A revised study of the View the MathML sourceLi2+ alkali-dimer using a model potential approach

Djamal Rabli, Ronald Mccarroll

A revised study of the Li_2^+ alkali-dimer using a model potential approach

Djamal Rabli, Ronald McCarroll

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

Abstract

The model potential approach is well adapted to study atomic and molecular systems involving a single active electron. Such is the case of the alkali-dimer lithium cation Li_2^+. However, a comparison of the model potential results of Magnier et al.[1] and those based on *ab-initio* techniques [2, 3, 4] raises a number of questions related to the existence of an important disagreement regarding several excited states,which are found to be repulsive by Magnier et al. [1] but attractive when *ab-initio* techniques are employed.

In this paper, we propose to re-investigate the Li_2^+ system, using a model potential technique to compute the adiabatic energy curves and the molecular spectroscopic constants. Our aim is to clarify whether this disagreement between the *ab-initio* and model potential methods originates from some conceptual defect of the model potential technique or whether there is some source of error in the calculations of Magnier et al. [1].

Keywords: model potential, Lithium cation, *ab-initio*, adiabatic energies, molecular spectroscopic constant

1. Introduction

The alkali-dimer lithium cation Li_2^+ is a simple diatomic molecular ion, that may be considered as a prototype for molecular systems involving a single active electron. It has been the subject of both theoretical and experimental studies and several accurate adiabatic potential energy curves and molecular spectroscopic

Email addresses: djamal.rabli@gmail.com (Djamal Rabli),
ronald_mccarroll@upcm.fr (Ronald McCarroll)

constants, based on different approaches, have been reported in the literature during the last decade [1, 2, 3, 4, 5, 6].

From the experimental side, several works mainly focusing on the $X^2\Sigma_g^+$ ground state were realized. To estimate the ground state dissociation energy, Mathur et al. [7] used an ionization process of the lithium dimer by exploiting two different lines of the Ar^+ ion laser; going from the lithium dimer $X^1\Sigma_g^+$ ground state trough its $B^1\Pi_u$ state, to finally reach the Li_2^+ cation ground state. On the other hand measurements accomplished by McGeoch et al. [8] also enabled the knowledge of molecular spectroscopic constants of the $X^2\Sigma_g^+$ ground state, while Bernheim et al. [9, 10] provided the same quantities, by investigating a Rydberg series of excited electronic states of the lithium dimer using an optical-optical double resonance spectroscopy.

From the theoretical point of view, a restricted Hartree-Fock-Roothaan approach was developed by Henderson et al. [11], while Müller et al. [12] carrying out calculations with frozen atomic core, generated adiabatic potential energy curves of states dissociating up to the $Li^+(1s^2)+Li(3d)$ limit. In a study by Konowalow et al. [13], the first eight lowest-lying electronic states were obtained by valence configuration calculations, whereas Schmidt-Mink et al. [14] employed *ab-initio* self-consistent-field (SCF) and valence CI techniques combined with a core polarization potential for a better description of the inter-shell correlation effects.

In addition to pseudo-potential method used by Fuentealba et al. [15] and local potential approach developed by D. Hasman [16], Jasik et al. [3], adopted an *ab-initio* approach where calculations were based on the SCF configuration interaction scheme. Similarly, Bouzouita et al. [2] adopted an *ab-initio* approach, based on a non-empirical pseudo-potential for the $Li(1s^2)$ core where core-core and core-valence correlations have been added to generate the adiabatic energy curves of states dissociating up to $Li^++Li(3d)$ asymptotic limit. More recently Musial et al. [4] used an *ab-initio* calculation with all inner shell electrons correlated to study the first 18 electronic states.

If *ab-initio* methods provided most available data describing the Li_2^+ cation, model potential techniques also were used by Henriet et al. [17] in a study focusing on the ground state. Similarly, Cerjan [18] adopted a model potential approach to determine molecular properties, of the lowest $^2\Sigma_g^+$ and $^2\Pi_u$ states. In a more detailed investigation, based on model potential techniques, Bottcher and Dalgarno [19] reported the potential energy curves of the first low-lying, four Σ, two Π and one Δ states. But to our best knowledge, the most extensive work exploiting model potential techniques remains the one by Magnier et al. [1] who used a potential

2

Table 1: Comparison of calculated and experimental energy levels in cm^{-1} of the lithium atom.

Level	Exp [23]	This work	[1]	[2]	[3]	[4]
Li(1s^2,2p)	14903.86	14904.52	14903.86	14905.40	14908.91	14914.80
Li(1s^2,3s)	27206.07	27174.03	27172.71	27211.78	27195.97	27186.52
Li(1s^2,3p)	30925.28	30904.22	30902.90	30925.94	30896.97	30922.48
Li(1s^2,3d)	31283.03	31284.78	31283.25	31286.10	31292.47	31259.62

of Klapisch [20] to report a complete set of 58 adiabatic states for internuclear distances in the range 4 to 40 a.u.

Having one single active electron, certainly makes the lithium cation a relatively simple system to investigate. However when comparing results obtained by different approaches, agreement is far from being guaranteed for all states. While different methods give results which are in reasonable agreement for the ground state, for several excited states, an important disagreement is observed when analyzing data resulting from a model potential approach [1] and those based on *ab-initio* methods [2, 3, 4]. The states $3^2\Sigma_u^+$ and $4^2\Sigma_u^+$ for example have been found to be repulsive by model potential techniques [1], but are found to be attractive when *ab-initio* approaches are employed. It is unclear from Magnier et al. [1] whether this disagreement is limited by some conceptual defect of the model potential technique or whether there is some other source of error.

