Simple model potential and model wave functions for (H–alkali)+ and (alkali–alkali)+ ions

S. H. Patil and K. T. Tang

Citation: J. Chem. Phys. 113, 676 (2000); doi: 10.1063/1.481843
View online: http://dx.doi.org/10.1063/1.481843
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v113/i2
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.
Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors
Simple model potential and model wave functions for (H–alkali)$^+$ and (alkali–alkali)$^+$ ions

S. H. Patil
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073, Göttingen, Germany
and Department of Physics, Indian Institute of Technology, Bombay 400 076, India

K. T. Tang
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073, Göttingen, Germany
and Department of Physics, Pacific Lutheran University, Tacoma, Washington 98447

(Received 18 October 1999; accepted 5 April 2000)

A simple model potential is proposed to describe the interaction of a valence electron with the alkali core, which incorporates the correct asymptotic behavior in terms of dipolar polarizabilities, and the short-range exchange effects in terms of a hard core adjusted to give the correct energy for the valence electron. Based on this potential, simple wave functions are developed to describe the (H–alkali)$^+$ and (alkali–alkali)$^+$ ions. These wave functions exhibit some important structures of the ions, and provide a universal description of the properties of all (H–alkali)$^+$ and (alkali–alkali)$^+$ ions, in particular, the equilibrium separations of the nuclei and the corresponding dissociation energies. They also allow us to calculate the dipolar polarizabilities of Li$_2^+$, Na$_2^+$, K$_2^+$, Rb$_2^+$, and Cs$_2^+$. © 2000 American Institute of Physics. [S0021-9606(00)01325-8]

I. INTRODUCTION

The H$_2^+$ ion is an ideal example for introducing the concepts and complications one encounters in the description of molecules and molecular ions. As such it has been analyzed from many different points of view. Within the Born–Oppenheimer approximation, the Schrödinger equation is separable in terms of elliptic coordinates, and the energies and wave functions have been obtained with high accuracy for several states. It has also been analyzed in terms of other approaches, such as a variational approach, which provide a deeper understanding of the system in terms of simple model wave functions, for example, the Guillemin–Zener wave function and the James wave function. In the development of these wave functions, local properties of the wave functions play a significant role. Alkali atoms are in some ways similar to the hydrogen atom. They have one electron outside the closed shell core, and many of their properties are determined primarily by the wave function of the valence electron. However, the interaction of this electron with the alkali core is more complicated than a simple Coulombic term. There have been many attempts to simulate this interaction by a model potential. However, in most cases, the model potential contains many parameters and the corresponding wave functions for (H–alkali)$^+$ and (alkali–alkali)$^+$ ions are generally made up of variational wave functions with many parameters. There is a lack of simple wave functions which give an accurate description of the properties of (H–alkali)$^+$ and (alkali–alkali)$^+$ ions, and provide a physical insight into their structure.

Here we consider a simple model potential which depends on only one parameter. It has the correct asymptotic behavior and an appropriate structure at small distances from the center of the core. We then develop a simple wave function for the description of (H–alkali)$^+$ ions based on some local and perturbative properties. These wave functions are used to obtain the interionic potential for (H–alkali)$^+$ ions. We also develop a wave function for the description of the (alkali–alkali)$^+$ ion, which is an extension of the Guillemin–Zener wave function. This wave function is used to obtain the interionic potential for (alkali–alkali)$^+$ ions. The predictions for the internuclear separation at equilibrium and the corresponding dissociation energies for all the 20 systems we have considered are in good agreement with the results from accurate calculations and with the experimental values. These wave functions also allow us to calculate the dipolar polarizabilities of Li$_2^+$, Na$_2^+$, K$_2^+$, Rb$_2^+$, and Cs$_2^+$, which are expected to play an important role in the description of Rydberg states of Li$_2$, Na$_2$, K$_2$, Rb$_2$, and Cs$_2$.

