

# Theoretical studies of molecular ions. The ionization potential and electron affinity of BH

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We have carried out a thorough study of the lowest energy  ${}^1\Sigma^+ \rightarrow {}^2\Sigma^+$  ionization potential and the  ${}^1\Sigma^+ \rightarrow {}^2\Pi$  electron affinity of BH at several internuclear distances within 0.5 a.u. of the equilibrium bond length. Potential energy curves and spectroscopic constants ( $R_e$ ,  $\omega_e$ ) are computed for the ground state ( ${}^2\Sigma^+$ ) of  $\text{BH}^+$  as well as for the  ${}^2\Pi$  diabatic state of  $\text{BH}^-$ . Comparisons with experimental results on the  ${}^2\Sigma^+$  state of  $\text{BH}^+$  are reasonably encouraging. The electron density in  $\text{BH} ({}^1\Sigma^+)$  is compared to that in the isoelectronic negative ion  $\text{BeH}^- ({}^1\Sigma^+)$  in an attempt to better understand the roles of electron repulsion and electron-nuclear attractions in the bonding in these two interesting species.

## I. INTRODUCTION

The  $\text{BH} ({}^1\Sigma^+) \rightarrow \text{BH}^+ ({}^2\Sigma^+)$  ionization potential and the  $\text{BH} ({}^1\Sigma^+) \rightarrow \text{BH}^- ({}^2\Pi)$  electron affinity have been studied at several internuclear separations by making use of the *ab initio* direct calculation technique developed by one of us in Ref. 1. This method permits us to effect a formal cancellation of those terms which contribute equally, through third order in perturbation theory, to the ion and molecule energies. The connections between our working equations, which are discussed briefly below, and the Dyson equation<sup>2</sup> of Green's function theory are described in Refs. 1 and 3. Additional remarks regarding the relationship of our method to the approaches of Cederbaum<sup>4</sup> and of Chong<sup>5</sup> are made in Sec. II of this paper.

An essential point to keep in mind is that the adjustment of the parent's (BH) Hartree-Fock molecular orbitals as well as the change in electron correlation energy which accompany ionization are treated in our theory in a manner which permits the ion-molecule energy difference to be obtained accurately through third order in the electron interactions  $\gamma_{ij}^{-1}$ . In earlier publications,<sup>6-8</sup> we have presented the results of applying our theory to the ionization energies of HF,  $\text{N}_2$ , and  $\text{OH}^-$ . We have also completed detailed studies<sup>9</sup> of  $\text{BeH}^-$  and  $\text{BeLi}^-$  and we are presently carrying out thorough investigations of  $\text{SH}^-$ ,  $\text{MgH}^-$ ,  $\text{NH}_2^-$ ,  $\text{CH}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{O}_3^-$ . In each of these projects our objectives are to determine the ion-molecule energy difference to within  $\pm 0.2$  eV and to understand the changes in charge density and bonding which accompany ion formation.

In the research described in Sec. III of this paper, we obtain a vertical electronic ionization potential of 9.53 ( $\pm 0.2$ ) eV for BH, which is in reasonable agreement with Herzberg's spectroscopic determination<sup>10</sup> of  $9.77 \pm 0.05$  eV made in 1964. Computed spectroscopic parameters for BH,  $\text{BH}^+$ , and  $\text{BH}^-$  are also compared with the known experimental values. Our results indicate that the electron affinity of BH is negative over the range of internuclear distances we have studied. Section III also contains a discussion of the bonding both in BH and the isoelectronic  $\text{BeH}^-$  as well as our concluding remarks.

## II. DESCRIPTION OF THE METHOD

In our theory of electron affinities and ionization potentials derived in Ref. 1, the excitation operator  $\Omega_\mu$ , which generates the, in principle exact, eigenstate  $|\mu^*\rangle$  of the positive ion when operating on the true neutral-molecule ground state  $|g\rangle$ ,

$$\Omega_\mu |g\rangle = |\mu^*\rangle, \quad (1)$$

is approximated in terms of the second-quantized Hartree-Fock orbital creation ( $C_i^\dagger$ ) and annihilation ( $C_i$ ) operators as follows<sup>11</sup>:

