

# Theoretical studies of molecular ions: BeH<sup>-</sup>

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In this paper we present the results of our theoretical work on BeH<sup>-</sup> in which we have used the equations-of-motion method to obtain the <sup>1</sup>Σ<sup>+</sup> → <sup>2</sup>Σ<sup>+</sup> vertical ionization energies of BeH<sup>-</sup> at several internuclear distances. Calculated potential energy curves, equilibrium internuclear distances, and spectroscopic constants are presented for BeH<sup>-</sup> and BeH. From the ion and neutral potential energy curves we are able to calculate a thermodynamic ionization energy and a dissociation energy for BeH<sup>-</sup> as well. We also report an interesting correlation between our equations-of-motion results and the Koopmans' theorem estimate of ionization energies. The effects of basis set optimization on our BeH<sup>-</sup> calculations are discussed.

## I. INTRODUCTION

In the equations-of-motion (EOM) method for calculating molecular electron affinities and ionization potentials, as developed by our research group,<sup>1</sup> the ion-molecule energy difference is obtained from a single calculation rather than by two separate variational calculations on the molecule and the ion. This method permits formal cancellation of terms contributing equally to the ion and molecule energies through third order. Changes in correlation energy associated with ionization and the adjustment of the Hartree-Fock orbitals of the parent species are included in our EOM theory so as to allow calculation of the ion-molecule energy difference through third order in the electron interactions  $r_{ij}^{-1}$ . The relationship between many body Green's function theory,<sup>2</sup> Rayleigh-Schrödinger (RS) perturbation theory, and our EOM theory has been discussed by us in Ref. 1 and elsewhere.<sup>3</sup> In Sec. II of this paper we give a brief description of our theory and some brief comments regarding its relationship to the work of Cederbaum<sup>4</sup> and of Chong.<sup>5</sup>

In Sec. III we present and analyze our BeH and BeH<sup>-</sup> data and compare it to the experimental data on BeH obtained by vibrational spectroscopy. Our calculated ionization energies for BeH<sup>-</sup> are compared with the BeH<sup>-</sup> photodetachment energy recently determined by Feldmann.<sup>6</sup> In our investigation of the influence of basis set optimization on our EOM results we compare results obtained with initial and optimized versions of a BeH<sup>-</sup> basis set at various internuclear separations. The almost constant difference between EOM and Koopmans' theorem ionization potentials as a function of  $R$ , which is observed in our calculations on the BeH, BeH<sup>-</sup> system is discussed and interpreted. The electron density of the BeH<sup>-</sup> ion is analyzed and compared to the electron density of the Hartree-Fock wavefunction for the neutral BeH reported by Cade and Huo.<sup>7</sup> We also compare the electron density in BeH<sup>-</sup> to that in the isoelectronic BH which has also been studied by our research group.<sup>8</sup>

## II. EOM THEORY

In applying our EOM theory to negative molecular ions such as BeH<sup>-</sup>, we attempt to find a good approximation to the excitation operator  $\Omega_\mu$  which generates the neutral molecule wavefunction  $|\mu^{N-1}\rangle$  from the ground state wavefunction of the negative ion  $|g^N\rangle$ :

$$\Omega_\mu |g^N\rangle = |\mu^{N-1}\rangle. \quad (1)$$

In the model we have proposed,  $\Omega_\mu$  is approximated by the second-quantized Hartree-Fock (HF) orbital creation and annihilation operators,  $\{C_i^\dagger\}$  and  $\{C_i\}$ , as shown below<sup>9</sup>:

$$\begin{aligned} \Omega_\mu = & \sum_i X_i(\mu) C_i \\ & + \sum_{m < n, \alpha} Y_{n\alpha m}(\mu) C_n C_\alpha^\dagger C_m + \sum_{\alpha < \beta, m} Y_{\alpha m \beta}(\mu) C_\alpha C_m^\dagger C_\beta. \end{aligned} \quad (2)$$

The greek indices in Eq. (2) refer to Hartree-Fock spin orbitals below the Fermi level, the indices  $n, m$  refer to Hartree-Fock spin orbitals above the Fermi level, and the indices  $i, j$  refer to either set. The  $X_i(\mu)$ ,  $Y_{n\alpha m}(\mu)$ ,  $Y_{\alpha m \beta}(\mu)$  are expansion coefficients determined from the EOM theory.

The approximation to the ground state wavefunction of the closed-shell negative ion parent is given by the Rayleigh-Schrödinger expression:

$$|g_{RS}^N\rangle = N_0^{-1/2} \left[ |0\rangle + \sum_{m < n, \alpha < \beta} \frac{\langle mn | \alpha \beta \rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n} C_m^\dagger C_n^\dagger C_\beta C_\alpha |0\rangle \right]. \quad (3)$$

In Eq. (3) the Hartree-Fock wavefunction of the closed-shell negative ion is represented by  $|0\rangle$ ,  $\epsilon_i$  is the energy of spin orbital  $\phi_i$ ,  $N_0$  is a normalization constant, and the  $\langle mn | \alpha \beta \rangle$  are antisymmetrized two electron integrals over the spin orbitals  $\phi_m, \phi_n, \phi_\alpha, \phi_\beta$ , as described in Ref. 1.

Assuming that both  $|\mu^{N-1}\rangle$  and  $|g^N\rangle$  are eigenfunctions of the Born-Oppenheimer Hamiltonian  $H$ , we can write

$$H |g^N\rangle = E_g^N |g^N\rangle, \quad (4)$$

$$H |\mu^{N-1}\rangle = E_\mu^{N-1} |\mu^{N-1}\rangle. \quad (5)$$

From Eqs. (1), (4), and (5) we develop the Heisenberg equations of motion,

$$[\Omega_\mu, H] |g^N\rangle = (E_g^N - E_\mu^{N-1}) \Omega_\mu |g^N\rangle \quad (6)$$

which we use to derive our matrix pseudoeigenvalue working equations for the iterative calculation of vertical ionization energies  $\Delta E_\mu = E_g^N - E_\mu^{N-1}$ :

$$\sum_j H_{ij}(\Delta E_\mu) X_j(\mu) = \Delta E_\mu X_i(\mu). \quad (7)$$

The matrix elements  $H_{ij}(\Delta E_\mu)$  are given by

$$H_{ij}(\Delta E_\mu) = A_{ij} + \sum_{\alpha < \beta, m} \frac{B_{i, \alpha m \beta} B_{j, \alpha m \beta}^*}{E_\alpha^m + \Delta E_\mu} + \sum_{m < n, \alpha} \frac{B_{i, m \alpha n} B_{j, m \alpha n}^*}{-E_\alpha^{mn} + \Delta E_\mu}, \quad (8)$$

where the terms appearing in Eq. (8) are defined by Eqs. (31d)–(35) of Ref. 1 which we reproduce here for completeness.