Since *ab-initio* methods predict for the states showing disagreement, large values of equilibrium distances (R_e > 18 a.u), where model potential techniques in principle should give an accurate description of the system, in the present work we propose to re-investigate the Li$_2^+$ system using a model potential of Klapisch [20]. We aim to sort out whether these disagreements were physical effects or numerical artifacts of particular implementation of the model potential method.

Except where stated, atomic units will be used throughout.

2. Theory

The interaction of an electron with a closed shell lithium core is described by the model potential of Klapisch [20]

$$V(r) = -\frac{1}{r} - \frac{2e^{-7.90875r} + 10.321re^{-3.90006r}}{r}, \tag{1}$$
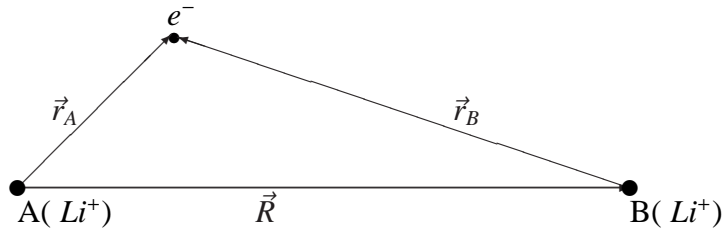
3

Figure 1: Relative coordinates for the active electron.

where r is the radial distance of the electron form the lithium nucleus. The eigenvalues of the corresponding model atomic Hamiltonian

$$H = T + V(r), \tag{2}$$

where T denotes the electronic kinetic energy operator, are compared with the experimental energy values of the neutral Lithium atom in Table 1. The precision of the computed energy levels is adequate for the particular applications of this work.

Taking the lithium nucleus at A and B (see Fig. 1), the Li_2^+ molecular cation is then treated as a set of two closed shell $Li^+(1s^2)$ cores and a single active electron, whose position is described in the Born-Oppenheimer approximation [21] by the effective Hamiltonian

$$H_e = T + V(r_a) + V(r_b) + U_{core}, \tag{3}$$

where T is the electronic kinetic energy operator, r_a and r_b the radial distances of the active electron from nuclei A and B respectively. U_{core} may be mainly taken as the nuclei repulsion modified by a polarization term, namely:

$$U_{core} = \frac{q_1 q_2}{R} - \frac{\alpha}{2R^4}, \tag{4}$$

where $q_1 = q_2 = 1$ is the ionic core charge and $\alpha = 0.19$ a.u. the polarizability of the lithium atom [22].

4

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

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

and ϕ is the azimuthal angle.

The basis set of Slater-type orbitals take the following form:

$$f_{sto}(\lambda.\mu,\phi) = N[(\lambda^2 - 1)(1 - \mu^2)]^{\frac{\Lambda}{2}} \lambda^p \mu^q e^{-\frac{R}{2}\zeta(\lambda+\epsilon\mu)} e^{im\phi}, \tag{6}$$

where N denotes a normalization factor, ϵ a parameter that takes the values ± 1 depending on whether the orbital is centered on nucleus A or nucleus B, (p,q) 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 the internuclear axis **R**) and $\Lambda = | m | = 0,1,2,\dots$ for Σ, Π and Δ molecular states respectively.

3. Results

We have computed the adiabatic potential energies of the attractive ground state dissociating to a ground state lithium atom Li($1s^2$,2s) and Li$^+$ and of the manifold of excited states correlated in the asymptotic region to Li$^+$+Li($1s^2$,nl), where nl=2s,2p,3s,3p and 3d. Graphics showing our adiabatic energies versus the internuclear separation R, ($R \leq 50$ Å), for Σ, Π and Δ states are presented in Fig.3, Fig.4 and Fig.5 respectively while comparison of the molecular constants obtained in the present work and selected theoretical and experimental data, is shown in Table 2, Table 3 and Table 4.