II. MODEL POTENTIAL FOR ALKALI ATOMS

For developing a reliable potential for the interaction of the valence electron with the core in alkali atoms, we note that when the electron is far away, the dominant interaction is given by the Coulombic term and the interaction with the induced dipole moment,

$$ V(r) = -\frac{q_A e}{r} - \frac{\alpha_a}{2r^4} \quad \text{for } r \to \infty, $$

(2.1)

where $q_A$ is the charge of the core A, and $\alpha_a$ is its dipolar polarizability. At small distances from the center of the core, the exclusion principle prevents the valence electron from entering the core to any significant extent, so that we effectively have a strong repulsive interaction at short distances. We therefore propose a model potential for describing the interaction of the valence electron with the core,
TABLE I. The input values of the valence electron energy \( E_v \), dipolar polarizability \( \alpha_e \), of the core, implied values of the radius \( R_a \), of the core, and the calculated values of the energies of the outer two electrons in the negative alkali ions along with the experimental values in brackets.

<table>
<thead>
<tr>
<th>Ion</th>
<th>( q_e )</th>
<th>(-E_v(\text{eV}))</th>
<th>( \alpha_e(\text{a.u}) )</th>
<th>( R_a(\text{a.u}) )</th>
<th>(-E_2(\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>5.390</td>
<td>0.192</td>
<td>0.833</td>
<td>5.908</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>5.138</td>
<td>0.099</td>
<td>0.963</td>
<td>5.658</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>4.339</td>
<td>5.5</td>
<td>1.436</td>
<td>4.833</td>
</tr>
<tr>
<td>Rb</td>
<td>1</td>
<td>4.176</td>
<td>9.2</td>
<td>1.595</td>
<td>4.668</td>
</tr>
<tr>
<td>Cs</td>
<td>1</td>
<td>3.893</td>
<td>15.7</td>
<td>1.857</td>
<td>4.374</td>
</tr>
</tbody>
</table>

\[
V(r) = -\frac{q_e}{r} - \frac{\alpha_e}{2(r^2 + R_a^2)^{3/2}} \quad \text{for} \quad r > R_a
\]
\[
= \infty \quad \text{for} \quad r \leq R_a, \quad (2.2)
\]

where \( R_a \) is to be regarded as the radius of the hard core \( A \). One has accurate values for the dipolar polarizabilities of the core deduced from Rydberg energies and from accurate calculations. The single parameter \( R_a \) is determined by requiring that the state of this potential is equal to the valence electron energy. The input values of the valence electron energy, dipolar polarizabilities of the core, and the deduced values of the core radius are given in Table I.

The quality of our potential can be tested by calculating the energies of the excited states and comparing them with the experimental values. For example, for Na, some of the experimental values of the excited state energies are 4s: -1.947, 5s: -1.022, 3p: -3.035, 4p: -1.386, 3d: -1.522, 4d: -0.855 eV, whereas the values predicted by our potential in Eq. (2.2) are -1.943, -1.023, -3.132, -1.415, -1.515, -0.851 eV, respectively. The agreement between the two is quite satisfactory. The predictions for other atoms are of similar quality. We can also test the quality of our potential by using it to calculate the energies of the two electrons outside the core in the negative ions Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, each experiencing the potential in Eq. (2.2), and an additional interaction,

\[
V_{12} = \frac{1}{r_{12}} - \frac{\alpha_e \cos \theta_{12}}{(r_1^2 + R_a^2)(r_2^2 + R_a^2)}, \quad (2.3)
\]

where \( \theta_{12} \) is the angle between the position vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) of the two electrons. The last term here incorporates the interaction of each electron with the dipole moment induced by the other electron. The predicted values for the energies of the two electrons are given in Table I and are close to the experimental values.

We now proceed with confidence to use the model potential in Eq. (2.2) to analyze the properties of (H–alkali)⁺ and (alkali–alkali)⁺ ions. Our hard-core potential is particularly suited for the analysis of these systems. The reason for this is that in the usual model potential one has large but finite repulsive potential at short distances and any deviation in the wave function at short distances leads to large changes in the energy. In our hard-core potential, this difficulty is avoided by the requirement that the wave function vanishes inside the hard core. But we must add a word of caution. It may be observed that the core of Li consists of only two s-wave electrons, and therefore, a hard core description may not be adequate. For other systems involving Na, K, Rb, Cs, we expect our potential to produce quite reliable results.

