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Calculation of adiabatic potentials of Li_2^+

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Abstract. We report adiabatic potential energy curves of the Li_2^+ molecule. Our curves are tabulated according to internuclear distance from $2\,a_0$ to $100\,a_0$. We compare our theoretical results with the ones calculated by other authors and potential energy curves derived from experiments. For the ground state and 17 excited states we calculate spectroscopic parameters and compare them with parameters obtained by other authors. For the first time we present three new minima for $3^2\Sigma_u^+$, $4^2\Sigma_u^+$ and $2^2\Pi_g$ excited states. In our approach we use the configuration interaction method where only the valence electrons of Li atoms are treated explicitly. The core electrons are represented by pseudopotential. All calculations are performed by means of MOLPRO program package.

1 Introduction

The lithium dimer and the ion of lithium dimer have attracted attention of experimentalists and theoreticians for many years, mainly because they are the next, just after the molecular hydrogen, smallest stable homonuclear molecules. It can serve as a convenient prototype for testing theoretical methods, which can be further applied to heavier alkali dimers. The first *ab initio* calculations on Li_2^+ using the RHFR method (restricted Hartree-Fock-Roothaan) were performed by Henderson and co-workers [1]. The frozen atomic core calculations were used by Müller and Jungen [2]to obtain several excited states of the ion of lithium dimer. Next, Konowalow and co-workers published series of papers where were presented adiabatic potential energy curves of Li_2 [3–7] and Li_2^+ [8, 9] molecules. Afterwards, Schmidt-Mink *et al.* [10] performed SCF/valence CI calculation where they obtained the 8 lowest lying states of Li_2^+ molecule. The last theoretical results were presented by Magnier *et al.* [11] where authors calculated adiabatic potential energy curves of 58 states of the ion of lithium dimer. Results of the first experimental studies of Li_2^+ molecule were presented by Mathur *et al.* [12]. Authors measured the ionization potential of Li_2 and the dissociation energy of Li_2^+. Their ionization process utilizes two different lines of Ar^+ laser to go from the $X^1\Sigma_g^+$ state via the $B^1\Pi_u$ state of Li_2 to the $X^2\Sigma_g^+$ state of Li_2^+. The most important experimental works where only ground state of Li_2^+ molecule was taken into account were performed by Bernheim *et al.* [13, 14] and McGeoch *et al.* [15]. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme which was used in our previous reports [16,17].

2 Theoretical methods

We consider the interaction between alkali atom and ion of alkali atom. Let $\mathbf{R}$ be the separation between the nuclei of these atoms. In the Born-Oppenheimer approximation we seek for the solutions of the Schrödinger equation

$$H\Psi_i(\mathbf{r},\mathbf{R}) = E_i(R)\Psi_i(\mathbf{r},\mathbf{R}), \tag{1}$$

where H is the hamiltonian of a diatomic system, $E_i(R)$ is the i-th adiabatic energy and $\Psi_i(\mathbf{r},\mathbf{R})$ describes the state of the system related to this energy, $\mathbf{r}$ represents the electronic coordinates and $\mathbf{R}$ is the relative position of the first atom to the second one. The Hamiltonian of the system can be written as

$$H = H_A + H_B + V_{AB}, \tag{2}$$

where H_A and H_B are the Hamiltonians of the isolated atoms and V_{AB} is the interaction between them. In the present approach only the valence electrons are treated explicitly, but the atomic cores are represented by l-dependent pseudopotentials. Consequently the total Hamiltonian in equations (1, 2) can be expressed as

$$H = T + V, \tag{3}$$

where T stands for the kinetic energy operator of the valence electrons and V represents the interaction operator. The latter is put into the form

$$V = \sum_{\lambda}(V^{\lambda} + V^{\lambda}_{pol}) + \sum_{j>i=1}^{N}\frac{1}{r_{ij}} + V_{cc}. \tag{4}$$

Here V^{λ} describes Coulomb and exchange interaction as well as the Pauli repulsion between the valence electrons and core λ and is defined as

$$V^{\lambda} = \sum_{i=1}^{N}\left(-\frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{l,k} B^{\lambda}_{l,k}\exp(-\beta^{\lambda}_{l,k}r^2_{\lambda i})P^{\lambda}_{l}\right), \tag{5}$$

where $Q_{\lambda} = 1$ denotes the net charge of lithium core λ, P^{λ}_{l} is the projection operator onto the Hilbert subspace of angular symmetry l with respect to the Li^{+}-core and N is the number of the valence electrons. The parameters $B^{\lambda}_{l,k}$ and $\beta^{\lambda}_{l,k}$ define the semi-local energy-consistent pseudopotentials. The second interaction term in equation (4) is the polarization term which describes, among others, core-valence correlation effects and, in the case of atom A, is taken as

$$V^{A}_{pol} = -\frac{1}{2}\alpha_A\mathbf{F}^2_A, \tag{6}$$

Table 1. Comparison of asymptotic energies with other theoretical and experimental results. Energies are shown in hartree units.