$$A_{ij} = \delta_{ij} \epsilon_i + \sum_{k, l} \langle ik | jl \rangle F_{kl}, \quad (1-31d)$$

$$B_{i, \alpha m \beta} = -\langle im | \alpha \beta \rangle - \frac{1}{2} \sum_{p, q} \langle im | pq \rangle K_{\alpha \beta}^{pq} + \sum_{\gamma, \rho} [\langle i\gamma | p\alpha \rangle K_{\beta \gamma}^{m\rho} - \langle i\gamma | p\beta \rangle K_{\alpha \gamma}^{m\rho}], \quad (1-31e)$$

$$B_{i, n \alpha m} = \langle i\alpha | mn \rangle + \frac{1}{2} \sum_{\gamma \rho} \langle i\alpha | \delta \gamma \rangle K_{\delta \gamma}^{mn} + \sum_{\gamma \rho} [\langle i\rho | \gamma m \rangle K_{\alpha \gamma}^{m\rho} - \langle i\rho | \gamma n \rangle K_{\alpha \gamma}^{n\rho}], \quad (1-31f)$$

$$F_{kl} = \sum_{\alpha < \beta, p} K_{\alpha \beta}^{pk} K_{\alpha \beta}^{p'l} - \sum_{p < q, \alpha} K_{\alpha l}^{pq} K_{\alpha k}^{p'q}, \quad (1-32)$$

$$E_\alpha^{mn} = \epsilon_m + \epsilon_n - \epsilon_\alpha - \langle \alpha n | \alpha m \rangle - \langle \alpha n | \alpha n \rangle + \langle mn | mn \rangle, \quad (1-34)$$

$$E_{\delta \gamma}^{\rho} = \epsilon_\rho - \epsilon_\delta - \epsilon_\gamma - \langle \delta \rho | \delta \rho \rangle - \langle \gamma \rho | \gamma \rho \rangle + \langle \delta \gamma | \delta \gamma \rangle, \quad (1-35)$$

and

$$K_{\alpha \beta}^{pq} = \frac{\langle pq | \alpha \beta \rangle}{(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)}. \quad (1-15)$$

For this paper it is sufficient to note that each of these terms can be calculated if the orbital energies  $\{\epsilon_i\}$  and the two electron integrals  $\{\langle ij | kl \rangle\}$  are known.

The physical significance of the summations in Eq. (8) is as follows. The  $\beta = N$  terms in the first summation contain the effects of charge redistribution on the calculated ionization energies, since these terms contribute to the ion-neutral Hartree-Fock energy difference. The  $\beta < N$  terms in the first summation give the approximate change in correlation energy of the  $N$  electrons of the negative ion parent caused by removal of an electron from the highest occupied molecular orbital  $\phi_N$  to form the neutral species. Finally, the second summation gives an approximation to the negative of the correlation energy of an electron in  $\phi_N$  of the negative ion, interacting with the  $N - 1$  other electrons.

In order to solve the matrix pseudoeigenvalue equation [Eq. (7)], the Hartree-Fock orbital energies  $\{\epsilon_i\}$  and two electron integrals  $\{\langle ij | kl \rangle\}$  are computed after which the necessary two electron integrals are transformed to the Hartree-Fock basis. A modified version of the Harris DIATOM program is used to obtain these values, from which the terms  $A_{ij}$ ,  $E_\alpha^{mn}$ ,  $E_{\alpha \beta}^m$ ,  $B_{i, n \alpha m}$ ,  $B_{j, n \alpha m}$ ,  $B_{i, \alpha m \beta}$ ,  $B_{j, \alpha m \beta}$  in the matrix elements  $H_{ij}$  [Eq. (8)], can be calculated. This step is carried out only once, and is not a part of the iteration process. An important feature of our theory is that the matrix  $\mathbf{H}(\Delta E_\mu)$  is block

diagonalized by molecular symmetry. The symmetry properties of  $\mathbf{H}(\Delta E_\mu)$  allow us to calculate only a limited set of the above terms. This simplifies the computational procedure and significantly reduces computer time.

Our equations-of-motion theory in its present form is limited to closed shell  $N$ -electron parent systems, such as BeH<sup>-</sup>, OH<sup>-</sup>, or BH. However, from equations-of-motion calculations of electron affinities or ionization energies of the parent, we can obtain energies for the corresponding  $N \pm 1$  electron species:

$$E^{N \pm 1} = E^N + \left\{ \begin{array}{l} -\text{E.A.}^N = \text{I.P.}^{N+1} \\ +\text{I.P.}^N = -\text{E.A.}^{N-1} \end{array} \right\}. \quad (9)$$

Only those systems not having a closed-shell parent or daughter are inaccessible to our method. Our research group is presently developing an extension of our theory to open-shell parent systems.

As an initial approximation to the ionization energy one can choose the Koopmans' theorem estimate<sup>10</sup>:

$$\Delta E_\mu \approx \epsilon_\mu. \quad (10)$$

For the "shake up" states in which both ionization and excitation occur, an initial estimate for  $\Delta E_\mu$  is chosen to be of the form,

$$\Delta E_\mu \approx \epsilon_\alpha + \epsilon_\beta - \epsilon_p, \quad (11)$$

where the subscripts  $\alpha$  and  $\beta$  refer to HF spin orbitals below the Fermi level and the subscript  $p$  refers to an HF spin orbital above the Fermi level, as noted earlier. Shake up states were not studied in our BeH<sup>-</sup> work and will not be discussed in any more detail here.

