

# A Variational Wave Function for $2p^2$ -Orbitals in Atomic Negative Ions

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A variational wave function is used to describe the binding energy of atomic negative ions using a two-electron system in the  $2p^2$ -state. Each electron is described by a modified screened hydrogenic wave function involving two free screening parameters denoted by  $c$  and  $a$ . The model is applied to hydrogen, helium, lithium, and boron anions, where the optimum values of the screening parameters are deduced through fitting the optimized energy to available experimental and theoretical values. The behavior of the optimum wave function for each anion is also investigated as a function of electronic radial distance and compared with its counterpart in the screened hydrogenic model and the Hartree–Fock method.

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## 1. INTRODUCTION

Negative ions play an important role in applied physics such as the development of gas lasers, gas discharge devices, plasma chemistry (Smirnov, 1982) and providing the basis for ultrasensitive accelerator mass spectroscopy (AMS) (Paul, 1993), and secondary negative-ion mass spectroscopy (SIMS) (Winter *et al.*, 1991).

The additional electron of a negative ion is bound by short-range potential rather than by a Coulomb potential. This implies that most negative ions only exist in one bound electronic configuration as opposed to the infinite number of Rydberg states present in neutral atoms and positive ions (Lee *et al.*, 1996). They are more sensitive to correlation effects than the corresponding isoelectronic neutral atoms or positive ions because for this member of a sequence the core field is weakest and, therefore, the masking of the interelectronic interaction is reduced (Weiss, 1995; Yamagami *et al.*, 1994).

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The electron affinity (EA) of an atom A is defined as the difference between the total energies ( $E_{\text{tot.}}$ ) of the ground states of A and its negative ion  $A^-$  (Andersen *et al.*, 1999; Hotop and Lineberger, 1985):

$$\text{EA}(A) = E_{\text{tot.}}(A) - E_{\text{tot.}}(A^-).$$

Calculation of excitation energies and electron affinities with suitable accuracy, is crucial in predicting new stable ions or excited states and help the experimentalist in narrowing the range to be scanned for a weak or hidden transition (Olsen *et al.*, 1994). Since the EA of the atom is much smaller than its ionization energy, one would expect that the size of the negative ion is much greater than the size of the atom.

The electron-binding energy of a negative ion can be calculated by a variational method, in a way similar to that used to determine the ionization energy of an atom (Waghmare, 1996). Reasonable simplifications of the variational technique can be used to calculate the electron-binding energy of negative ions conferring a large number of electrons. The reliability of the final result then depends on the extent to which these simplifications are justified Arias de Saavedra *et al.*, 1994; Baker *et al.*, 1990; Weiss, 1995.

Two-electron atomic models involving single-particle orbitals are useful for exploring the electronic screening and correlation effects. The single-particle orbitals could be screened hydrogenic (SH), with a single free parameter, or modified using two or more parameters (Porras, 1995).

In this paper, Slater-type 2p atomic orbitals with two free screening parameters are used to describe the two outermost valence electrons in  $H^-$ ,  $He^-$ ,  $Li^-$ , and  $B^-$ . The first parameter,  $c$ , manifests a constant average electronic screening of the nuclear charge whilst the second one,  $a$ , provides spatial correlation correction through its variable screening effect built in the radial wave function. The total energy of each anion is calculated using a variational method. A similar approach was applied to the ground state of helium-like neutral atoms by Porras (1995). Banyard and Keeble (1994) used configuration-interaction wave functions to investigate Coulomb correlations in  $He(2p^2:3P)$ -like ions.

## 2. THEORY

Using atomic units, the Hamiltonian of the two-electron system can be written as (Lindgren and Morrison, 1986; Weissbluth, 1978)

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (1)$$

where  $\nabla^2$  is the Laplacian operator,  $r_1$  and  $r_2$  are the respective distances between the electrons and the center of the nucleus, and  $r_{12}$  is the distance between the two

electrons. The total energy of the system is

$$E = T + V_1 + V_{12}, \quad (2)$$

where the first term,  $T$ , is the total kinetic energy for the two electrons, the second term,  $V_1$ , represents the Coulomb interaction between the two electrons and the nucleus, and the third term,  $V_{12}$ , is the electron–electron interaction.

