p'''_\sigma$Na	(0.1500)	$2s'_\sigma$O	(1.8792)
$2p'_\pi$Li	(0.3500)	$2p_\sigma$F	(4.2784)	$2p_\pi$Na	(4.1742)	$2p_\sigma$O	(3.4198)
$1s_\sigma$H	(1.5657)	$2p'_\sigma$F	(2.3732)	$2p'_\pi$Na	(2.2828)	$2p'_\sigma$O	(1.7405)
$1s'_\sigma$H	(0.8877)	$2p''_\sigma$F	(1.4070)	$3p_\pi$Na	(0.9636)	$2p''_\sigma$ O	(1.0626)
*$2s_\sigma$H	(0.4000)	$2p_\pi$F	(2.3291)	$1s_\sigma$H	(0.7808)	$2p_\pi$O	(3.4198)
$2p_\sigma$H	(1.3765)	$2p'_\pi$F	(1.3584)	*$2s_\sigma$H	(0.4000)	$2p'_\pi$O	(1.7405)

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TABLE II. Equation-of-motion electron affinities and Koopmans' theorem estimates (eV).

	LiH(5.88)[a]	LiF(6.33)	LiCl(7.13)	NaH(6.98)	BeO(7.41)
EOM[b]	0.2986	0.4645	[0.54, 0.61]	0.3618	1.7692
$-\epsilon_{LUMO}$[b]	0.1997	0.4252	0.48	0.2897	1.4144
Orbital relaxation and correlation corrections[c]	0.0989	0.0393	0.13	0.0721	0.3548

[a]The quantities in parenthesis are the dipole moments in debye. The dipole moment of BeO has not been experimentally determined. The value listed is that calculated by Yoshimine (Ref. 19). For the other molecules the experimental dipole moments are listed. These values are taken from the tables of R. D. Nelson, D. R. Lide, A. A. Maryott, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase* (U. S. Department of Commerce, Natl. Bur. Stand., Washington, D. C., 1967).

[b]The LiCl LUMO orbital energy is from Jordan and Luken (Ref. 9). An EOM calculation has not been performed on LiCl. The value of 0.54 eV was obtained from a ΔE_{HF} [$\Delta E_{HF} = E_{HF}(\text{LiCl}) - E_{HF}(\text{LiCl}^-)$] calculation, while the value of 0.61 eV is the experimental value of Carlsten, Peterson, and Lineberger (Ref. 8).

[c]For LiH, LiF, NaH, and BeO the orbital relaxation and correlation corrections are obtained by subtracting the Koopmans' theorem estimate of the electron affinity from the EOM value. For LiCl the experimental electron affinity is used in place of the EOM value.

The basis for LiF was formed from $1s$, $1s'$, $2s$, $2s'$, $2s''$, $2s'''$, $2p_\sigma$, $2p_\pi$ STO's on the lithium atom together with the most important fluorine orbitals from the CH basis for HF. Our resulting LiF basis[15] consists of seven σ and four π orbitals on the fluorine (taken from the CH HF bases), and seven σ and two π orbitals on Li. The diffuse $2s$ and $2p_\sigma$ orbitals on the Li were then optimized to give maximum binding of LiF^-. The BeO basis consists of two $1s$, three $2s$, three $2p_\sigma$, and two $2p_\pi$ orbitals centered on the beryllium and one $1s$, two $2s$, three $2p_\sigma$, and two $2p_\pi$ orbitals on the oxygen. The exponents of the most diffuse $2s$ and $2p_\sigma$ orbitals on the beryllium were varied in order to maximize the binding energy of the anion.

For the LiH, BeO, NaH, and LiF molecules, optimization of the exponents of the diffuse orbitals leads to a *negative* orbital energy for the lowest unoccupied molecular orbital (LUMO). For each of these species the LUMO has σ symmetry. Thus even with the results obtained from the application of Koopmans' theorem, the $^2\Sigma$ states of the ions are stable at the equilibrium geometry of the parent neutral.

After optimization of the exponents at the experimental R_e, Hartree–Fock and EOM calculations were carried out for several other internuclear separations. The Hartree–Fock calculations with the STO basis sets employed a modified version of the Harris DIATOM program. The electron affinities and potential energy curves are reported in the following sections of the paper.

IV. RESULTS

A. Electron affinities

In Table II the KT and EOM electron affinities are presented for the equilibrium bond length of the parent neutral. Perhaps the most striking observation to be drawn from these data is that orbital relaxation and correlation corrections to the EA's are small, in marked contrast to the situation encountered with covalent molecules such as OH, O_2, and NO, for which orbital relaxation and correlation corrections to the electron affinities are typically 1 eV or more. The small correlation and relaxation energy changes which occur with the formation of the ions from the neutrals are in accord with a description in which the "extra" electron resides in a region of space which is essentially unoccupied by other electrons. Apparently, the orbital picture provides a good first approximation to the binding of electrons to highly polar molecules. The nonbonding nature of the LUMO's is illustrated in Figs. 1, 3–5, and in Table III we list the coefficients of the dominant atomic orbitals for each of the LUMO's.

In Fig. 1 the charge distribution of our LiH LUMO is plotted. The diffuse lithium $2s$ and $2p$ orbitals have "hybridized" such that most of the charge density of the LiH LUMO is behind the lithium atom, or more correctly the lithium positive ion since, near R_e, the molecule is predominantly Li^+H^-. This nonbonding nature of the LUMO explains the small orbital relaxation and correlation corrections to the Koopmans' theorem approximation. There are also maxima in the charge distribution near the hydrogen and lithium atoms.

Figure 2 displays the variation in the KT and EOM electron affinities of LiH (for a 17 STO bases identical to that of Table I except for the omission of the Li $2p_\pi$ orbitals) as the orbital exponents of the most diffuse Li $2s$ and $2p$ STO's ($2s'''$ and $2p_\sigma''''$) are simultaneously varied from 0.25 to 0.35. The minima of the KT and EOM electron affinities occur for $\zeta \simeq 0.29$ and 0.31, respectively. For ζ varying between 0.25 and 0.35 the change in the EA's is less than 0.007 eV. From this

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TABLE III. Coefficients of the lowest unoccupied molecular orbitals of LiH, LiF, NaH, and BeO at their equilibrium separations[a].

