Adiabatic potential energy curves of $\mathbf{Li_2}$

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ABSTRACT

Adiabatic potential energy curves for twenty six low-lying electronic states of Li_2 dimer have been computed in the large range of internuclear distances ($3.2\ a_0 \leq R \leq 80\ a_0$). Four singlet states ($4^1\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$ and $1^1\Delta_g$) and four triplet states ($5^3\Sigma_u^+$, $2^3\Pi_u$, $2^3\Pi_g$ and $1^3\Delta_u$) are presented for the first time. In the calculations, the complete-active-space multi-configuration self-consistent-field (CASSCF) method has been used. The core-polarization potential (CPP) has been also added to the hamiltonian. A good agreement with previous theoretical and experimental results has been obtained.

Keywords: Adiabatic potential energy curves, Li_2 dimer, cold molecules

1. INTRODUCTION

The Li_2 molecule, for many years, has attracted attention of experimentalists and theoreticians. It is the second, just after H_2, smallest stable homonuclear molecule. Li_2 has been studied by means of spectroscopical methods and a large number of electronic states has been tabulated. As an example, it can be given the recent experiment performed in Orsay[1] providing a better description of the $1^1\Pi_u$ state which correlates to $2s + 2p$ asymptote. Here, the lithium molecules were produced by molecular beam and next they were excited by a tunable dye laser. Two kinds of measurements were performed: first, several hundred transitions to the ground $1^1\Sigma_g{}^+$ state were accurately measured and second, the dissociation rates in quasibond levels were determined. In turn Pashov *et al.*[2] and Jastrzębski *et al.*[3] reported an accurate potential energy curves of $3^1\Sigma_g{}^+$ and $4\Sigma_g{}^+$ states. Their method was based on the inverted perturbation approach which reproduced positions of the experimental energy levels for all three isotopomers of Li_2. We want to underline the recent experiments on photoassociative spectroscopy of long-range states of ultracold lithium dimers (Abraham *et al.*)[4]

There have also been several theoretical studies concerning the ground and excited states. We note the first accurate *ab initio* calculations of the ground state reported by Das and Wahl.[5] Next, we have to mention results of a few excited states obtained by Kutzelnigg *et al.*[6] Two very extensive calculations using the multi-configuration self-consistent-field (MC SCF) were performed by Olson and Konowalow[7] and next by Schmidt-Mink *et al.*[8] We compare our theoretical results with the both last approaches.

Very recently, there were also intensive experimental studies on the Bose-Einstein condensation of the Li_2 molecules in an optical trap (for example: Jochim *et al.*[9] and Bartenstein *et al.*[10]) and on fermionic pairing in an ultracold two-component gas of the Li atoms (for example: Chin *et al.*[11] and Jochim *et al.*[12]). Both experiments require high lying adiabatic energy curves, which nowadays are only partly available.

The aim of our theoretical approach is to proof validity of other methods based on the MOLPRO[13] program package in order to obtain high lying potential curves of the Li_2 dimer. In our calculations we use the complete-active-space multi-configuration self-consistent-field (CASSCF) method. Core electrons are treated by the effective-core potential (ECP) with the additional basis for the d electrons. Correlation is taken into account by employing the core-polarization potential (CPP). After CASSCF the configuration interaction (CI) calculations are performed. The spin-orbit coupling is not taken into account.

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2. THEORETICAL METHOD

We solve the Schrödinger equation, which in the Born-Oppenheimer approximation, can be written in the following form

$$(H_1 + H_2 + V_{12})\Psi_\kappa(\mathbf{r}, \mathbf{R}) = E_\kappa(R)\Psi_\kappa(\mathbf{r}, \mathbf{R}),$$

when H_1 and H_2 are the atomic hamiltonians of separated lithium atoms, V_{12} is the interaction between these two atoms, $E_\kappa(R)$ is the adiabatic energy in the κ^{th} state which is described by the wavefunction $\Psi_\kappa(\mathbf{r}, \mathbf{R})$. Here, the $\mathbf{r}$ are coordinates of all electrons of considered system and $\mathbf{R}$ is the position vector giving the position of the first atom in relation to the second atom. In our calculations only the valence electrons of the lithium atoms are treated explicitly, what means that we consider effectively the two-electron system. The core electrons of Li atoms are represented by l-depended pseudopotential ECP2SDF.[14] The basis for the s and p orbitals which comes with this potential is enlarged by functions for d orbitals given by P. Feller[15] and assigned by CC-PV5Z. Additionally, our basis set was augmented by nine short range correlation functions and five diffuse functions. For details see Table 1. To account for the valence-core correlation the core-polarization potential is used. Detailed formulas can be found for instance in Czuchaj *et al.* papers.[16–18]

Table 1. The basis set for s, p and d orbitals with augmented functions (bold numbers).

