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# Three-Parameter Wave Functions for $ns^2$-Orbitals in Alkali–Metal Negative Ions

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A three-parameter variational wave function is used to describe the binding energy of alkali–metal negative ions using a two-electron system in the $ns^2$-state. Each electron is described by a modified screened hydrogenic wave function involving two free screening parameters denoted by $c$ and $a$ in addition to the core-screened nuclear charge, $\overset{*}{Z}$. The model is applied to lithium, sodium, potassium, rubidium, and cesium anions, where the optimum values of the variational parameters are deduced through fitting the optimized energy to the available experimental values. It is also applied to group-II isoelectronic neutral atoms of Be, Mg, Ca, Sr, and Ba. The results of our calculation are compared with other two-electron methods.

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**KEY WORDS:** electronic structure of atomic negative ions; variational techniques; electron affinity; photodetachment.

## 1. INTRODUCTION

The physical properties of alkali–metal negative ions are mainly determined by the nature of the Coulomb field acting on the two outer s electrons and the mutual repulsion between them. Although two-electron theoretical models have been applied successfully to helium-like atoms and positive ions (Tripathy, *et al.*, 1995), the only negative ion studied extensively is $H^-$ (Le Sech, 1997; Moumeni *et al.*, 1990; Patil, 1999; Porras, 1995; Siebbeles *et al.*, 1993; Siebbeles and Le Sech, 1994; Blondel, 1995).

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):

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

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Thus, the EA of an atom is numerically equal to the binding energy of the extra electron in the anion. The two outer electrons in alkali–metal anions are strongly correlated (Weiss, 1968). Vosko and Wilk (1983) used self-interaction-corrected local correlation energy functional to calculate $\langle r_2 \rangle$ for $Li^-$, $Na^-$, and $K^-$ and the electron affinities of their parent neutral atoms. Christensen-Dalsgaard (1985) calculated the sizes of $Li^-$, $Na^-$, and $K^-$ and the electron affinities of their parent neutral atoms using two-electron model wave functions. This work is an extension of the previous work of Abbadi *et al.* (2001), where a two-parameter wave function for $2p^2$-orbitals was employed to deduce the optimum effective screened nuclear charge in few light anions, using a variational technique.

In this paper, modified screened atomic hydrogen-like orbitals with three adjustable input parameters are used to describe the two outermost valence electron in $Li^-$, $Na^-$, $K^-$, $Rb^-$, and $Cs^-$. The first parameters, $\overset{*}{Z}$, represents the effective core-screened nuclear charge, the second one, $c$, manifests a constant average electronic screening of the nuclear charge while the third 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 by Porras (1995) to the ground state of helium neutral atom and its isoelectronic sequence. Le Sech (1997) used simple two- and three-parameter wave functions for the ground state of $H^-$; then, Magnier *et al.* (1999) extended that method to calculate the ground state energies of alkali–metal anions.

## 2. THEORY

The alkali–metal negative ion is assumed to consist of two outer *ns* valence electrons moving in a spherically symmetric screened Coulomb field due to the nucleus and more electrons. Thus, the core region of the anion is replaced by an effective screened nuclear charge, $\overset{*}{Z}$. The nonrelativistic Hamiltonian of the two-electron system, using atomic units, is (Bethe and Salpeter, 1957):

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{\overset{*}{Z}}{r_1} - \frac{\overset{*}{Z}}{r_2} + \frac{1}{r_{12}}, \tag{1}$$

where $r_1$ and $r_2$ are the radial coordinates of electrons 1 and 2 relative to the center of the nucleus, respectively. The distance between the two electrons is $r_{12}$ and $\nabla^2$ is the Laplacian operator. The total energy of the system is:

$$E = T + V_1 + V_{12}, \tag{2}$$

where $T$ is the total kinetic energy, $V_1$ is the total potential energy of attraction between the two electrons and the nucleus, and $V_{12}$ is the potential energy of inter-electronic repulsion. The Schrodinger equation corresponding to the Hamiltonian of Eq. (1) cannot be separated in any coordinate system due to the presence of the interelectronic distance, $r_{12}$, therefore a variational method will be used. The trial wave function of the system is written as a product of symmetric space function and antisymmetric spin function, according to Pauli exclusion principle, i.e.,

