Post-print of: Jasik P., Sienkiewicz J.: Calculation of adiabatic potentials of Li2. CHEMICAL PHYSICS. Vol. 323, (2006), p. 563-573.
DOI: 10.1016/j.chemphys.2005.10.025

Calculation of adiabatic potentials of Li_2

P. Jasik *, J.E. Sienkiewicz

Department of Theoretical and Mathematical Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,
ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

Abstract

We report adiabatic potential energy curves of the lithium dimer. Our curves are tabulated according to internuclear distance from $3.2a_0$ to $88a_0$. We compare our theoretical results with the ones calculated by other authors and potential energy curves derived from experiments. In our approach we use the configuration interaction method where only the valence electrons of Li atom are treated explic-itly. The core electrons are represented by pseudopotential. All calculations are performed by means of MOLPRO program package.

PACS: 31.15.Ar; 31.15.Ne; 31.25.Nj; 32.80.Pj; 33.80.Ps; 34.20.Cf

Keywords: Adiabatic potential energy curves; Li_2 dimer; Cold molecules

1. Introduction

The lithium dimer has attracted attention of experimentalists and theoreticians for many years, mainly because it is the second, just after the molecular hydrogen, smallest stable homonuclear molecule. 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 were performed by Konowalow and coworkers [1–5], including the work of Konowalow and Fish [5] where they computed and analyzed the potential energy curves in the long-range region of the 26 lowest lying states. They accounted for atomic polarizabilities in order to describe the atomic multiple interaction and the molecular valence-shell polarization. By using the atomic effective-core potential (ECP) and high quality basis set they were able to perform self-consistent-field (SCF) and configuration-interaction (CI) calculations. Obtained results allowed for valuable comparisons with experimental spectroscopic data of He et al. [6]. Nevertheless, as discussed by Müller and Mayer [7] the usage by Konowalow and co-workers of the originally atomic ECP leads to defect of an unbalanced treatment of core polarization effects in molecule since it lacks electron–other core polarization contributions. Next, Schmidt-Mink et al. [8] performed SCF/valence CI calculation where they implemented the effective potential to reduce the above defect. In this approach, they employed the technique of self-consistent electron pairs (SCEP) to simultaneously optimize several electronic states, combined with a core polarization potential (CPP) for an efficient treatment of inter-shell correlation effect. Their results also achieved very good agreement with experimental data of He et al. [6]. In turn, Poteau and Spiegelmann [9] reported results for 49 states obtained by calculations, where effective core pseudopotentials and *l*-dependent core polarization potentials were employed. Recently, Song et al. [10] studied both theoretically and experimentally the $5^1\Sigma_g^+$ and $6^1\Sigma_g^+$ Rydberg states. Several spectroscopic studies of lithium dimer were repeated. These include analysis of the $1^1\Sigma_u^+$–$1^1\Sigma_g^+$ band system [11], near infrared two-photon laser spectroscopy of the $2^1\Sigma_g^+$ state [6], ultrafast spectroscopy of wavelength-dependent coherent photoionization in the $5^1\Sigma_g^+$ state [12], state to state

---

doi:10.1016/j.chemphys.2005.10.025

collision energy transfer in singlet state [13] and observation of predissociation in the $2^1\Pi_u$ state in the ^{6}Li^{7}Li isotopomer [14]. Quite recently need for theoretical description of long range potential curves has been caused by molecular photoassociative spectroscopy of cold alkali atoms [15]. Two-photon photoassociation of colliding ultracold lithium atoms was used by Abraham et al. [16] to probe the lowest triplet state $1^3\Sigma_u^+$ of Li_2 in order to determine the scattering lengths necessary to predict the Bose–Einstein condensate (BEC). Also photoassociative spectroscopy was used to obtain high-lying vibrational levels of $1^1\Sigma_u^+$ and $1^3\Sigma_g^+$ states [17] and the intensity dependent rate and shift of a transition in a quantum degenerate gas [18]. Very recently our motivation to calculate the potential curves of highly excited states of the lithium dimer was strengthened by Johim et al. [19] who reported on the BEC of more than 10^5 Li_2 molecules in an optical dipole trap and Chin et al. [20] who studied fermionic pairing in an ultracold two-component degenerate gas of lithium atoms by observing a pairing gap in radio-frequency excitation spectra. The experimentally observed states can be characterized by their potential curves which may serve for direct comparison with theoretical curves. For instance, the application of Doppler-free UV–visible optical–optical double resonance polarization spectroscopy allowed for determination of $2^1\Sigma_u^+$ and $C^1\Pi_u$ states [21]. Quite recently, Jastrzębski et al. [22] and Pashov et al. [23] reported potential curves for the $3^1\Sigma_g^+$ and $4^1\Sigma_g^+$ states. They used the inverted perturbation approach (IPA) developed by Pashov et al. [24]. In turn, Bouloufa et al. [25] constructed the potential energy curve for the $1^1\Pi_u$ state by combining a short-range potential obtained by direct fit of accurate spectroscopic measurements with a long-range potential generated by asymptotic calculation of Coulombic and exchange energies. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme. We use a substantially richer basis set than in our first report [26]. The present calculation also use the ECP which enables us to provide high lying adiabatic potential curves not calculated in previous theoretical approaches.