The variational technique is simply based on the calculation of the expectation value of the energy of the two-electron system assuming a trial wave function with two independent parameters ( $a$  and  $c$ ), and then the minimization of the energy with respect to both parameters ( $\partial E/\partial a = 0$  and  $\partial E/\partial c = 0$ ). The optimum values of these parameters are obtained when the least approximate energy of the system is closest to the real value. Consequently, the energy and the wave function of the system are determined.

According to the one electron approximation the total wave function of the system is

$$\Psi(\bar{r}_1, \bar{r}_2) = \Phi(r_1)\Phi(r_2)Y_{lm}(\theta_1, \varphi_1)Y_{l'm'}(\theta_2, \varphi_2), \quad (3)$$

where the radial part of the single-particle wave function  $\Phi(r)$  for a 2p-orbital is assumed to be modified screened hydrogenic (MSH):

$$\Phi(r) = Br \exp\left\{-Z\left[\frac{(1-c)r}{2} - \frac{c}{2a}e^{-ar}\right]\right\}, \quad (4)$$

where  $a$  and  $c$  are free parameters. When  $c = 0$  we obtain the radial unscreened hydrogenic wave function of the 2p state, that is,

$$\Phi_0(r) = B_0r \exp\left\{-\frac{Zr}{2}\right\}. \quad (5)$$

When  $a \rightarrow \infty$ , we obtain the radial SH wave function of the 2p state, that is,

$$\Phi_1(r) = B_1r \exp\left\{-Z\left[\frac{(1-c)r}{2}\right]\right\}, \quad (6)$$

where  $Zc$  is the screening parameter. The normalization constant  $B$  in Eq. (4) can be determined from the normalization condition by introducing the following coordinate transformation:

$$x = \exp(-ar). \quad (7a)$$

We obtain the following expression for  $B$ :

$$B^2 = \frac{a^5}{I\left(4, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right)}, \quad (7b)$$

where  $I$  is defined by the relation

$$I(n, \alpha, \beta) = \int_0^1 (-\ln x)^n x^{\alpha-1} e^{\beta x} dx, \quad (8a)$$

or

$$I(n, \alpha, \beta) = \sum_{k=0}^n \frac{\beta^k}{k!} \frac{n!}{(k + \alpha)^{n+1}} \quad (8b)$$

The expectation value of the total kinetic energy of the two electrons is

$$T = \langle \Psi | -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) | \Psi \rangle. \quad (9)$$

From the symmetry of the two electrons, the total kinetic energy of the system is

$$T = 2 \int_0^\infty r^2 \Phi(r) \left[ -\frac{1}{2r^2} \frac{d}{dr} \left( r^2 \frac{d\Phi(r)}{dr} \right) + \frac{l(l+1)}{2r^2} \Phi(r) \right] dr, \quad (10)$$

where  $l$  is the orbital angular momentum of the electron. The result of integration leads to nine energy terms besides the last term, which arises from the centrifugal barrier,  $V_c$ .

$$T = T_1 + T_2 + T_3 + T_4 + T_5 + T_6 + T_7 + T_8 + T_9 + T_{10}, \quad (11)$$

where

$$\begin{aligned} T_1 &= Z(1-c)B^2 \int_0^\infty r^3 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\ &= \frac{Z(1-c)B^2}{a^4} I\left(3, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right), \end{aligned} \quad (12)$$

$$\begin{aligned} T_2 &= ZcB^2 \int_0^\infty r^3 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) \exp(-ar) dr, \\ &= \frac{ZcB^2}{a^4} I\left(3, \frac{Z(1-c)}{a} + 1, \frac{Zc}{a}\right), \end{aligned} \quad (13)$$

$$\begin{aligned} T_3 &= -\frac{ZcaB^2}{2} \int_0^\infty r^4 \exp(-ar) \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\ &= -\frac{ZcaB^2}{2a^5} I\left(4, \frac{Z(1-c)}{a} + 1, \frac{Zc}{a}\right), \end{aligned} \quad (14)$$

$$\begin{aligned} T_4 &= -\frac{Z^2(1-c)^2B^2}{4} \int_0^\infty r^4 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\ &= -\frac{Z^2(1-c)^2B^2}{4a^5} I\left(4, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right), \end{aligned} \quad (15)$$