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1)\,\Psi(\vec{r}_2)\,[\chi^{+}(1)\chi^{-}(2) - \chi^{+}(2)\chi^{-}(1)]/\sqrt{2}, \tag{3}$$

with $\chi^{\pm}(1)$ and $\chi^{\pm}(2)$ for the spin functions of electrons 1 and 2, respectively. In fact, the spin wave function in Eq. (3) has no effect on the value of the total energy presented in Eq. (2) (Levine, 1974; Lowe, 1993). Therefore, the ground-state wave function of the alkali anion can be written as a product of two single-electron radial functions as follows:

$$\Psi(\vec{r}_1, \vec{r}_2) = \Phi(r_1)\Phi(r_2), \tag{4}$$

such that each function comprises a product of two functions:

$$\Phi_n(r) = N_n F_{1n}(r) F_{2n}(r), \tag{5}$$

where $N_n$ are the normalization constants corresponding to the principal quantum numbers, $n$. The first function is the screened hydrogen-like wave function:

$$F_{1n}(r) = \left[\sum_{m=0}^{m=n-1} p_m r^m\right] \exp\left[-\frac{\overset{*}{Z}}{n} r\right], \tag{6}$$

with the associated Laguerre polynomials of order $n-1$ in the first bracket being multiplied by an exponential factor, which involves the core-screened nuclear charge, $\overset{*}{Z}$.

The associated Laguerre polynomials for alkali negative ions are

$$\mathrm{Li}^{-}(n=2) : \left[1 - \left(\frac{\overset{*}{Z}}{2}\right) r\right], \tag{7a}$$

$$Na^{-}(n=3) : \left[1 - 2\left(\frac{\overset{*}{Z}}{3}\right) r + \frac{2}{3}\left(\frac{\overset{*}{Z}}{3}\right)^2 r^2\right], \tag{7b}$$

$$\mathrm{K}^{-}(n=4) : \left[1 - 3\left(\frac{\overset{*}{Z}}{4}\right) r + 2\left(\frac{\overset{*}{Z}}{4}\right)^2 r^2 - \frac{1}{3}\left(\frac{\overset{*}{Z}}{4}\right)^3 r^3\right], \tag{7c}$$

$$\mathrm{Rb}^{-}(n=5) : \left[1 - 4\left(\frac{\overset{*}{Z}}{5}\right) r + 4\left(\frac{\overset{*}{Z}}{5}\right)^2 r^2 - \frac{4}{3}\left(\frac{\overset{*}{Z}}{5}\right)^3 r^3 + \frac{2}{15}\left(\frac{\overset{*}{Z}}{5}\right)^4 r^4\right], \tag{7d}$$

$$\mathrm{Cs}^{-}(n=6):\left[1-5\left(\frac{\overset{*}{Z}}{6}\right)r+\frac{20}{3}\left(\frac{\overset{*}{Z}}{6}\right)^{2}r^{2}-\frac{10}{3}\left(\frac{\overset{*}{Z}}{6}\right)^{3}r^{3}+\frac{2}{3}\left(\frac{\overset{*}{Z}}{6}\right)^{4}r^{4}\right.$$
$$\left.-\ \frac{2}{45}\left(\frac{\overset{*}{Z}}{6}\right)^{5}r^{5}\right]. \tag{7e}$$

The second function is chosen to manifest the screening effect of each valence electron through the use of two parameters, $c$ and $a$:

$$F_{2n}(r)=\exp\left[\frac{\overset{*}{Z}c}{n}\left\{r+\frac{1}{a}\ \exp(-ar)\right\}\right]. \tag{8}$$

When the two electrons are close to the nucleus ($r \to 0$), the total wave function of Eq. (5) satisfies Kato's cusp condition:

$$\lim_{r\to 0}\left[\frac{d}{dr}|\Phi_n(r)|^2\right]=-2\overset{*}{Z}\lim_{r\to 0}[|\Phi_n(r)|^2]. \tag{9}$$

The asymptotic behavior at large distances ($r \to \infty$) is also guaranteed since the function in Eq. (5) approaches zero in this case.