3.1. Σ states

A basis set of 345 vectors were used to generate the Σ states for different internuclear separation. For the $1^2\Sigma_g^+$ ground state, present calculations yield a dissociation energy D_e =10494 cm^{-1} and an equilibrium distance R_e=3.083 Å. These values may be compared to the experimental ones of Bernheim et al. [9, 10], D_e =10464 cm^{-1} and R_e=3.11 Å. Our results also show small differences when they are compared to the *ab-initio* ones of Jasik et al. [3] R_e=3.093 Å and D_e=10498 cm^{-1}, to those of Bouzouita et al. [2], R_e=3.095 Å and D_e=10475 cm^{-1} and to the recent ones of Musial et al. [4] R_e=3.103 and D_e=10439 cm^{-1}.
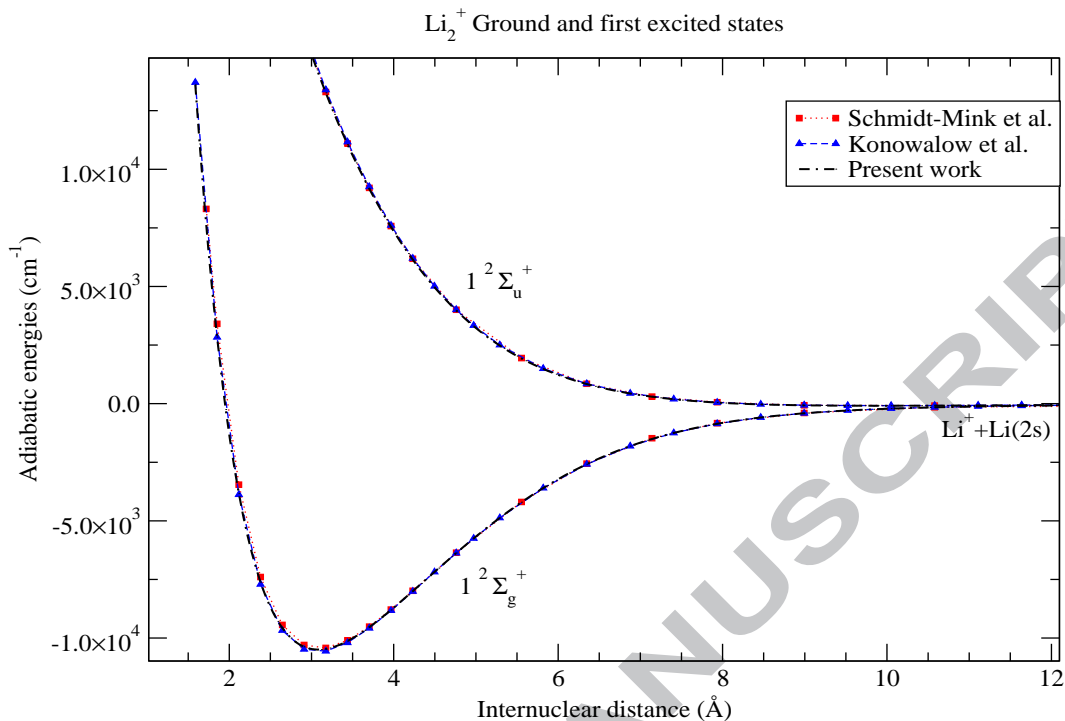
5

Figure 2: Li_2^+: The adiabatic energies of the ground $^2\Sigma_g^+$ and the first excited $^2\Sigma_u^+$ states. The red curve corresponds to Schmidt-Mink et al. [14] results, blue curve to Konowalow et al. [25] results, while the black curve indicates the present results.

As mentioned in Table 2, for the $1^2\Sigma_g^+$ ground state, it is interesting to notice that our vibration constants ω_e=262.771 cm^{-1} and $\omega_e\chi_e$=1.645 cm^{-1}, compare well to the experimental values [9, 10], ω_e=262 cm^{-1} and $\omega_e\chi_e$=1.7 cm^{-1}.

Present calculations also show that the first excited state $1^2\Sigma_u^+$ correlated to Li($1s^2$,2s)+Li$^+$ in the asymptotic limit, has a repulsive character at short internuclear distances, however it possesses a weak potential minimum of 89 cm^{-1} occurring at an equilibrium internuclear distance R$_e$=9.929 Å. These values may be compared to the *ab-initio* ones of Bouzouita et al. [2] D$_e$=88 cm^{-1} and R$_e$ =9.911 Å and to those of Jasik et al. [3] D$_e$=89 cm^{-1} and R$_e$ =9.942 Å. The present results also perfectly agree with the ones by Musial et al. [4] R$_e$= 9.954 Å and D$_e$=88 cm^{-1}. On the other hand, our vibration constants ω_e=16.312 cm^{-1} and $\omega_e\chi_e$=0.750 cm^{-1}, related to the shape of the potential energy curve, compare well to those of Bouzouita et al. [2] resulting from an *ab-initio* approach, ω_e=15.81 cm^{-1} and $\omega_e\chi_e$=0.74 cm^{-1}.

6

For the $2^2\Sigma_g^+$ state correlated to Li$^+$+Li(2p) in the asymptotic limit, the present study shows that the potential energy curve has a well pronounced minimum of 2522 cm^{-1} occurring at an equilibrium distance R$_e$= 6.823 Å. These results are in good agreement with those of Musial et al. [4] R$_e$= 6.826 Å and D$_e$=2529 cm^{-1}. An excellent agreement is also observed when comparing our results to the *ab-initio* ones of Jasik et al. [3], giving a dissociation energy D$_e$=2517 cm^{-1} and an equilibrium distance R$_e$=6.819 Å.

The analysis of the present results shows that the second excited state $2^2\Sigma_u^+$ dissociating in the asymptotic limit to Li$^+$+Li(2p), exhibits a relatively weak minimum of 127 cm^{-1} occurring at an equilibrium distance R$_e$ = 13.203 Å, with vibration constants ω_e=13.069 cm^{-1} and $\omega_e\chi_e$=0.335 cm^{-1}. As shown in Table 2, these results compare favorably to other values resulting from different approaches [1, 2, 3, 4].