LiH			LiF			NaH			BeO		
STO	ζ	$C_{3\sigma}$	STO	ζ	$C_{4\sigma}$	STO	ζ	$C_{5\sigma}$	STO	ζ	$C_{5\sigma}$
$2s$ Li	1.200	−0.226	$1s'$ Li	2.474	−0.058	$3s'$ Na	0.911	0.137	$1s'$ Be	3.530	−0.094
$2s'$ Li	0.797	0.851	$2s$ Li	1.635	−0.075	$3s''$ Na	0.400	0.151	$2s$ Be	1.196	0.121
$2s''$ Li	0.600	−0.881	$2s'$ Li	1.029	0.193	$3s'''$ Na	0.200	0.208	$2s'$ Be	0.856	0.392
$2s'''$ Li	0.300	0.552	$2s''$ Li	0.535	0.128	$3p'_\sigma$ Na	0.711	−0.186	$2s''$ Be	0.468	0.422
$2p''_\sigma$ Li	0.737	−0.168	$2s'''$ Li	0.322	0.676	$3p''_\sigma$ Na	0.400	−0.591	$2p'_\sigma$ Be	0.856	−0.273
$2p'''_\sigma$ Li	0.600	0.103	$2p_\sigma$ Li	0.407	−0.499	$3p'''_\sigma$ Na	0.150	−0.126	$2p''_\sigma$ Be	0.468	−0.287
$2p''''_\sigma$ Li	0.300	−0.795				$1s$ H	0.781	−0.123	$2p_\sigma$ O	3.420	0.060
$2s$ H	0.400	0.514				$2s$ H	0.400	0.449	$2p''_\sigma$ O	1.063	0.101

[a]Only coefficients of magnitude greater than 0.05 are listed.

we conclude that it is not essential to determine precisely the value of ζ which maximizes the EA. We have also performed calculations in which the exponents of the diffuse $2s$ and $2p$ orbitals were varied separately; we did not find a significant increase in the EA as a result of this increased flexibility. Omission of the diffuse $2s'''$ and $2p''''_\sigma$ Li orbitals from the basis resulted in a positive value of ϵ(LUMO), the energy of the lowest unoccupied orbital, but still gave a bound LiH^- ion (EA = 0.11 eV) when orbital relaxation and correlation effects were included through the EOM procedure. If the $2s''$ and $2p'''_\sigma$ Li STO's ($\zeta = 0.6$) were also deleted both the KT and EOM values of the electron affinity were found to be negative. This underscores the necessity of inclusion of diffuse functions for adequate representation of the LUMO and the corresponding negative ion.

Our LiH calculations employed 19 STO basis functions. It is not really necessary to use such an extensive basis to describe the binding of the extra electron in the anions of polar molecules. It is, however, essential to include the proper diffuse functions to allow the hybridization of the LUMO. To illustrate this we have also performed calculations on LiH using a simple Gaussian basis (the Gaussian basis is given in Table IV). On the H atom we have employed the 4–31 G $1s$, $1s'$ basis of Pople and co-workers.[16,17] On the Li atom we have employed a $1s$, $2s$, $2s'$, $2p$, $2p'$ basis constructed from the $1s$, $2s$, $2p$ portion of the 6–31 G basis[16,17] for Li, replacing the $2s'$, $2p'$ functions of the 6–31 G basis by $2s'$ and $2p'$ STO's (with exponents of 0.30) which are least-squares represented by three Gaussians. Although the Hartree–Fock ground state energy for LiH (at R_e) obtained with this basis was 0.2 eV higher than that with our 19 STO basis, the binding energy of the LUMO was only 0.003 eV less than with the STO basis. Except for the cusp behavior at the nuclei, the charge distribution of the LUMO obtained from the Gaussian basis is in excellent agreement with

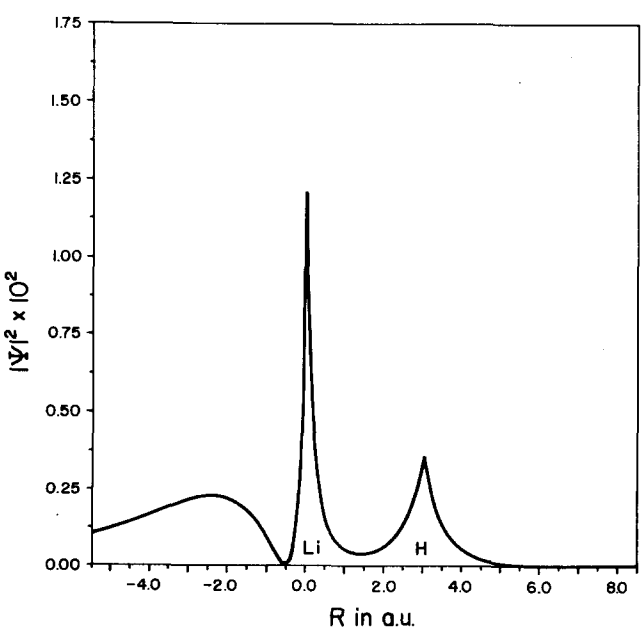

FIG. 1. Charge distribution of the LUMO (σ_3) of LiH at internuclear separation of 3.015 a.u.

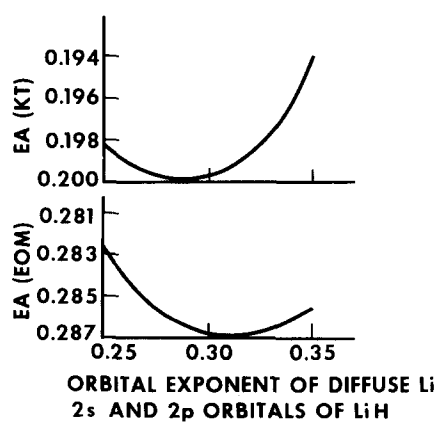

FIG. 2. Variation of the LiH electron affinity with the diffuse lithium $2s$ and $2p$ orbital exponents. The upper curve shows the variation in the value of $-\epsilon$(LUMO) as the exponent of the most diffuse $2s$ and $2p$ orbitals are simultaneously varied from 0.25–0.35. The bottom curve plots the change in the EOM value of the electron affinity over the same range of orbital exponents.