$$\begin{aligned}
 T_5 &= -\frac{Z^2c(1-c)B^2}{2} \int_0^\infty r^4 \exp(-ar) \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= -\frac{Z^2c(1-c)B^2}{2a^5} I\left(4, \frac{Z(1-c)}{a} + 1, \frac{Zc}{a}\right), \tag{16}
 \end{aligned}$$

$$\begin{aligned}
 T_6 &= -\frac{Z^2c^2B^2}{4} \int_0^\infty r^4 \exp(-2ar) \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= -\frac{Z^2c^2B^2}{4a^5} I\left(4, \frac{Z(1-c)}{a} + 2, \frac{Zc}{a}\right), \tag{17}
 \end{aligned}$$

$$\begin{aligned}
 T_7 &= -2B^2 \int_0^\infty r^2 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= -\frac{2B^2}{a^3} I\left(2, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right), \tag{18}
 \end{aligned}$$

$$\begin{aligned}
 T_8 &= Z(1-c)B^2 \int_0^\infty r^3 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= \frac{Z(1-c)B^2}{a^4} I\left(3, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right), \tag{19}
 \end{aligned}$$

$$\begin{aligned}
 T_9 &= ZcB^2 \int_0^\infty r^3 \exp(-ar) \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= \frac{ZcB^2}{a^4} I\left(3, \frac{Z(1-c)}{a} + 1, \frac{Zc}{a}\right), \tag{20}
 \end{aligned}$$

$$\begin{aligned}
 T_{10} &= 2B^2 \int_0^\infty r^2 \exp(-Z(1-c)r) \exp\left(\frac{Zc}{a} e^{-ar}\right) dr, \\
 &= \frac{2B^2}{a^3} I\left(2, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right). \tag{21}
 \end{aligned}$$

The second step now is to calculate the expectation value of the Coulomb electron–nucleus interaction operator:

$$V_1 = \langle \Psi | -\frac{Z}{r_1} - \frac{Z}{r_2} | \Psi \rangle. \tag{22}$$

Assuming that the two electrons are identical, it becomes

$$V_1 = -2Z \int_0^\infty r |\Phi(r)|^2 dr. \tag{23}$$

Using the same mathematical approach applied to calculate the first term of the kinetic energy, we will obtain the final result as

$$V_1 = \frac{-2ZB^2}{a^4} I\left(3, \frac{Z(1-c)}{a}, \frac{Zc}{a}\right). \quad (24)$$

Finally we will calculate the electron–electron interaction:

$$V_{12} = \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle, \quad (25)$$

where the detailed calculations of this term are shown in Appendix A.

$$V_{12} = 2 \frac{B^4}{a^9} J\left(\frac{Z(1-c)}{a}, \frac{Zc}{a}\right) + 2.537039896 \frac{B^4}{a^9} J_1\left(\frac{Z(1-c)}{a}, \frac{Zc}{a}\right), \quad (26)$$

where the  $J$ -integrals are defined as follows:

$$J(\alpha, \beta) = \int_0^1 (-\ln x)^3 x^{\alpha-1} e^{\beta x} \left[ \int_x^1 (-\ln y)^4 y^{\alpha-1} e^{\beta y} dy \right] dx, \quad (27a)$$

and

$$J_1(\alpha, \beta) = \int_0^1 (-\ln x)^{\alpha-1} e^{\beta x} \left[ \int_x^1 (-\ln y)^6 y^{\alpha-1} e^{\beta y} dy \right] dx. \quad (27b)$$

These integrals are described in Appendix B.

