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Theoretical study of the lowest electronic states of the LiNa$^+$ molecule

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Abstract

The potential energy curves and the spectroscopic constants of the molecular ion LiNa$^+$ electronic states dissociating into Li(2s, 2p, 3s, 3p, 3d, 4s and 4p) + Na$^+$ and Li$^+$ + Na(3s, 3p, 4s, 4p, 5s and 4d) are calculated using an ab initio approach involving a non-empirical pseudopotential for the Li (1s^2) and Na (1s^{2}2s^{2}2p^6) cores and core–valence correlation correction. A very good agreement has been obtained for the ground state for the spectroscopic constants with the available theoretical and experimental works. On the other hand for several excited states a clear discrepancy between this study and the model potential work of Magnier et al. [J. Phys. Chem. A 105, 2001] is observed. They found that the 2, 4, 6, 8, 10 $^2\Sigma$ and 4 $^2\Pi$ states are dissociative although they are in our work attractive with potential wells of some hundreds of cm^{-1}.
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1. Introduction

Diatomic molecules and their cations composed by hydrogen and alkali atoms, have been the subject of numerous theoretical and experimental investigations. This is due to the simplicity of such systems with no more than two valence electrons. Alkali and hydrogen alkali dimers form a prototype systems for investigation of non-adiabatic coupling, collison process radiative association and dissociation, diabatisation and predissociation. In theory, several techniques have been used to study alkali dimers. Most of them have proposed to reduce the number of electrons to only valence electrons, by using pseudopotential or model potential replacing the effect of core electrons on the valence electron. The use of pseudopotentials for Li and Na cores reduce the number of active electrons to only one valence electron, where the SCF calculation produces the exact energy in the basis and the main source of errors corresponds to the basis-set limitations. Furthermore we correct the energy by taking into account the core–core and core–electron correlation following the formalism of Foucrault et al. [1]. This formalism was used first for Rb$_2$ and RbCs molecules and later for several systems (LiH, LiH$^+$, Li$_2^+$) and its use was demonstrated efficiency. The non-empirical pseudopotentials permit the use of very large basis sets for the valence and Rydbergs states

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and allow accurate descriptions for the highest excited states.

In this case LiNa$^+$, having only one active electron, is one of the simplest heteromolecular systems and the computing time is reduced. For our best knowledge only the ground state is experimentally explored [2]. In theory, in the past, the ground state has also been studied by Müller et al. [3] using a similar method to the method used in this work. In that work, the aim was to test the effective core polarization potentials formalism, which contains only a single adjustable atomic parameter, for alkali dimers and their cations having two and one valence electrons. Recently a model potential calculation for the ground state and various excited states has been realized by Magnier et al. [4]. The data produced were used to perform a simulation of one and two-color experiments [5] in above threshold dissociation (ATD) by monitoring an avoided crossing with femtosecond spectroscopy. The same wok has been done recently for Na$_2^+$ and Li$_2^+$ [6, 7] using the available potential energy curves [8,9]. This molecular process involves both bound-free and free–free transition and requires accurate potentials.

This paper presents the first ab initio calculations on high excited states of LiNa$^+$ molecule since we treat nearly all the states dissociating into Li$^+$ + Na(3s, 3p, 4s, 3d, 4p, 5s and 4d) and Li(2s, 2p, 3s, 3p, 3d, 4s and 4p) + Na$^+$.

In Section 2 we briefly present the computational method. The spectroscopic constants and their comparison with previous works, for the 25 lower electronic states of $^2\Sigma$, $^2\Pi$ and $^2\Delta$ symmetries, will be reported in Section 3. Finally we summarize our conclusion in Section. 4.