III. WAVE FUNCTIONS FOR (H–ALKALI)⁺ IONS

In the analysis of the energies of (H–alkali)⁺ ions, we need to consider the interaction of a charge not only with the dipole moment induced by it in the core, but also with the dipole moment induced by the other charge. Therefore the potential describing the interaction in the (H–alkali)⁺ ion is given by

\[
V = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R} + \frac{\alpha_e}{2(r_1^2 + R_a^2)^{3/2}} - \frac{\alpha_e}{2(r_2^2 + R_a^2)^{3/2}} - \frac{\alpha_e \cos \theta_2}{(r_1^2 + R_a^2)(r_2^2 + R_a^2)} \quad \text{for} \quad r_2 > R_a
\]
\[
= \infty \quad \text{for} \quad r_2 < R_a. \quad (3.1)
\]

Here \( R \) is the distance between proton and the alkali core, \( r_1 \) and \( r_2 \) are the distances of the electron from the proton and the alkali core with radius \( R_a \) and dipolar polarizability \( \alpha_e \), and

\[
\cos \theta_2 = \frac{r_2^2 - r_1^2 + R^2}{2 r_2 R}. \quad (3.2)
\]

For developing the wave function of the electron in this potential, we first consider some of its properties.

A. Cusp condition

As the electron approaches the proton, the dominant terms in the Schrödinger equation are

\[
\left(-\frac{1}{2}\nabla^2 + \frac{1}{r_1}\right) \psi = O(1) \quad \text{for} \quad r_1 \rightarrow 0. \quad (3.3)
\]

Expanding the wave function for a particular angular momentum \( l \) state,

\[
\psi_l = r_1^{l} (a_0 + a_1 r_1 + \cdots) P_l(\cos \theta_1), \quad (3.4)
\]

we get from Eq. (3.3),

\[
a_1 = -\frac{a_0}{l+1}, \quad (3.5)
\]

which for \( l = 0 \) leads to the usual Kato condition,\(^1^8\)

\[
\psi_0 - a_0 (1 - r_1) \quad \text{for} \quad r_1 \rightarrow 0. \quad (3.6)
\]

For small \( r_1 \) this is the most important condition.

B. First-order perturbed wave function

When the alkali ion is at a large distance from the hydrogen atom, we can describe the system as a hydrogen atom perturbed by the potential
The corresponding induced dipole moment is given by

\[ V_p = \frac{1}{R} \frac{1}{|R - r|} \]

\[ = - \sum_{l=1}^{\infty} \frac{r_l^l}{R^{l+1}} P_l(\cos \theta_1) \quad \text{for large } R. \tag{3.7} \]

The leading perturbation comes from the \( l = 1 \) term and the corresponding perturbation to the ground-state wave function satisfies the equation

\[ \frac{1}{2} \left( \frac{\nabla^2}{r} + \frac{1}{r} - \frac{1}{2} \right) \delta \psi_1 = - \frac{r_1}{R^2} (\cos \theta_1) N e^{-r_1}, \]

where \( N = \pi^{-1/2} \) is the normalization constant for the ground state. The solution to this equation is the well-known Dalgarno–Lewis solution,

\[ \delta \psi_1 = \frac{1}{2R^2} (r_1^2 + 2r_1)(\cos \theta_1) N e^{-r_1}. \tag{3.9} \]

The corresponding induced dipole moment is given by

\[ p = 2 \langle \psi | r_1 \cos \theta_1 | \delta \psi_1 \rangle = \frac{9}{2} \left( \frac{1}{R^2} \right). \tag{3.10} \]

\section*{C. Second-order perturbed wave function}

It is quite useful to consider the perturbation in the \( s \)-wave component of the wave function. The leading term in this will come from the second-order change in the wave function produced by the \( l = 1 \) term in Eq. (3.7),

\[ \delta \psi^{(2)} = - \frac{1}{E_0 - H_0} \left( - \frac{r_1^2}{R^2} \cos \theta_1 \right) \delta \psi_1 \]

\[ = - \left( \frac{1}{2R^2} \right) \left( \frac{1}{E_0 - H_0} \right) (r_1^2 + 2r_1^2)(\cos^2 \theta_1) N e^{-r_1}. \tag{3.11} \]

where \( H_0 \) is the hydrogenic Hamiltonian with the ground-state energy \( E_0 \) and we have used the \( \delta \psi_1 \) in Eq. (3.9). Of course the ground-state wave function has to be projected out before \( (E_0 - H_0)^{-1} \) operates on the function. Though one could get an estimation for the perturbation \( \delta \psi^{(2)} \) by using the Unsöld approximation, the main point to observe is that the leading order perturbation in the \( l = 0 \) state coming from \( \delta \psi^{(2)} \) is of order \( (1/R^3) \).

