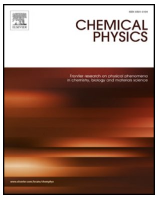
Chemical Physics 511 (2018) 63–70

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



Theoretical study of the low-lying adiabatic states of the NaLi$^+$ molecular ion

Djamal Rabli*, Ronald McCarroll

Sorbonne Université, Université Pierre et Marie Curie, UMR 7614 du CNRS, Laboratoire de Chimie Physique-Matiére et Rayonnement, 75231-Paris Cedex 05, France

ARTICLE INFO

Keywords:
Model potential
NaLi$^+$
Ab initio
Adiabatic energies
Molecular spectroscopic constant

ABSTRACT

With one active electron, the NaLi$^+$ cation is a relatively simple system to study, and a good candidate for which results issue from different approaches can be compared to cross check the reliability of different theoretical methods for the calculation of the adiabatic potential energies. However, comparison of the *ab initio* results of Berriche (2003) and those of Magnier and Frécon (2001), employing model potential methods, is showing a serious disagreement concerning several molecular states. In particular, the low-lying states $2^2\Sigma^+$, $4^2\Sigma^+$, $6^2\Sigma^+$, $8^2\Sigma^+$, $10^2\Sigma^+$ and $4^2\Pi$ obtained by Magnier and Frécon, are found to be repulsive whereas they are attractive when *ab initio* methods are used.

To clarify the origin of such a disagreement, in this work, the NaLi$^+$ cation is re-investigated within the framework of the model potential approach. Adiabatic energies and corresponding molecular spectroscopic constants of states dissociating up to the limit Li$^+$ + Na(4d) are computed. A good agreement with the previous *ab initio* calculations is observed.

1. Introduction

For the calculation of potential energy surfaces, most *ab initio* techniques make use of Gaussian-type orbitals basis functions. In such a basis set, matrix elements involving the electron–electron repulsion terms in the electronic Hamiltonian can be calculated analytically. On the other hand, such matrix elements in a Slater-type basis involve a numerical integration. However, for certain types of problems, a Slater-type basis does have certain particular virtues for the description of long-range interactions involving excited Rydberg states. For such states, the passive electrons may be represented by a model potential, designed to reproduce the experimental energies of the interacting atoms or ions. Molecules having only effective active electron provide a way to test the effectiveness of model potential methods for the calculation of excited electronic states, for which a Slater-type basis is well adapted. Such methods have proved to be very successful in providing an accurate description of avoided crossings of energy curves of excited adiabatic states. In practice, there are two types of systems which are amenable to the use of model potential techniques, namely the alkali molecular ions and the alkali-rare gas systems, both of which involve one active electron. Typical homo-nuclear alkali molecular ions such as Li_2^+, Na_2^+, K_2^+, ..., and hetero-nuclear species such as LiNa$^+$, NaK$^+$, LiK$^+$, ..., have been the subject of several extensive studies [3–9]. Typical alkali-rare gas, such as Na-He, Na-Ne, Na-Xe require a special treatment since in order to take account of the Pauli principle, it is necessary to preclude the active electron from the closed shell implicitly [10,11]. An extensive review of more recent work has been presented by Ben Salem et al. [12].

In this paper, we will be concerned with the LiNa$^+$ molecular ion. From the experimental prespective, direct measurements of crossed-beam reaction rate coefficients for the production of NaLi$^+$ ions, have been reported by Johnson et al. [13]. Several other experimental studies involving indirectly this molecular ion, have been motivated by the measurement of cross sections of charge transfer process which occurs in Li$^+$/Na collisions [14–18]. From the theoretical point of view, besides computation of charge transfer cross sections which has motivated several studies [19–23], theoretical determination of the adiabatic energy curves of the NaLi$^+$ ion, has also received considerable attention. Indeed, the ground state $X^2\Sigma^+$ of this system has been computed in Hartree-Fock approximation by Bertoncini et al. [24], while the first systematic calculation of both the ground and excited states was carried out by Magnier and Frécon [2] using a model potential originally proposed by Klapisch [25] to describe the interaction of the valence electron with the lithium and sodium cores. Results were presented of the first eighteen low-lying molecular states (ten Σ^+, six Π and two Δ).