2. Summary of the method

In this work the Li and Na atoms are treated trough a one electron pseudopotential proposed by Barthelat et al. [10] and used in many previous works [11–14]. In addition we account the core valence correlation by the use of the operatorial formulation of Müller, Flesh, and Meyer [15] where the core polarization potential is written:

$$V_{CPP} = -\frac{1}{2}\sum_{\lambda}\alpha_{\lambda}f_{\lambda}f_{\lambda},$$

The summation runs over all the polarizable cores λ with a dipole polarizabilty α. f_{λ} is the electric field created on center λ produced by valence electrons and all other cores, modified by a cutoff function F with an l-dependent adjustable parameter according to the formulation of Foucrault, Millie, and Daudey [1].

$$f_{\lambda} = \sum_{i}\frac{\vec{r}_{i\lambda}}{r_{i\lambda}^3}F(r_{i\lambda},\rho_{\lambda}) - \sum_{\lambda'\neq\lambda}\frac{\vec{R}_{\lambda'\lambda}}{R_{\lambda'\lambda}^3}Z_{\lambda}$$

where $r_{i\lambda}$is a core–electron vector and $R_{\lambda'\lambda}$, is a core–core vector. $F(r_{i\lambda},\rho_{\lambda})$ is the cutoff operator, expressed following the Foucroult formalism by a step function defined by

$$F(r_{i\lambda},\rho_{\lambda}) = \begin{cases} 0, & r_{i\lambda} < \rho_{\lambda} \\ 1, & r_{i\lambda} > \rho_{\lambda} \end{cases}$$

which has a physical meaning of excluding the valence electrons from the core region for calculating the electric field. The cutoff radius is taken to be a function of l as following:

$$F(r_{i\lambda},\rho_{\lambda}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}F_l(r_{i\lambda},\rho_{\lambda}^l)|lm\lambda\rangle\langle lm\lambda|,$$

where $|lm\lambda\rangle$ is the spherical harmonic centered on λ. In Müller et al. formalism this cutoff function is unique for a given atom, generally adjusted to reproduce the first ionization potential.

The cutoff radii, reported in Table 1, were optimized in order to reproduce the ionization potentials and the lowest valence s, p, and d one-electron states as deduced from the atomic data tables. The Gaussian-type orbitals basis sets on Li and Na atoms were, respectively, 9s/8p/4d/1f and 12s/12p/9d/2f. They are reported in Table 2. The core dipole polarizability of Li$^+$ and Na$^+$ are, respectively, 0.1915 and 0.993 a_0^3.

Table 1
l-dependant cutoff radii (in bohr) for Li and Na atoms

l	Li	Na
s	1.434	1.455
p	0.982	1.600
d	0.600	0.700
f	0.400	0.700

Table 2
Basis set for lithium and sodium (exponent and coefficients)

	Lithium		Sodium	
	Expt.	Coef.	Expt.	Coef.
	2.464	0.013829	2.8357	0.007043
	1.991	− 0.032077	0.49318	− 0.1871
	0.582	1	0.072085	1
	0.2	1	0.036061	1
	0.07	1	0.016674	1
	0.031	1	0.00693	1
	0.015	1	0.00287	1
	0.008	1		
	0.003037	1		
p	0.63	0.052433	0.431	− 0.1778
	0.24	0.078566	0.09276	0.2003
	0.098	1	0.03562	1
	0.043	1	0.01447	1
	0.02	1	0.0058	1
	0.01	0.01445	0.0023	1
	0.005	0.006587		
	0.002734	1		
d	0.2	1	0.292	0.01454
	0.07	1	0.06361	0.123
	0.022796	0.491521	0.02273	1
	0.008574	0.549272	0.008852	1
	0.008574	0.549272	0.00352	1
f	0.01	1	0.015	1
			0.0055	0.70461
			0.0020	0.11743

Table 3 presents a comparison between our ab initio, the model potential [4] and the experimental [16] dissociation limit for all the electronic states dissociating into $Li^+ + Na(3s, 3p, 4s, 3d, 4p, 5s$ and 5d)) and $Li(2s, 2p, 3s, 3p, 3d, 4s$ and 4d)) + Na^+. Our dissociation energies are in very good agreement with the experiment dissociation energies. The difference between our work and the experimental values does not exceed $3.4 \times 10^{-5} a_0$ (7 cm^{-1}). The model potential energies were calculated at 200 a_0.