\section*{D. Model wave function}

We consider a simple wave function for the ground state of \((\text{H–alkali})^+ \) ions,

\[ \psi = Ce^{-b_1r_1} \cosh(b_2r_1) e^{-b_2r_2}[1 - e^{-b_3(r_2 - R_a)}] \]

for \( r_2 > R_a \)

\[ = 0 \quad \text{for } r_2 < R_a, \tag{3.12} \]

where \( b_0, b_1, b_2, b_3 \) are constant parameters, \( R_a \) is the radius of the alkali ion core, and \( C \) is the normalization constant. We now analyze this wave function in terms of the general properties just described.

The cusp condition in Eq. (3.6) for the case when the electron approaches the proton, implies that

\[ b_0 = 1. \tag{3.13} \]

This in a sense is the most important property.

For large \( R \), we expect the corrections to the hydrogenic wave function to be small and hence parameters \( b_1 \) and \( b_2 \) are expected to be small. Using the expansion

\[ r_2 = (R^2 - 2Rr_1 \cos \theta_1 + r_1^2)^{1/2} \]

\[ = R - r_1 \cos \theta_1 + \frac{1}{2} \left( \frac{r_1^2}{R^2} \right) - \frac{1}{2 R^2} r_1^2 \cos^2 \theta_1 + \cdots, \tag{3.14} \]

we have

\[ e^{-r_1-b_2r_2} \approx e^{-r_1-b_2R}(1 + b_2r_1 \cos \theta_1 + \cdots). \tag{3.15} \]

Therefore the leading \( p \)-wave perturbation is given by

\[ \delta \psi_1 = b_2r_1 \cos \theta_1 \psi_0(r_1), \tag{3.16} \]

where \( \psi_0(r_1) \) is the unperturbed hydrogenic ground-state wave function. Requiring that the dipole moment due to this perturbed wave function is equal to the corresponding dipole moment in Eq. (3.10) due to the exact first-order perturbed wave function, we get

\[ 2b_2 \int r_1^2 \cos^2 \theta_1 e^{-2r_1} d^3r_1 \]

\[ = 2 \left( \frac{1}{2R^2} \right) \int (r_1^2 + 2r_1^2) \cos^2 \theta_1 e^{-2r_1} d^3r_1, \tag{3.17} \]

which leads to

\[ b_2 = \frac{9}{4R^2}. \tag{3.18} \]

To ensure the correct behavior for the \( s \)-wave perturbation, we use the expansion in Eq. (3.14) to obtain

\[ e^{-b_2r_2} \approx e^{-b_2R} \left[ 1 + b_2r_1 \cos \theta_1 + \frac{1}{2} b_2^2 r_1^2 \cos^2 \theta_1 \right. \]

\[ \left. - \frac{1}{2R} b_2 r_1^2 + \frac{1}{2R} b_2 r_1^2 \cos^2 \theta_1 + \cdots \right]. \tag{3.19} \]

Projecting out the \( l = 0 \) term, we have for the leading term

\[ \delta \psi_0 = - \frac{3}{4R} b_2 r_1^2 N e^{-r_1} = \left( 1 + \frac{3}{4R} b_2 r_1^2 \right) N e^{-r_1}, \tag{3.20} \]

where we have substituted the relation from Eq. (3.18). However, we have shown in Eq. (3.11) that the leading perturbation in the \( s \)-wave is of order \( 1/R^3 \). We therefore demand that the additional term coming from the expansion of the \( \cosh(b_1r_1) \) factor in the wave function in Eq. (3.12),

\[ \cosh(b_1r_1) N e^{-r_1} = (1 + \frac{3}{4R} b_2 r_1^2 + \cdots) N e^{-r_1} \tag{3.21} \]

should cancel the \( 1/R^3 \) term, in Eq. (3.20),

\[ \frac{1}{2} b_1^2 - \frac{3}{4R^3} = 0 \tag{3.22} \]

or

\[ b_1 = \left( \frac{3}{2R^3} \right)^{1/2}. \tag{3.23} \]