A little later, Berriche [1] developed a method combining *ab initio* methods together with a non-empirical pseudo-potential to describe the Li$^+$ and Na$^+$ cores and taking into account the core-valence correlation

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* Corresponding author.
E-mail addresses: djamal.rabli@gmail.com (D. Rabli), ronald_mccarroll@upmc.fr (R. McCarroll).

https://doi.org/10.1016/j.chemphys.2018.06.004
Received 18 April 2018; Accepted 8 June 2018

as a correction. This method was used to calculate the adiabatic energies of the ground $X^2\Sigma^+$ state and of all the excited molecular states dissociating up to the Na(4d) + Li^+ limit. Subsequently, Khelifi et al. [26], following the formalism of Foucrault et al. [27] reproduced the spectroscopic constants of both, the NaLi alkali dimer and the $NaLi^+$ cation.

While different experimental and theoretical results show a global agreement for the $X^2\Sigma^+$ ground state, the lack of experimental data for the excited states of the $NaLi^+$ system makes it difficult to reach a final conclusion. However, there are significant disagreements between some of the theoretical results. Comparison between the *ab initio* data [1,26] and those of Magnier and Frécon [2] based on model potential techniques, exhibit a significant number of serious disagreement concerning several excited states. Some states are found to be repulsive by Magnier and Frécon [2] but attractive when *ab initio* techniques are used. According to the model potential results [2], the molecular states $2^2\Sigma^+$, $4^2\Sigma^+$, $6^2\Sigma^+$, $8^2\Sigma^+$, $10^2\Sigma^+$ and $4^2\Pi$ states do not exhibit any energy minimum whereas a well pronounced energy minimum is observed for these states in the *ab initio* approach [1].

Bearing in mind that the disagreement between the *ab initio* [1,26] and the model potential results [2] occurs for states for which the energy minimum occurs at large equilibrium distances ($14 < R_e < 44$ a.u), where model potential methods are expected to provide an accurate description of the system, in the present work we re-investigate the $NaLi^+$ system using the model potential of Klapisch [25], previously employed by Magnier and Frécon [2]. We aim to clarify the origin of these existing disagreements: either due to a numerical artifact, or more seriously to some unknown limitation of either the *ab initio* or model potential methods.

Except where stated, atomic units will be used throughout.

2. Theory

The interaction of the electron of valence with the closed shells, $Li^+(1s^2)$ and $Na^+(2p^6)$ cores, is described by model potentials $V_{model}^{Na/Li}$ previously used in the work by Magnier and Frécon [2] and originally proposed by Klapisch [25] in the form:

$$V_{model}(r) = -\frac{q}{r} - \frac{Z-1}{r}(e^{-\alpha_1 r} + \beta r e^{-\alpha_2 r}), \tag{1}$$

where r denotes the radial distance of the electron form the nucleus, q the ionic core charge and Z the atomic number. The set of parameters () shown in Table 2, has been optimised such that the eigenvalues of the model atomic Hamiltonian

$$H_{model} = T + V_{model}, \tag{2}$$

where T is the kinetic energy operator, reproduce the experimental energies of the ground and the first few excited states of the corresponding ion, Li^+ and Na^+ in the present study (see Table 1).

Table 1
Comparison of calculated and experimental energy levels of the Na atom in a.u.

Level	Present work	[1]	[2]	Exp [28]
Li(2s) + Na^+	0.0000000	0.0000000	0.0000000	0.0000000
Li^+ + Na(3s)	0.0092790	0.0092820	0.0093060	0.0092840
Li(2p) + Na^+	0.0679080	0.0679140	0.0679380	0.0679070
Li^+ + Na(3p)	0.0866030	0.0865920	0.0865500	0.0865940
Li(3s) + Na^+	0.1238130	0.1239860	0.1238400	0.1239600
Li^+ + Na(4s)	0.1264450	0.1265580	0.1264720	0.1265630
Li(3p) + Na^+	0.1407930	0.1409090	0.1408340	0.1409060
Li^+ + Na(3d)	0.1422030	0.1422070	0.1421810	0.1422050
Li(3d) + Na^+	0.1425490	0.1425500	0.1425750	0.1425360
Li^+ + Na(4p)	0.1470870	0.1472120	0.1471290	0.1472070
Li(4s) + Na^+	0.1594310	0.1595390		0.1595270
Li^+ + Na(5s)	0.1604810	0.1605610		0.1605570
Li(4p) + Na^+	0.1659840	0.1661870		0.1661680
Li^+ + Na(4d)	0.1665060	0.1667330		0.1667000