3. Potential energy curves and spectroscopic constants

Molecular potential energies for all the electronic states dissociating into $Li^+ + Na(3s, 3p, 4s, 3d, 4p, 5s, 4d)$ and $Li(2s, 2p, 3s, 3p, 3d, 4s, 4p) + Na^+$ have been calculated for a large and dense grid of intermolecular distance from 3 to 200 a_0. The potential energy curves are displayed in Fig. 1 for $^2\Sigma$ states and Fig. 2 for $^2\Pi$ and $^2\Delta$ states.

The ground state has the deepest well ($D_e = 8061$ cm^{-1}) compared to the $^2\Sigma$ excited states or other symmetries showing the electron delocalisation and the formation of a chemical bond. Further more, the LiNa$^+$ ionic system is more bound than the neutral LiNa ($D_e = 7066$ cm^{-1}) molecule in contrast to similar systems like LiK$^+$–LiK and NaK$^+$–NaK

Table 3
Dissociation Energies (in a. u): comparison between our calculated energy, the Magnier et al. [4] Model Potential calculated energy and corresponding Experimental dissociation

Dissociation unit	Our work	Magnier et al. [4]	Experiment [15]	ΔE
Li(2s) + Na$^+$	− 0.198141	− 0.198142	− 0.198142	10^{-6}
Li$^+$ + Na(3s)	− 0.188859	− 0.188836	− 0.188858	10^{-6}
Li(2p) + Na$^+$	− 0.130227	− 0.130204	− 0.130235	8×10^{-6}
Li$^+$ + Na(3p)	− 0.111549	− 0.111592	− 0.111548	10^{-6}
Li(3s) + Na$^+$	− 0.074155	− 0.074302	− 0.074182	27×10^{-6}
Li$^+$ + Na(4s)	− 0.071583	− 0.071670	− 0.071579	4×10^{-6}
Li(3p) + Na$^+$	− 0.057232	− 0.057308	− 0.057236	4×10^{-6}
Li$^+$ + Na(3d)	− 0.055934	− 0.055961	− 0.055937	3×10^{-6}
Li(3d) + Na$^+$	− 0.055591	− 0.055567	− 0.055606	15×10^{-6}
Li$^+$ + Na(4p)	− 0.050929	− 0.051013	− 0.050935	6×10^{-6}
Li(4s) + Na$^+$	− 0.038602		− 0.038615	13×10^{-6}
Li$^+$ + Na(5 s)	− 0.037580		− 0.037585	5×10^{-6}
Li(4p) + Na$^+$	− 0.031954		− 0.031974	20×10^{-6}
Li$^+$ + Na(4d)	− 0.031408		− 0.031442	34×10^{-6}