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TABLE IV. Contracted Gaussian basis set for LiH calculation.

Orbital type	Exponent	s coefficients	p coefficients
Li(1s)	642.41895	0.00214	...
	96.79849	0.01621	...
	22.09109	0.07732	...
	6.20107	0.24579	...
	1.93512	0.47019	...
	0.63674	0.34547	...
Li(2sp)[a]	2.19146	−0.03509	0.00894
	0.59613	−0.19123	0.14101
	0.07455	1.08399	0.94535
Li(2$s'p'$)	0.08948	−0.09997	0.15559
	0.02079	0.39951	0.60768
	0.00676	0.70012	0.39196
H(1s)	18.73110	0.03349	...
	2.82539	0.23473	...
	0.64012	0.81376	...
H(1s')	0.16128	1.00000	...

[a]The (nsp) designation refers to a ns_σ, and np_π set of orbitals which share a common set of exponents.

that given in Fig. 1.

In Fig. 3 the charge distribution of the LiF LUMO is plotted. The similarity of this charge distribution to that of the LiH LUMO should be noted. As in the LiH case, the orbital is nonbonding with most of the charge located behind the lithium. The LiF LUMO has a node near the fluorine nucleus to ensure orthogonality to the $n=1$ and $n=2$ occupied fluorine orbitals. The calculated electron affinity (EA) of LiF is greater than that of LiH (0.47 vs 0.30 eV in the EOM theory), not a surprising result since the positive charge on the lithium is greater in LiF than in LiH.[18] This difference is demonstrated in Figs. 1 and 3; the LUMO of LiF has

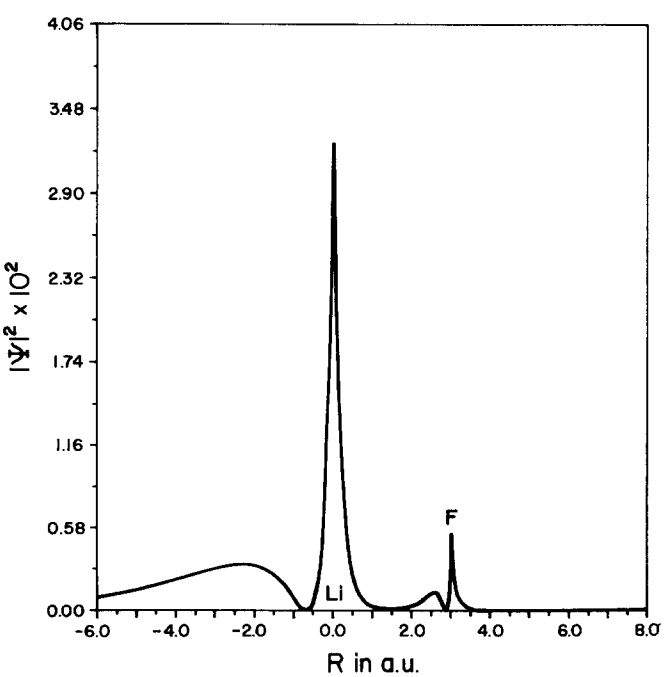

FIG. 3. Charge distribution of the LUMO (σ_4) of LiF at internuclear separation of 2.955 a.u.

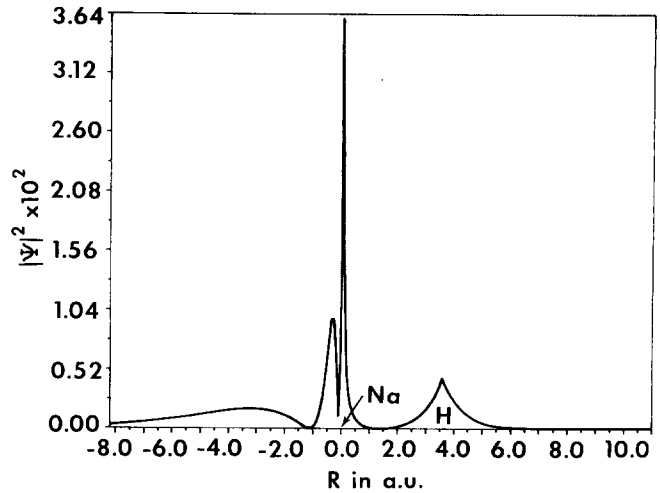

FIG. 4. Charge distribution of the LUMO (σ_5) of NaH at internuclear separation of 3.566 a.u.

more of its charge density located near the lithium than does the LUMO of LiH.

The charge distribution of the LiCl LUMO is similar to those of LiF and LiH; the charge density of LiCl LUMO is slightly more localized near the lithium than is the case for LiH and LiF. The increased localization of the LiCl LUMO is consistent with the fact that the LiCl electron affinity is greater than that of LiF or LiH. For these three molecules the electron affinity is found to increase with increasing dipole moment. These results indicate that other ionic molecules possessing large dipole moments such as LiOH and LiCN, with lithium as the electropositive atom, may also form stable negative ions.

As indicated in Table III, the nonbonding LUMO of NaH is essentially a $3s$–$3p$ hybrid on the sodium atom. Due to the nodal structure of these higher quantum number orbitals, the LUMO charge density now has, in addition to a peak on the sodium, *two* peaks "behind" the sodium, as may be seen in Fig. 4. Because the $2s$ and $2p$ orbitals are already occupied in the core, the LUMO cannot be a $2s$–$2p$ hybrid. We have also performed calculations in which a diffuse $3d_\sigma$ function was added to the sodium atom. The $3d_\sigma$ function did not significantly mix with the $3s$–$3p$ hybrid, and the orbital energy and EOM electron affinity were unchanged to 0.01 eV.