In summary, we have the wave function in Eq. (3.12),
ψ = Ce^{-bφ} \cos(b_1 r_1) e^{-b_2 r_2^2\left[1 - e^{-b_3 (r_2 - R_a)}\right]}

for R_a \geq R_a

= 0 \quad \text{for } R_a < R_a. \quad (3.24)

Imposing some general conditions on this wave function allows us to obtain the parameters b_0, b_1, b_2, b_3.

cusp condition \rightarrow b_0 = 1, \quad (3.25)

dipole condition in Eq. (3.10) \rightarrow b_2 = \frac{9}{4R_e^2}, \quad (3.26)

s-wave condition in Eq. (3.11) \rightarrow b_1 = \left(\frac{3}{2R_e^3}\right)^{1/2}. \quad (3.27)

The remaining parameter b_3 in the last factor which ensures that the wave function vanishes at the hard core, is determined variationally.

E. Results

We use the wave function in Eq. (3.24) with parameters b_0, b_1, b_2, b_3 given in Eqs. (3.25)–(3.27) to calculate the energies of (H−alkali)^+ ions, as a function of the internuclear separation. The parameter b_3, which is sensitive to the behavior of the wave function close to the alkali ion, is determined variationally. The calculations are carried out conveniently in terms of elliptic coordinates

\[ u = \frac{r_1 + r_2}{R}, \quad v = \frac{r_1 - r_2}{R}, \quad (3.28) \]

\[ \nabla^2 = \frac{2}{R^2} \frac{1}{u^2 - v^2} \left[ \frac{d}{du} (u^2 - 1) \frac{d}{du} + \frac{d}{dv} (1 - v^2) \frac{d}{dv} \right], \quad (3.29) \]

\[ dV = 2\pi \left(\frac{R}{2}\right)^3 \left(u^2 - v^2\right) dudv, \quad (3.30) \]

where we have left out the \( \phi \) dependent terms. The results for the equilibrium separation of the nuclei and the corresponding dissociation energies, and the energies at some other separations, are given in Table II.

For comparison with the results of the earlier calculations, we note that for (HLi)^+, our dissociation energy \( D(R_e) = 0.0806 \text{ eV} \) is fairly close to the recommended value \( ^{19} \text{ of } 0.09 \pm 0.06 \text{ eV} \), which, however, has large uncertainties. The basis calculations of Browne\(^{20}\) give a value of about 0.103 eV whereas the calculations of Rosmus and Meyer\(^{21}\) and of Fuentebalba et al.\(^{14}\) give somewhat larger values of 0.13–0.15 eV. The equilibrium separation suggested by them is about 4.2 a.u., compared with our value of 4.55 a.u. As mentioned earlier, since the core of Li has only two s-wave electrons, the description of its potential may require finer details than a simple hard core.