ΔE is the difference between our calculated and the experimental energies.
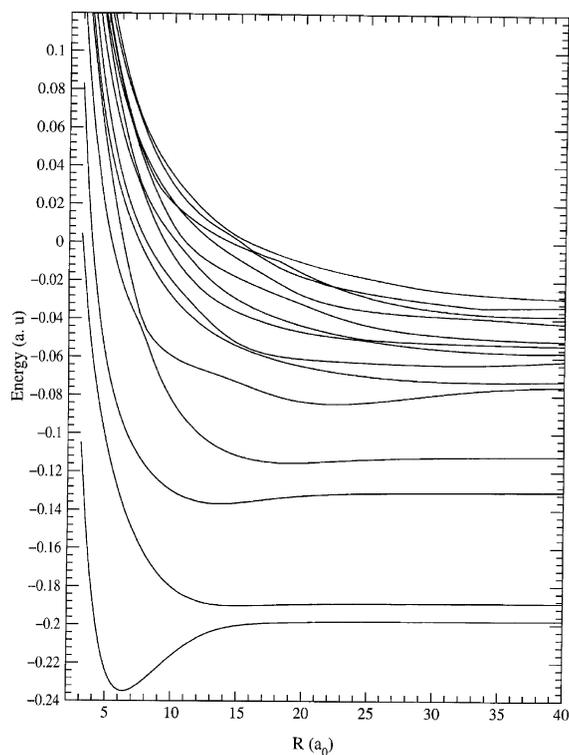
Fig. 1. Potential energy curves for the lowest $^2\Sigma$ electronic states of LiNa$^+$ dissociating into Li(2s, 2p, 3s, 3p, 3d, 4s, 4p) + Na$^+$ and Li$^+$ + Na (3s, 3p, 4s, 3d, 4p, 5s, 4d).
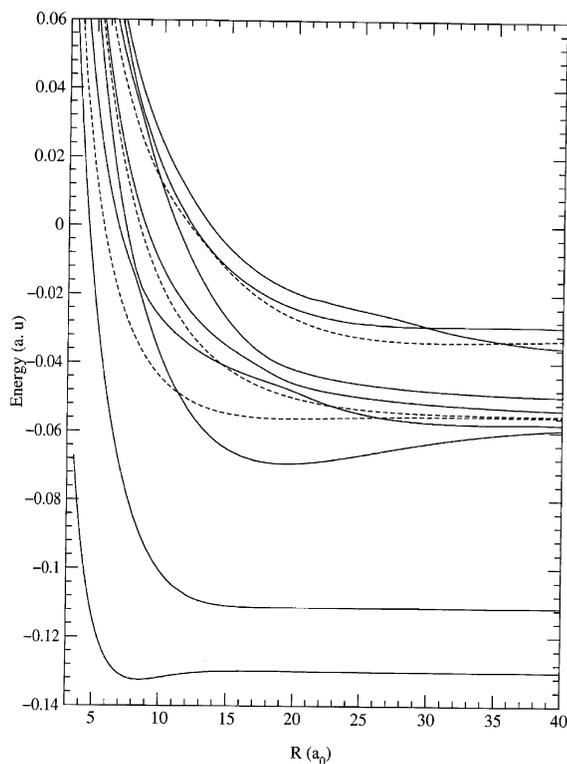

Fig. 2. Potential energy curves for the $^2\Pi$(solid lines) and the $^2\Delta$ (dashed lines) lowest electronic states of LiNa$^+$ dissociating into Li(2p, 3p, 3d, 4p) + Na$^+$ and Li$^+$ + Na (3p, 3d, 4p, 4d).

[3], where the neutral molecule is more bound than the ionic. The spectroscopic constants of the ground and low lying $^2\Sigma$ states are presented in Table 4 and compared with other theoretical [3,4] and experimental [2] works. For our best knowledge, the only ab initio theoretical work realized for LiNa$^+$ is the work of Müller at al [3]. They report the spectroscopic constants for many neutral and ionic alkali dimers but only for the ground state. Our work can be considered as the first ab initio calculation on the excited states. Our ground state equilibrium distance (R_e) is in good agreement as well as the well depth (D_e) with their work. We find for R_e and D_e, respectively, 6.37 a_0 and 8061 cm^{-1} and they found 6.35 a_0 and 8114 cm^{-1}. The difference between our and their values is 0.02 a_0 for R_e and 53 cm^{-1} for D_e. This good agreement between our results and those of Müller et al. for the ground states is also observed for ω_e, $\omega_e\chi_e$ and β_e spectroscopic constants. Our values for ω_e, $\omega_e\chi_e$ and

β_e, are respectively, 192.98, 1.11 and 0.2786 cm^{-1} and their values are 193, 1.09 and 0.277 cm^{-1}. This excellent agreement for all spectroscopic constants for the ground state is not surprising since we used similar methods. In contrast our D_e value is in better agreement than their value compared to the experimental [2] value of 7985 ± 242 cm^{-1}. In the same time there is a good agreement for the ground state between our spectroscopic constants and that of Magnier et al. [4]. They found for R_e, D_e and ω_e, respectively, 6.35 a_0, 7988 and 192.04 cm^{-1}. As it's said in their paper the cutoff parameters were adjusted in order to reproduce the experimental [2] dissociation energy and the ab initio theoretical [3] equilibrium distance.