In BeO, the LUMO resulting from our calculation is found to be mainly a $2s$–$2p$ hybrid (see Fig. 5). The binding energy of the BeO LUMO is much greater than that of any of the other molecules considered in this paper. The experimental value of the dipole moment for the $^1\Sigma^+$ ground state of BeO is not known, but *ab initio* calculations[19] give a value of 7.41 D. Although the dipole moment of BeO is nearly the same as the dipole moment of LiCl, the electron affinity of BeO is about 2.9 times greater than that of LiCl. This can be understood from consideration of the charge distributions[20] in the two neutral molecules: Li^+Cl^- and $Be^{1.5+}O^{1.5-}$ (near their respective equilibrium positions). Assuming the validity of the dipole model, and neglect-

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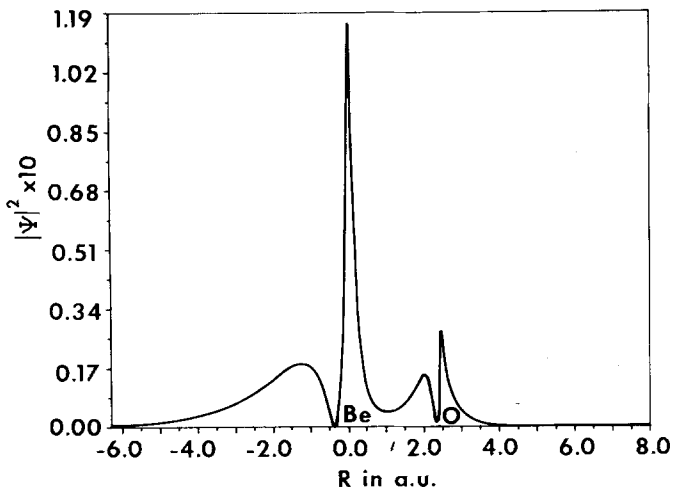

FIG. 5. Charge distribution of the LUMO (σ_5) of BeO at internuclear separation of 2.516 a.u.

ing the small difference between the BeO and LiCl dipole moments, the ratio of the EA's of BeO and LiCl should be proportional to the ratio of the square of their equilibrium nuclear distances[9]:

$$\frac{\mathrm{EA(BeO)}}{\mathrm{EA(LiCl)}} = \left[\frac{R_e(\mathrm{LiCl})}{R_e(\mathrm{BeO})}\right]^2 . \tag{9}$$

Upon substitution of the equilibrium distance of LiCl and BeO, we find that this approximation predicts the electron affinity of BeO to be 2.5 times greater than that of LiCl, which is in agreement with the ratio of 2.9 quoted above.

While BeO, LiH, LiF, LiCl, and NaH have dipole moments well in excess of the critical moment of 1.625 D, the dipole moment of HF (1.82 D) is only slightly greater than the critical value. For a dipole moment of this magnitude, the ground state of the ion predicted by the dipole model is bound[2,7] by only $\sim 10^{-5}$ eV. This corresponds to a very diffuse orbital. In our preliminary investigation we reported HF^- to be bound by 0.36 eV. However, it now seems that this result is not correct and that HF^- is actually unstable relative to electron detachment. Apparently, the quadrature procedure used in the integral evaluations in the Hartree–Fock program was inadequate for the diffuse hydrogen functions. In order to minimize such numerical difficulties, we have repeated calculations on HF using a Gaussian basis so that all integrals could be evaluated analytically.

In these HF^- check calculations, the fluorine orbitals were obtained from the 6–31 G $1s$, $2s$, $2s'$, $2p$, $2p'$ Gaussian basis of Pople and co-workers,[16] while for hydrogen we supplemented the 4–31 G $1s$, $1s'$ Guassian basis[16] with diffuse $1s$, $2s$, and $2p$ STO's (least-squares fit to Gaussians). Extensive variation of these exponents did *not* give rise to a bound LUMO at the 1.733 a.u. equilibrium internuclear separation of HF. The energy of the LUMO approached zero as the orbitals were made more diffuse. This calculation is in agreement with the results of earlier investigations,[21] which also indicated that at $R = 1.73$ a.u. HF^- has no bound state with respect to HF plus a free electron. We also find, in agreement with Weiss and Krauss,[21] that the $^2\Sigma$ HF^- potential curve intersects the $^1\Sigma$ HF potential curve near an internuclear separation of 2.4 a.u.

We conclude this section with a few comments on the possibility of bound excited negative ion states. As was mentioned in the discussion of the dipole model, for dipole moments greater than 1.625 D, this model predicts an infinity of bound states. Thus it is appropriate to determine whether the *ab initio* calculations also predict more than one bound negative ion state for the molecules being considered in this paper.

The second unoccupied σ orbital of LiCl was found to have a negative energy (~ -0.007 eV) when very diffuse $3s$ and $3p_\sigma$ functions were placed on the lithium. A similar result is observed for LiF, and probably would be observed for NaH, BeO, and LiH if sufficiently diffuse functions of the appropriate symmetry were included in the basis sets. However, one should not attach much physical significance to such weakly bound states, since they would probably become unbound if corrections to the Born–Oppenheimer approximation were included.[6] It is possible that molecules with substantially larger dipole moments such as CsCl ($\mu = 10.4$ D) could, near the equilibrium separation of the parent molecule, have two stable negative ion states. Certainly if the dipole moment becomes large enough, the first excited anion state will remain stable even when corrections to the Born–Oppenheimer approximation are included. At present, none of our calculations provide convincing evidence that such excited anions exist for any of the systems we have studied.

B. Potential curves

In Tables V–VIII we present our Hartree–Fock ground state energies and the EOM and Koopmans' theorem estimates of the electron affinity as a function of internuclear separation. The potential curve studies employ the orbital exponents derived at the equilibrium distances. The basis sets are sufficiently flexible, so that it is not necessary to repeat the orbital exponent variation at each internuclear separation.

Figures 6–9 display the ground state potential energy curves of LiH, LiF, NaH, BeO, and their anions. The potential energy curves of the neutral parent molecules are constructed from experimental data via the Padé approximant procedure[22]

TABLE V. EOM and Koopman's theorem estimates (eV) for the electron affinity of LiH vs internuclear separation.