ECP2SDF	ECP2SDF	CC-PV5Z
s	p	d
392.169555	**96.625417**	**3.751948**
77.676373	**19.845562**	**1.9783**
15.38253	**4.076012**	**1.043103**
3.047327	0.837158	0.55
0.603579	0.171941	0.29
0.069138	0.052079	0.14
0.026502	0.019172	0.061
0.010159	**0.007058**	**0,026579**
0.003894	**0.002598**	

We check the quality of our basis set performing the CI calculation for the ground and excited states of isolated lithium atom. The results are given in Table 2. The agreement with experimental values is quite reasonable.The potential energy curves are calculated with multi-reference CASSCF calculation followed by CI calculation.

Table 2. Comparison asymptote energy with other theoretical and experimental results. Energies are shown in cm^{-1} units.

	Present work	Schmidt-Mink[8]	Bashkin[19]
2s + 2p	14916	14938	14904
2s + 3s	27201	27209	27206
2p + 2p	29822	29876	29808
2s + 3p	30931	31078	30925
2s + 3d	32113		31283

3. RESULTS AND DISCUSSION

Calculation of the adiabatic energy curves are performed for the internuclear separation R in the range from $3.2a_0$ to $80a_0$ with the various step, according to the internuclear distance. Results for all singlet and triplet states are shown respectively in Fig. 1 and Fig. 2. The states $5^3\Sigma_u^+$, $4^1\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$ are calculated for the first time and were not known previously. In Fig. 3, we compare our ground and the first excited molecular state correlating to ground state of lithium atoms with the theoretical results of Olson and Konowalow[20, 21] and Schmidt-Mink *et al.*[8] As one might see, the agreement is excellent. We make comparisons with potential curves derived from experiments. In Fig. 4, we show comparison with results derived from experiment by Bouloufa *et al.*[1] and theoretical results of Schmidt-Mink *et al.*[8] Once again we note the almost excellent agreement. In turn in Fig. 5, we display the comparison with two states of symmetry ${\Sigma_g}^+$ derived from experiment by Pashov *et al.*[2] and Jastrzębski *et al.*[3] Here, in the case of $4^1{\Sigma_g}^+$ state once again the agreement is excellent, while in the case of the lower $3^1{\Sigma_g}^+$ state, correlating to $2s + 3s$ atomic energy, we find the disagreement for small internuclear distance.

4. CONCLUSION

We provide previously unknown adiabatic potential curves. These are $5^3\Sigma_u^+$, $4^1\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$. We believe in quality of our results, since comparison with chosen theoretical curves given by other authors is excellent. Also the agreement with the curves derived from spectroscopical measurements is excellent except the $3^1{\Sigma_g}^+$ state, where in the repulsive part of the potential curve some disagreement is noted.

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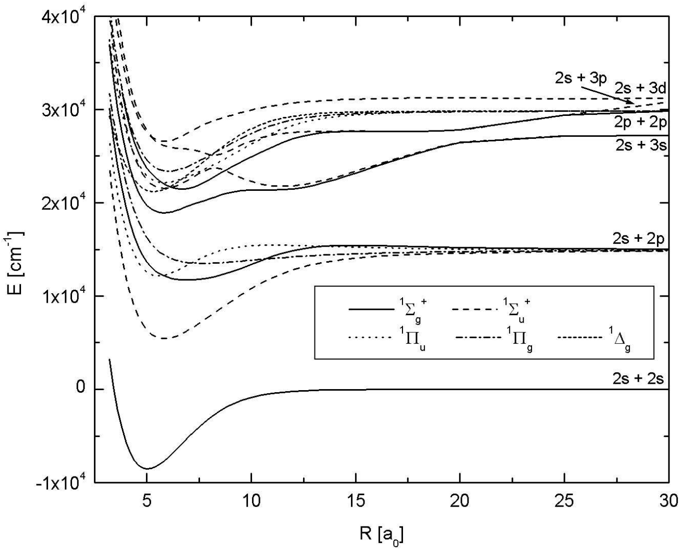

Figure 1. Adiabatic potential energy curves for ground and excited singlet states of the Li_2 molecule correlating to the $2s + 2s$, $2s + 2p$, $2s + 3s$, $2p + 2p$, $2s + 3p$ and $2s + 3d$ asymptotes.

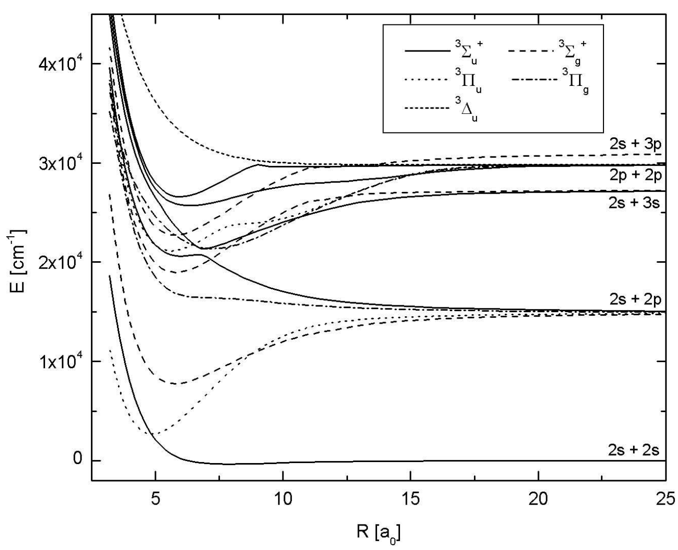

Figure 2. Adiabatic potential energy curves for excited triplet states of the Li_2 molecule correlating to the $2s + 2s$, $2s + 2p$, $2s + 3s$, $2p + 2p$ and $2s + 3p$ asymptotes.