Our results for (HNa)^+ and (HK)^+ are in very good agreement with the earlier reliable calculations. For (HNa)^+, our values of dissociation energy \( D(Re) = 0.073 \text{ eV} \) and \( R_e = 4.75 \text{ a.u.} \) compare well with the recommended values \( D(R_e) = 0.064 \pm 0.01 \text{ eV}, \ R_e = 4.91 \text{ a.u.} \) of Olson et al.\(^{22}\)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_e (\text{equil}) )</td>
<td>4.55</td>
<td>4.75</td>
<td>5.45</td>
<td>5.6</td>
<td>6.0</td>
</tr>
<tr>
<td>( D(R_e) )</td>
<td>0.0806</td>
<td>0.0734</td>
<td>0.0502</td>
<td>0.0487</td>
<td>0.0429</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>3.34</td>
<td>3.22</td>
<td>2.91</td>
<td>2.32</td>
<td>2.75</td>
</tr>
<tr>
<td>( E(4.0) )</td>
<td>-0.0449</td>
<td>-0.0100</td>
<td>0.224</td>
<td>0.336</td>
<td>0.623</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>2.77</td>
<td>2.47</td>
<td>1.66</td>
<td>1.57</td>
<td>1.43</td>
</tr>
<tr>
<td>( E(4.5) )</td>
<td>-0.0803</td>
<td>-0.0691</td>
<td>0.0247</td>
<td>0.0679</td>
<td>0.188</td>
</tr>
<tr>
<td>( b_3 )</td>
<td>3.34</td>
<td>3.02</td>
<td>2.11</td>
<td>1.93</td>
<td>1.68</td>
</tr>
<tr>
<td>( E(5.0) )</td>
<td>-0.0728</td>
<td>-0.0705</td>
<td>-0.0394</td>
<td>-0.0255</td>
<td>0.0215</td>
</tr>
<tr>
<td>( b_4 )</td>
<td>3.62</td>
<td>3.40</td>
<td>2.60</td>
<td>2.39</td>
<td>2.04</td>
</tr>
<tr>
<td>( E(5.5) )</td>
<td>-0.0566</td>
<td>-0.0570</td>
<td>-0.0502</td>
<td>-0.0481</td>
<td>-0.0329</td>
</tr>
<tr>
<td>( b_5 )</td>
<td>3.83</td>
<td>3.63</td>
<td>2.94</td>
<td>2.77</td>
<td>2.44</td>
</tr>
<tr>
<td>( E(6.0) )</td>
<td>-0.0419</td>
<td>-0.0429</td>
<td>-0.0438</td>
<td>-0.0455</td>
<td>-0.0429</td>
</tr>
<tr>
<td>( b_6 )</td>
<td>4.02</td>
<td>3.81</td>
<td>3.20</td>
<td>3.02</td>
<td>2.75</td>
</tr>
<tr>
<td>( E(6.5) )</td>
<td>-0.0307</td>
<td>-0.0316</td>
<td>-0.0342</td>
<td>-0.0356</td>
<td>-0.0382</td>
</tr>
<tr>
<td>( b_7 )</td>
<td>4.18</td>
<td>3.95</td>
<td>3.37</td>
<td>3.22</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Similarly, for (HK)^+, our values of \( D(R_e) = 0.050 \text{ eV} \) and \( R_e = 5.45 \text{ a.u.} \) compare well with the recommended values \( D(R_e) = 0.05 \pm 0.02 \text{ eV}, \ R_e = 5.68 \pm 0.38 \text{ a.u.} \) of Olson et al.\(^{2}\)

There are essentially no reliable estimations\(^{23}\) of the dissociation energies for (HRb)^+, (HCs)^+. Considering the quality of our results for (HNa)^+ and (HK)^+, we are confident that our predictions for (HRb)^+ and (HCs)^+ also are quite reliable.

It may be mentioned that though we have given our results for the values of the parameters \( b_0, b_1, b_2, b_3 \) given by Eqs. (3.25)–(3.27), we have varied their values and found that the variational minima are essentially the same as those given by the values in Eqs. (3.25)–(3.27). This demonstrates the usefulness of incorporating some general properties of the wave function into the model wave functions. Overall, our wave function in Eq. (3.24) with each factor representing some physical properties such as the cusp condition, perturbation limits, etc., brings out the physical aspects of the system in a transparent manner, and gives accurate values for the energies.

IV. WAVE FUNCTION FOR (ALKALI−ALKALI)^+ IONS

In the analysis of (alkali−alkali)^+ systems, we need to consider the dipoles induced in both alkali cores. The potential describing the (alkali−alkali)^+ ions is therefore given by

\[ V = \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{R} = \frac{\alpha_a}{2(r_1^2 + R_a^2)^{1/2}} - \frac{\alpha_b}{2(r_2^2 + R_a^2)^{1/2}} \]

\[ = \frac{\alpha_a}{2(R_a^2 + R_b^2)^{1/2}} - \frac{\alpha_b}{2(R_a^2 + R_b^2)^{1/2}} + \frac{\alpha_a \cos \theta_1}{(r_1^2 + R_a^2)^{1/2}} + \frac{\alpha_b \cos \theta_2}{(r_2^2 + R_b^2)^{1/2}} \]