R(a.u.)	E_{HF}(a.u.)	EA(EOM)	EA(KT)	Orbital relaxation and correlation corrections
2.000	−7.91271	0.1028	0.0185	0.0844
2.250	−7.95158	0.1491	0.0637	0.0854
2.750	−7.98344	0.2441	0.1546	0.0895
3.015	−7.98662	0.2985	0.1997	0.0988
3.500	−7.98078	0.4193	0.2925	0.1268
4.000	−7.96734	0.5703	0.4117	0.1586
4.500	−7.95145	0.7436	0.5502	0.1935

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TABLE VI. EOM and Koopman's theorem estimates (eV) for the electron affinity of LiF vs internuclear separation.

R(a.u.)	E_{HF}(a.u.)	EA(EOM)	EA(KT)	Orbital relaxation and correlation corrections
2.50	−106.55525	0.3428	0.3020	0.0408
2.855	−106.58411	0.4378	0.3980	0.0398
2.905	−106.58508	0.4512	0.4115	0.0397
2.955	−106.58542	0.4645	0.4252	0.0393
2.985	−106.58547	0.4727	0.4335	0.0392
2.005	−106.58538	0.4781	0.4390	0.0391
3.005	−106.58479	0.4920	0.4532	0.0388
3.105	−106.58422	0.5064	0.4677	0.0387
3.50	−106.57066	0.6293	0.5928	0.0365
4.00	−106.54265	0.8077	0.7722	0.0355

$$U_{PA}(X) = a_0X^2/[1 - a_1X + (a_1^2 - a_2)X^2], \tag{10}$$

where $X = (R - R_e)/R_e$ and a_0, a_1, a_2 are determined from the spectroscopic constants[23] ω_e, $\omega_e\chi_e$, B_e, and α_e as follows:

$$a_0 = \omega_e^2/4B_e, \tag{11}$$

$$a_1 = -\omega_e\alpha_e/6B_e^2 - 1, \tag{12}$$

$$a_2 = \tfrac{5}{4}a_1^2 - \tfrac{2}{3}(\omega_e\chi_e/B_e). \tag{13}$$

The Padé approximant given by Eq. (10) provides a particularly good representation of the potential curves of ionic molecules near their equilibrium configurations. For example, for the range of R considered in Fig. 6 the potential curve for LiH, given by Eq. (10), is essentially indistinguishable from the RKR curve and is very close to the potential curve of Docken and Hinze[24] obtained from a configuration interaction calculation. In Table IX we list the spectroscopic constants ω_e, $\omega_e\chi_e$, β_e, α_e and R_e for the molecules being considered in this paper.

For each molecule two approximations to the $^2\Sigma$ negative ion potential curves are obtained by subtracting, at various internuclear separations, the EOM and Koopmans' theorem estimates of the electron affinity from the LiH potential curve.

From Fig. 6, which presents the results for LiH and LiH$^-$, we see that there is a small increase in the equilibrium internuclear separation upon going from the parent molecule to the anion [R_e(LiH) = 3.015 a.u., R_e(LiH$^-$) = 3.20 a.u.] and that there is a corresponding decrease in the value of ω_e upon ion formation [ω_e(LiH) = 1406 cm^{-1}, ω_e(LiH$^-$) ≃ 1250 cm^{-1}]. The relatively

TABLE VII. EOM and Koopman's theorem estimates (eV) for the electron affinity of NaH vs internuclear separation.

R(a.u.)	E_{HF}(a.u.)	EA(EOM)	EA(KT)	Orbital relaxation and correlation corrections
3.000	−161.92395	0.2750	0.2378	0.0372
3.250	−161.93409	0.2962	0.2371	0.0591
3.566	−161.94217	0.3619	0.2897	0.0722
3.750	−161.94091	0.4018	0.3239	0.0779
4.000	−161.93346	0.4626	0.3755	0.0871
4.250	−161.93082	0.5252	0.4299	0.0927

TABLE VIII. EOM and Koopman's theorem estimates (eV) for the electron affinity of BeO vs internuclear separation.

R(a.u.)	E_{HF}(a.u.)	EA(EOM)	EA(KT)	Orbital relaxation and correlation corrections
2.250	−89.334593	1.6204	1.2418	0.3786
2.300	−89.341195	1.6505	1.2736	0.3769
2.350	−89.344943	1.6800	1.3059	0.3741
2.400	−89.346513	1.7084	1.3385	0.3700
2.425	−89.346539	1.7221	1.3550	0.3671
2.450	−89.346123	1.7357	1.3714	0.3643
2.515	−89.343186	1.7692	1.4144	0.3548
2.540	−89.341428	1.7814	1.4308	0.3506
2.600	−89.335922	1.8088	1.4699	0.3389
2.800	−89.328486	1.8215	1.4907	0.3208

small changes in ω_e and R_e upon formation of the ion are another manifestation of the nonbonding nature of the charge density of the extra electron. As may be seen from Figs. 7–9, the situation is similar for LiF$^-$, NaH$^-$, and BeO$^-$. In Table IX we have also summarized the calculated values of R_e and ω_e for the anions.

C. Discussion

In our preliminary communication we suggested that the EOM method probably underestimates the stability of the anions by 0.1–0.2 eV. At the time of publication of the communication there was no experimental data which could be used to evaluate the above error estimate. The recent measurement[8] together with the theoretical calculation[9] of the electron affinity of LiCl allow us to refine our error estimate. The experimental electron affinity of LiCl is 0.61 ± 0.02 eV, while that obtained from the difference between the anion and neutral Hartree–Fock energies is 0.54 eV. The 0.07 (eV) error in the Hartree–Fock determination of the LiCl electron affinity leads us to estimate that the EOM electron affinities presented in this paper are probably correct to 0.05–0.1 eV. Our confidence in this small error estimate arises from the fact that the EOM method allows for both orbital relaxation and correla-

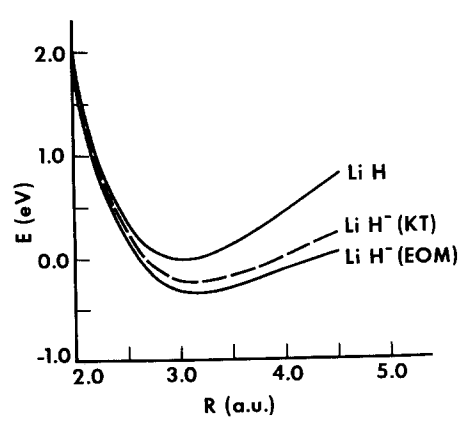

FIG. 6. Potential curves for LiH and LiH$^-$. The LiH potential curve is obtained from a Padé approximant fit to the experimental data. The negative ion curves labeled LiH$^-$ (KT) and LiH$^-$ (EOM) are obtained by subracting respectively the Koopmans' theorem and EOM estimates of the electron affinity from the LiH potential curve.