The spectroscopic constants for $^2\Sigma$ excited states are presented here and compared with the available calculation. For our best knowledge, there are not experimental results for the excited states.

Table 4
Spectroscopic constants for the $^2\Sigma$ electronic states of LiNa$^+$ (R_e in a_0, D_e, T_e, ω_e, $\omega_e\chi_e$ and β_e are in cm^{-1})

State		R_e	D_e	T_e	ω_e	$\omega_e\chi_e$	β_e	Reference
1	$^2\Sigma$	6.37	8061		192.98	1.11	0.278607	This work
		6.35	8115		193.00	1.09	0.277	Theory [3]
		6.35	7988		192.04			Theory [4]
			7985 ± 242					Exp [2]
2	$^2\Sigma$	14.90	294	9805	36.39	1.51	0.050840	This work
			Repulsive					Theory [4]
3	$^2\Sigma$	13.65	1423	21543	58.14	0.21	0.060663	This work
		13.64	1495	21401	58.24			Theory [4]
4	$^2\Sigma$	18.94	847	26219	32.45	13.76	0.031677	This work
			Repulsive					Theory [4]
5	$^2\Sigma$	22.41	2262	33011	41.12	0.33	0.022492	This work
		22.43	2300	32879	40.00			Theory [4]
6	$^2\Sigma$	34.24	265	35575	13.59	4.09	0.009606	This work
			Repulsive					Theory [4]
7	$^2\Sigma$		Repulsive					This work
			Repulsive					Theory [4]
8	$^2\Sigma$	37.47	375	38896	43.29	13.00	0.008025	This work
			Repulsive					Theory [4]
9	$^2\Sigma$		Repulsive					This work
			Repulsive					Theory [4]
10	$^2\Sigma$	44.95	127	40242	2.83	19.36	0.005090	This work
			Repulsive					Theory [4]
11	$^2\Sigma$		Repulsive					This work
12	$^2\Sigma$	62.05	201	44103	6.97	0.03	0.002933	This work
13	$^2\Sigma$	33.91	488	44138	41.99	18.99	0.009791	This work
14	$^2\Sigma$		Repulsive					This work

Equilibrium distance of all these states is found for intermediate and large values of the internuclear distance, from 13.65 to 73.76 a_0. We remark that the 7 and 9 $^2\Sigma$ states, which are dissociating into Li(3p and 3d) + Na$^+$ are repulsive in agreement with the model potential calculation [4]. They studied 1–10 $^2\Sigma$, 1–6 $^2\Pi$ and 1–2 $^2\Delta$ states. In their work and from their Table 2, they found only 1, 3, 5 $^2\Sigma$ and 1, 3 $^2\Pi$ and 1 $^2\Delta$ states were bound states. The other studied states were repulsive. For the 3 and 5 $^2\Sigma$ states, we remark a good agreement for R_e between our values and those of the model potential calculation. We find, respectively, 13.65 and 22.41 a_0 and they found 13.64 and 22.43 a_0. The difference between the two calculated R_e is about 0.02 a_0. For D_e we find for the 3, 5 $^2\Sigma$ states, respectively, 1423, and 2262 cm^{-1} and they found 1495 and 2300 cm^{-1}. We remark that our D_e, for the two states, is lower than theirs values but the difference does not exceed 72 cm^{-1}, showing a good