If the initial Koopmans' theorem estimate for the ionization energy is quite far from the true value,  $\Delta E_\mu - \epsilon_\mu \geq 1$  eV, we must consider the possibility of iterative convergence to an excited-state ion-molecule energy difference. Due to the symmetry diagonalization of the matrix pseudoeigenvalue problem expressed in Eq. (7), this possibility is restricted to states having the same symmetry as the state of interest with true ionization energies close to the initial Koopmans' theorem estimate for  $\Delta E_\mu$ . A more careful study of the dependence of the solution to Eq. (7) on the initial estimate for  $\Delta E_\mu$  would be necessary for this uncommon situation. Such excited state convergence problems have not been encountered in any of our calculations to date.

Once an initial guess for  $\Delta E_\mu$  has been formulated, and the terms given in Eqs. (1-31d)–(1-35) are computed, the matrix elements  $H_{ij}(\Delta E_\mu)$  belonging to the proper symmetry block can be constructed. The eigenvalue of  $\mathbf{H}(\Delta E_\mu)$  closest to the first approximation of  $\Delta E_\mu$  can then be used to form a new set of matrix elements  $H'_{ij}(\Delta E'_\mu)$ , for the next approximation in the iterative process. This iterative solution of our matrix pseudoeigenvalue working equations [Eq. (7)] in conjunction with Aiken's method<sup>11</sup> for improving the rate of convergence has been used to generate the vertical ionization energy results for BeH<sup>-</sup> reported in this paper.

The second order Dyson equation of Reinhardt and Doll<sup>2</sup> can be generated from the matrix pseudoeigenval-

ue equation [Eq. (7)] by making the substitutions

$$K_{\alpha\beta}^{mn} = 0, \quad (12a)$$

$$E_{\alpha\beta}^m = \epsilon_m - \epsilon_\alpha - \epsilon_\beta, \quad (12b)$$

$$E_\alpha^{mn} = \epsilon_m + \epsilon_n - \epsilon_\alpha, \quad (12c)$$

which eliminate the third order terms in  $\mathbf{H}(\Delta E_\mu)$ . The relationship between the matrix representations of the one particle Green's function and our equations-of-motion is,

$$\mathbf{G}(E) = [\mathbf{E}\mathbf{1} - \mathbf{H}(E)]^{-1} \quad (13)$$

from which we can see that the third order poles of the Green's function  $\mathbf{G}(E)$  correspond to the energy solutions of the third order pseudo-eigenvalue equation [Eq. (7)]. Based upon atomic ionization potential calculations employing the Dyson equation, Reinhardt and Doll concluded that highly accurate results can be obtained only if one includes third and perhaps the higher order interactions. Thus we feel the inclusion of the third order terms is a significant aspect of our theory.

Recently, Chong and co-workers<sup>5</sup> computed neutral-molecule ionization potentials using third order Rayleigh-Schrödinger perturbation theory together with geometrical approximations to higher orders. This procedure is equivalent in our theory to a calculation, for ionization from spin orbital  $\phi_\alpha$ , in which the single third order matrix element  $H_{\alpha\alpha}(\Delta E_\mu)$  is evaluated at  $\Delta E_\mu = \epsilon_\alpha$  with geometrical approximations to fourth and higher order energy differences:

$$\Delta E^{(3)}/\Delta E^{(2)} = \Delta E^{(4)}/\Delta E^{(3)} = \Delta E^{(5)}/\Delta E^{(4)} = \dots \quad (14)$$

In the excellent formulation of Cederbaum,<sup>4</sup> third order Green's function calculations are used to compute molecular ionization potentials. These calculations are equivalent to iteratively solving the matrix pseudo-eigenvalue equations [Eq. (7)] without the two electron integrals in the energy denominators and without the third order components of  $H_{ij}(\Delta E)$ , and then evaluating the third order contributions at the value of  $\Delta E$  obtained

from the iterative second order calculation. The geometric approximation used by Cederbaum to approximate fourth and higher order terms corresponds to our use of "shifted" energy denominator terms in Eq. (1-37). In addition to the work of Cederbaum and of Chong,<sup>5</sup> Pickup and Goscinski<sup>12</sup> have derived second order expressions for charge reorganization and correlation energy corrections to Koopmans' theorem. Recently, Smith and Day<sup>13</sup> and Parr and Levy<sup>14</sup> have also made very interesting and important contributions toward developing useful extensions of Koopmans' theorem.

### III. RESULTS AND DISCUSSION

#### A. Basis sets; BeH<sup>+</sup>

An initial basis set for the closed-shell (<sup>1</sup>Σ<sup>+</sup>) BeH<sup>+</sup> consisting of 20 Slater-type orbitals (STO's) was adopted from the optimized BeH basis set reported by Cade and Huo.<sup>6</sup> To accommodate the extra electron correlation, 2*p<sub>r</sub>* functions and diffuse *s* and 2*p<sub>σ</sub>* 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<sup>+</sup> 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<sup>+</sup> equilibrium internuclear distance of 2.660 a.u. The initial and optimized BeH<sup>+</sup> basis sets and expansion coefficients for occupied molecular orbitals are listed in Table I. 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<sup>+</sup> basis set caused dramatic increases in the importance of the diffuse 2*s*Be and 1*s*H basis functions describing the 3σ HOMO.

Substitution of a 2*p<sub>σ</sub>* STO ( $\zeta = 2.500$ ) for the 2*s* STO ( $\zeta = 2.500$ ) on the hydrogen resulted in a slightly better value for the BeH<sup>+</sup> energy. The energy was again slightly improved by making the 2*p<sub>σ</sub>*H orbital more diffuse.

TABLE I. Original and optimized 20 STO basis sets for BeH<sup>+</sup>. Original basis set;  $R_e = 2.660$  a.u.,  $E = -15.12104$  a.u.,  $\epsilon_{1\sigma} = -4.51210$  a.u.,  $\epsilon_{2\sigma} = -0.28926$  a.u.,  $\epsilon_{3\sigma} = -0.02032$  a.u.; I. P. = 0.02751 a.u. Optimized basis set;  $R_e = 2.670$  a.u.,  $E = -15.12308$  a.u.,  $\epsilon_{1\sigma} = -4.50693$  a.u.,  $\epsilon_{2\sigma} = -0.27730$  a.u.,  $\epsilon_{3\sigma} = -0.01877$  a.u., I. P. = 0.02913 a.u.