### 3. RESULTS

The total energy for the negative ions of hydrogen, helium, lithium, and boron is computed using a Fortran program, which minimizes the total energy expressed in Eq. (2) with respect to both parameters  $a$  and  $c$ . The necessary quantities to calculate the electron affinity for the parent neutral atom of each anion are tabulated in Tables I and II. In Table I, we present the free parameters  $a$  and  $c$ , the total energy of the two-electron system in 2p-state, and the electron affinity (EA). In our calculations we use atomic units (a.u.) for total energy and eV for the EA, where 1 a.u. = 27.211 3957 eV (Cohen and Taylor, 1987). In Table II, we display the calculated values of the following quantities for  $H^-$ ,  $He^-$ ,  $Li^-$ , and  $B^-$ : the normalization constant,  $B$ , the Coulomb interaction between the nucleus and the two-electron system,  $V_1$ , the interaction potential between the two electrons,  $V_{12}$ , the total kinetic energy,  $T$ , and the virial ratio  $-V/T$ , where  $V = V_1 + V_{12}$ . From Table II, the virial ratio is satisfied up to 4 decimal digits in all cases and the corresponding electron affinity in Table I is set very close to the latest available experimental value. Although we were able to satisfy the virial coefficient up to 15 decimal digits, the corresponding calculated value of the EA in all cases was

**Table I.** Calculated Optimum Values of Total Energy,  $E$ , and the Corresponding Electron Affinity, EA, for  $H^-$ ,  $He^-$ ,  $Li^-$ , and  $B^-$ 

$Z$	$c$	$a$	$-E$ (a.u.)	EA (eV) [this work]	EA (eV) [experimental]
1	0.305 226 46	0.224 106 33	0.152 716 66	0.754 209 003	0.754 195 (19) <sup>d</sup>
2	0.157 563 79	0.143 110 00	0.906 399 68	0.077 400 350	0.077 516 (6) <sup>b</sup>
3	0.170 943	0.477 9336	1.842 771 108	0.618 001 847	0.618 049 (21) <sup>c</sup>
5	0.131 670	0.612 725 40	5.517 929 62	0.279 001 6679	0.279 723 (25) <sup>d</sup>

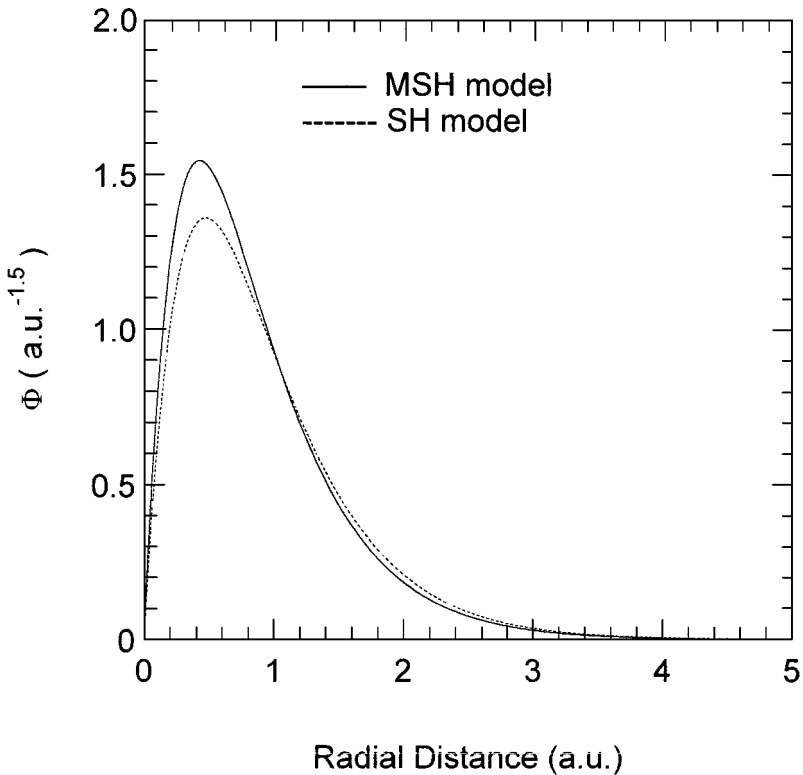
<sup>a</sup>Lykke *et al.*, 1991.<sup>b</sup>Kristensen *et al.*, 1997.<sup>c</sup>Haeffler *et al.*, 1996.<sup>d</sup>Scheer *et al.*, 1998.

less closer to the experimental value within 0.3%, whereas the change in optimum values of  $a$  and  $c$  never exceeds  $10^{-4}$ . The reference energy is chosen to be the unperturbed  $2p$  level in a single-electron ion and the binding energy of the anion is assumed equal to the energy required to remove an electron from this orbital according to Koopmans theorem (Weissbluth, 1978). Recent elaborate numerical calculations of the EA of hydrogen by Drake and Martin (1998), Baker *et al.* (1990), and Arias de Saavedra *et al.* (1994) yield values with uncertainties of  $10^{-7}$  eV. The theoretical result of Xi and Fischer (1996) for helium is 0.077 37 eV, using multi-configuration H-F (MCHF) orbitals. Recently, Moccia and Spizzo (1990) obtained a theoretical value of 0.6175 eV for lithium. The recent theoretical values of EA of boron include 0.279 eV obtained by Eliav *et al.* (1997), using the relativistic coupled-cluster (RCC) method, and 0.2795 eV obtained by Fischer *et al.* (1995), using MCHF method.