For the $3^2\Sigma_g^+$ state, our study shows that the corresponding potential energy curve has an energy minimum occurring at 11.059 Å, with a corresponding dissociation energy of 3139 cm^{-1}. Those values are compared to the *ab-initio* calculations of Bouzouita et al. [2] D$_e$=3093 cm^{-1} and R$_e$=11.08 Å and to those of Musial et al. [4] D$_e$=3119 cm^{-1} and R$_e$=11.071 Å. For this state, we also report that our calculated vibration constants, ω_e =55.449 cm^{-1} and $\omega_e\chi_e$= 0.245 cm^{-1}, are in good agreement with those of of Musial et al. [4], using an *ab-initio* approach.

As previously mentioned, *ab-initio* studies [2, 3, 4] have shown that the $3^2\Sigma_u^+$ state has an attractive character, while Magnier et al. [1] exploiting model potential techniques, described a such state as completely repulsive. The present study based on a model potential approach, shows that the potential energy curve of the $3^2\Sigma_u^+$ state is exhibiting an energy minimum occurring at 19.413 Å, with a corresponding dissociation energy D$_e$=165 cm^{-1}, vibration constants ω_e = 11.131 cm^{-1}, $\omega_e\chi_e$= 0.188 cm^{-1} and a value of 37498 cm^{-1} for T$_e$. Those new results agree with the *ab-initio* ones of Jasik et al. [3] and with those of Bouzouita et al. [2] as well. A very good agreement is also obtained when comparison is made with those of Musial et al. [4] giving R$_e$=19.475 Å, D$_e$=168 cm^{-1}, ω_e=11.06 cm^{-1}, $\omega_e\chi_e$= 0.20 cm^{-1} and T$_e$=37457 cm^{-1}.

As shown in Table 2, there is a good agreement of our 4 $^2\Sigma_g^+$ state spectroscopic constants and those resulting from previous works. The present work yields a dissociation energy D$_e$=1678 cm^{-1} and an internuclear equilibrium distance R$_e$=16.334 Å. Those may be compared to the *ab-initio* values [2] D$_e$=1674 cm^{-1}, R$_e$=16.499 Å and to the recent results of Musial et al. [4] D$_e$=1678 cm^{-1}

7
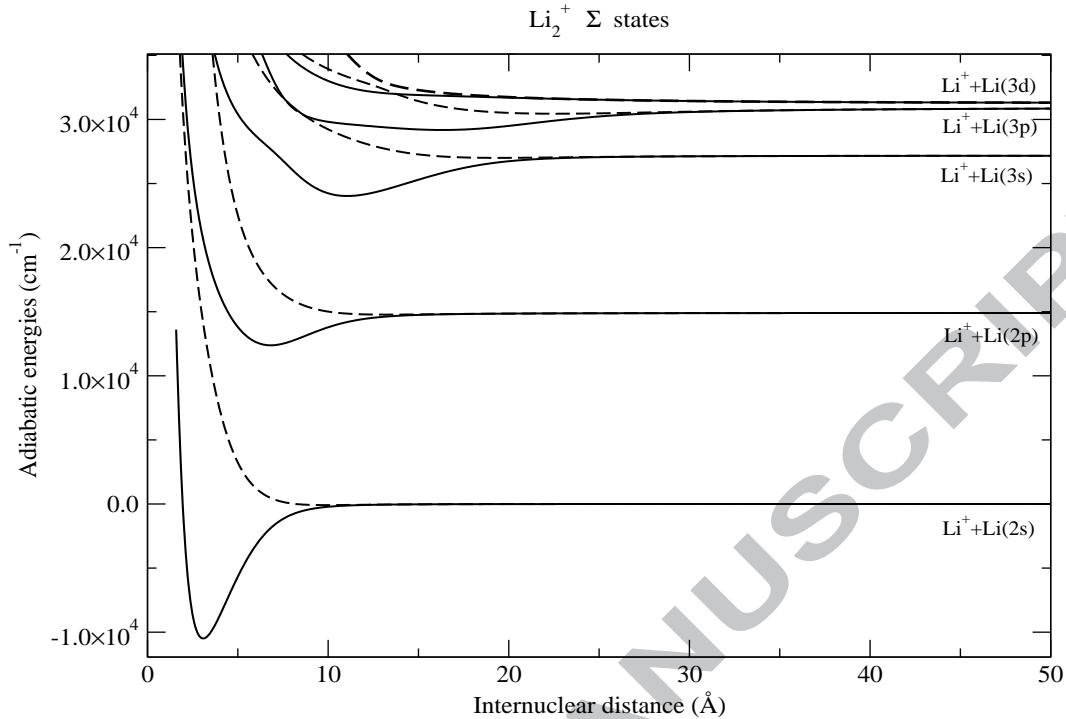
Figure 3: Li_2^+ potential energy curves of the $^2\Sigma^+$ states. Solid lines correspond to $^2\Sigma_g^+$ states, dashed lines to $^2\Sigma_u^+$ states.

and R_e=16.472 Å.

As previously mentioned, there is a serious disagreement between the *ab-initio* results [2, 3, 4] and those based on model potential approach [1] for the $4^2\Sigma_u^+$ state. Contrary to results of Magnier et al. [1], describing this state as repulsive, our potential energy curve for the $4^2\Sigma_u^+$ state, clearly shows the existence of an energy minimum at an equilibrium distance R_e=22.631 Å, with a corresponding dissociation energy D_e= 409 cm^{-1}. The analysis of the potential energy curve relative to this state, gives vibration constants ω_e=11.471 cm^{-1}, $\omega_e\chi_e$=0.080 cm^{-1} and a value of 40942 cm^{-1} for T_e. As shown in Table 2, it is easy to notice that these new results exploiting model potential techniques, compare favorably with all *ab-initio* results [2, 3, 4].