BeH basis	Orbital	$\zeta$ (original)	$\zeta$ (optimized)	$C_{1\sigma}^{(or.)}$	$C_{1\sigma}^{(op.)}$	$C_{2\sigma}^{(or.)}$	$C_{2\sigma}^{(op.)}$	$C_{3\sigma}^{(or.)}$	$C_{3\sigma}^{(op.)}$
*	1 <i>s</i> Be	2.9448		0.84377	0.85361	-0.16987	-0.15081	-0.09822	-0.08297
*	1 <i>s'</i> Be	5.7480		0.23092	0.22616	-0.00186	-0.01022	-0.01053	-0.01590
	2 <i>s</i> Be	0.4000	0.4250	0.01243	-0.03928	0.01391	-0.09120	0.63441	1.08018
*	2 <i>s'</i> Be	0.8925	1.1500	0.07154	0.10249	0.29861	0.39163	0.63860	0.56833
	2 <i>s''</i> Be	1.7238		-0.11599	-0.16573	0.12175	-0.02368	0.06845	-0.05475
	2 <i>p<sub>σ</sub></i> Be	0.4000		0.01257	-0.01303	0.03299	-0.03817	-0.13953	-0.01752
*	2 <i>p<sub>σ</sub>'</i> Be	0.8080		0.03336	0.01491	0.03954	-0.01068	-0.11016	-0.28577
*	2 <i>p<sub>σ</sub>''</i> Be	1.0460		-0.04211	-0.00897	0.12792	0.13322	-0.08124	0.05031
*	2 <i>p<sub>σ</sub>'''</i> Be	1.5000		0.01356	0.00198	0.09628	0.08734	-0.10446	-0.12637
	2 <i>p<sub>r</sub></i> Be	0.8080		0.0	0.0	0.0	0.0	0.0	0.0
	2 <i>p<sub>r</sub>'</i> Be	1.0460		0.0	0.0	0.0	0.0	0.0	0.0
	2 <i>p<sub>r</sub>''</i> Be	1.5000		0.0	0.0	0.0	0.0	0.0	0.0
	1 <i>s</i> H	0.4000	0.3000	-0.05489	0.03915	0.05648	0.15939	-0.47443	-0.73778
	1 <i>s'</i> H	1.0000	1.0500	0.01772	-0.02409	0.71242	0.64325	-0.19299	-0.19021
*	2 <i>s</i> H	2.5000		-0.00019	0.01496	0.01453	-0.01514	0.00898	0.00635
	2 <i>p<sub>r</sub></i> H	1.4500		0.0	0.0	0.0	0.0	0.0	0.0

TABLE II. Energy vs internuclear separation data in a. u. for BeH and BeH<sup>-</sup>, original and optimized basis sets.

$R$ (a. u.)	$E_{\text{BeH}}^{(\text{or.})}$	$E_{\text{BeH}}^{(\text{op.})}$	$E_{\text{BeH}^-}^{(\text{or.})}$	$E_{\text{BeH}^-}^{(\text{op.})}$	I. P. $_{\text{BeH}}^{(\text{or.})}$	I. P. $_{\text{BeH}}^{(\text{op.})}$	$-\epsilon_{3\sigma}^{(\text{or.})}$	$-\epsilon_{3\sigma}^{(\text{op.})}$
2.380	-15.11607	-15.11785	-15.09207	-15.09201	0.02400	0.02584		0.01559
2.420	-15.11750	-15.11935	-15.09307	-15.09311	0.02443	0.02624	0.01781	0.01595
2.460	-15.11868	-15.12056	-15.09381	-15.09392	0.02487	0.02664	0.01818	0.01633
2.500	-15.11959	-15.12150	-15.09422	-15.09441	0.02537	0.02709	0.01857	0.01673
2.538	-15.12023	-15.12217	-15.09439	-15.09465	0.02584	0.02752	0.01895	0.01715
2.580	-15.12070	-15.12269	-15.09429	-15.09467	0.02641	0.02802	0.01940	0.01763
2.620	-15.12096	-15.12297	-15.09401	-15.09446	0.02695	0.02851	0.01985	0.01812
2.660	-15.12104	-15.12308	-15.09353	-15.09409	0.02751	0.02899	0.02032	0.01864
2.700	-15.12097	-15.12303	-15.09284	-15.09348	0.02813	0.02955	0.02081	0.01918
2.740	-15.12076	-15.12284	-15.09201	-15.09275	0.02875	0.03009	0.02133	0.01975
2.780	-15.12042	-15.12251	-15.09101	-15.09184	0.02941	0.02067	0.02188	0.02035

The diffuse 2sBe and 1sH functions continued to dominate the description of the 3 $\sigma$  HOMO even with the hydrogen polarized radial correlation modifications.

In almost all of the calculations involving basis set optimization, the energies of the occupied molecular orbitals decreased in magnitude and the ionization energy increased in magnitude with basis set choices giving better approximations to the total electronic energy of BeH<sup>-</sup>. In Sec. III. D we amplify our discussion of this behavior and offer explanations for its occurrence.

### B. Calculated potential energy curves, BeH, BeH<sup>-</sup>

In Table II we present our calculated BeH and BeH<sup>-</sup> energies for both the original and optimized basis sets. SCF calculations for  $E_{\text{BeH}}(R)$  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 min. Vertical ionization energies of BeH<sup>-</sup>, I. P.  $_{\text{BeH}^-}(R)$ , were calculated by our third order equations-of-motion program. Execution time for each ionization energy calculation on the Univac 1108 was approximately 25 sec. BeH energies were calculated by adding the vertical ionization energy of BeH<sup>-</sup> energy,

$$E_{\text{BeH}}(R) = E_{\text{BeH}^-}(R) + \text{I. P.}_{\text{BeH}^-}(R). \quad (15)$$

Introduction of angular correlation into the BeH<sup>-</sup> basis set, while necessary for a good description of the electron correlation effects associated with negative-ion ionization energy calculations, resulted in total electronic energy values for both BeH and BeH<sup>-</sup> which were not as good as those obtained from calculations employing a sigma-only HF basis set. To see this we compare the BeH minimum energy of -15.15312 a. u. determined by the HF calculations of Cade and Huo with our optimized minimum SCF-EOM BeH energy result of -15.09446 a. u.

In Fig. 1 the calculated BeH and BeH<sup>-</sup> potential curves are presented for the original and optimum basis sets. The energy scale shown in this figure is relative energy in a. u. where the zeros of the curves have all been adjusted so their shapes may be compared. It is evident from these figures that BeH<sup>-</sup> has a shallower potential and a larger equilibrium internuclear distance than BeH.