The normalization constants are calculated from Eq. (5) by applying the normalization condition with the following coordinate transformation:

$$x=\exp(-ar). \tag{10}$$

The number of integral terms in the resulting expression for $N_n$ is $n(n+1)/2$, and the resulting expression for $N_2$ is:

$$N_2^2=a^3\div\left[I(2,\alpha,\beta)-\frac{\overset{*}{Z}}{a}I(3,\alpha,\beta)+\left\{\frac{\overset{*}{Z}}{2a}\right\}^{2}I(4,\alpha,\beta)\right], \tag{11}$$

where

$$\alpha=2\overset{*}{Z}(1-c)/na,\ \beta=2\overset{*}{Z}c/na,\ \text{and}$$
$$I(m,\alpha,\beta)=\int_0^1(-\ln x)^m x^{\alpha-1}\ \exp(\beta x)dx=m!\sum_{s=0}\frac{\beta^s}{S!(s+\alpha)^{m+1}}. \tag{12}$$

The total kinetic energy of the two electrons is:

$$T=\left\langle\Psi(\vec{r}_1,\vec{r}_2)\left|-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)\right|\Psi(\vec{r}_1,\vec{r}_2)\right\rangle. \tag{13}$$

The symmetry of the two electrons leads to the following expression:

$$T=2\int_0^\infty\Phi(r)\left[-\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d\Phi(r)}{dr}\right)\right]r^2dr. \tag{14}$$

The result of integration leads to a certain number of kinetic energy terms for each anion, $[7n(n+1)-2]/2$. There are 20 kinetic energy terms for Li$^-$, which could be grouped into 11 terms:

$$T_1 = \frac{1}{a}\left(\alpha + \frac{\overset{*}{Z}}{a}\right) N_2^2 I(1, \alpha, \beta) \tag{15a}$$

$$T_2 = -\frac{1}{2a}\left(\frac{\alpha^2}{2} + \frac{3\overset{*}{Z}\alpha}{a} + \left\{\frac{\overset{*}{Z}}{a}\right\}^2\right) N_2^2 I(2, \alpha, \beta) \tag{15b}$$

$$T_3 = \frac{\overset{*}{Z}\alpha}{2a^2}\left(\frac{\alpha}{2} + \frac{\overset{*}{Z}}{a}\right) N_2^2 I(3, \alpha, \beta) \tag{15c}$$

$$T_4 = -\frac{1}{a}\left(\frac{\overset{*}{Z}\alpha}{4a}\right) N_2^2 I(4, \alpha, \beta) \tag{15d}$$

$$T_5 = \frac{\beta}{a} N_2^2 I(1, \alpha+1, \beta) \tag{15e}$$

$$T_6 = -\frac{\beta}{2a}\left(1 + \alpha + \frac{3\overset{*}{Z}}{a}\right) N_2^2 I(2, \alpha+1, \beta) \tag{15f}$$

$$T_7 = \frac{\overset{*}{Z}\beta}{2a^2}\left(1 + \alpha + \frac{\overset{*}{Z}}{\alpha}\right) N_2^2 I(3, \alpha+1, \beta) \tag{15g}$$

$$T_8 = -\frac{\beta}{2a}\left\{\frac{\overset{*}{Z}}{2a}\right\}^2 (1+\alpha) N_2^2 I(4, \alpha+1, \beta) \tag{15h}$$

$$T_9 = -\frac{\beta^2}{4a} N_2^2 I(2, \alpha+2, \beta) \tag{15i}$$

$$T_{10} = \frac{\overset{*}{Z}\beta^2}{4a} N_2^2 I(3, \alpha+2, \beta) \tag{15j}$$

$$T_{11} = -\frac{1}{a}\left\{\frac{\overset{*}{Z}\beta}{4a}\right\}^2 N_2^2 I(4, \alpha+2, \beta) \tag{15k}$$

Assuming that the two electrons are identical, their energy of Coulomb attraction due to the nucleus becomes:

$$V_1 = \left\langle \Psi(\vec{r}_1, \vec{r}_2) \left| -\frac{\overset{*}{Z}}{r_1} - \frac{\overset{*}{Z}}{r_2} \right| \Psi(\vec{r}_1, \vec{r}_2) \right\rangle = -2\overset{*}{Z} \int_0^\infty |\Phi(r)|^2 r\,dr. \tag{16}$$