for \( r_1 > R_a, r_2 > R_b \),

\[ \Rightarrow \quad \text{for } r_1 < R_a \text{ or } r_2 < R_b. \quad (4.1) \]
This wave function vanishes inside either of the two cores. We therefore propose a wave function to be found close to either of the alkali ions. We therefore of the two alkali atoms are of comparable magnitude, and

\[ r \approx \frac{R_a + R_b}{2}, \]

\[ R_a \] and \( R_b \) are the distances of the electron from the cores A and B with core radii \( R_a \) and \( R_b \) and dipolar polarizabilities \( \alpha_a \) and \( \alpha_b \), respectively, and

\[ \cos \theta_1 = \frac{r_1^2 - r_2^2 + R^2}{2r_1 R}, \quad \cos \theta_2 = \frac{r_2^2 - r_1^2 + R^2}{2r_2 R}. \]

In the (alkali–alkali)\(^+\) systems, the ionization energies of the two alkali atoms are of comparable magnitude, and therefore there will be substantial probability for the electron to be found close to either of the alkali ions. We therefore propose a wave function

\[ \psi = [e^{-\frac{1}{2}(|z_1| + |z_2|)} + Ge^{-\frac{1}{2}(|z_1| + |z_2|)}](r_1 - R_a)(r_2 - R_b) \]

for \( r_1 > R_a, \ r_2 > R_b \)

\[ = 0 \quad \text{for} \quad r_1 < R_a \ \text{or} \ r_2 < R_b, \]

with \( z_1, z_2 \), and \( G \) as variational parameters. This is a simple extension of the Guillemin–Zener wave function\(^3\) for H\(_2\)\(^+\), modified to incorporate the property that there is very little penetration of the valence electron into the alkali cores. This wave function vanishes inside either of the two cores.

As in the case of (H–alkali)\(^+\) ions, here also it is convenient to evaluate the operations in terms of elliptic coordinates. We simplify the variational analysis by writing

\[ \psi = \phi_1 + G \phi_2, \]

\[ \phi_1 = e^{-|z_1| r_1 - |z_2| r_2}(r_1 - R_a)(r_2 - R_b), \]

\[ \phi_2 = e^{-|z_1| r_1 - |z_2| r_2}(r_1 - R_a)(r_2 - R_b). \]

With matrix elements

\[ H_{ij} = \langle \phi_i | -\frac{1}{2} \nabla^2 + V | \phi_j \rangle, \]

\[ S_{ij} = \langle \phi_i | \phi_j \rangle, \]

the extremum condition for the parameter \( G \) leads to

\[ G = \frac{-c_2 \pm (c_2^2 - 4c_1c_3)^{1/2}}{2c_1}, \]

\[ c_1 = H_{12}S_{11} - H_{11}S_{22}, \]

\[ c_2 = H_{22}S_{11} - H_{11}S_{22}, \]

\[ c_3 = H_{12}S_{11} - H_{11}S_{22}. \]

This effectively reduces the problem to that of variation of only two parameters, \( z_1 \) and \( z_2 \).
A. Energies

We use the wave function in Eq. (4.3), and the potential in Eq. (4.1), to calculate the energies of all (alkali–alkali)$^+$ ions, as functions of internuclear separation. The parameters $z_1$ and $z_2$ are determined variationally, and parameter $G$ is determined by making use of Eqs. (4.9) and (4.10). We have presented the results for the internuclear separation at equilibrium, and the corresponding dissociation energy, in Table III.

Our predictions for the internuclear separation at equilibrium and the corresponding dissociation energies are in good agreement with the results of other calculations and with the experimental values$^{29-32}$ whenever available. For example, for Na$_2^+$, our values of $R_e = 6.8$ a.u. and $D(R_e) = 0.958$ eV compare well with the values 6.89 a.u. and 0.93 eV of Flad et al.$^{24}$ and the experimental values of 6.8 a.u. and 0.984 eV. The largest deviation is about 25% for Li$_2^+$, for which we have, as mentioned before, some reservation in using a hard-core potential. For some systems, there are very few earlier calculations, and they differ substantially from ours.