agreement between the two calculations. The same agreement is observed for ω_e where we find, respectively, 58.14 and 41.12 cm^{-1} and they found, respectively, 58.24 and 40 cm^{-1}. The 2, 4, 6, 8 and 10 $^2\Sigma$ states are in our work attractive and they have potential wells at, respectively, 14.90, 18.94, 34.24, 37.47 and 44. 95 a_0 of, respectively, depth of 294, 847 and 265 cm^{-1}. In contrast to the 1, 3, 5, 7 and 9 $^2\Sigma$ states, where the agreement between our work and the model potential calculation is good, there is a disagreement for the 2, 4, 6 8, and 10 $^2\Sigma$ states. In the model potential calculation the five states are repulsive. In our work the 2, 4, 6, 8 and 10 $^2\Sigma$ states have been found to be attractive with potential wells of, respectively, 294, 847, 265, 375 and 127 cm^{-1} at, 14.90, 18.94, 34.24, 37.47 and 44.95 a_0 equilibrium distances. Their vibrational frequencies (ω_e) are, respectively, 36.39, 32.45, 13.59, 43.29 and 2.83 cm^{-1}. As we remark the equilibrium distances

are at intermediate and large distance and their dissociation energies (D_e) are of the order of some 100 cm^{-1}. The model potential curves have been calculated from $R = 2.5$ to $R_{max} = 40 \, a_0$ and our equilibrium distance ($R_e = 43.29 \, a_0$) for the 10 $^2\Sigma$ state is larger than R_{max}. This explains the raison why they do not find the potential well associated to such state. Although, our equilibrium distance (R_e) for the 2, 4, 6 and 8 $^2\Sigma$ states is shorter than R_{max}, these states are purely repulsive in the model potential calculations. The 11, 12 13 and 14 $^2\Sigma$ sates are studied here for the first time. The 11 and 14 $^2\Sigma$ states are found to be repulsive although the 12 and 13 $^2\Sigma$ sates are found to be bound states. Their R_e, D_e and ω_e spectroscopic constants are, respectively, 62.05 a_0, 201 and 6.97 cm^{-1} for the 12 $^2\Sigma$ state, and 33.91 a_0, 488 and 41.99 cm^{-1} for the 13 $^2\Sigma$ state.

The eight lower $^2\Pi$ and the three $^2\Delta$ electronics states are presented in Fig. 2. Their spectroscopic constants are reported in Table 4 and compared to the model potential data. Unfortunately, to our knowledge there is no experimental information for the $^2\Pi$ and $^2\Delta$ states. As can be seen in Table 4, only the 1– 6 $^2\Pi$ electronics states were studied in the model potential calculation [4]. Furthermore, only the 1 $^2\Pi$ and 3 $^2\Pi$

states were found to be bound states in their calculation. Our spectroscopic constants (R_e, D_e and ω_e) are, respectively, 8.53 a_0, 496 and 68.70 cm^{-1} for 1 $^2\Pi$ state and 19.35 a_0, 2667 and 37.27 cm^{-1} for the 3 $^2\Pi$ state, to be compared with 8.56 a_0, 614 and 58.24 cm^{-1}, and 19.09 a_0, 2863 and 38.34 cm^{-1}. We remark that our bond length (R_e) is in good agreement with that of Magnier et al. as well as the vibrational frequency (ω_e), while the dissociation energy is in a rather good agreement. The 4 $^2\Pi$ state exhibits two minimums lie at, respectively, $R_e = 34.76$ and 41.28 a_0 with well depths $D_e = 398$ and 422 cm^{-1}. This state is found to be repulsive in the model potential calculation. A good agreement, between our calculation and the model potential calculation for the 2, 5 and 6 $^2\Pi$ states, was observed. In both calculations the three states are repulsive. The higher 7 and 8 $^2\Pi$ excited states are studied here for the first time. They are bound states and present minimums at large distances. The minimum of the state 7 $^2\Pi$ lies at $R_e = 46.01 \, a_0$ with a well depth $D_e = 1098 \, cm^{-1}$. For the 8 $^2\Pi$ state, we find two minimums at, respectively, 79.30 and 118.38 a_0 with a depth of 108 and 81 cm^{-1}.