The number of integral terms in the resulting expression for $V_1$ is $n(n+1)/2$, and the result for Li$^-$ is:

$$V_1 = -\frac{2\overset{*}{Z}}{a^2} N_2^2 \left[ I(1, \alpha, \beta) - \frac{\overset{*}{Z}}{a} I(2, \alpha, \beta) + \left\{ \frac{\overset{*}{Z}}{2a} \right\}^2 I(3, \alpha, \beta) \right]. \tag{17}$$

The energy of mutual electronic repulsion is:

$$V_{12} = \left\langle \Psi(\vec{r}_1, \vec{r}_2) \left| \frac{1}{r_{12}} \right| \Psi(\vec{r}_1, \vec{r}_2) \right\rangle, \tag{18}$$

which can be expressed as follows (Porras, 1995; Weissbluth, 1978):

$$V_{12} = 2 \int_0^\infty r[\Phi(r)]^2 \, dr \int_0 s^2 [\Phi(s)]^2 \, ds. \tag{19}$$

The last integral is performed through expanding the exponential as a power series, and the result for Li$^-$ is:

$$V_{12} = N_2^4 a^{-9} J(\alpha, \beta), \tag{20}$$

where the $J$ integral has the following expression:

$$\begin{aligned} J(\alpha, \beta) = {} & \frac{1}{2} a^2 I(1, \alpha, \beta) \{4a^2 I(2, \alpha, \beta) - 4\overset{*}{Z} a I(3, \alpha, \beta) + \overset{*}{Z}{}^2 I(4, \alpha, \beta)\} \\ & + \frac{1}{2} \overset{*}{Z} a I(2, \alpha, \beta) \{-4a^2 I(2, \alpha, \beta) + 5\overset{*}{Z} a I(3, \alpha, \beta) - \overset{*}{Z}{}^2 I(4, \alpha, \beta)\} \\ & + \frac{1}{8} \overset{*}{Z}{}^3 I(3, \alpha, \beta) \{-4a I(3, \alpha, \beta) + \overset{*}{Z} I(4, \alpha, \beta) \\ & + \sum_{q=0} \frac{\beta^q}{q!(\alpha + q)} [J_1 + J_2 + J_3 + J_4 + J_5 + J_6 + J_7]. \end{aligned} \tag{21}$$

with

$$J_1 = \frac{4a^2}{(\alpha + q)^4} I(1, 2\alpha + q, \beta) \{-3\overset{*}{Z}{}^2 + 3\overset{*}{Z} a(\alpha + q) - a^2(\alpha + q)^2\} \tag{22a}$$

$$\begin{aligned} J_2 = {} & \frac{4a}{(\alpha + q)^4} I(2, 2\alpha + q, \beta) \{3\overset{*}{Z}{}^3 - 6\overset{*}{Z}{}^2 a(\alpha + q) \\ & + 4\overset{*}{Z} a^2 (\alpha + q)^2 - a^3 (\alpha + q)^3\} \end{aligned} \tag{22b}$$

$$\begin{aligned} J_3 = {} & \frac{1}{(\alpha + q)^4} I(3, 2\alpha + q, \beta) \{-3\overset{*}{Z}{}^4 + 15\overset{*}{Z}{}^3 a(\alpha + q) - 19\overset{*}{Z}{}^2 a^2 (\alpha + q)^2 \\ & + 10\overset{*}{Z} a^3 (\alpha + q)^3 - 2a^4 (\alpha + q)^4\} \end{aligned} \tag{22c}$$

$$J_4 = \frac{\overset{*}{Z}}{(\alpha+q)^3} I(4, 2\alpha+q, \beta)\{-3\overset{*}{Z}^3 + 9\overset{*}{Z}^2 a(\alpha+q) - 9\overset{*}{Z}a^2(\alpha+q)^2 + 4a^3(\alpha+q)^3\} \tag{22d}$$

$$J_5 = \frac{\overset{*}{Z}^2}{2(\alpha+q)^2} I(5, 2\alpha+q, \beta)\{-3\overset{*}{Z}^2 + 7\overset{*}{Z}a(\alpha+q) - 6a^2(\alpha+q)^2\} \tag{22e}$$

$$J_6 = \frac{\overset{*}{Z}^3}{2(\alpha+q)} I(6, 2\alpha+q, \beta)\{-\overset{*}{Z} + 2a(\alpha+q) \tag{22f}$$