Level	Bashkin - exp. [27]	Present work	Magnier - theory [11]
$Li^{+} + Li(2s)$	−0,198142	−0,198102	−0,198107
$Li^{+} + Li(2p)$	−0,130235	−0,130172	−0,130200
$Li^{+} + Li(3s)$	−0,074182	−0,074188	−0,074299
$Li^{+} + Li(3p)$	−0,057236	−0,057325	−0,057303
$Li^{+} + Li(3d)$	−0,055606	−0,055523	−0,055570

where $\alpha_A = 0.1915a_0$ [18] is the dipole polarizability of the A^+ core and $\mathbf{F}_A$ is the electric field generated at its site by the valence electrons and the other core. The latter can be written as

$$\mathbf{F}_A = \sum_i \frac{\mathbf{r}_{Ai}}{r_{Ai}^3}[1 - \exp(-\delta_A r_{Ai}^2)] - \frac{Q_B \mathbf{R}}{R^3}[1 - \exp(-\delta_A R^2)], \tag{7}$$

where $\delta_A = 0.831\, a_0^{-2}$ [18] is the cutoff parameter. The third term in equation (4) represents the Coulomb repulsion between the valence electrons, whereas the last term describes the core-core interaction. Since the alkali atoms cores are well separated, we choose a simple point-charge Coulomb interaction in the latter case. Detailed formulas are given in the papers of Czuchaj and co-workers [19–24].

3 Computational details

All calculations reported in this paper were performed by means of the MOLPRO program package [25]. The core electrons of Li atoms are represented by pseudopotential ECP2SDF [18], which was formed from the uncontracted ($9s9p8d3f$) basis set. The basis for s and p orbitals, which comes with this potential is enlarged by functions for d and f orbitals given by P.O. Widmark et al. [26] and assigned by ROOS. Additionally, our basis set was augmented by three s short range correlation functions (392.169555, 77.676373, 15.385230), three p functions (96.625417, 19.845562, 4.076012) and three d functions (10.495627, 3.673469, 1.285714). Also, we added to the basis a set of nine diffused functions: three s functions (0.010159, 0.003894, 0.001493), three p functions (0.007058, 0.002598, 0.000956) and three d functions (0.006753, 0.002364, 0.000827). We checked the quality of our basis set performing the CI calculations for the ground and several excited states of isolated lithium atom. The calculated Li_2^+ adiabatic

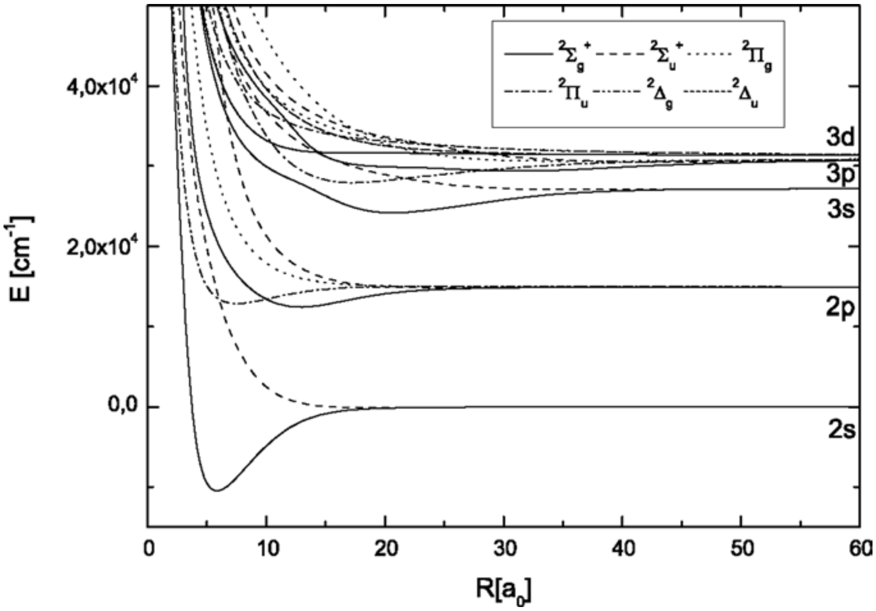

Fig. 1. Adiabatic potential energy curves for all, calculated by us, states of the Li_2^+ molecule correlating to the Li^+ + Li(2s), Li^+ + Li(2p), Li^+ + Li(3s), Li^+ + Li(3p) and Li^+ + Li(3d) asymptotes.