For the $^2\Delta$ states we present the three lower states dissociating into Li(3d) + Na$^+$ and Li$^+$ + Na(3d and

Table 5

Spectroscopic constants for the $^2\Pi$ and $^2\Delta$ electronic states of LiNa$^+$ (R_e in a_0, D_e, T_e, ω_e, $\omega_e\chi_e$ and β_e are in cm^{-1})

State		R_e	D_e	T_e	ω_e	$\omega_e\chi_e$	β_e	Reference
1	$^2\Pi$	8.53	496	22471	68.70	1.40	0.155188	This work
		8.56	614	22282	58.24			Theory [4]
2	$^2\Pi$	Repulsive						This work
		Repulsive						Theory [4]
3	$^2\Pi$	19.35	2667	36319	37.27	0.13	0.030175	This work
		19.09	2863	36020	38.34			Theory [4]
4	$^2\Pi$	34.76	398	38872	7.12	42.57	0.009550	This work
		41.28	422	38849	16.76	42.57	0.009550	This work
		Repulsive						Theory [4]
1	$^2\Delta$	19.59	57	39216	18.48	0.35	0.029415	This work
		17.97	340	38900	22.0			Theory [4]
5	$^2\Pi$	Repulsive						This work
		Repulsive						Theory [4]
2	$^2\Delta$	Repulsive						This work
6	$^2\Pi$	Repulsive						This work
		Repulsive						Theory [4]
7	$^2\Pi$	46.01	1098	43442	71.71	10.08	0.006647	This work
8	$^2\Pi$	79.30	108	44524	4.61	0.10	0.011436	This work
		118.38	81	44551	1.92	0.10	0.011436	This work
3	$^2\Delta$	31.10	522	44110	14.15	8.43	0.011596	This work

4d). Their spectroscopic constants are reported in Table 4 and their potential energy curves are presented in Fig. 2. For the 1 $^2\Delta$ a rather good agreement is observed between our equilibrium distance ($R_e = 19.59\ a_0$) and that of the model potential calculation ($R_e = 17.97\ a_0$). In contrast, a disagreement is observed for D_e where we find a potential well of 57 cm^{-1}, while their well is deeper 340 cm^{-1}. The 2 $^2\Delta$ state is repulsive, in good agreement with the model potential calculation, and the 3 $^2\Delta$ state present a deep well, compared to the 1 $^2\Delta$, of 522 cm^{-1} at an equilibrium distance $R_e = 45.92\ a_0$.

From the comparison between our work and that of the model potential calculation, we remark first, a good agreement between the two works for 1, 3, 5, 7 and 9 $^2\Sigma$ and 1, 3 and 5 $^2\Pi$ states. Second a disagreement for 2, 4, 6, 8 and 10 $^2\Sigma$ and 2, 4 and 6 $^2\Pi$ states. In our work all the last states are attractive in contrast to model potential calculation where all such electronic states are repulsive.

We remark in the potential energy curves many avoided crossing due to the electron transfer between Li$^+$ and Na$^+$. Many works on measuring of the total electron transfer cross-sections have been done by Daley et al. [17] and Aquilanti et al. [18] on Li$^+$ + Na(3s) and Li(2s) + Na$^+$ systems, and Machholm et al. [19] and Thomsen et al. [20] on Li$^+$ + Na(3p) system. In a recent work of Magnier and Toniolo [5] The avoided crossing between the 4 $^2\Sigma$ and 5 $^2\Sigma$ states was used to monitor the a simulation of the non-adiabatic dynamics by two-color ATD experiment. In Table 4 we present the intermolecular distance R_c, which corresponds to the avoided crossing between 4/5, 5/6, 6/7, 7/8, 8/9, 9–10, 10/11, 11/12, and 12/13 $^2\Sigma$, and 3/4, 4/5, 5/6, 6/7, and 7/8 $^2\Pi$ states. A comparison is done with the values found by Magnier et al. [4] for only 4/5, 5/6, 6/7 and 8/9 $^2\Sigma$ states and 3/4, 4/5 and 5/6 $^2\Pi$ states avoided crossing. For the first, a very good agreement is observed between the two results, 7.75 a_0 compared to 7.73 a_0. For 5/6 states, we observe two avoided crossing at, respectively, 4.29 and 15.61 a_0. Magmier et al. [4] mentioned only the first ($R_c = 4.25\ a_0$) where the agreement with our value is good. The same thing is observed for the 6/7 states, we find two avoided crossings at, respectively, 7.86 and 16.02 a_0 and they find only one at 16.5 a_0. For the 8/9 states