The differences in energies  $\Delta E_{\text{BeH}^-}$ ,  $\Delta \text{I. P.}_{\text{BeH}^-}$ , and  $\Delta E_{\text{BeH}}$  between the two basis sets are plotted as a function of  $R$  in Fig. 2. Since orbital exponents were optimized at the initially calculated equilibrium internuclear distance of BeH<sup>-</sup> to give the best BeH<sup>-</sup> energy it is not surprising that  $E_{\text{BeH}^-}$  was more sensitive to this basis set optimization than  $E_{\text{BeH}}$ . For both BeH and BeH<sup>-</sup> the qualitative effect of BeH<sup>-</sup> basis set optimization was to slightly increase the slope of the potential curves for  $R \leq R_e$  and to decrease the slope for  $R \geq R_e$ , with  $R_e^{\text{BeH}^-}$  and  $R_e^{\text{BeH}}$  becoming slightly larger. We can visualize this by considering the effect of subtracting the  $\Delta E$  curves in Fig. 2 from the original basis BeH and BeH<sup>-</sup> curves in Fig. 1.

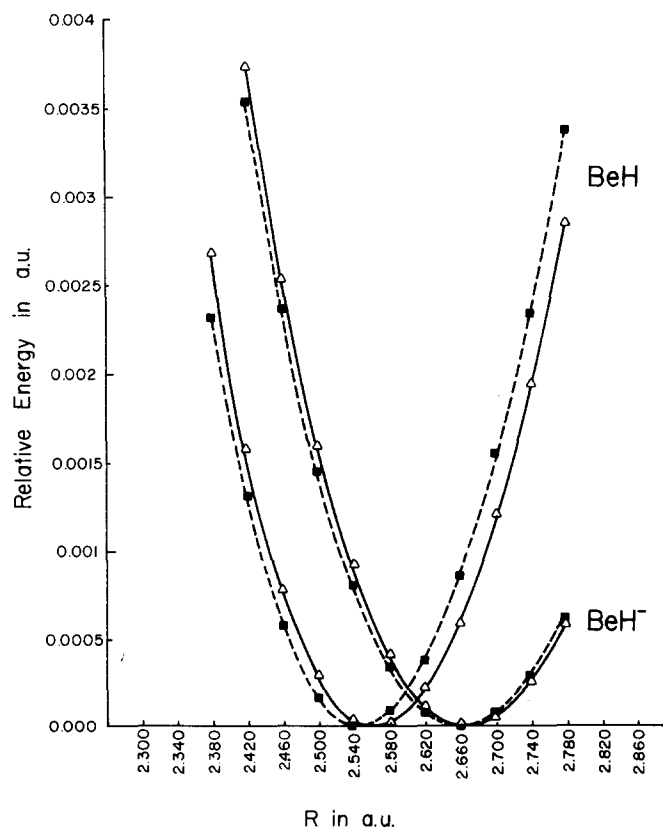


FIG. 1. Relative energies of BeH<sup>-</sup> ( $^1\Sigma^+$ ) and BeH ( $^2\Sigma^+$ ) generated from our SCF calculations and from Eq. (15), for our original  $\blacksquare$  and optimized  $\triangle$  BeH<sup>-</sup> basis sets.

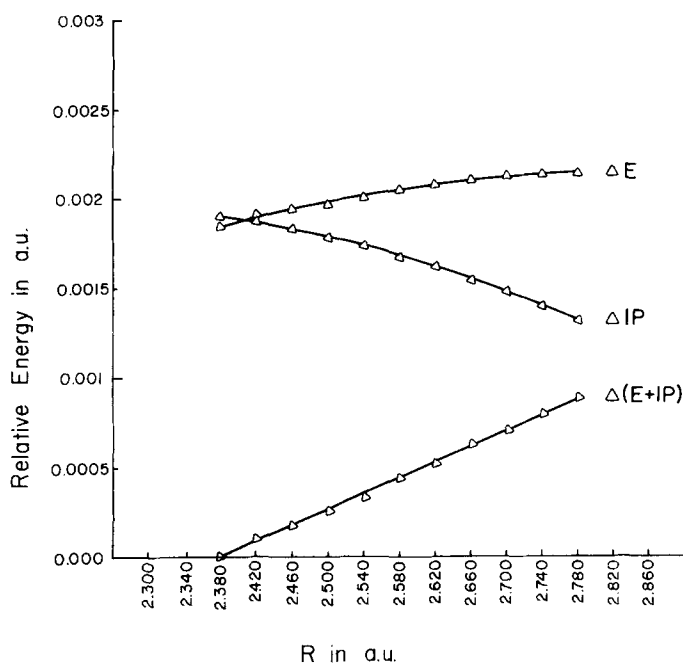


FIG. 2. Changes in the optimized basis set—original basis set energy differences,  $\Delta E_{\text{BeH}^-}$ ,  $\Delta \text{I. P.}_{\text{BeH}^-}$  and  $\Delta E_{\text{BeH}^-} = \Delta(E_{\text{BeH}^-} + \text{I. P.}_{\text{BeH}^-})$ , with internuclear separation.

### C. Spectroscopic parameters

Our calculated spectroscopic parameters for BeH and BeH<sup>-</sup> are presented in Table III. Hartree–Fock values and experimental values have been included in this table for comparison with our theoretical results.