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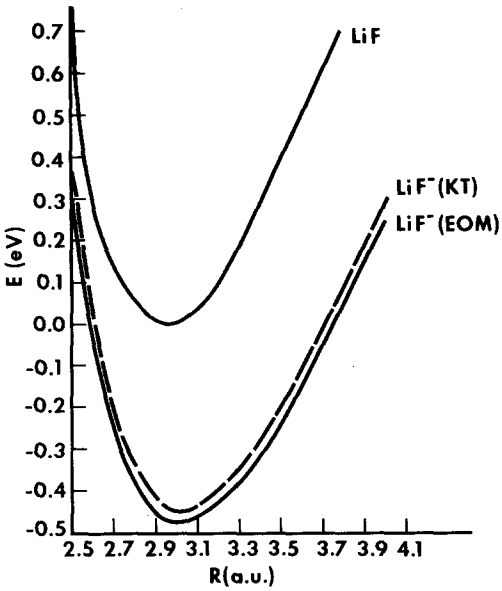

FIG. 7. Potential curves for LiF and LiF^-. The LiF potential curve is obtained from a Padé approximant fit to the experimental data. The negative ion curves labeled LiF^- (KT) and LiF^- (EOM) are obtained by subtracting respectively the Koopmans' theorem and EOM estimates of the electron affinity from the LiF potential curve.

tion corrections, while the Hartree–Fock calculations of the LiCl electron affinity neglected correlation corrections.

It is appropriate at this point to compare our calculated electron affinities with those of the fixed finite dipole model.[2–7,9] In Fig. 10 we have plotted the binding energy of the first three states of an electron in the field of a fixed dipole moment as a function of the dipole moment. Here we have specifically considered the case of a dipole arising from two charges $+q$ and $-q$, where $q=1$. For LiH, LiF, LiCl, and NaH, q is close to 1 so the choice of $q=1$ introduces only a small error. As was pointed out in Ref. 9, one should

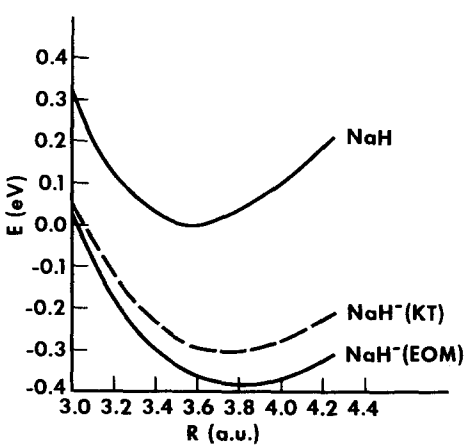

FIG. 8. Potential curves for NaH and NaH^-. The NaH potential curve is obtained from a Padé approximant fit to the experimental data. The negative ion curves labeled NaH^- (KT) and NaH^- (EOM) are obtained by subtracting respectively the Koopmans' theorem and EOM estimates of the electron affinity from the NaH potential curve.

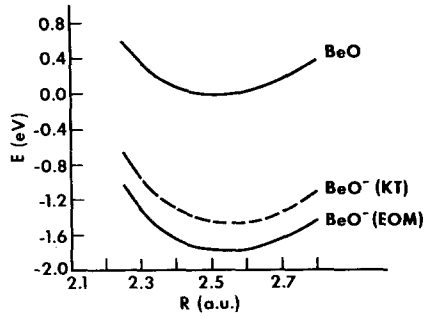

FIG. 9. Potential curves for BeO and BeO^-. The BeO potential curve is obtained from a Padé approximant fit to the experimental data. The negative ion curves labeled BeO^- (KT) and BeO^- (EOM) are obtained by subtracting respectively the Koopmans' theorem and EOM estimates of the electron affinity from the BeO potential curve.

not attempt to correlate the ground state negative ions of these molecules with the (0, 0, 0) ground state of the dipole model, since this state of the dipole model does not have the correct nodal behavior. There is, however, a qualitative correlation between the ground state negative ions where lithium is the electropositive species and the first excited (1, 0, 0) state of the dipole model. Similarly, for species where sodium is the electropositive species there is a qualitative correlation of the negative ions with the second excited state (2, 0, 0) of the dipole model. This correlation is apparent from Fig. 10. These correlations would become much more quantitative if core penetration effects were incorporated in the dipole model. For example, near R_e LiCl is well described as Li^+Cl^-, where the Li^+ has a $(1s)^2$ core. In the negative ion the nonbonding LUMO has a node ~ 0.8 a.u. behind the lithium, while the dipole model, for a dipole moment of 7.2 D, locates the node 2.7 a.u. behind the positive center.[9]

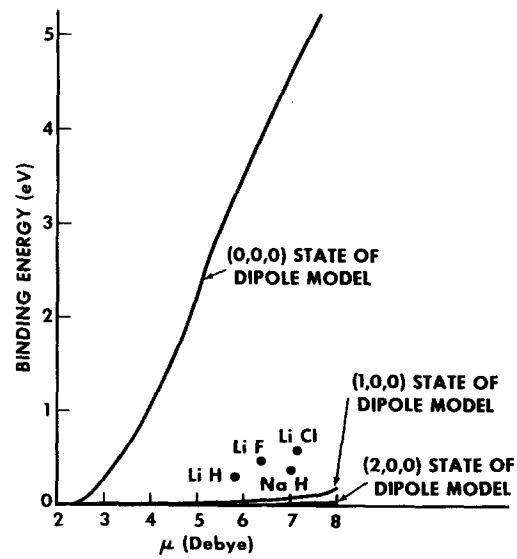

FIG. 10. Binding energy of an electron vs dipole moment for the (0, 0, 0), (1, 0, 0), and (2, 0, 0) states of the dipole model. For dipole moment $\mu < 1.625$ D, there are no bound states in the dipole model. The (0, 0, 0), (1, 0, 0), and (2, 0, 0) states of dipole model coalesce at 1.625 D. The EOM electron affinities of LiH, LiF, LiCl, and NaH are also indicated in the figure.