8

Table 2: Spectroscopic constants for $^2\Sigma^+$ states, R_e in Å, D_e, ω_e, $\omega_e\chi_e$, B_e and T_e in cm^{-1}.

State	Reference	R_e	D_e	ω_e	$\omega_e\chi_e$	B_e	T_e
$1\ ^2\Sigma_g^+$	Present work	3.083	10494	262.771	1.645	0.505	0
	Theory [1]	3.122	10466	263.08	1.477	0.4945	0
	Theory [2]	3.095	10475	264	1.94	0.506	0
	Theory [3]	3.093	10498	263.39			0
	Theory [4]	3.103	10439	262.58	1.58		0
	Exp [7]		10276				0
	Exp [8]	3.032	10807	263.45	1.35		0
	Exp [9, 10]	3.11	10464	262(2)	1.7	0.496	0
	Theory [14]	3.099	10441	263.76	1.646	0.5006	0
	Theory [24]	3.096	10444	265.5	1.89	0.501	0
	Theory [25]	3.127	10324				0
$2\ ^2\Sigma_g^+$	Present work	6.823	2522	78.602	0.612	0.103	22874
	Theory [1]	6.879	2525	84.16	0.684	0.1154	22844
	Theory [2]	6.741	2424	79.23	0.49	0.106	22955
	Theory [3]	6.819	2517	79.04			22800
	Theory [4]	6.826	2529	78.67	0.86		22825
	Theory [14]	6.654	2390	82.94	0.623	0.1085	22987
$3\ ^2\Sigma_g^+$	Present work	11.059	3139	55.449	0.245	0.039	34524
	Theory [1]	11.113	3143	56.62	0.212	0.0405	34496
	Theory [2]	11.08	3093	54.56	0.16	0.039	34593
	Theory [3]	10.947	3058	57.9			34533
	Theory [4]	11.071	3119	55.58	0.20		34506
$4\ ^2\Sigma_g^+$	Present work	16.334	1678	22.014	0.072	0.018	39673
	Theory [1]	16.404	1724	22.14	0.095	0.0178	39644
	Theory [2]	16.499	1674	25.27	0.10	0.017	39714
	Theory [3]	16.6	1512	24.03			39768
	Theory [4]	16.472	1678	21.47	0.12		39683
$5\ ^2\Sigma_g^+$	Present work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	repulsive					
$1\ ^2\Sigma_u^+$	Present work	9.929	89	16.312	0.750	0.0487	10405

9

	Theory [1]	10.001	90	16.01	0.79	0.0493	10376
	Theory [2]	9.911	88	15.81	0.74	0.048998	10387
	Theory [3]	9.942	89	15.92			10285
	Theory [4]	9.954	88	15.98	0.81		10351
	Theory [14]	9.95	90	20.1	0.13	0.0490	10350
	Theory [25]	10.3	86				
$2^2\Sigma_u^+$	Present work	13.203	127	13.069	0.335	0.028	25268
	Theory [1]	13.229	131	13.07	0.401	0.0278	25239
	Theory [2]	13.276	125	12.44	0.34	0.027565	25255
	Theory [3]	13.225	127.5	12.96			25156
	Theory [4]	13.217	130	12.98	0.40		25223
$3^2\Sigma_u^+$	Present work	19.413	165	11.131	0.188	0.013	37498
	Theory [1]	repulsive					
	Theory [2]	19.478	169	11.05	0.17	0.012805	37518
	Theory [3]	19.492	162	10.94			37405
	Theory [4]	19.475	168	11.06	0.20		37457
$4^2\Sigma_u^+$	Present work	22.631	409	11.471	0.080	0.009	40942
	Theory [1]	repulsive					
	Theory [2]	23.03	421	14.21	0.15	0.004227	40967
	Theory [3]	23	383.5	11.25			40885
	Theory [4]	22.710	467	12.90	0.11		40894
$5^2\Sigma_u^+$	Present work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	repulsive					