Dissociation energies for BeH<sup>-</sup> were calculated according to the procedure depicted in Fig. 3 from which the following equations can be written:

$$D_e^{\text{BeH}^-} = D_e^{\text{BeH}} + \Delta D_e \quad (16)$$

$$\Delta D_e = \text{I. P.}_{\text{BeH}^-}(R_e^{\text{BeH}}) + E_{\text{BeH}^-}(R_e^{\text{BeH}}) - E_{\text{BeH}^-}(R_e^{\text{BeH}^-}) - E. A. H. \quad (17)$$

*Ab initio* approximations to  $D_e^{\text{BeH}^-}$  were obtained using the HF value for  $D_e^{\text{BeH}}$  of 2.18 eV reported by Cade and

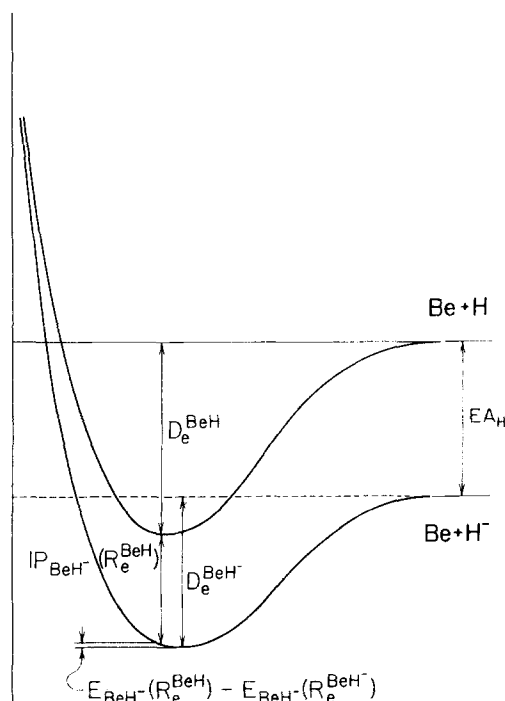


FIG. 3. Calculation of BeH<sup>-</sup> dissociation energy.

Huo.<sup>7</sup> Semiempirical BeH<sup>-</sup> dissociation energy results were calculated using Herzberg's BeH dissociation energy of 2.33 eV.<sup>16</sup> Referring to the  $D_e^{\text{BeH}^-}$  values in Table III we can see that the ion–molecule dissociation energy difference,  $\Delta D_e$ , is small, and that it changes sign with basis set optimization. Herzberg, and more recently Gaydon<sup>15</sup> both note the large uncertainty in experimental  $D_e^{\text{BeH}^-}$  values. Gaydon reports for  $D_e^{\text{BeH}^-}$   $2.3 \pm 0.3$  eV, an uncertainty which is of course much larger than our calculated  $\Delta D_e$  value. We must therefore assume a corresponding uncertainty is introduced into our semiempirical calculations of the negative ion dissociation energy.

Approximate vibrational force constants and fundamental vibrational frequencies for the BeH and BeH<sup>-</sup>

TABLE III. Calculated and experimental spectroscopic parameters for BeH and BeH<sup>-</sup>.

Parameter	Units	BeH <sup>(exp.)</sup>	BeH <sup>(HF)</sup>	BeH <sup>(or.)</sup>	BeH <sup>(op.)</sup>	BeH <sup>(or.)</sup>	BeH <sup>(op.)</sup>	BeH <sup>(exp.)</sup>
$R_e$	a. u.	2.538 <sup>a</sup>	2.528 <sup>c</sup>	2.540	2.560	2.660	2.670	
$k_e$	dyn/cm $\times 10^{-5}$	2.246 <sup>a,h</sup>	2.461 <sup>c</sup>	2.345	2.118	1.903	1.753	
$\nu_e$	cm <sup>-1</sup>	2058.6 <sup>a</sup>	2154.6 <sup>c,h</sup>	2103.2 <sup>h</sup>	1998.6 <sup>h</sup>	1894.9 <sup>h</sup>	1818.5 <sup>h</sup>	
$D_e$	eV	(2.33) <sup>a,b</sup>	2.18 <sup>c</sup>			2.15 <sup>e</sup>	2.20 <sup>d,e</sup>	
						2.31 <sup>f</sup>	2.35 <sup>d,f</sup>	
$E. A._{\text{BeH}}(R_e^{\text{BeH}})$	eV			0.7031	0.7560 <sup>d</sup>			
$\text{I. P.}_{\text{BeH}^-}(R_e^{\text{BeH}^-})$	eV					0.7485	0.7926 <sup>d</sup>	
$\text{I. P.}_{\text{BeH}^-}$ (Thermo.)	eV					0.7253	0.7727 <sup>d</sup>	0.74 <sup>g</sup>

<sup>a</sup>Herzberg, Ref. 16.

<sup>b</sup>Gaydon, Ref. 15, reports 2.3 eV with an uncertainty of  $\pm 0.3$  eV.

<sup>c</sup>Cade and Huo, Ref. 7.

<sup>d</sup>Results obtained from SCF and EOM calculations at  $R$  values not reported in Table II.

<sup>e</sup>Calculated from Cade and Huo HF  $D_e^{\text{BeH}}$  of 2.18 eV and Eqs. (16) and (17).

<sup>f</sup>Calculated from Herzberg's  $D_e^{\text{BeH}}$  of 2.33 eV and Eqs. (16) and (17).

<sup>g</sup>Feldmann, Ref. 6, photodetachment energy value corrected for zero point vibrational energy difference by Eq. (19).

<sup>h</sup>Calculated from  $k_e$  or  $\nu_e$  assuming  $\nu_e = 1/2\pi c \sqrt{k_e/\mu}$ .

systems were obtained by fitting a least squares quadratic polynomial to each potential energy curve. Agreement of these calculations with the experimental BeH values<sup>16</sup> was quite good. For the original basis set,  $\nu_e^{(\text{calc})} - \nu_e^{(\text{exp})}$  was +44.6 cm<sup>-1</sup>, a +2.17% deviation, and for the optimized basis set the deviation was -60.0 cm<sup>-1</sup> or -2.91%. For comparison, the value for  $\nu_e^{\text{BeH}}$  reported by Cade and Huo deviated from the experimental value by +96.0 cm<sup>-1</sup> or +4.66%. It is reasonable to assume our calculated fundamental vibrational frequencies for BeH<sup>-</sup> are at least this accurate. These results for BeH<sup>-</sup> should prove extremely useful to experimentalists in the rapidly developing area of negative ion spectroscopy. The smaller vibrational force constant and the correspondingly lower vibrational frequency for BeH<sup>-</sup> as compared to BeH is expected from the relative shapes of their potential energy curves as shown in Fig. 1. The fundamental vibrational frequencies for both the negative ion and the neutral decrease with basis set optimization. This trend follows from the widening of the optimized potential wells of the two species described earlier in Sec. III.B.