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TABLE IX. Experimental spectroscopic constants for the neutral molecules, and calculated spectroscopic constants for the anions.[a]

Parameter	Units	LiH	LiF	LiCl	NaH	BeO
R_e	a.u.	3.015	2.956	3.814	3.566	2.516
ω_e	cm^{-1}	1405.6	910.3	662	1172.2	1487.3
$\omega_e\chi_e$	cm^{-1}	23.20	7.929	4.501	19.72	11.83
B_e	cm^{-1}	7.5131	1.3454	0.625	4.9001	1.6510
α_e	cm^{-1}	0.2132	0.0201	0.0079	0.1353	0.0190
		LiH^-	LiF^-	$LiCl^-$	NaH^-	BeO^-
R_e	a.u.	3.20	3.00	4.01	3.80	2.54
ΔR_e	Å	0.08	0.02	0.10	0.12	0.01
ω_e[b]	cm^{-1}	1250	840	525	960	1360
% change in ω_e	%	11	8	21	18	8
D_e	eV	1.94	3.02	1.84	1.65	4.86

[a]The values of $\omega_e\chi_e$ for LiCl, and the values of α_e for LiF and LiCl are from P. Brumer and M. Karplus, J. Chem. Phys. 58, 3903 (1973). The rest of the data for the neutral species are from Ref. 23.

[b]The ω_e are obtained by fitting points on the negative ion curve obtained by substracting the EOM electron affinity from the potential curve of the neutral parent molecule. The uncertainty in ω_e, due to our fitting procedure, is probably $\sim \pm 50$ cm^{-1}.

The *ab initio* calculations allow lithium 2*s* and 2*p* electrons to penetrate the $(1s)^2$ core and "feel" the +3 nuclear charge, while this important effect is not accounted for in the dipole model. This is a major source of the discrepancy between the dipole model and the more realistic *ab initio* calculations.

From Eq. (8) we see that the ground state negative ion of BeO should also correlate with the (1, 0, 0) state of the dipole model. The electron affinity of BeO has not been included in Fig. 10 since BeO is not a monovalent species. To compare the electron affinity of BeO with the dipole model predictions, we would have to repeat the calculations for $q \simeq 1.5$.

LiH, LiF, LiCl, and NaH all have dipole moments between 5.8 and 7.2 D and all have computed (vertical) electron affinities between 0.3 and 0.6 eV. It would be of interest to determine the electron affinities of molecules with dipole moments in the 3–6 D range. For dipole moments $\lesssim 6$ D the electron affinities should be $\lesssim 0.3$ eV. These cases may pose special difficulties. The considerations of this paper have assumed the validity of the Born–Oppenheimer approximation. As stressed by Garrett,[6] one should allow for the fact that the dipole is nonstationary. Anions which are weakly bound under the assumption of the validity of the Born–Oppenheimer approximation may turn out to be unbound when corrections to the Born–Oppenheimer approximation are included.

We now turn to a discussion of the differences in frequencies and bond lengths between the anions and their parent neutrals. These differences cannot be understood from the magnitude of the dipole moments of the parents. There is, however, a correlation between the dissociation energy of the anion and the frequency and bond length changes. The smaller the dissociation energy of the anion, the greater the frequency decrease and the greater the bond length increase. This correspondence is depicted in Fig. 11, where we have plotted ΔR_e vs D_e. ΔR_e is the difference between the anion and the parent equilibrium separations, and D_e is the dissociation energy of the anion,

$$MX^- \rightarrow M + X^-,$$

where M is the electropositive species and X is a halogen or hydrogen atom. To actually obtain the dissociation energy, we locate the $M+X^-$ asymptote relative

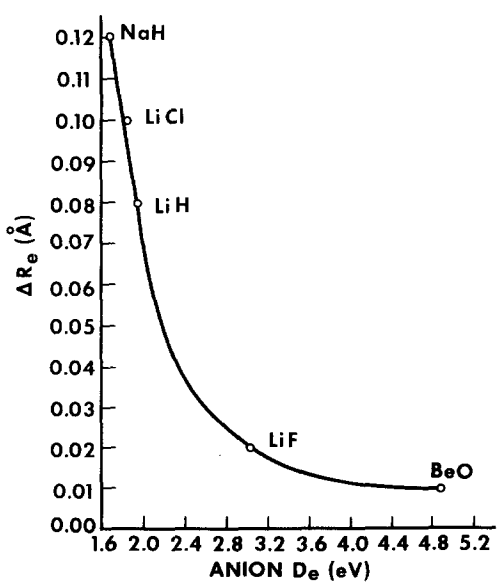

FIG. 11. Change of equilibrium separation (ΔR_e) vs the dissociation energy (D_e) of the anion. Our results for NaH, LiCl, LiH, LiF, and BeO are indicated by circles. The solid line is included merely to emphasize the trend.

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to the minimum of the MX potential curve[9] and add the electron affinity (at the equilibrium separation of the neutral species) to this value.

From consideration of the dissociation energies we can, for example, understand why ΔR_e is greater for $LiCl^-$ than for LiF^-. The dissociation energy of LiF^- is 3.02 eV while that for $LiCl^-$ is 1.84 eV. Consequently, near their respective equilibrium separations, the $LiCl^-$ potential curve changes more abruptly from that of LiCl than the change in the LiF^- curve from that of LiF. In other words near R_e, the LiF^- potential curve "tracks" the LiF curve more closely than the $LiCl^-$ potential curve "tracks" the LiCl curve.