3.2. Π *states*

A basis set of 311 vectors were used to generate the Π states. For the $1^2\Pi_u$ first excited state in the Π_u symmetry, correlated to $Li^+ + Li(2p)$ in the asymptotic limit, present calculations yield a dissociation energy D_e=2107 cm^{-1} and an equilibrium distance R_e= 3.964 Å. It is clear from Table 3, that present results compare favorably to the previous ones based on *ab-initio* [2, 3, 4] and to those exploiting model potential methods [1] as well. Our vibration constants ω_e = 105.146 cm^{-1} and $\omega_e\chi_e$=1.311 cm^{-1}, shown in Table 3, agree well when comparison is made with other values resulting from different approaches.
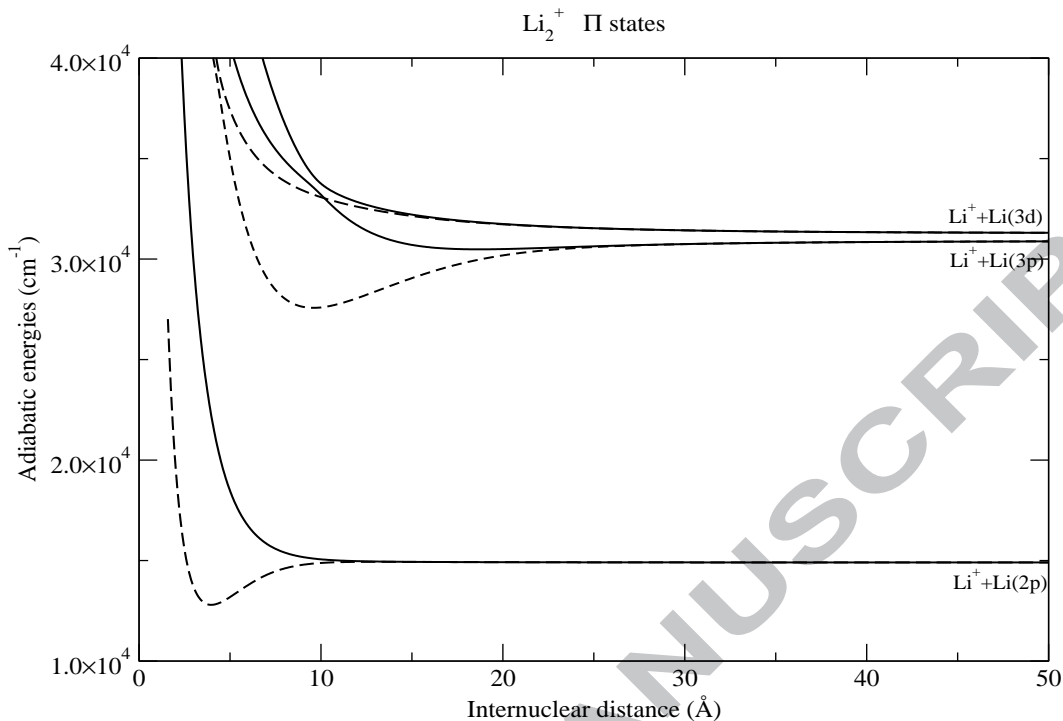
10

Figure 4: Li_2^+ potential energy curves of the $^2\Pi$ states. Solid lines correspond to $^2\Pi_g$ states, dashed lines to $^2\Pi_u$ states.

For the $1^2\Pi_g$ first excited state in the Π_g symmetry, also correlated to Li^+ + $Li(2p)$ in the asymptotic limit, our results indicate that a such state has a repulsive character since the corresponding potential energy curve does not exhibit any energy minimum.

For the $2^2\Pi_u$ state, present study shows that the potential energy curve has an energy minimum occurring at an equilibrium distance R_e = 9.587 Å and a dissociation energy D_e=3312 cm^{-1}. The analysis of the potential energy curve relative to this state gives for vibration constants ω_e = 50.220 cm^{-1} and $\omega_e\chi_e$=0.190 cm^{-1} and 38067 cm^{-1} for T_e. As mentioned in Table 3, it is easy to notice that these results agree with the ones resulting from different approaches [1, 2, 3, 4].

On the other hand, as predicted by previous studies based on different approaches [1, 3, 2, 4], the analysis of the present results, shows that both the $3^2\Pi_u$ and $3^2\Pi_g$ states are completely repulsive, since their potential energy curves do not possess any energy minimum.

The $2^2\Pi_g$ state has been the subject of a disagreement when comparing exist-

11

ing *ab-initio* [2, 3, 4] and model potential results of Magnier [1]. For this state, present calculations indicate the existence of a well pronounced energy minimum corresponding to an energy dissociation D_e= 401 cm^{-1}, occurring at an equilibrium distance R_e = 18.677 Å, as expected by *ab-initio* results [2], giving for dissociation energy and equilibrium radius the values D_e= 411 cm^{-1}, R_e = 18.65 Å, respectively. A good agreement is also observed when comparison is made between present results and those of Musial et al. [4] giving D_e=425 cm^{-1} and R_e=18.799 Å. Other spectroscopic constants ω_e=13.301 cm^{-1}, $\omega_e\chi_e$= 0.110 cm^{-1} and T_e= 40978 cm^{-1} compare favorably to values resulting from other approaches as shown in Table 3.

Table 3: Spectroscopic constants for $^2\Pi$ states, R_e in Å, D_e, ω_e, $\omega_e\chi_e$, B_e and T_e in cm^{-1}.

State	Reference	R_e	D_e	ω_e	$\omega_e\chi_e$	B_e	T_e
$1^2\Pi_u$	Present work	3.964	2107	105.146	1.311	0.306	23291
	Theory [1]	4.022	2100	108.26	1.246	0.3108	23270
	Theory [2]	3.952	1995	110.5	1.19	0.310921	23388
	Theory [3]	3.981	2133	105.25			23197
	Theory [4]	3.978	2102	105.38	1.03		23251
	Theory [14]	3.976	2103	105.58	0.922	0.3040	23277
	Theory [25]	4.014	1852				
$2\,^2\Pi_u$	Present work	9.587	3312	50.220	0.190	0.052	38067
	Theory [1]	9.631	3330	50.79	0.186	0.0527	38039
	Theory [2]	9.99	2979	45.74	0.08	0.048655	38565
	Theory [3]	9.107	3008	60.06			38285
	Theory [4]	9.516	3283	52.20	0.21		38078
$3^2\Pi_u$	Present work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	repulsive					
$1\,^2\Pi_g$	Present work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	repulsive					
$2\,^2\Pi_g$	Present work	18.677	401	13.301	0.110	0.014	40978