$$J_7 = \frac{\overset{*}{Z}^4}{8} I(7, 2\alpha+q, \beta). \tag{22g}$$

The initial value of the parameter $\overset{*}{Z}$ is estimated from the exact solution to Schrodinger equation for the parent neutral atom (ns$^1$ orbital) whose first ionization potential energy, $E_1$, is:

$$E_1 = \overset{*}{Z}^2/(2n^2). \tag{23}$$

The experimental value of the ground-state energy of the anion is the sum of $E_1$ and the electron affinity of the corresponding parent neutral atom, $E_2$, *i.e.*,

$$|E| = E_1 + E_2. \tag{24}$$

## 3. RESULTS

The ground-state energy of each alkali negative ion is computed using a computer program, which minimizes the total energy expressed in Eq. (2) with

**Table I.** Theoretical Values of Effective Nuclear Charge, $\overset{*}{Z}$th, and the Experimental Values of Binding Energies ($E_1$, $E_2$, $E$) for Alkali–Metal Anions

| Anion | Z | $\overset{*}{Z}$th | $E_1$(eV)[a] | $E_2$(eV) | $-E$(a.u.) |
|---|---|---|---|---|---|
| Li$^-$ | 3 | 1.259 | 5.391 72 | 0.618 049(21)[b] | 0.220 85(2) |
| Na$^-$ | 11 | 1.844 | 5.139 08 | 0.547 926(25)[c] | 0.208 994(1) |
| K$^-$ | 19 | 2.259 | 4.340 66 | 0.501 459(12)[d] | 0.177 945(4) |
| Rb$^-$ | 37 | 2.770 | 4.177 13 | 0.485 916(20)[e] | 0.171 365(1) |
| Cs$^-$ | 55 | 3.210 | 3.893 90 | 0.471 626(25)[f] | 0.160 431(1) |

[a] Lide, 2000.

[b] Haeffler *et al.*, 1996.

[c] Hotop and Lineberger, 1985.

[d] Andersson *et al.*, 2000.

[e] Andersen *et al.*, 1999.

**Table II.** Calculated Optimum Values of the Ground-State Energy, $E$, and the Variational Parameters of $Li^-$, $Na^-$, $K^-$, $Rb^-$, and $Cs^-$

| Anion | $\overset{*}{Z}$ | $c$ | $\overset{*}{Z}c$ | $a$ | $-E$(a.u.) |
|---|---|---|---|---|---|
| $Li^-$ | 1.246 45 | 0.2159 | 0.2691 | 0.458 | 0.220 85(2) |
| $Na^-$ | 1.671 780 | 0.1550 | 0.2590 | 0.379 | 0.208 994(1) |
| $K^-$ | 1.982 861 | 0.1258 | 0.2495 | 0.894 | 0.177 945(4) |
| $Rb^-$ | 2.361 425 | 0.1067 | 0.2519 | 0.829 | 0.171 365(1) |
| $Cs^-$ | 2.691 890 | 0.0947 | 0.2550 | — | 0.160 431(1) |

respect to both parameters $c$ and $a$. The initial value for $\overset{*}{Z}$ is calculated from Eq. (23) using the latest available experimental values of $E_1$ taken from Lide (2000) and the references therein. The variational procedure is iterated using other values of $\overset{*}{Z}$ until the least energy of the system is closest to the well-established experimental value given by Eq. (24). The experimental values of $E_2$ are taken from Andersen *et al.* (1999) and the references therein while the conversion factor for energy units (1 a.u. = 27.211 3961(81) eV) is taken from Cohen and Taylor (1987). Theoretical values of effective nuclear charge, $\overset{*}{Z}$th, and the experimental values of binding energies ($E_1$, $E_2$, $E$) for alkali–metal anions are presented in Table I. The optimum values of the parameters for all alkali anions are listed in Table II. The optimum values of $\overset{*}{Z}$ are slightly less than the corresponding theoretical ones, $\overset{*}{Z}$th, due to mutual repulsion and angular correlation effects among the core electrons (Christensen-Dalsgaard, 1985; Moumeni *et al.*, 1990). They increase with increasing atomic number while those of $c$ decrease, reflecting the decrease in average screening due to the valence electrons as the principal quantum number increases. The screening constant, $\overset{*}{Z}c$, does not change appreciably and its average value is 0.257 ± 0.003. The corresponding values of the parameter $a$ show no systematic change, except for the overall variable screening character. No specific value of $a$ was obtained for $Cs^-$ due to the multiple-node structure of its wave function. In Table III, we display the calculated values of $N_n$, $V_1$, $V_{12}$, $V$, and $T$,