Exchange effects at short distances, are expected to play an important role in the analysis of Rydberg states of alkali dimers. The perturbation to the wave function in the presence of a unit external electric field $\mathbf{n}$ is given by

$$\eta = -\frac{1}{2} \nabla^2 + V - E_0 \mathbf{r} \cdot \mathbf{n} \psi,$$

(4.11)

where the potential $V$ is given in Eq. (4.1), $\mathbf{r}$ is the position vector of the electron with respect to the center of mass, and the unperturbed wave function $\psi$ is given in Eq. (4.3). We obtain $\eta$ variationally by using a basis of two terms,

$$\eta = C_1 \eta_1 + C_2 \eta_2,$$

(4.12)

$$\eta_1 = r(\mathbf{r} \cdot \mathbf{n}) \psi,$$

(4.13)

$$\eta_2 = (\mathbf{r} \cdot \mathbf{n}) \psi.$$  

(4.14)

The variational solution for the coefficients of $C_i$ is given by

$$C_i = \sum_j (B^{-1})_{ij} A_j,$$

(4.15)

B. Dipolar polarizabilities

We can use the wave function in Eq. (4.3) to calculate dipolar polarizabilities of alkali dimer cations, which are expected to play an important role in the analysis of Rydberg states of alkali dimers. The perturbation to the wave function in the presence of a unit external electric field $\mathbf{n}$ parallel and perpendicular to $\mathbf{R}$ is obtained by taking $\mathbf{n}$ parallel and perpendicular to $\mathbf{R}$. The calculated values of the parallel and perpendicular components of the polarizabilities of Li$^+_2$, Na$^+_2$, K$^+_2$, Rb$^+_2$, and Cs$^+_2$ are given in Table IV, along with the average values.

$$A_i = \langle \eta_i | \mathbf{r} \cdot \mathbf{n} | \psi \rangle,$$

(4.16)

$$B_{ij} = \langle \eta_i | (-\frac{1}{2} \nabla^2 + V - E_0) \eta_j \rangle,$$

(4.17)

and

$$\alpha_n = 2 \sum_i C_i A_i / \langle \psi | \psi \rangle.$$  

(4.18)

The component of $\alpha$ parallel and perpendicular to $\mathbf{R}$ is obtained by taking $\mathbf{n}$ parallel and perpendicular to $\mathbf{R}$. The calculated values of the parallel and perpendicular components of the polarizabilities of Li$^+_2$, Na$^+_2$, K$^+_2$, Rb$^+_2$, and Cs$^+_2$ are given in Table IV, along with the average values

$$\bar{\alpha} = \frac{1}{2} (\alpha_\parallel + 2 \alpha_\perp).$$

V. SUMMARY

We have developed a simple potential to simulate the interaction of the valence electron with the core, in alkali atoms, which has the correct asymptotic behavior and an effective hard-core radius. Based on this we have constructed a wave function to describe (H–alkali)$^+$ ions, which incorporates the cusp condition and has the correct perturbative structure. For the (alkali–alkali)$^+$ ions, we have constructed a Guillemin–Zener type of wave function generalized to incorporate the hard-core structure of closed shells. These wave functions provide reliable values for the potentials, in particular for dissociation energies for all (H–alkali)$^+$ and (alkali–alkali)$^+$ ions, and provide a good physical insight into their structures. They also allow us to consider perturbations in the presence of external dipolar interaction, and calculate dipolar polarizabilities of Li$^+_2$, Na$^+_2$, K$^+_2$, Rb$^+_2$, and Cs$^+_2$.

| Ion      | $\alpha_\parallel$ | $\alpha_\perp$ | Average
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+_2$</td>
<td>109</td>
<td>63</td>
<td>78</td>
</tr>
<tr>
<td>Na$^+_2$</td>
<td>123</td>
<td>77</td>
<td>92</td>
</tr>
<tr>
<td>K$^+_2$</td>
<td>175</td>
<td>149</td>
<td>158</td>
</tr>
<tr>
<td>Rb$^+_2$</td>
<td>189</td>
<td>176</td>
<td>180</td>
</tr>
<tr>
<td>Cs$^+_2$</td>
<td>217</td>
<td>231</td>
<td>226</td>
</tr>
</tbody>
</table>

TABLE IV. Polarizabilities of Li$^+_2$, Na$^+_2$, K$^+_2$, Rb$^+_2$, Cs$^+_2$ for the electric field parallel and perpendicular to $\mathbf{R}$, and the average polarizabilities.