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

The operator  $C_i^\dagger (C_i)$  creates (destroys) an electron in the Hartree-Fock spin orbital  $\varphi_i$ . Green indices  $\alpha$ ,  $\beta$ , and  $\gamma$  label "occupied" Hartree-Fock spin orbitals;  $m$ ,  $n$ ,  $p$ , and  $q$  label "unoccupied" spin orbitals; and  $i$ ,  $j$ ,  $k$ , and  $l$  label either set. The  $X_i(\mu)$ ,  $Y_{n\alpha m}(\mu)$ , and  $Y_{\alpha m \beta}(\mu)$  are expansion coefficients which are determined by making use of the theory of Ref. 1 whose pertinent aspects are briefly reviewed below. An analogous expansion for the operator  $\Omega_\lambda^*$  which generates negative-ion eigenstates when operating on  $|g\rangle$  is also given in Ref. 1.

By assuming that  $|g\rangle$  and  $|\mu^*\rangle$  exactly obey the following Schrödinger equations:

$$H|g\rangle = E|g\rangle, \quad (3a)$$

and

$$H|\mu^*\rangle = E_\mu^*|\mu^*\rangle, \quad (3b)$$

one immediately obtains the basic equations of motion,

$$[H, \Omega_\mu]|g\rangle = (E_\mu^* - E)\Omega_\mu|g\rangle, \quad (3c)$$

which were used in Ref. 1 to derive the working matrix pseudoeigenvalue problem involving the electron affinities or ionization potentials and the coefficients  $X_i(\lambda)$ , or  $X_i(\mu)$ ,

$$\sum_j H_{ij}(\Delta E_\lambda) X_j(\lambda) = \Delta E_\lambda X_i(\lambda), \quad (4a)$$

or

$$\sum_j H_{ij}(\Delta E_\mu) X_j(\mu) = \Delta E_\mu X_i(\mu), \quad (4b)$$

where  $\Delta E_\lambda = E_\lambda^- - E$  and  $\Delta E_\mu = E - E_\mu^+$ . These results can be derived by using the approximation to  $\Omega_\mu$  given in Eq. (2), or its electron-affinity analog, and the Rayleigh-Schrödinger approximation to  $|g\rangle$ ,

$$|g_{\text{RS}}\rangle = N_0^{-1/2} \left[ |0\rangle + \sum_{m < n, \alpha < \beta} \langle mn | \alpha\beta \rangle (\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n)^{-1} \times C_m^* C_n^* C_\beta C_\alpha |0\rangle \right], \quad (5)$$

in Eq. (3c). The coefficients  $Y_{n\alpha m}$  and  $Y_{\alpha m \beta}$  have been eliminated by partitioning the resulting equations. In Eq. (5),  $N_0$  is a normalization constant,  $\epsilon_i$  is the Hartree-Fock energy of spin orbital  $\varphi_i$ , and the  $\langle mn | \alpha\beta \rangle$  are antisymmetrized two-electron integrals over the spin orbitals  $\varphi_m, \varphi_n, \varphi_\alpha, \varphi_\beta$ . The Hartree-Fock wavefunction of the neutral parent is represented by  $|0\rangle$ . The elements of the matrix  $H_{ij}(\Delta E)$  are given in Eq. (37) of Ref. 1 as

$$H_{ij}(\Delta E) = A_{ij} + \sum_{\alpha < \beta, m} \frac{B_{i, \alpha m \beta} B_{j, \alpha m \beta}^*}{E_{\alpha\beta}^m + \Delta E} + \sum_{m < n, \alpha} \frac{B_{i, n \alpha m} B_{j, n \alpha m}^*}{-E_{\alpha}^{mn} + \Delta E}, \quad (1-37)$$

where  $\Delta E$  is either  $\Delta E_\lambda$  or  $\Delta E_\mu$  and the quantities appearing in this equation, which are defined in Eqs. (31d)–(35) of Ref. 1, are reproduced here for the sake of completeness:

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

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

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

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

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

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

and

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

Although the above quantities are rather complicated, it should be kept in mind that a knowledge of the orbital energies ( $\epsilon_i$ ) and two-electron integrals ( $\langle ij | kl \rangle$ ) is sufficient to permit the formation of  $H_{ij}(\Delta E)$ . The physical content of the terms in the above expression for  $H_{ij}(\Delta E)$ , which is discussed more completely in Ref. 1, can be summarized, for the case of ionization from  $\varphi_N$ , as follows (analogous statements can be made for ionization from or into other spin orbitals):

(i) The  $\beta = N$  terms in the first sum in Eq. (1-37) contribute to the ion-neutral Hartree-Fock energy difference; therefore, these terms contain the effects of charge redistribution on the calculated ionization energies.