The behavior of the normalized radial wave function of  $B^-$  is presented in Fig. 1. The solid curve represents the present model using Eq. (4) and the values of  $c$  and  $a$  listed in Table I, whereas the corresponding radial SH wave function of Eq. (6) is represented by the dashed curve. The two curves intersect at a core radius,  $r_c$ , of 1.042 a.u. The peak of the solid curve lies at  $r = 0.421$  a.u. whereas

**Table II.** Calculated Values of the Normalization Constant and the Energy Terms Used to Obtain the Total Energy of  $H^-$ ,  $He^-$ ,  $Li^-$ , and  $B^-$  Listed in Table I

	$H^-$	$He^-$	$Li^-$	$B^-$
$B^2$	0.004 715 490 384	0.126 566 742 084	2.504 175 300 039	36.437 506 740 115
$-V_1$	0.390 026 071 936	1.903 678 388 88	4.070 562 071 828	11.742 447 021 470
$V_{12}$	0.084 595 498 971	0.090 968 000 023	0.385 152 571 525	0.706 815 260 4548
$-V$	0.305 430 572 965	1.812 710 388 866	3.685 409 500 303	11.035 631 761 015
$T$	0.152 713 910 652	0.906 310 711 038	1.842 698 417 568	5.517 702 141 578
$-V/T$	2.000 018 018 408	2.000 098 163 683	2.000 006 873 163	2.000 004 1226 919



**Fig. 1.** The normalized radial wave function of  $B^-$  plotted as a function of electronic radial distance over the range 0–5 a.u., using the present model (solid curve) and the SH model (dashed curve).

the dashed curve has its peak at  $r = 0.461$  a.u., which implies that the parameter  $a$  produces an inward shift in the electronic charge density. The properties of all wave functions are summarized in Table III, where  $r_m$  is the most probable radial location of the electron and  $r_c$  is the core radius at which the MSH and SH functions are equal. It shows that the extent of the wave function and the characteristic core radius decrease with increasing atomic number. The core radius is slightly less than  $\langle r \rangle$ . We found that the MSH electronic charge density falls down to 31% of its maximum value at  $r = r_c$  for all anions.

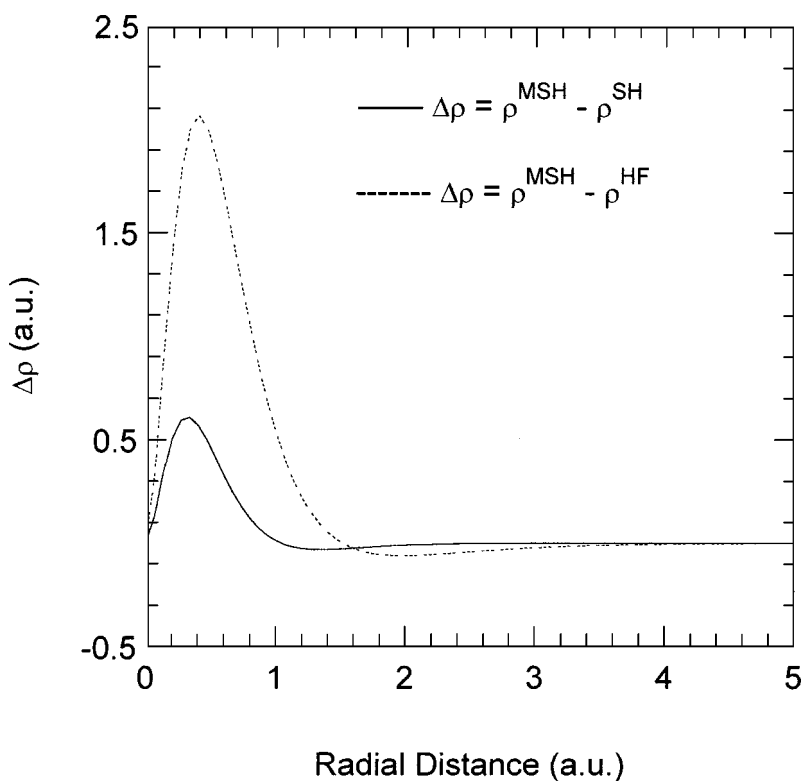
To demonstrate the correlation effect of the parameter  $a$ , the difference between the electronic charge densities of the present model and the SH model is plotted as a function of radial distance, for  $B^-$ , in Fig. 2. It shows that this difference is positive in the core region ( $r < r_c$ ) and very close to zero in the outer region.