V. CONCLUSIONS AND FUTURE WORK

In this paper we have presented the results of calculations on the ground state anions of LiH, LiF, NaH, and BeO. In each case the extra electron is found to occupy a predominantly nonbonding orbital. This results in small orbital relaxation and correlation corrections, as well as a small increase of the internuclear separation and a small (10%–20%) decrease in ω_e upon formation of the ion. The electron affinities predicted by the dipole model are found to be in poor agreement with those of our *ab initio* calculations. We attribute this disagreement to the neglect of core penetration in the dipole model.

There are several possible extensions and applications of the work presented in this paper. We intend to report on negative ions of various polar polyatomic molecules in future publications. We are also investigating whether the stable negative ions of ionic molecules may influence the mechanisms of certain chemical reactions. In collisions between an ionic molecule and an atom or molecule with a low ionization potential, an electron jump mechanism may play a role. For example, an excited cesium atom could lose an electron to LiCl. Further, this would tend to favor a "backside" attack proceeding through a $Cs^+(LiCl)^-$ intermediate, as opposed to LiClCs. The possibility of formation of LiX^- from the reaction of Li^- with X_2 is particularly interesting. Although alkali–halogen reactions have long been a favorite in studies of collision dynamics, to date the experimental studies have dealt with neutral species or positively charge species.

One of the reactions that we are currently studying[25] is

$$e^- + (LiX)_2 \rightarrow (LiX)_2^- \rightarrow LiX^- + Li + X,$$

where X = H, F, or Cl. This reaction has been employed by Ebinghaus[26] to produce the LiF^- and $LiCl^-$ anions. From the appearance potential of the monomer anion, the dissociation energy of LiX, and the dimerization energy of the neutral dimer, Ebinghaus was able to deduce an EA $\geq$ 1.35 eV for LiF and an EA $\geq$ 1.28 eV for LiCl. However, as is discussed in Ref. 25, it seems that the appearance potential for LiX^- production via the above reaction is due to fragmentation of the linear dimer and not the cyclic dimer as was assumed by Ebinghaus. When the EA's of Ebinghaus are corrected by an energy equal to the difference in stability between the linear and cyclic neutral dimers, they turn out to be in good agreement with those reported in this paper.

It is hoped that the calculations and suggested new reaction pathways presented in this paper will stimulate experimental investigations of the anions of highly polar molecules. It is our intention to continue our theoretical research in this highly fruitful area.

ACKNOWLEDGMENTS

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APPENDIX: EOM THEORY

In this Appendix we briefly review the EOM theory of electron affinities. A more thorough discussion may be found in Refs. 10 and 11. In the EOM theory, electron affinities are calculated directly without the need of performing separate calculations on the neutral molecule and on its anion. This is accomplished by introducing an operator Ω_λ^+ which generates the negative ion wavefunction $|\lambda^{N+1}\rangle$ from the ground state wavefunction of the neutral parent molecule $|g^N\rangle$,

$$\Omega_\lambda^+ |g^N\rangle = |\lambda^{N+1}\rangle . \tag{A1}$$

We represent Ω_λ^+ in terms of second-quantized Hartree–Fock (HF) orbital creation and annihilation operators $\{C_i^+\}$ and $\{C_i\}$

$$\Omega_\lambda^+ = \sum_i X_i(\lambda) C_i^+ + \sum_{m<n,\alpha} Y_{n\alpha m}(\lambda) C_n^+ C_\alpha C_m + \sum_{\alpha<\beta,m} Y_{\alpha m\beta}(\lambda) C_\alpha^+ C_m C_\beta^+ , \tag{A2}$$

where α, β refer to HF spin orbitals below the Fermi level, and m, n refer to HF spin orbitals above the Fermi level, and the index i refers to either set. The $X_i(\lambda)$, $Y_{n\alpha m}(\lambda)$, and $Y_{\alpha m\beta}(\lambda)$ are expansion coefficients determined from the EOM theory.

The ground state wavefunction of the closed-shell neutral parent is given by the Rayleigh–Schrödinger expression

$$|g_{RS}^N\rangle = N_0^{-1/2} \left[|0\rangle + \sum_{m<n,\alpha<\beta} \frac{\langle mn|\alpha\beta\rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n} C_m^+ C_n^+ C_\beta C_\alpha |0\rangle \right], \tag{A3}$$

where the Hartree–Fock wavefunction of the parent is represented by $|0\rangle$, N_0 is a normalization constant, ϵ_i is the orbital energy of the ϕ_i spin orbital, and the $\langle mn|\alpha\beta\rangle$ are antisymmetrized two electron integrals.[10,11]

Assuming that both $|\lambda^{N+1}\rangle$ and $|g^N\rangle$ are eigenfunctions of the Born–Oppenheimer Hamiltonian H, we have

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$$H|g^N\rangle = E_g^N|g^N\rangle, \tag{A4}$$

$$H|\lambda^{N+1}\rangle = E_\lambda^{N+1}|\lambda^{N+1}\rangle. \tag{A5}$$

From Eqs. (3)–(5) we derive the EOM theory of electron affinities,

$$\langle g^N|\{\delta\Omega_\lambda, H, \Omega_\lambda^+\}|g^N\rangle = \Delta E_\lambda \langle g^N|\{\delta\Omega_\lambda, \Omega_\lambda^+\}|g^N\rangle, \tag{A6}$$

where the commutators are defined as

$$\{x, y, z\} = \tfrac{1}{2}\{x, [y, z]\} + \tfrac{1}{2}\{[x, y], z\}, \tag{A7}$$

$$\{A, B\} = AB + BA, \tag{A8}$$

$$[A, B] = AB - BA, \tag{A9}$$

and $\Delta E_\lambda \equiv E_g^N - E_\lambda^{N+1}$ is the vertical electron affinity.

The details concerning the solution of Eq. (6) may be found in Refs. 10–12. The electron affinities (EA) obtained from the EOM contain the second order correlation and orbital relaxation corrections as well as the most important third and higher order corrections to the Koopmans' theorem estimate to the electron affinity. The Koopmans' theorem approximation equates the electron affinity with $-\epsilon$(LUMO), where ϵ(LUMO) is the orbital energy of the lowest unoccupied molecular orbital.

*University of Utah Graduate Research Fellow.

†Alfred P. Sloan Fellow.

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