(ii) The second sum approximates the negative of the correlation energy of an electron in  $\varphi_N$ , which is vacant in the positive ion, interacting with all other electrons.

(iii) The  $\beta < N$  terms in the first sum give the approximate change in correlation energy of the parent's  $N$  electrons caused by the removal of an electron from  $\varphi_N$ .

To make use of Eq. (4a) or (4b), one must first carry out a Hartree-Fock calculation on the parent molecule of interest, after which the necessary<sup>12</sup> two-electron integrals must be transformed to the Hartree-Fock basis. In its present form, the theory is restricted, because<sup>13</sup> of the use of Eq. (5) for  $|g\rangle$ , to closed-shell parent molecules. This does not prohibit us from computing the electron affinity of, for example, the BeH radical, however, because we can obtain the desired energy difference by calculating the ionization potential of the closed-shell species BeH<sup>-</sup>. Only those energy differences for which neither the ion nor the molecule are closed shell are presently outside the capability of our method. We are currently devoting considerable effort toward developing an extension of our theory for use on such open-shell systems.

Once the Hartree-Fock orbital energies and two-electron integrals have been computed, the quantities  $A_{ij}$ ,  $E_{\alpha}^{mn}$ ,  $E_{\alpha\beta}^m$ ,  $B_{i, n \alpha m} B_{j, n \alpha m}$  and  $B_{i, \alpha m \beta} B_{j, \alpha m \beta}$ , which are defined in Eqs. (1-31d)–(1-35), can be formed. This step is carried out only once; it is not part of the iterative procedure used to solve Eq. (4a) or (4b) which is described below. The fact that  $\mathbf{H}(\Delta E)$  is block diagonalized by molecular symmetry allows us to compute only a limited set of the above-mentioned quantities, which leads to a very important savings in computation quantities.<sup>1</sup> As an initial approximation to the desired ionization potential  $\Delta E_\mu$  or electron affinity  $\Delta E_\gamma$ , one can choose the Koopmans' theorem<sup>14</sup> value.

$$\Delta E \cong \epsilon_i, \quad (6)$$

for ionization from (or into) orbital  $\varphi_i$ . In this approximation, we assume that the state of the ion being studied is related, through zeroth order, to the parent's Hartree-Fock wavefunction by the addition or removal of an electron from a single spin orbital. For the so-called shake-up states<sup>15</sup> of a positive ion, in which ionization is accompanied by excitation of the ion, the initial estimate for  $\Delta E_\mu$  should be taken to be of the form  $\epsilon_\alpha + \epsilon_\beta - \epsilon_p$ , where the meaning of the subscripts was dis-

TABLE I. Twenty-Function Hartree-Fock wavefunction for BH.  $R=2.3299$  a.u.,  $E = -25.1143$  a.u.,  $\epsilon_{1\sigma} = -7.69897$ ,  $\epsilon_{2\sigma} = -0.65413$ ,  $\epsilon_{3\sigma} = -0.34163$ .

$\sigma$ atomic orbitals	$1\sigma$	$2\sigma$	$3\sigma$	$\pi$ atomic orbitals	$1\pi$
B1s(3.9139)	0.8982	-0.1848	-0.1383	B2p(0.7000)	0.4490
B2s(1.5657)	0.1396	0.6306	0.2663	B2p'(1.5401)	0.323
B2p(0.9108)	-0.0064	-0.0320	-0.1860		
B1s'(7.3276)	0.1788	-0.0112	-0.0041	B2p''(1.0000)	-0.2003
B2s'(0.9796)	-0.0699	0.0299	0.6274	H2p(0.4000)	0.6057
B2p'(1.5401)	0.0067	0.4251	-0.3808		
B2s''(0.4000)	-0.0060	0.0115	0.2204		
B2p''(0.4000)	-0.0073	-0.0029	0.0727		
B2s'''(2.5000)	-0.1645	-0.0667	0.0492		
H1s(1.1827)	-0.0027	0.4734	-0.2741		
H1s'(0.4000)	0.0281	0.0331	-0.4256		
H2s(1.9822)	-0.0033	0.0138	-0.0255		