**Table III.** Properties of the Modified Screened Hydrogenic (MSH) Wave Functions

Anion	$r_m$	$r_c$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$
H <sup>-</sup>	2.2846	6.2124	6.588 839	53.223 763	0.195 013	0.052 497
He <sup>-</sup>	1.0220	2.5650	2.648 852	8.487 421	0.475 920	0.304 713
Li <sup>-</sup>	0.7101	1.7836	1.865 663	4.228 766	0.677 904	0.622 809
B <sup>-</sup>	0.4208	1.0421	1.074 349	1.396 515	1.174 245	1.857 377

The dashed curve represents the same property calculated relative to HF wave functions of  $2p$  orbital used in the calculation of Ramsbottom and Bell (1995), where the difference is almost three times its value compared with the SH case. The core radius relative to HF function is 1.5180 and 1.0352 a.u. relative to SH



**Fig. 2.** The difference in electronic charge density,  $\Delta\rho$ , between the present model and the SH [HF] model, represented by solid [dashed] curve, as a function of radial distance over the range 0–5 a.u.

function. The reason for that is the lack of proper correlation among electrons of opposite spin in the Hartree–Fock method (Weissbluth, 1978).

Table I shows that the boron anion has the smallest  $c$ -value but the largest  $a$ -value, which implies that electron correlations play a dominant role in boron anion, which is the most weakly bound stable ion among the lightest elements. The lightest anion,  $H^-$ , has a  $c$ -value, which is double each other value reflecting the strong screening effect of the core 1s-electron.

#### 4. CONCLUSION

In this work, the ground state of a negative ion is treated as a two-electron system in the  $2p^2$  configuration. Each electron is described by a MSH wave function that involves two free adjustable parameters. The binding energy of the extra electron in each atomic anion is calculated using a variational technique which leads to a set of input parameters ( $a$  and  $c$ ) for optimizing the total energy of the anion keeping  $V/T = -2.0000$  in all cases. Although the HF method will always give the most accurate value for the energy, the accuracy of an approximate wave function is not entirely determined by the accuracy of the corresponding variational energy.

The optimum radial wave function allows an inward shift for the electronic charge density, increasing its value in the core region ( $r < 6.21$  a.u. for  $H^-$  and  $r < 1.04$  a.u. for  $B^-$ ) and lowering it in the outer region ( $r > 6.21$  a.u. for  $H^-$  and  $r > 1.04$  a.u. for  $B^-$ ). The screening effect is thus improved by introducing the second screening parameter  $a$ . In other words, the electron correlation is taken into account through the variable screening effect of the parameter  $a$ .

The size of the anion is determined by the expectation value of the electronic radial distance,  $\langle r \rangle$ , which is larger than the size of the parent neutral atom. We found that the optimum wave functions deduced from the MSH model lead to values of  $\langle r \rangle$  that are almost inversely proportional to the atomic number,  $Z$ , but  $\langle r^{-1} \rangle$  values are directly proportional to  $Z$ .