potentials correlate to the Li$^+$ + Li(2s) ground atomic asymptote and Li$^+$ + Li(2p), Li$^+$ + Li(3s), Li$^+$ + Li(3p), Li$^+$ + Li(3d) excited atomic asymptotes. The comparison of experimental and theoretical asymptotic energies for different states is shown in Table 1. The spin-orbit coupling (SO) and core-core polarization effect contribute insignificant part to energy of our system, so we do not take them into consideration in our calculations. The potential energy curves for Li_2^+ are calculated using the complete-active-space self-consistent-field (CASSCF) method to generate the orbitals for the subsequent CI calculations.

4 Results and discussion

Calculations of the adiabatic energy curves are performed for the internuclear separation R in the range from $2a_0$ to $100a_0$ with the various steps adjusted to the internuclear distance. Numerical values of the calculated potential energies are available on request. Equilibrium positions R_e and depths of the potential wells D_e are obtained using cubic spline approximation to the calculated potentials around their equilibrium positions. Spectroscopic parameters ω_e and T_e are calculated by solving the Schrödinger equation with calculated adiabatic potentials. These values are shown in Table 2. As it is seen, overall agreement all our spectroscopic constants and other theoretical and experimental data is very reasonable. Present results for all, calculated by us, states are plotted relative to the corresponding experimental values of the atomic terms in Fig. 1. All our states are calculated for the first time, for the long distance in the nuclear separation R (up to 100 a_0). We obtain asymptotic energies for ground and excited states, which are in very good agreement with experimental and other theoretical values (Table 1.). In Fig. 2, we compare our ground and the first excited molecular state correlating to the ground state of lithium atoms along with the theoretical results of Konowalow and Rosenkrantz (1979) [8] and Schmidt-Mink *et al.* (1985) [10]. As one may see, the agreement is very good. For the first time we present spectroscopic parameters for three states $3^2\Sigma_u^+$, $4^2\Sigma_u^+$ and $2^2\Pi_g$, previously known as repulsive potentials (Table 2.). We obtained these adiabatic potential

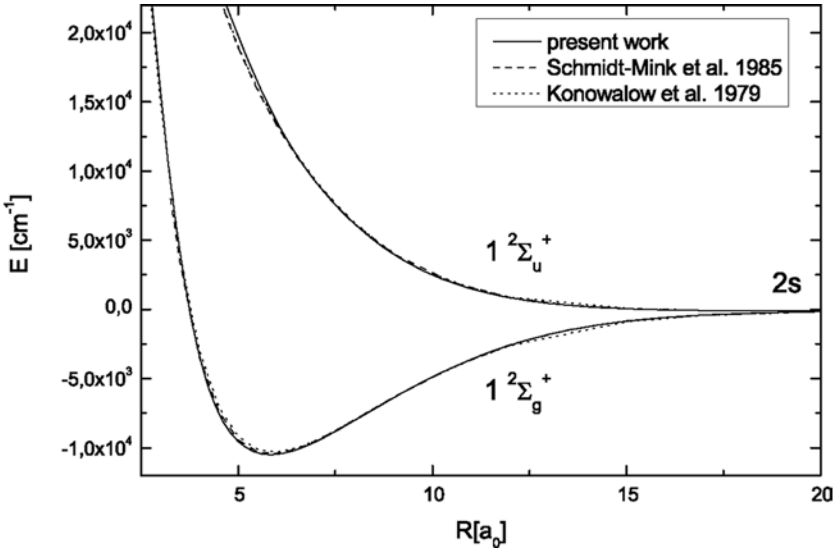

Fig. 2. Comparison of the ground and the first excited molecular state correlating to Li$^+$ + Li(2s) asymptote with the theoretical results of Konowalow and Rosenkrantz [8] and Schmidt-Mink *et al.* [10].

Table 2. Spectroscopic parameters R_e (Å), D_e, ω_e and T_e (cm^{-1}) for the ground and excited states of Li_2^+ molecule.