cussed earlier. Such states are not treated in our studies of BH and will not be discussed further here. The fact that the Koopmans' theorem initial guess may be quite far ( $\geq 1$  eV) from the correct  $\Delta E$  leads one to inquire about the possibility of the iterative procedure converging to some ion-molecule energy difference other than the energy which is appropriate to the state of interest. Because the pseudoeigenvalue problem expressed in Eq. (4a) or (4b) is symmetry-diagonalized,

this problem will arise only if there exists a state whose symmetry is the same as that of the state of interest and whose ionization energy is close to the initial Koopmans' theorem estimate. In this uncommon situation, a more detailed analysis of the dependence of the solution to Eq. (4a) or (4b) upon the initial estimate for  $\Delta E$  is required; in all of our calculations to date, such difficulties have not arisen.

Given the quantities appearing in Eqs. (1-31d)-(1-35) and an initial approximation to  $\Delta E$ , the matrix elements  $H_{ij}(\Delta E)$  belonging to the proper symmetry block can be formed in a straightforward manner, as shown in Eq. (1-37). The particular eigenvalue of  $\mathbf{H}(\Delta E)$  which lies closest to the previous approximation to  $\Delta E$  can then be used as the next approximation in forming a new  $\mathbf{H}(\Delta E)$  matrix. This iterative solution of the working equations [Eq. (4a) or (4b)] of our theory, in combination with Aiken's method<sup>15</sup> for improving the rate of convergence, has been successfully employed to generate the results presented below for the ionization potential and electron affinity of BH as well as analogous ion-molecule energy differences for the other interesting species discussed in our Introduction.

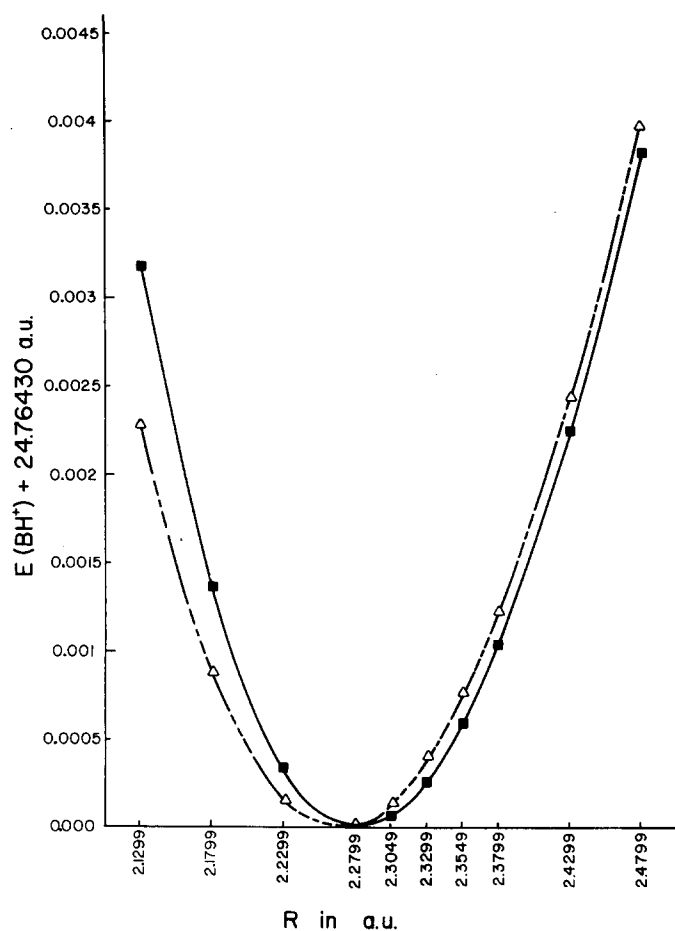


FIG. 1. The energy of  $\text{BH}^+(\Sigma^+)$  generated from our SCF calculation on  $\text{BH}(\Sigma^+)$  ■ and from a Morse potential curve for  $\text{BH}(\Sigma^+)$  △.