Table 2
Klapisch model potential parameters [25].

	q	Z	α_1	α_2	β
Li	1	3	7.90875	3.90006	1.0321
Na	1	11	7.88747	2.69155	2.354102

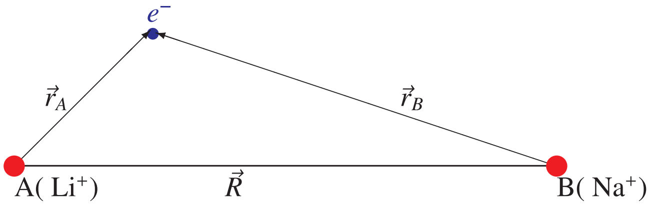

Fig. 1. Relative coordinates for the active electron.

Fixing the lithium and sodium cores at A and B positions respectively as shown in Fig. 1, the $NaLi^+$ molecular cation is then treated as a set of two closed shells $Li^+(1s^2)$ and $Na^+(2p^6)$ cores and a single active electron moving in the field created by the two ionic cores, whose position is described in the Born-Oppenheimer approximation [34], by the electronic Hamiltonian

$$H_e = T + V_{model}^{Li^+}(r_A) + V_{model}^{Na^+}(r_B) + U_{core}, \tag{3}$$

where T denotes the electronic kinetic energy operator, r_A and r_B the radial distances of the active electron from the cores Li^+ and Na^+ respectively. Since we are concerned with intermediate and large internuclear distances only ($R \geqslant 4$ a.u), U_{core} in previous Eq. (3), is mainly the nuclei repulsion modified by polarization terms namely:

$$U_{core} = \frac{q_{Li}\cdot q_{Na}}{R} - \frac{\alpha_d^{Li} + \alpha_d^{Na}}{2R^4} - \frac{\alpha_q^{Li} + \alpha_q^{Na}}{2R^6}, \tag{4}$$

where $q_{Li} = q_{Na} = 1$ denotes the ionic core charge, α_d and α_q are dipole and quadrupolar polarizabilities, respectively. In the present study, as in the work by Magnier and Frécon [2], we have used $\alpha_d^{Li} = 0.1915$ a.u [29], $\alpha_q^{Li} = 0.0156$ a.u [31] for lithium, and $\alpha_d^{Na} = 0.9965$ a.u [32], $\alpha_q^{Na} = 0.376$ a.u [32] for sodium.

The spectrum of the effective Hamiltonian H_e defined in Eq. (3) is determined by conventional variational techniques, using a basis set of Slater-type orbitals f_{sto}, expressed in prolate spheroidal coordinates $\lambda \in [1, \infty]$, $\mu \in [-1, 1]$ and, $\phi \in [0, 2\pi]$ where

$$\lambda = \frac{1}{2R}(r_A + r_B), \quad \mu = \frac{1}{2R}(r_A - r_B), \quad \phi, \tag{5}$$

is the azimuthal angle.

In this prolate spheroidal coordinates system, the basis functions of Slater-type orbitals take the form:

$$\langle \lambda, \mu, \phi | f_{sto} \rangle = A[(\lambda^2-1)(1-\mu^2)]^{\frac{\Lambda}{2}} \lambda^l \mu^k e^{-\frac{R}{2}\zeta(\lambda+\epsilon\mu)} e^{im\phi}, \tag{6}$$

where A denotes a normalisation factor, ϵ a parameter that takes the values ± 1 depending on whether the orbital is centred on lithium or sodium cores, (l, k) integers, ζ a variational parameter describing the decay of the orbital, m the projection of the electronic angular momentum on the z-axis (coinciding with **R**) and $\Lambda = |m| = 0, 1, 2, \ldots$ for Σ^+, Π and Δ molecular states respectively.

3. Results

We have computed the adiabatic potential energies of the attractive ground state dissociating into a sodium ion Na^+ and a lithium atom in its ground state Li(2s), and of the manifold of excited states correlated in the asymptotic region to Na^+ + $Li(1s^2,nl)$, nl = 2p, 3s, 3p, 3d, 4s, 4d and Li^+ + $Na(2p^6,nl)$, nl = 3s, 3p, 4s, 3d, 4p, 5s, 4d.