#### APPENDIX A: THE INTERACTION TERM

The general definition of the interaction term is

$$V_{12} = \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle, \quad (\text{A.1})$$

where  $\Psi$  is the two-electron wave function defined as

$$\Psi(r_1, r_2, \theta_1, \theta_2, \varphi_1, \varphi_2) = \Phi(r_1)Y_{lm}(\theta_1, \varphi_1)\Phi(r_2)Y_{l'm'}(\theta_2, \varphi_2), \quad (\text{A.2})$$

Now we will rewrite Eq. (A.1) in the integral form as

$$V_{12} = \int \Psi^*(r_1, r_2, \theta_1, \theta_2, \varphi_1, \varphi_2) \frac{1}{r_{12}} \Psi(r_1, r_2, \theta_1, \theta_2, \varphi_1, \varphi_2) d\bar{r}_1 d\bar{r}_2. \quad (\text{A.3})$$

Write  $1/r_{12}$  in terms of the Legendre polynomial as follows:

$$\frac{1}{r_{12}} = \sum_{L=0} \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos \omega_{12}) = \sum_{L=0} \frac{r_{<}^L}{r_{>}^{L+1}} \sum_{M=-L}^L \frac{4\pi}{2L+1} Y_{LM}(\theta_1, \varphi_1) Y_{LM}(\theta_2, \varphi_2). \quad (\text{A.4})$$

The integral in Eq. (A.3) vanishes unless the triangle conditions are satisfied ( $-m' + m + M = 0$  and  $l' + l + L$  is an even integer) (Weissbluth, 1978) with  $L = 0, 2; m' = m = 0$ , for the case  $l' = l = 1$ .

For the case  $L = 0$ , the angular part in Eq. (A.3) equals unity and the radial part is

$$(V_{12})_{L=0} = \int_{r_1=0}^{\infty} \left[ \int_{r_2=0}^{r_1} \Phi^2(r_2) r_2^2 \frac{1}{r_1} dr_2 + \int_{r_1}^{\infty} \Phi^2(r_2) r_2^2 \frac{1}{r_2} dr_2 \right] \Phi^2(r_1) r_1^2 dr_1. \quad (\text{A.5})$$

The second term in Eq. (A.5) is equivalent to

$$\int_{r_1=0}^{\infty} \left[ \int_{r_1}^{\infty} \Phi^2(r_2) r_2^2 \frac{1}{r_2} dr_2 \right] \Phi^2(r_1) r_1^2 dr_1 = \int_{r_2=0}^{\infty} \left[ \int_0^{r_2} \Phi^2(r_1) r_1^2 dr_1 \right] \Phi^2(r_2) r_2 dr_2, \quad (\text{A.6})$$

then

$$\begin{aligned} (V_{12})_{L=0} &= \int_0^{\infty} dr_1 r_1 \Phi^2(r_1) \int_0^{r_1} dr_2 r_2^2 \Phi^2(r_2) \\ &\quad + \int_0^{\infty} dr_2 r_2 \Phi^2(r_2) \int_0^{r_2} dr_1 r_1^2 \Phi^2(r_1). \end{aligned} \quad (\text{A.7})$$

The final result is

$$(V_{12})_{L=0} = 2 \int_0^{\infty} r \Phi^2(r) dr \int_0^r s^2 \Phi^2(s) ds. \quad (\text{A.8})$$

The interaction term for the case  $L = 2$  is

$$\begin{aligned} (V_{12})_{L=2} &= \frac{8}{25} \sqrt{5\pi} \int_0^{\infty} dr_1 r_1^2 \Phi^2(r_1) \\ &\quad \times \left[ \int_0^{r_1} dr_2 r_2^2 \Phi^2(r_2) \frac{r_2^2}{r_1^3} + \int_{r_1}^{\infty} dr_2 r_2^2 \Phi^2(r_2) \frac{r_1^2}{r_2^3} \right]. \end{aligned} \quad (\text{A.9})$$

This integral is equivalent to

$$(V_{12})_{L=2} = \frac{16}{25} \sqrt{5\pi} \int_0^\infty dr_1 r_1^2 \Phi^2(r_1) \left[ \int_0^{r_1} dr_2 r_2^2 \Phi^2(r_2) \frac{r_2^2}{r_1^3} \right]. \tag{A.10}$$

Then, the interaction term becomes

$$V_{12} = 2 \int_0^\infty r \Phi^2(r) dr \int_0^r s^2 \Phi^2(s) ds + \frac{16}{25} \sqrt{5\pi} \int_0^\infty dr \frac{1}{r} \Phi^2(r) \left[ \int_0^r ds s^4 \Phi^2(s) \right]. \tag{A.11}$$