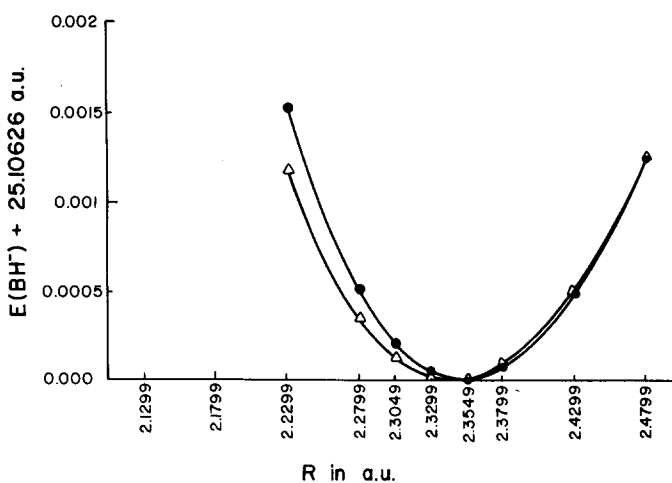


FIG. 2. The energy of  $\text{BH}^+(\Sigma^+)$  generated from our SCF calculation on  $\text{BH}(\Sigma^+)$  ● and from a Morse potential curve for  $\text{BH}(\Sigma^+)$  △.

Chong and co-workers<sup>5</sup> have used third-order Rayleigh-Schrödinger perturbation theory plus geometric approximations to higher orders to compute ionization potentials of neutral molecules with good success. For ionization from spin orbital  $\varphi_\alpha$ , such an approach is equivalent to a calculation using our theory in which the single third-order matrix element  $H_{\alpha\alpha}(\Delta E)$  is evaluated at  $\Delta E = \epsilon_\alpha$ , and fourth- and higher-order energy differences are approximated geometrically:

$$\Delta E^{(3)}/\Delta E^{(2)} = \Delta E^{(4)}/\Delta E^{(3)} = \Delta E^{(5)}/\Delta E^{(4)} = \dots \quad (7)$$

Cederbaum<sup>4</sup> has pioneered the use of third-order Green's function calculations in computing molecular ionization potentials and intensities. Such calculations are equivalent to solving Eq. (4a) or (4b) without the two electron integrals in the energy denominators and without the third-order components of  $H_{ij}(\Delta E)$ , then evaluating the third-order contributions once and for all at the value of  $\Delta E$  which was obtained from the second-order iterative calculation. The geometric approximation which Cederbaum employs to approximate the contributions of fourth- and higher-order terms is included within our theory by the presence of the "shifted" energy denominators in Eq. (1-37). In addition to this excellent third-order work of Cederbaum, Pickup and Goscinski<sup>16</sup> have derived second-order expressions for the charge-reorganization and correlation-energy corrections to Koopmans' theorem.

With this brief review of our theoretical methods now complete, let us now turn to a discussion of our numerical results.

### III. RESULTS FOR BH

Our calculations on the  ${}^1\Sigma^+ \rightarrow {}^2\Sigma^+$  ionization potential and the  ${}^1\Sigma^+ \rightarrow {}^2\pi$  electron affinity of BH were carried out within the twenty-function Slater-type basis described in Table I. This basis was constructed by taking the dominant  $\sigma$  orbitals from Cade and Huo's basis<sup>17</sup> for BH and adding  $\pi$  functions to permit the inclusion of angular correlation as well as more diffuse  $\sigma$  and  $\pi$  functions to enable us to adequately treat the charge density in  $\text{BH}^-$ . The orbital exponents of the diffuse boron and hydrogen basis functions were initially varied in an attempt to determine whether  $\text{BH}^-$  is stable with respect

to BH and an electron at infinity. We found that the electron affinity of BH is not positive, i.e., that optimization of the orbital exponents of the diffuse functions gave a negative electron affinity (at all values of  $R$ ) which approached zero (BH plus an electron) as the exponents were made smaller. Therefore, in an attempt to compute an approximation to the diabatic  $\text{BH}^-$  potential energy curve, we chose the orbital exponents of the diffuse functions to be reasonable for the "separated-atom" limit rather than for a BH molecule plus an electron at infinity. Because the diffuse orbitals have not been fully optimized for the separated species, the diabatic  $\text{BH}^-$  curve obtained by this procedure will probably not be highly accurate. However, we feel that our conclusion that the electron affinity of BH is negative is correct.