The thermodynamic ionization energy of BeH<sup>-</sup> was calculated using the relationship

$$I. P._{\text{BeH}^-}(\text{Thermo.}) = E_{\text{BeH}}(R_e^{\text{BeH}}) - E_{\text{BeH}^-}(R_e^{\text{BeH}^-}), \quad (18)$$

in which  $E_{\text{BeH}}(R_e^{\text{BeH}})$  was determined indirectly from our EOM results and the BeH<sup>-</sup> energies as defined in Eq. (9). Vertical ionization energies of BeH<sup>-</sup> and vertical electron affinities of BeH were calculated directly from our EOM theory. The threshold photodetachment energy for BeH<sup>-</sup>,  $\Delta E_{\text{BeH}^-}^{h\nu}(\nu^{\text{BeH}^-} = 0 \rightarrow \nu^{\text{BeH}} = 0)$ , recently determined by Feldmann<sup>6</sup> is related to  $I. P._{\text{BeH}^-}(\text{Thermo.})$  by the following equation:

$$I. P._{\text{BeH}^-}(\text{Thermo.}) = \Delta E_{\text{BeH}^-}^{h\nu}(0, 0) - h/2(\nu_e^{\text{BeH}} - \nu_e^{\text{BeH}^-}). \quad (19)$$

The second term in Eq. (19), which gives the difference in zero point vibrational energies between BeH and BeH<sup>-</sup>, takes into account the fact that the photodetachment energy is the energy difference between zero point vibrational levels of the negative ion and the neutral, rather than the difference between their potential minima. Calculations

of this zero point vibrational frequency correction gives -0.0129 and -0.0111 eV for the original and optimized basis set data, respectively. In reporting Feldmann's value for  $I. P._{\text{BeH}^-}(\text{Thermo.})$  of 0.74 eV in Table III, we have thus subtracted 0.01 eV from the BeH<sup>-</sup> photodetachment energy value of 0.75 eV. Calculated thermodynamic ionization potentials for BeH<sup>-</sup> deviate from the experimental value by [-0.01 eV, -1.4%]<sup>(or)</sup>, [+0.03 eV, +4.1%]<sup>(op)</sup>. 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<sup>-</sup> our vertical EOM ionization energy calculations at  $R_e^{\text{BeH}}$  and  $R_e^{\text{BeH}^-}$  are quite good.

#### D. Bonding in BeH<sup>-</sup>

In Table IV we list for comparison the dominant Slater orbitals and expansion coefficients for the 2σ and 3σ MO's of BeH, BeH<sup>-</sup>, and BH, which is isoelectronic with BeH<sup>-</sup>. From this table we observe that the 2σ MO's of BeH<sup>-</sup> and BeH are predominantly a bonding combination of a 1sH STO and a partial *sp* hybrid on the Be, with higher density localized on the more electronegative hydrogen nucleus. In BH, the 2σ MO is also a bonding combination of 1sH, 1sBe, 2*p*<sub>z</sub>Be STO's, but in this case the higher density is localized on the boron since it is more electronegative than hydrogen. The dominant STO's contributing to the 3σ MO of BeH<sup>-</sup> form an antibonding combination of diffuse 1s H and 2s Be functions, with less 2*p*<sub>z</sub>Be character than in the 3σ MO of the neutral BeH. The 3σ MO of BH, an antibonding combination of 1s H and 2sB STO's, has a larger 2*p*<sub>z</sub>B contribution than the corresponding 2*p*<sub>z</sub>Be contribution to the 3σ MO's of both BeH and BeH<sup>-</sup>.

In the isoelectronic pair BeH<sup>-</sup>, BH, the higher effective nuclear charge of the BH system draws electron density in closer to the boron nucleus where it can partially contribute to the bonding, whereas in the BeH<sup>-</sup> system the electron-electron repulsions tend to cause electron density to become more spread out and less involved in bonding. The diffuse nonpolarized 3σ MO of BeH<sup>-</sup> and the relatively polarized 3σ MO of BH are

TABLE IV. 2σ and 3σ MO's of BeH ( $R_e = 2.538$  a. u.), BeH<sup>-</sup><sup>(op)</sup> ( $R_e = 2.670$  a. u.), and BH ( $R_e = 2.330$  a. u.).

MO	BeH <sup>a</sup>			BeH <sup>-b</sup>			BH <sup>b,c</sup>		
	STO	ζ	<i>C</i> <sub>no</sub>	STO	ζ	<i>C</i> <sub>no</sub>	STO	ζ	<i>C</i> <sub>no</sub>
2σ	1sBe	2.945	-0.152	1sBe	2.945	-0.151	1sB	3.914	-0.185
	2sBe	1.274	0.286	2sBe	1.150	0.392	2sB	1.566	0.631
	1sH	1.065	0.573	1sH	1.050	0.643	1sH	1.183	0.473
	2 <i>p</i> <sub>z</sub> Be	1.500	0.085	1sH	0.300	0.159	2 <i>p</i> <sub>z</sub> B	1.540	0.245
	2 <i>p</i> <sub>z</sub> Be	1.046	0.136	2 <i>p</i> <sub>z</sub> Be	1.046	0.133			
	2sBe	1.274	-0.236	2sBe	1.150	0.568	2sB	0.980	0.659
3σ	2sBe	0.892	-0.581	2sBe	0.425	1.080	2sB	1.566	0.258
	1sH	1.065	0.164	1sH	1.050	-0.190	2sB	0.400	0.224
	2 <i>p</i> <sub>z</sub> Be	1.046	0.214	1sH	0.300	-0.738	1sH	1.183	-0.265
	2 <i>p</i> <sub>z</sub> Be	0.808	0.380	2 <i>p</i> <sub>z</sub> Be	0.808	-0.286	1sH	0.400	-0.432
	2 <i>p</i> <sub>z</sub> Be	1.500	0.044	2 <i>p</i> <sub>z</sub> Be	1.500	-0.126	2 <i>p</i> <sub>z</sub> B	1.540	-0.390

<sup>a</sup>Cade and Huo, Ref. 7.

<sup>c</sup>Griffing and Simons, Ref. 8.

<sup>b</sup>Results obtained from SCF calculations.