State	R_e	D_e	ω_e	T_e
$1^2\Sigma_g^+$				
Exp.[12]		10280		
Exp.[14, 13]	3.110	10464(6)	262(2)	0
Exp.[15]	3.032	10807	263.45	0
Theory[10]	3.099	10441	263.76	0
Theory[8]	3.127	10324	-	0
Theory[11]	3.122	10466	263.08	0
Present work	3.093	10498	263.39	0
$2^2\Sigma_g^+$				
Theory[10]	6.654	2390	82.94	22987
Theory[11]	6.879	2525	84.16	22844
Present work	6.819	2516.5	79.04	22800
$3^2\Sigma_g^+$				
Theory[11]	11.113	3143	56.62	34496
Present work	10.947	3058	57.90	34533
$4^2\Sigma_g^+$				
Theory[11]	16.404	1724	22.14	39644
Present work	16.600	1512	24.03	39768
$1^2\Sigma_u^+$				
Theory[10]	9.950	90	20.10	10350
Theory[8]	10.300	86	-	-
Theory[11]	10.001	90	16.01	10376
Present work	9.942	89	15.92	10285
$2^2\Sigma_u^+$				
Theory[11]	13.229	131	13.07	25239
Present work	13.225	127.5	12.96	25156
$3^2\Sigma_u^+$				
Present work	19.492	162	10.94	37405
$4^2\Sigma_u^+$				
Present work	23	383.5	11.25	40885
$2^2\Pi_g$				
Present work	19.144	349	12.14	40920
$1^2\Pi_u$				
Theory[10]	3.976	2103	105.58	23277
Theory[8]	4.014	1852	-	-
Theory[11]	4.022	2100	108.26	23270
Present work	3.981	2133	105.25	23197
$2^2\Pi_u$				
Theory[11]	9.631	3330	50.79	38039
Present work	9.107	3008	60.06	38285
$1^2\Delta_g$				
Theory[11]	9.578	324	28.14	41425
Present work	repulsive potential			

energy curves with minima, because all our states were calculated for large internuclear separations R (up to 100 a_0). Previous calculations were performed only to 30 a_0 (Konowalow *et al.* [8] and Schmidt-Mink *et al.* [10]) and 40 a_0 (Magnier *et al.* [11]). All of our new minima are very shallow and very wide: $3^2\Sigma_u^+$ - R_e = 19.492 Å and D_e = 162 cm^{-1}; $4^2\Sigma_u^+$ - R_e = 23 Å and D_e= 383.5 cm^{-1}; $2^2\Pi_g$ - R_e = 19.144 Å and D_e = 349 cm^{-1}. In Fig. 3 we present these minima near their equilibrium positions which are lain in the large distance on the internuclear separations scale.

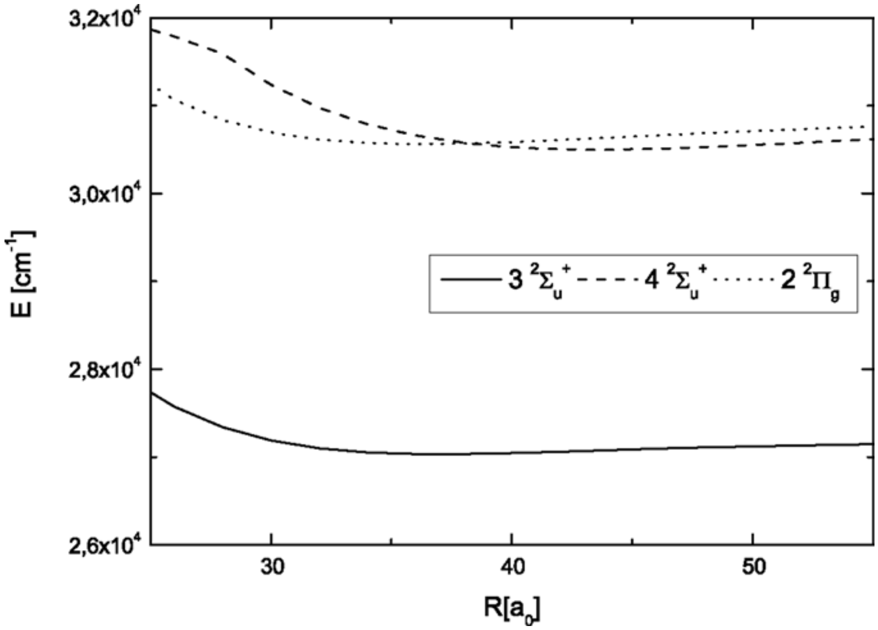

Fig. 3. Three states $3^2\Sigma_u^+$, $4^2\Sigma_u^+$ and $2^2\Pi_g$ with previously unknown minima near their equilibrium positions.