We should also note that since our calculated ion-molecule energy differences are presumably more accurate (third order) than the SCF energies of BH, it may not be wise to compute potential energy curves for  $\text{BH}^+$  and  $\text{BH}^-$  by simply adding the ionization potential or electron affinity of BH to the SCF potential energy curve of BH. On the other hand, the spectroscopic constants of BH ( $R_e$ ,  $D_e$ , and  $\omega_e$ ) are not known to high precision. This means that a Morse potential curve which uses these uncertain spectroscopic constants may be even less reliable than our SCF curve. Therefore, we have chosen to construct the two pairs of ionic potential curves shown in Figs. 1 and 2 and listed in Tables II and III by adding our computed ionization potential and electron affinity to both the SCF energy of BH and a Morse potential for BH which makes use of the experimental values for  $R_e$ ,  $\omega_e$ , and  $D_e$ .<sup>18</sup> Since we have restricted the internuclear separation to lie within 0.5 a.u. of the equilibrium value for BH, we are probing only the bottom portions of the  $\text{BH}^+({}^2\Sigma^+)$  and  $\text{BH}^-({}^2\pi)$  potential energy curves.

In Table II we also present our computed SCF energies for BH, the  ${}^2\Sigma^+$  ionization potential, and the  ${}^2\pi$  electron affinity for internuclear distances between 1.8299 and 2.8299 a.u. At the experimental equilibrium bond length of BH ( $R_e = 2.3299$  a.u.), our computed vertical ionization potential is 9.53 eV; Herzberg's spectroscopic measurements give  $9.77 \pm 0.05$  eV. The minimum SCF energy in our work occurs at  $R = 2.3049$  a.u., which is

TABLE II. Energy vs internuclear separation data for BH,  $\text{BH}^+$ , and  $\text{BH}^-$  (in a. u.).

$R$ (a. u.)	$E(\text{BH})$	IP( $\text{BH} \rightarrow \text{BH}^+$ )	$E(\text{BH}^+)$	EA( $\text{BH} \rightarrow \text{BH}^-$ )	$E(\text{BH}^-)$
1.8299	-25.073240 <sup>a</sup>	0.34687	-24.726370	-0.02079	-25.05245
2.1299	-25.109892	0.34877	-24.761122	-0.02087	-25.089022
2.1799	-25.112081	0.34915	-24.762931	-0.02105	-25.091031
2.2299	-25.113491	0.34953	-24.763961	-0.00875	-25.104741
2.2799	-25.114212	0.34991	-24.764302	-0.00846	-25.105752
2.3049	-25.114347	0.35010	-24.764247	-0.00829	-25.106057
2.3290	-25.114341	0.35030	-24.764041	-0.00812	-25.106221
2.3549	-25.114198	0.35049	-24.763708	-0.00794	-25.106258
2.3799	-25.113941	0.35067	-24.763271	-0.00774	-25.106201
2.4299	-25.113084	0.35103	-24.762054	-0.00731	-25.105774
2.4799	-25.111839	0.35136	-24.760479	-0.00682	-25.105019
2.8299	-25.095770	0.35229	-24.743480	-0.00216	-25.09361

<sup>a</sup>The energy of BH is obtained from our SCF calculation.

TABLE III. Energy vs internuclear separation data for BH, BH<sup>+</sup>, and BH<sup>-</sup> (in a. u.).

$R$ (a. u.)	$E$ (BH)	$E$ (BH <sup>+</sup> ) - 0.34997	$E$ (BH <sup>-</sup> ) - 0.00817
2.1299	0.00348 <sup>a</sup>	0.00228	0.01618
2.1799	0.00170	0.00088	0.01458
2.2299	0.00059	0.00015	0.00117
2.2799	0.00006	0.00000	0.00035
2.3049	0.00000	0.00013	0.00012
2.3299	0.00006	0.00039	0.00001
2.3549	0.00023	0.00075	0.00000
2.3799	0.00052	0.00122	0.00009
2.4299	0.00137	0.00243	0.00051
2.4799	0.00258	0.00397	0.00123

<sup>a</sup>The energy of BH is obtained from a Morse curve using the spectroscopic data of Ref. 18. The zero of energy is chosen to coincide with the minimum energy point of our SCF calculations on BH.