2. Theoretical method

We consider the interaction between two alkali atoms. Let **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, **r** represents the electronic coordinates and **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 Eqs. (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

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

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

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

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^{λ}_{lk} and β^{λ}_{lk} define the semi-local energy-consistent pseudopotentials. The second interaction term in Eq. (4) is the polarization term which describes, among others, core–valence correlation effects [20] and, in the case of atom A, is taken as

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

where $\alpha_A = 0.1915a_0$ [27] 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

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

where $\delta_A = 0.831a_0^{-2}$ [27] is the cutoff parameter. The third term in Eq. (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 [28–33].

Table 1
Comparison of asymptotic energies with other theoretical and experimental results

	Present work	Schmidt-Mink [8]	Poteau [9]	Bashkin [39]
2s + 2p	14911	14924	14904	14904
2s + 3s	27201	27209	27212	27206
2p + 2p	29822	29876	–	29808
2s + 3p	30931	30934	30927	30925

Energies are shown in cm^{-1} units.

Table 2
The Li_2 molecule adiabatic potential energy curves for $1^1\Sigma_g^+$, $2^1\Sigma_g^+$, $3^1\Sigma_g^+$, $4^1\Sigma_g^+$, $1^1\Sigma_u^+$, $2^1\Sigma_u^+$ and $3^1\Sigma_u^+$ states