12

	Theory [1]	repulsive					
	Theory [2]	18.653	411	18.15	4.69	0.014183	41009
	Theory [3]	19.144	349	12.14			40920
	Theory [4]	18.799	425	12.90	0.11		40935
$3^2\Pi_g$	Present work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	repulsive					

3.3. Δ states

A basis set of 300 vectors were used to generate the Δ states adiabatic energies. The obtained results are summarized in Table 4 and the corresponding energy curves are plotted in Fig. 5 for different internuclear distances up to 50 Å.

The $1^2\Delta_g$ state, correlated in the asymptotic limit to Li^++Li(3d), exhibits an energy minimum at an equilibrium distance R_e=9.502 Å, with a corresponding dissociation energy D_e= 330 cm^{-1}. These values, as shown in Table 4, are in good agreement with those of Magnier et al. [1], but they cannot be compared to the *ab-initio* [2, 3] results, describing a such state as completely repulsive. A reasonable agreement is obtained when the present results are compared to those based on an *ab-initio* approach of Musial et al. [4], giving R_e=9.394 Å and D_e=174 cm^{-1}.

From Table 4, it is also easy to see that our frequencies ω_e=27.004 cm^{-1} and $\omega_e\chi_e$=0.552 cm^{-1}, compare favorably to the *ab-initio* results [4] ω_e=26.64 cm^{-1} and $\omega_e\chi_e$=0.56 cm^{-1}. On the other hand, our calculations are giving a value of 41453 cm^{-1} for T_e, which may be compared to T_e =41528 cm^{-1} of Musial e al. [4], exploiting an *ab-initio* approach.

For the excited state $1^2\Delta_u$, the present study shows that the corresponding potential energy curve does not have a minimum, therefore the $1^2\Delta_u$ is a completely repulsive state, as predicted by previous studies of Magnier et al. [1] and Musial et al. [4]. However, it is important to mention that the $1^2\Delta_u$ state remains a subject of disagreement when comparison is made with *ab-initio* results of Bouzouita et al. [2], describing a such state as attractive with an energy minimum occurring at an equilibrium distance around 21 Å and a very weak dissociation energy of 52 cm^{-1}.
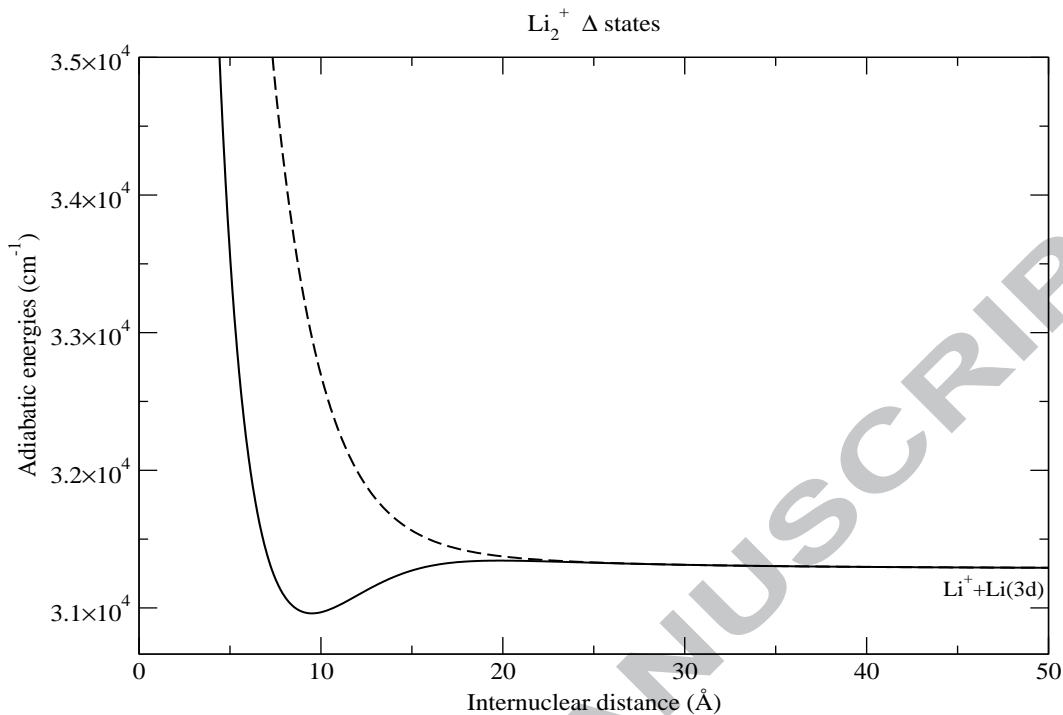
13

Figure 5: Li_2^+ potential energy curves of the $^2\Delta$ states. Solid lines correspond to $^2\Delta_g$ states, dashed lines to $^2\Delta_u$ states.

Table 4: Spectroscopic constants for $^2\Delta$ states, R_e in Å, D_e, ω_e, $\omega_e\chi_e$, B_e and T_e in cm^{-1}.