0.025 a. u. shorter than the experimentally determined bond length. However, the computed vertical ionization potential at  $R = 2.3049$  a. u. is also 0.53 eV. We have also investigated the relative accuracy of Koopmans' theorem and our third-order results as a function of  $R$  for the BH ionization potential. We find that the difference between our calculated ionization energy and  $-\epsilon_{3\sigma}$  varies by only 0.06 eV over the range of internuclear distances studied here. This leads us to speculate that, if one is interested in results whose precision is  $\pm 0.2$  eV, then it may be sufficient to carry out a third-order calculation at a single internuclear separation to establish the (approximately constant) Koopmans' theorem defect followed by Koopmans' theorem (SCF) calculations at other values of  $R$ . We are presently investigating the validity of this approach for other ion-neutral energy differences.

We have used the results of Tables II and III to calculate the equilibrium bond lengths and vibrational frequencies of BH<sup>+</sup> and BH<sup>-</sup> given in Table IV. Because there is no available experimental data on the spectroscopic parameters for the diabatic potential curve of BH<sup>-</sup>, we cannot make any firm conclusions concerning the values of  $\omega_e$  and  $R_e$  that are reported for BH<sup>-</sup> in Table IV. The fact that our atomic orbital basis is not optimum for describing the BH<sup>-</sup> diabatic curve probably means that our computed spectroscopic parameters for this curve are not highly accurate.

On the other hand,  $R_e$  and  $\omega_e$ , the spectroscopic parameters which we obtain for BH<sup>+</sup>(<sup>2</sup> $\Sigma^+$ ), can be seen from Table IV to be in reasonable agreement with those listed in Herzberg's tabulation.<sup>18</sup> The vibrational frequencies which result from either the SCF energy curve or the Morse curve for BH are within 152 cm<sup>-1</sup> of the experimental quantity. The equilibrium bond lengths obtained for BH<sup>+</sup> lie within 0.03 a. u. of the experimental  $R_e$ . Because BH<sup>+</sup> has both a shorter bond length and a higher vibrational frequency than BH, we can infer that the 3 $\sigma$  orbital of BH is somewhat antibonding in character. Analogous observations concerning BH<sup>-</sup> suggest that the 1 $\pi$  orbital of BH is also somewhat antibonding.

To better understand the bonding in BH, consider the

data of Table V in which the dominant expansion coefficients of the 2 $\sigma$  and 3 $\sigma$  molecular orbitals of BH and the isoelectronic BeH<sup>-</sup>, which has also been investigated in our research laboratory,<sup>9</sup> are listed next to the corresponding Slater-type basis functions. We find that the 2 $\sigma$  orbital of BH is a bonding combination of a 1 $s_H$  function and a partial 2  $sp$  hybrid on the boron nucleus, with higher density on the more electronegative boron. In comparison, the 2 $\sigma$  orbital of BeH<sup>-</sup> is a bonding combination of a 1 $s_H$  function and a partial  $sp$  hybrid on the Be, with higher density in this case on the more electronegative hydrogen atom. The 3 $\sigma$  orbitals of BH and BeH<sup>-</sup> differ in that the 3 $\sigma$  orbital of BH is an antibonding combination of 2 $s_B$  functions and 1 $s_H$  functions with a contribution of -0.39 from a 2 $p_B$  function, whereas the more diffuse 3 $\sigma$  orbital of BeH<sup>-</sup> is an antibonding combination of 2 $s_{B^*}$  functions and 1 $s_H$  functions with somewhat less 2 $p_{B^*}$  character involved. Thus the principal differences between the electron density of BH and that of BeH<sup>-</sup> are the more diffuse nature of the BeH<sup>-</sup> 3 $\sigma$  orbital and the polarization of the electron density toward the boron nucleus in BH and toward the hydrogen nucleus in BeH<sup>-</sup>.

In conclusion, we see that our third-order EOM calculations are capable of yielding valuable new information concerning the <sup>2</sup> $\Sigma^+$  state of BH<sup>+</sup> and the <sup>2</sup> $\pi$  diabatic state of BH<sup>-</sup>. The  $R_e$  and  $\omega_e$  values obtained for BH from our SCF calculation and for BH<sup>+</sup> from our ionization potential calculation are in reasonable agreement with experimental results. Our computed ionization potential is also in quite good agreement with experiment. The <sup>2</sup> $\pi$  state of BH<sup>-</sup> was found to be energetically less stable than a BH molecule and an electron infinitely far away. Thus the electron affinity of BH is negative and the <sup>2</sup> $\pi$  curve which we compute is probably a rather crude approximation to the diabatic <sup>2</sup> $\pi$  curve of BH<sup>-</sup>.