**APPENDIX B: CALCULATION OF  $J$  INTEGRAL**

The usual definition of the integral  $J$  is

$$J(\alpha, \beta) = \int_0^1 (-\ln x)^3 x^{\alpha-1} \exp(\beta x) dx \int_x^1 (-\ln y)^4 y^{\alpha-1} \exp(\beta y) dy. \tag{B.1}$$

The integration on  $y$  is written as follows:

$$\int_x^1 (-\ln y)^4 y^{\alpha-1} \exp(\beta y) dy = - \int_0^x (-\ln y)^4 y^{\alpha-1} \exp(\beta y) dy + \int_0^1 (-\ln y)^4 \exp(\beta y) y^{\alpha-1} dy,$$

where the last term is defined by integral  $I$ :

$$\int_0^1 (-\ln y)^4 \exp(\beta y) y^{\alpha-1} dy = I(4, \alpha, \beta), \tag{B.2}$$

and the first term is written as

$$\int_0^x (-\ln y)^4 \exp(\beta y) y^{\alpha-1} dy = \left[ \frac{d^4}{ds^4} \int_0^x \exp(\beta y) y^{\alpha-s-1} dy \right]_{s=0}. \tag{B.3}$$

Expressing the exponential as a power series, the integral becomes

$$\sum_{k=0} \frac{\beta^k}{k!} \left[ \frac{d^4}{ds^4} \int_0^x y^{\alpha+k-s-1} dy \right]_{s=0} = \sum_{k=0} \frac{\beta^k}{k!} \frac{d^4}{ds^4} \left( \frac{x^{k+\alpha-s}}{k+\alpha-s} \right)_{s=0}, \tag{B.4}$$

when  $s = 0$ , then this equation becomes

$$\sum_{k=0} \frac{\beta^k}{k!} \frac{d^4}{ds^4} \left( \frac{x^{k+\alpha-s}}{k+\alpha-s} \right)_{s=0} = \sum_{k=0} \frac{\beta^k}{k!} \left[ \frac{x^{k+\alpha}(-\ln x)^4}{(k+\alpha)} + 4 \frac{x^{k+\alpha}(-\ln x)^3}{(k+\alpha)^2} + 12 \frac{x^{k+\alpha}(-\ln x)^2}{(k+\alpha)^3} + 24 \frac{x^{k+\alpha}(-\ln x)}{(k+\alpha)^4} + 24 \frac{x^{k+\alpha}}{(k+\alpha)^5} \right]. \quad (\text{B.5})$$

Substituting Eq. (B.5) into Eq. (B.1), we obtain

$$J(\alpha, \beta) = I(3, \alpha, \beta)I(4, \alpha, \beta) - \sum_{k=0} \frac{\beta^k}{k!(\alpha+k)} \left[ I(7, 2\alpha+k, \beta) + \frac{4}{\alpha+k} I(6, 2\alpha+k, \beta) + \frac{12}{(\alpha+k)^2} I(5, 2\alpha+k, \beta) + \frac{24}{(\alpha+k)^3} \times I(4, 2\alpha+k, \beta) + \frac{24}{(\alpha+k)^4} I(3, 2\alpha+k, \beta) \right]. \quad (\text{B.6})$$

The  $J_1$ -integral can be done in the same mathematical manipulation, the final result is

$$J_1(\alpha, \beta) = I(1, \alpha, \beta)I(6, \alpha, \beta) - \sum_{k=0} \frac{\beta^k}{k!(\alpha+k)} \left[ I(7, 2\alpha+k, \beta) + \frac{6}{\alpha+k} I(6, 2\alpha+k, \beta) + \frac{30}{(\alpha+k)^2} I(5, 2\alpha+k, \beta) + \frac{120}{(\alpha+k)^3} \times I(4, 2\alpha+k, \beta) + \frac{360}{(\alpha+k)^4} \times I(3, 2\alpha+k, \beta) + \frac{720}{(\alpha+k)^5} I(2, 2\alpha+k, \beta) + \frac{720}{(\alpha+k)^6} \times I(1, 2\alpha+k, \beta) \right]. \quad (\text{B.7})$$

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