State	Reference	R_e	D_e	ω_e	$\omega_e\chi_e$	B_e	T_e
$1\ ^2\Delta_g$	This work	9.502	330	27.004	0.552	0.053	41453
	Theory [1]	9.578	324	28.14	0.431	0.0556	41425
	Theory [2]	repulsive					
	Theory [3]	repulsive					
	Theory [4]	9.394	174	26.64	0.56		41528
$1\ ^2\Delta_u$	This work	repulsive					
	Theory [1]	repulsive					
	Theory [2]	21.52	52	20.52	0.38	0.037447	41877
	Theory [3]	repulsive					
	Theory [4]	repulsive					

14

4. Conclusion

We have used a model potential approach to compute the adiabatic potential energies and the molecular spectroscopic constants of the Li_2^+ molecular ion, dissociating up to $Li^+ + Li(1s^2,3d)$ limit. A good agreement between our calculations and those based on *ab initio* methods has been obtained in the present work. This confirms the accuracy of model potential techniques in studying molecular systems with a single active electron.

It is also interesting to note that the previous disagreement between *ab-initio* [2, 3, 4] and model potential [1] results for the excited states $3^2\Sigma_u^+$, $4^2\Sigma_u^+$ and $2^2\Pi_g$, has been sorted out in the present work. Contrary to the claims of Magnier et al. [1] that these states are repulsive, our model potential results has shown that they are attractive as predicted by other studies exploiting *ab-initio* approach.

Although there are still a few unexplained features of the computed potential energy curves for Δ states. Certainly, an experimental study in the near future of such states would be of great interest.

Finally, it should be remarked that the model potential method used in this work can be applied to the calculation of more highly excited states, if required. Obviously, a larger basis set may be needed, but it is to be expected that the precision of the adiabatic states of Li_2^+, correlated to atomic states $Li(1s^2,nl)$, for which l=n-1, should be of the same order as for the states correlated to $Li(1s^2,2p)$ or $Li(1s^2,3d)$. For l < n-1, the precision is expected to be of the same order as for the states correlated to $Li(1s^2,3s)$ or $Li(1s^2,3p)$. The interaction potential for the higher excited states of Li_2^+ should also be given to the same level of precision.

5. References

[1] S. Magnier, S. Rousseau, A.R. Allouche, G. Hadinger, M. Aubert-Frècon, Chem. Phys. 246 (1999) 57

[2] H. Bouzouita, C. Ghanmi, H. Berriche, J. Mol. Struc. THEOCHEM 777 (2006) 75

[3] P. Jasik , J. Wilczyński, J.E. Sienkiewicz, Eur. Phys. J. Special Topics 144 (2007) 85

[4] M. Musial, M. Medrek, S.A. Kucharski, Mol. Phys. 113 (2015) 2943

[5] A. V. Nemukhin, N.F. Stepanov, Chem Phys. Lett. 60 (1979) 421

[6] D. Eisel, W. Demtröder, W. Müller, P. Botschwina, Chem. Phys. 80 (1983) 329

[7] B.P. Mathur, E.W. Rothe, G.P. Reck, A.J. Lightman, Chem. Phys. Lett. 56 (1978) 336

[8] M.W. McGeoch, R.E. Schlier, Chem. Phys. Lett. 99 (1983) 347

[9] R.A. Bernheim, L.P. Gold, T. Tipton, J. Chem. Phys. 78 (1983) 3635

[10] R.A. Bernheim, L.P. Gold, T. Tipton, D.D. Konowalow, Chem. Phys. Lett. 105 (1984) 201

[11] G.A. Henderson, W.T. Zemke, A.C. Wahl, J. Chem. Phys. 58 (1973) 2654

[12] W. Müller, M. Jungen, Chem. Phys. Lett. 40 (1976) 199

[13] D.D. Konowalow, J.L. Fish, Chem. Phys. Lett. 104 (1984) 210

[14] I. Schmidt-Mink, W. Müller, W. Meyer, Chem. Phys. 92 (1985) 263

[15] P. Fuentealba, H. Preuss, H. Stoll, L. van Szentpaly, Chem. Phys. Lett. 89 (1982) 418

[16] D. A. Hasman, Chem. Phys. Lett. 29 (1974) 260

[17] A. Henriet, F. Masnou-Seeuws, Chem. Phys. Lett. 101 (1983) 535

[18] C.J. Cerjan, Chem. Phys. Lett. 36 (1975) 569

[19] C. Bottcher, A. Dalgarno, Chem. Phys. Lett. 36 (1975) 137

[20] M. Klapisch, Comput. Phys. Commun. 2 (1971) 239

[21] M. Born, R. Oppenheimer, Ann. Phys. 84 (1927) 457

[22] J . N . Wilson, R . M . Curtis, J . Phys. Chem. 74 (1970) 187

[23] S. Bashkin, J.O. Stoner, Atomic Energy Levels and Grotrian Diagrams, vol. 1, North-Holland Publishing, Amsterdam, (1978)

[24] W. Müller, W. Meyer, J. Chem. Phys. 80 (1984) 3311

[25] D.D. Konowalow, M.E. Rosenkrantz, Chem. Phys. Lett. 61 (1979) 489

16

Li_2^+ adiabatic energies