5 Conclusion

We have calculated the adiabatic potential energy curves of the ion of lithium dimer using CASSCF/MRCI method. Comparisons with available lowly-lying theoretical curves provide almost perfect agreement. Calculated asymptotic energies and spectroscopic parameters are also in very good accordance with other theoretical and experimental results. We would like to underline that for three adiabatic potential energy curves $3^2\Sigma_u^+$, $4^2\Sigma_u^+$ and $2^2\Pi_g$, previously known as repulsive potentials we found minima, which are very shallow and very wide and lain in the large distance on the internuclear separations scale. In the near future, we plan to calculate adiabatic potential energy curves for heavier homo- and heteronuclear alkali systems.

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References

1. G.A. Henderson, W.T. Zemke, A.C. Wahl, J. Chem. Phys. **58**, 2654 (1973)
2. W. Müller, M. Jungen, Chem. Phys. Lett. **40**, 199 (1976)
3. M.L. Olson, D.D. Konowalow, Chem. Phys. Lett. **39**, 281 (1976)
4. M.L. Olson, D.D. Konowalow, Chem. Phys. **22**, 29 (1977)
5. M.L. Olson, D.D. Konowalow, Chem. Phys. **21**, 393 (1977)
6. D.D. Konowalow, M.L. Olson, J. Chem. Phys. **71**, 450 (1979)
7. D.D. Konowalow, J.L. Fish, Chem. Phys. **77**, 435 (1983)
8. D.D. Konowalow, M.E. Rosenkrantz, Chem. Phys. Lett. **61**, 489 (1979)
9. D.D. Konowalow, J.L. Fish, Chem. Phys. Lett. **104**, 210 (1984)
10. I. Schmidt-Mink, W. Müller, W. Meyer, Chem. Phys. **92**, 263 (1985)
11. S. Magnier, S. Rousseau, A.R. Allouche, G. Hadinger, M. Aubert-Frécon, Chem. Phys. **245**, 57 (1999)
12. B.P. Mathur, E.W. Rothe, G.P. Reck, A.J. Lightman, Chem. Phys. Lett. **56**, 336 (1978)
13. R.A. Bernheim, L.P. Gold, T. Tipton, Chem. Phys. **78**, 3635 (1983)
14. R.A. Bernheim, L.P. Gold, T. Tipton, D. Konowalow, Chem. Phys. Lett. **105**, 201 (1984)
15. M.W. McGeoch, R.E. Schlier, Chem. Phys. Lett. **99**, 347 (1983)
16. P. Jasik, J.E. Sienkiewicz, Chem. Phys. **323**, 563 (2006)
17. P. Jasik, J.E. Sienkiewicz, SPIE Proc. **5849**, 82 (2005)
18. P. Fuentealba, H. Preuss, H. Stoll, L. Von Szentply, Chem. Phys. Lett. **89**, 418 (1982)
19. E. Czuchaj, M. Krośnicki, H. Stoll, Chem. Phys. **265**, 291 (2001)
20. E. Czuchaj, M. Krośnicki, H. Stoll, Chem. Phys. **292**, 101 (2003)
21. E. Czuchaj, M. Krośnicki, H. Stoll, Theor. Chem. Acc. **107**, 27 (2001)
22. E. Czuchaj, M. Krośnicki, H. Stoll, Chem. Phys. Lett. **371**, 401 (2003)
23. E. Czuchaj, M. Krośnicki, H. Stoll, Theor. Chem. Acc. **110**, 28 (2003)
24. E. Czuchaj, F. Rebentrost, H. Stoll, H. Preuss, Theor. Chem. Acc. **100**, 117 (1998)
25. MOLPRO is a package of *ab initio* programs written by H.J. Werner, P.J. Knowles with contributions from R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Leininger, R. Lindh, A.W. Lloyd, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A.J. Stone, T. Thorsteinsson
26. P.O. Widmark, P.A. Malmqvist, B.O. Roos, Theor. Chim. Acta **77**, 291 (1990)
27. S. Bashkin, J.O. Stoner Jr., *Atomic energy levels and grotrian diagrams*, Vol. 1 (North-Holland, Amsterdam, 1975)