**Table III.** Calculated Values of the Normalization Constant and the Energy Terms Used to Obtain the Ground-State Energies Listed in Table II

| $Li^-$ | $Na^-$ | | $K^-$ | $Rb^-$ | $Cs^-$ |
|---|---|---|---|---|---|
| $N^2$ | 0.213 749 | 0.147 123 | 0.094 282 | 0.074 144 | 0.056 |
| $-V_1$ | 0.565 751 | 0.445 137 | 0.335 255 | 0.301 018 | 0.267 |
| $V_{12}$ | 0.152 898 | 0.094 80 | 0.063 918 | 0.049 157 | 0.039 04 |
| $-V$ | 0.412 853 | 0.350 337 | 0.271 337 | 0.251 861 | 0.228 |
| $T$ | 0.191 993 | 0.141 342 | 0.093 392 | 0.80 496 | 0.068 |

**Table IV.** Calculated Optimum Values of the Ground-State Energy, $E$, and the Variational Parameters of Group-II Isoelectronic Neutral Atoms

| Element | $\overset{*}{Z}$ | $c$ | $\overset{*}{Z}c$ | $a$ | $-E$(a.u.) |
|---|---|---|---|---|---|
| Be | 2.314 260 | 0.1261 | 0.2918 | 0.868 663 | 1.011 850 |
| Mg | 3.036 138 | 0.0915 | 0.2778 | 2.509 790 | 0.833 530 |
| Ca | 3.545 350 | 0.0801 | 0.2840 | 1.981 110 | 0.660 932 |
| Sr | 4.210 458 | 0.0711 | 0.2994 | 1.725 140 | 0.614 633 |
| Ba | 4.774 845 | 0.0651 | 0.3108 | — | 0.559 163 |

where $V = V_1 + V_{12}$. They follow a general trend of decreasing absolute values as the principal quantum number, $n$, increases. The calculation is applied to reproduce the ground-state energies of the isoelectronic neutral atoms of Be, Mg, Ca, Sr, and Ba. The results are presented in Table IV, where $(-E)$ is the sum of the first and second ionization energies obtained from the experimental data. The average value of $(\overset{*}{Z}c)$ in this case is $0.293 \pm 0.005$, which is slightly larger than that for the anions due to larger nuclear charge $(\Delta Z = +1)$ although the corresponding $c$ values are less. The values of $a$ are larger for neutral atoms compared to the corresponding anions.

The calculated expectation values for the ground-state wave functions of alkali–metal anions $(\langle r\rangle, \langle r^2\rangle, \langle 1/r\rangle, \langle 1/r^2\rangle, \langle 1/r_{12}\rangle)$ are listed in Table V. It shows a rapid increase in the values of $\langle r\rangle$ and $\langle r^2\rangle$ with increasing atomic numbers, with $\langle r\rangle$ being slightly less than $\langle r^2\rangle^{1/2}$ for each individual anion.

## 4. CONCLUSION

In this work, the ground state of each alkali–metal negative ion is described by a two-electron theoretical model for the ns$^2$-state. The wave function of each electron involves three adjustable parameters whose optimum values are determined from a variational calculation. The screening effect due to the core electrons is manifested through the parameter, $\overset{*}{Z}$, while the mutual screening of the valence

**Table V.** Calculated Expectation Values for the Ground-State Wave Functions of Alkali–Metal Anions

| Anion | $\langle r\rangle$ | $\langle r^2\rangle$ | $\langle 1/r\rangle$ | $\langle 1/r^2\rangle$ | $\langle 1/r_{12}\rangle$ |
|---|---|---|---|---|---|
| Li$^-$ | 5.9063 | 40.4289 | 0.226 945 | 0.175 155 | 0.152 898 |
| Na$^-$ | 9.5052 | 99.6901 | 0.133 133 | 0.078 046 | 0.094 80 |
| K$^-$ | 14.1567 | 215.77 | 0.084 538 | 0.032 193 | 0.063 918 |
| Rb$^-$ | 18.4612 | 362.955 | 0.063 736 | 0.020 653 | 0.049 157 |
| Cs$^-$ | 23.309 | 574.374 | 0.049 659 | 0.013 189 | 0.039 04 |

electrons is represented by the parameters $c$ and $a$. The expectation values of the wave function are useful in estimating the size of the anion and its detachment cross-section. The calculated values of $\langle r \rangle$ are larger than those obtained by Christensen-Dalsgaard (1985) because all differences in nodal structure were contained in the angular functions used there. The results are useful for the physical interpretation of interaction processes involving negative ions.