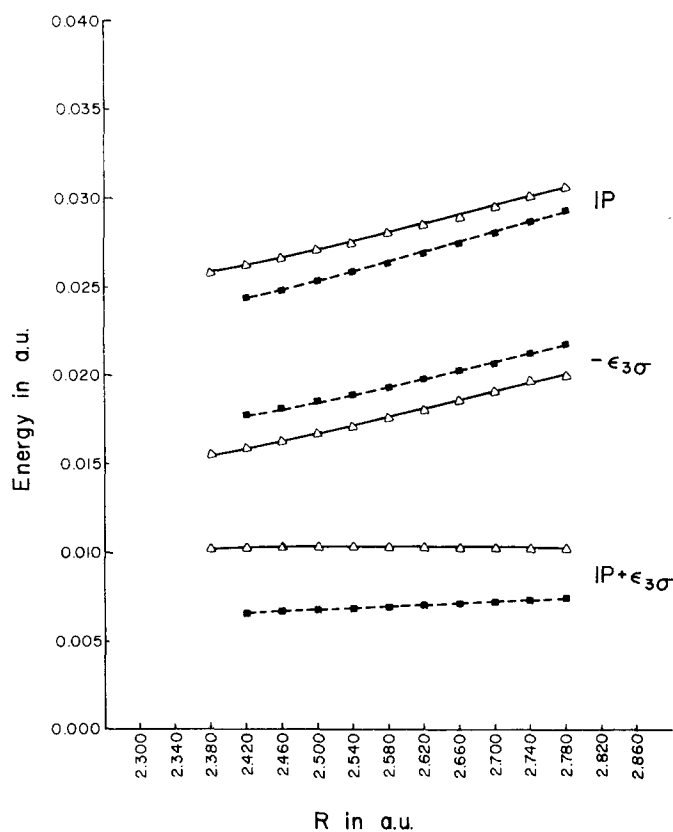


FIG. 4. Comparison between EOM and Koopmans' theorem BeH<sup>-</sup> ionization energy estimates for original ■ and optimized Δ basis sets.

seen to be manifestations of these trends. In the isonuclear pair BeH, BeH<sup>-</sup>, we see that the extra electron density of the negative ion is distributed over the entire system, effectively weakening the Be-H bond as compared to its neutral counterpart. These bonding trends are in agreement with the force constant data presented in Table III where we see  $k_e^{\text{BeH}} > k_e^{\text{BeH}^-}$ .

### E. EOM-Koopmans' theorem comparison

Comparisons between the equations-of-motion and the Koopmans' theorem ionization energy estimates for BeH<sup>-</sup> are illustrated in Fig. 4 for the original and optimum basis set choices. The almost constant difference between the two ionization energy estimates indicates that for the range of internuclear separations studied, the effects of orbital reorganization and correlation energy are essentially independent of  $R$ :

$$\partial \Delta I.P. / \partial R \approx 0. \quad (20)$$

To clarify this statement we refer to Eqs. (8) and (1-31d) to obtain the EOM-Koopmans' theorem ionization energy difference,  $\Delta I.P.$ :

$$\begin{aligned} \Delta I.P. = & \sum_{k,l} \langle ik | jl \rangle F_{kl} + \sum_{\alpha < \beta, m} \frac{B_{i, \alpha m \beta} B_{j, \alpha m \beta}^*}{E_{\alpha \beta}^m + \Delta E_{\mu}} \\ & + \sum_{m < n, \alpha} \frac{B_{i, m \alpha n} B_{j, m \alpha n}^*}{-\Delta E_{\mu} + E_{\alpha \beta}^m}, \end{aligned} \quad (21)$$

where the orbital energy  $\epsilon_i$  has been cancelled out by

the subtraction, and only the orbital reorganization and correlation terms remain. In our study of BH we have also found the corrections to the Koopmans' theorem ionization energy to be slowly varying functions of internuclear separation. We are now investigating the generality of this effect in conjunction with our studies on SH<sup>-</sup>, MgH<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and O<sub>3</sub><sup>-</sup>.

Another feature apparent from Fig. 4 is that while  $\Delta I.P.$  increases with basis set optimization, it has a noticeably weaker  $R$  dependence. This is an example of the trends associated with basis set optimization briefly discussed in Sec. III.A. In explaining these trends it is important to note from Table II that the Koopmans' theorem estimates of the ionization energy becomes smaller with basis set optimization. This means a greater correlation error is introduced with the Koopmans' theorem estimate for the optimized basis, but at the same time a better set of orbitals is available for describing the correlation effects. The equations-of-motion result for the optimized basis is therefore expected to vary more dramatically from the Koopmans' theorem estimate, but to provide a more accurate overall approximation to the ionization energy. From the weaker  $R$  dependence for  $\Delta I.P.$  with the optimized BeH<sup>-</sup> basis we infer a better correlation model has indeed been established. This phenomenon will be studied further in our work on other negative ions now in progress.

### F. Conclusion

Our SCF calculations on the <sup>1</sup>Σ<sup>+</sup> BeH<sup>-</sup> molecular ion and our third order EOM (BeH<sup>-</sup> → BeH) ionization energy calculations are capable of producing *ab initio* results for  $R_e^{\text{BeH}}$ ,  $\nu_e^{\text{BeH}}$ , and I.P.<sub>BeH</sub>(Thermo) in excellent agreement with experiment. These theoretical methods are also capable of yielding new information about BeH<sup>-</sup>, such as  $R_e^{\text{BeH}^-}$ ,  $\nu_e^{\text{BeH}^-}$ , which should be of great value to current experimental efforts in negative ion spectroscopy. Comparisons of the occupied MO's of BeH, BeH<sup>-</sup>, and BH make it possible to better understand the influences of electronic and nuclear charge changes in the bonding of these systems.

Our studies of basis set optimization in BeH<sup>-</sup> show that good approximations to ion and neutral potential curves, ionization energies, and spectroscopic parameters may be obtained with a carefully chosen non-optimized basis set. The small differences between I.P.<sub>BeH</sub>-( $R_e^{\text{BeH}^-}$ ), I.P.<sub>BeH</sub>-( $R_e^{\text{BeH}}$ ) and I.P.<sub>BeH</sub>(Thermo.) indicate threshold photodetachment energies and thermodynamic ionization potentials can be predicted to within ± 0.05 eV by single EOM vertical ionization energy calculations near the minima of the ion or neutral potential wells.

The EOM-Koopmans' theorem correlation we have observed in our BeH<sup>-</sup> and BH ionization energy calculations suggests we may be able to account for orbital reorganization and electron correlation effects at many internuclear distances by calculating the EOM correction to Koopmans' theorem ionization energy at a single internuclear distance. The generality of this effect and its theoretical implications we feel to be worthy of much more extensive study.

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