We believe that the above comparison between the electron densities of BH and BeH<sup>-</sup> has shed new light on the bonding both in the negative molecular ion BeH<sup>-</sup> and in BH itself. In this isoelectronic pair, the electron density difference can be interpreted in terms of the effects of electron-electron repulsions and electron-nuclear attractions. The larger electron repulsions in BeH<sup>-</sup>

TABLE IV. Vibrational frequencies and bond lengths.

Species	$\omega_e$ (cm <sup>-1</sup> )	$R_e$ (a. u.)	Source of $E$ (BH)
BH( <sup>1</sup> $\Sigma^+$ )	2531	2.317	SCF energy of BH
	2343	2.305	Morse curve for BH <sup>a</sup>
	2366	2.330	Herzberg <sup>b</sup>
BH <sup>+</sup> ( <sup>2</sup> $\Sigma^+$ )	2587	2.284	SCF energy for BH
	2483	2.270	Morse curve for BH <sup>a</sup>
	2435	2.296	Herzberg <sup>b</sup>
BH <sup>-</sup> ( <sup>2</sup> $\pi$ )	2262	2.355	SCF energy for BH
	2087	2.355	Morse curve for BH <sup>a</sup>

<sup>a</sup>A least-squares fit to a quadratic function of  $R$  was made to data points generated from an analytical Morse potential whose parameters are given by Herzberg.<sup>b</sup>

<sup>b</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1961), p. 510.

TABLE V. The  $2\sigma$  and  $3\sigma$  orbitals of BH ( $R=2.3299$  a. u.) and  $\text{BeH}^-$  ( $R=2.660$  a. u.).

	$\text{BeH}^-$			BH		
	$\zeta$	A. O.	Coefficient	$\zeta$	A. O.	Coefficient
$2\sigma$	2.948	$1s_{\text{Be}}$	-0.151	3.9139	$1s_{\text{B}}$	-0.185
	1.1500	$2s_{\text{Be}}$	0.392	1.5657	$2s_{\text{B}}$	0.631
	1.0500	$1s_{\text{H}}$	0.643	1.1827	$1s_{\text{H}}$	0.473
	0.3000	$1s_{\text{H}}$	0.159	1.5401	$2p\sigma_{\text{B}}$	0.245
	1.046	$2p\sigma_{\text{Be}}$	0.133			
$3\sigma$	1.1500	$2s_{\text{Be}}$	0.568	0.9796	$2s_{\text{B}}$	0.659
	0.4250	$2s_{\text{Be}}$	1.080	1.5657	$2s_{\text{B}}$	0.258
	1.0500	$1s_{\text{H}}$	-0.190	0.4000	$2s_{\text{B}}$	0.224
	0.3000	$1s_{\text{H}}$	-0.738	1.1827	$1s_{\text{H}}$	-0.265
	0.8080	$2p\sigma_{\text{Be}}$	-0.286	0.4000	$1s_{\text{H}}$	-0.432
	1.5000	$2p\sigma_{\text{Be}}$	-0.126	1.5401	$2p\sigma_{\text{B}}$	-0.39

tend to make the valence orbitals of this ion more diffuse than those of BH. The higher effective nuclear charge, and hence electronegativity, of boron tends to polarize the electron density in BH toward the boron, whereas the charge density in  $\text{BeH}^-$  is polarized toward the hydrogen atom.

Our observation that the difference between our third-order  $^1\Sigma^+ \rightarrow ^2\Sigma^+$  ionization potential of BH and the Koopmans' theorem estimate varies by only 0.06 eV over the range of internuclear distances studied here is, we believe, very worthy of much future investigation. In our study of  $\text{BeH}^-$  we have also found the Koopmans' theorem defect to be a slowly varying function of internuclear distance. We are presently investigating this question in the course of our work on  $\text{SH}^-$ ,  $\text{MgH}^-$ ,  $\text{NH}_2^-$ ,  $\text{CH}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{O}_3^-$ . If similar observations of slowly varying Koopmans' theorem defects are made for such a wide range of species, we will be in a position to infer that the orbital reorganization and correlation energy contributions to computed ion-molecule energy differences is not very strongly dependent upon  $R$  for the range of internuclear distances which we have studied. Our conclusions concerning this very interesting and important question will be published in papers dealing with the stability and bonding of the previously mentioned group of negative molecular ions.

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