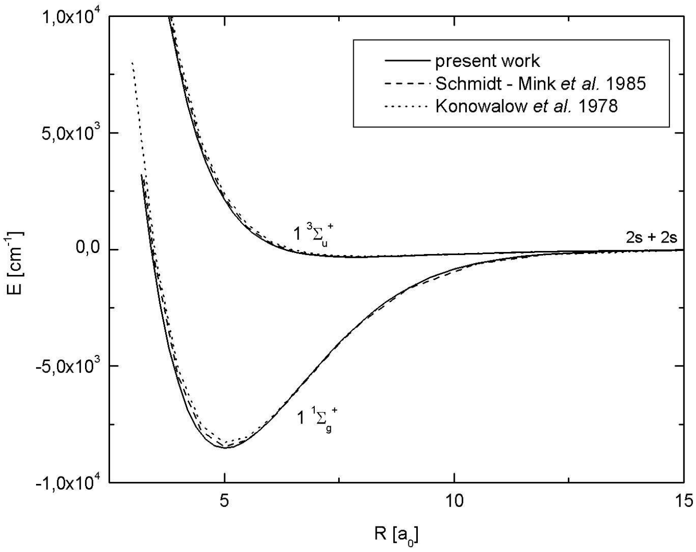

Figure 3. Comparison the ground and the first excited molecular state correlating to $2s + 2s$ asymptote with the theoretical results of Olson and Konowalow[20, 21] and Schmidt-Mink *et al.*[8]

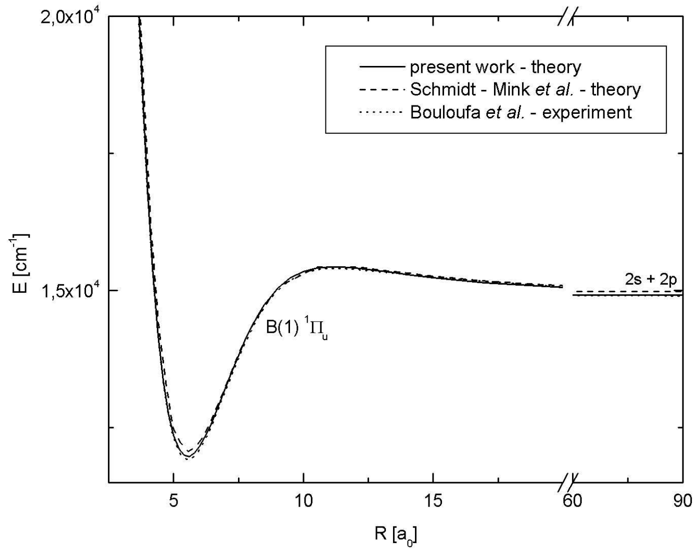

Figure 4. Comparison $B(1)^1\Pi_u$ state correlating to $2s + 2p$ asymptote with results derived from experiment by Bouloufa *et al.*[1] and theoretical results of Schmidt-Mink *et al.*[8]

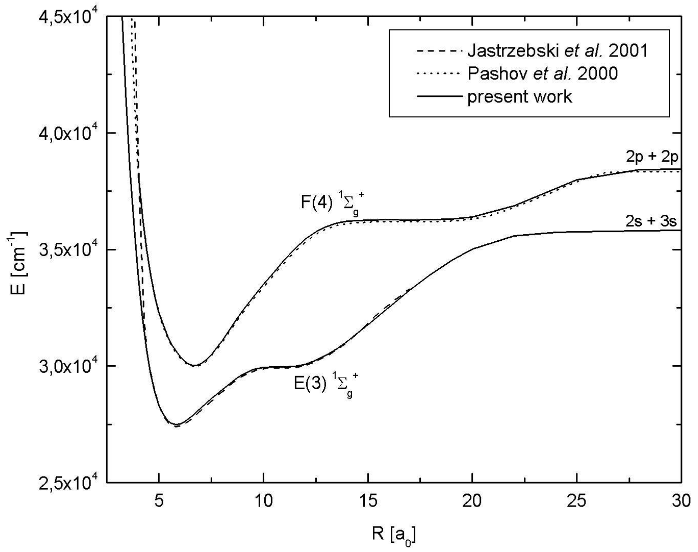

Figure 5. Comparison $E(3)^1\Sigma_g^+$ and $F(4)^1\Sigma_g^+$ states correlating respectively to $2s + 3s$ and $2p + 2p$ asymptotes with potential curves derived from experiment by Jastrzebski *et al.*[3] and Pashov *et al.*[2]