## REFERENCES

Abbadi, M. A., Bani-Hani, N. M., and Khalifeh, J. M. (2001). A variational wave function for $2p^2$-orbitals in atomic negative ions. *International Journal of Theoretical Physics* **40**(11), 2053–2066.

Andersen, T., Haugen, H. K., and Hotop, H. (1999). Binding energies in atomic negative ions: III. *Journal of Physical and Chemical Reference Data* **28**(6), 1511–1533.

Andersson, K. T., Sandstrom, J., Kiyan, I. Y., Hanstorp, D., and Pegg, D. J. (2000). Measurement of the electron affinity of potassium. *Physical Review A* **62**(2), 022503(5).

Bethe, H. A. and Salpeter, E. E. (1957). *Quantum Mechanics of the One- and Two-Electron Atoms*, Academic Press, New York.

Blondel, C. (1995). Recent experimental achievements with negative ions. *Physica Scripta T* **58**, 31–42.

Christensen-Dalsgaard, B. L. (1985). On the size of negative alkali ions $Li^-$, $Na^-$ and $K^-$. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **18**, L407–L411.

Cohen, E. R. and Taylor, B. N. (1987). The 1986 adjustment of the fundamental physical constants. *Reviews of Modern Physics* **59**(4), 1121–1148.

Haeffler, G., Hanstorp, D., Kiyan, I., Klinkmuller, A. E., Ljungblad, U., and Pegg, D. J. (1996). Electron affinity of Li: A state-selective measurement. *Physical Review A* **53**, 4127.

Hotop, H. and Lineberger, W. C. (1985). Binding energies in atomic negative ions: II. *Journal of Physical and Chemical Reference Data* **14**(3), 731–750.

Le Sech, C. (1997). Accurate analytic wave functions for two-electron atoms. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **30**, L47–L50.

Levine, I. N. (1974). *Quantum Chemistry*, 2nd edn., Allyn and Bacon, Boston.

Lide, D. R. (2000). *Handbook of Chemistry and Physics*, 80th edn., CRC Press, New York.

Lowe, J. P. (1993). *Quantum Chemistry*, 2nd edn., Academic Press, San Diego, CA.

Magnier, S., Aubert-Frecon, M., Hanssen, J., and Le Sech, C. (1999). Two-electron wave functions for the ground state of alkali negative ions. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **32**, 5639–5643.

Moumeni, A., Dulieu, O., and Le Sech, C. (1990). Correlated wave functions for two-electron systems using new screened hydrogen-like orbitals. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **23**, L739–L745.

Patil, S. H. (1999). Wave functions for two- and three-electron atoms and isoelectronic ions. *The European Physical Journal D* **6**, 171–177.

Porras, I. (1995). A two-parameter single-particle description of the ground state of two-electron atoms. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **28**, 4391–4398.

Siebbeles, L. D. A. and Le Sech, C. (1994). A simple method to calculate potential curves of two-electron molecules at intermediate nuclear distances. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **27**, 4443–4452.

Siebbeles, L. D. A., Marshall, D. P., and Le Sech, C. (1993). Simple and accurate wave functions for two-electron atoms in S, P and D states. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **26**, L321–L325.

Tripathy, D. N., Padhy, B., and Rai, D. K. (1995). Two-parameter wave functions for the ground state of the helium isoelectronic sequence. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **28**, L41–L46.

Vosko, S. H. and Wilk, L. (1983). A comparison of self-interaction-correlated local correlation energy functionals. *Journal of Physics B: Atomic, Molecular, and Optical Physics* **16**, 3687–3702.

Weiss, A. W. (1968). Theoretical electron affinities for some for the alkali and alkali-earth elements. *Physical Review* **166**(1), 70–74.

Weissbluth, M. (1978). Atoms and Molecules. Student edn., Academic Press, London.