Table 6
R_c (in a_0) the avoided crossing distances

States		Our work	Theory [4]
4/5	$^2\Sigma$	7.73	7.75
5/6	$^2\Sigma$	4.29, 15.61	4.25
6/7	$^2\Sigma$	7.86, 16.02	16.5
7/8	$^2\Sigma$	11.4	
8/9	$^2\Sigma$	7.52, 24.59	7.5, 25
9/10	$^2\Sigma$	10.82	
10/11	$^2\Sigma$	6.7, 20.19	
11/12	$^2\Sigma$	10.26, 33.50	
12/13	$^2\Sigma$	16.00, 22.25	
13/14	$^2\Sigma$	14.51	
3/4	$^2\Pi$	8.18	8.25
4/5	$^2\Pi$	19.59	20
5/6	$^2\Pi$	18.19	18.25
6/7	$^2\Pi$	8.34	
7/8	$^2\Pi$	29.75	

a good agreement is observed in both works for the two avoided crossings at, respectively, 5.52 and 24.59 a_0 for our values and 7.5 and 25 a_0 for their values. The higher avoided crossings are not observed in the Magnier et al. work, we present only our values. For the $^2\Pi$ states the avoided crossings occur at 8.18, 19.59, 18.19, 8.34, and 24.87 a_0 for, respectively, 3/4, 4/5, 5/6, 6/7, and 7/8 states. Magnier et al. presented in their work the position 8.25 a_0 for 3/4 states, 20 a_0 for 4/5 states and 18.25 a_0 for 5/6 states. These values agree well with our values (Tables 5 and 6).

4. Conclusion

Using the pseuodopotential approach for Li and Na atoms, the LiNa$^+$ was considered as a one-electron system. This leads to a trivial full CI ab-initio calculation, where 25 potential energy curves were computed with a good accuracy. The agreement between the spectroscopic constants obtained in our work and those of the available references [3,4] for the ground state is very good. For the 3, 5 $^2\Sigma$ and 1, 3 $^2\Pi$ excited states (where no experimental data are available), our D_e and R_e are in good agreement with the model potential calculation [4]. It seems that our values for D_e are always smaller than their values. In contrast, for the other excited states, they found that the 2, 4, 6, 7, 8 9,10 $^2\Sigma$ and 2, 4, 5, 6, and $^2\Pi$ are

repulsive. In our work only the 7, 9 and 14 $^2\Sigma$ states are repulsive. The other states present minima at large distance and wells of some 100 of cm^{-1}. The discrepancies between the two works cannot be due to the core–core and core–valence correlation effects, which strongly influence the lithium and sodium asymptotic spectrum and the shape of the potential curves, because this is present in the two methods of calculation. In fact, this discrepancy can be understood by the optimization, in the model potential calculation, of the cutoff radius to produce only the spectroscopic constants of the ground state. In order to understand clearly the discrepancy between the two works for the 2, 4, 6, 8, 10 $^2\Sigma$ and 4 $^2\Pi$ and 1 $^2\Delta$ excited states, further theoretical (by realizing full electron calculation) and experimental investigations have to be done.

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