$R(a_0)$	$1^1\Sigma_g^+$	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$	$1^1\Sigma_u^+$	$2^1\Sigma_u^+$	$3^1\Sigma_u^+$
3.20	3152.98	30025.64	36910.79	38600.08	23805.44	40291.92	45645.37
3.40	113.42	26708.38	33099.65	35351.71	19921.24	36302.24	41591.55
3.60	−2360.41	23815.65	29908.77	33081.52	16686.71	32977.51	38214.89
3.80	−4319.57	21350.95	27280.51	31283.14	14031.58	30250.43	35445.64
4.00	−5825.09	19290.59	25147.36	29559.44	11878.69	28043.92	33204.93
4.20	−6940.40	17594.63	23440.98	27802.53	10154.24	26282.04	31415.18
4.40	−7 725.27	16217.03	22097.39	26395.05	8792.34	24895.49	30005.55
4.60	−8234.16	15111.26	21059.21	25275.40	7734.62	23823.01	28913.55
4.80	−8515.69	14233.49	20276.19	24388.85	6930.38	23011.62	28085.09
5.00	−8612.28	13544.32	19704.92	23687.39	6336.43	22416.30	27473.47
5.20	−8560.29	13009.42	19308.30	23129.82	5916.51	21999.21	27035.66
5.40	−8390.55	12599.50	19054.76	22682.32	5640.35	21728.76	26710.54
5.60	−8129.00	12289.97	18917.43	22319.40	5482.83	21578.71	26423.57
5.80	−7797.39	12060.44	18873.29	22024.42	5423.09	21527.25	26203.19
6.00	−7413.95	11894.19	18902.28	21788.77	5443.79	21556.19	26053.22
6.20	−6994.00	11777.77	18986.63	21609.86	5530.44	21650.18	25958.83
6.40	−6550.41	11700.50	19110.35	21488.64	5670.92	21796.22	25903.36
6.60	−6094.00	11654.19	19259.04	21427.35	5855.04	21983.12	25869.93
6.80	−5633.86	11632.74	19420.33	21427.67	6074.28	22201.13	25841.35
7.00	−5177.55	11631.90	19584.69	21489.02	6321.42	22441.53	25800.41
7.25	−4621.95	11655.68	19786.12	21644.86	6660.47	22760.95	25708.88
7.50	−4091.69	11704.33	19980.75	21873.31	7023.90	23085.33	25558.10
7.75	−3593.92	11776.54	20170.75	22153.53	7403.70	23391.57	25360.50
8.00	−3133.66	11871.87	20358.27	22465.18	7793.30	23638.05	25168.37
8.25	−2713.92	11990.01	20542.62	22791.55	8187.28	23748.75	25077.64
8.50	−2336.04	12130.31	20720.04	23120.19	8581.13	23668.09	25161.95
8.75	−1999.86	12291.43	20884.64	23442.59	8971.14	23456.53	25373.24
9.00	−1704.02	12471.31	21029.85	23753.80	9354.22	23198.46	25634.13
9.50	−1223.52	12875.55	21240.84	24338.50	10089.61	22693.47	26164.63
10.00	−869.96	13314.59	21337.98	24886.61	10771.22	22284.85	26626.13
10.50	−615.93	13756.34	21355.05	25417.22	11388.01	21998.86	26988.21
11.00	−436.27	14170.58	21350.53	25930.29	11933.40	21836.14	27251.50
11.50	−310.36	14533.24	21375.63	26407.47	12405.03	21788.15	27432.13
12.00	−222.46	14829.31	21461.25	26822.23	12804.56	21842.02	27551.08
12.50	−161.08	15054.13	21618.56	27148.37	13137.09	21982.53	27627.17
13.00	−118.08	15212.27	21844.20	27373.47	13410.12	22193.45	27674.38
13.50	−87.76	15314.24	22126.37	27510.51	13632.32	22458.78	27702.26
14.00	−66.21	15372.76	22450.24	27587.01	13812.42	22763.65	27717.05
14.50	−50.70	15399.83	22801.54	27626.90	13958.49	23095.07	27722.89
15.00	−39.41	15405.41	23168.32	27645.62	14077.49	23442.27	27722.72
16.00	−24.77	15380.14	23913.39	27652.98	14256.23	24151.54	27712.76
17.00	−16.31	15334.30	24636.13	27649.11	14381.82	24843.40	27701.26
18.00	−11.14	15284.80	25308.41	27654.44	14473.99	25487.80	27701.50
19.00	−7.84	15238.37	25908.46	27687.70	14544.17	26059.95	27731.69
20.00	−5.65	15197.18	26407.30	27777.87	14599.15	26527.49	27823.15
22.00	−3.11	15130.94	26970.36	28265.30	14679.00	27026.23	28320.66
24.00	−1.82	15082.47	27123.67	29004.87	14733.24	27150.08	29050.11
26.00	−1.42	15063.32	27150.98	29370.28	14771.65	27181.42	29747.75
28.00	−0.72	15020.30	27182.53	29811.97	14799.70	27191.52	30346.21
30.00	−0.48	15000.18	27189.78	29815.96	14820.67	27195.55	30766.47
32.00	−0.33	14984.68	27193.64	29818.17	14836.68	27197.49	30896.14
34.00	−0.24	14972.55	27195.91	29819.52	14849.12	27198.56	30919.88
36.00	−0.17	14962.94	27197.35	29820.37	14858.93	27199.21	30926.13
38.00	−0.13	14955.23	27198.30	29820.94	14866.77	27199.64	30928.35
40.00	−0.10	14948.97	27198.95	29821.33	14873.12	27199.93	30929.36
42.00	−0.08	14943.84	27199.41	29821.59	14878.31	27200.13	30929.92
44.00	−0.07	14939.60	27199.74	29821.78	14882.60	27200.28	30930.26
46.00	−0.06	14936.06	27199.98	29821.92	14886.17	27200.39	30930.49
48.00	−0.05	14933.08	27200.15	29822.02	14889.17	27200.47	30930.66
50.00	−0.05	14930.56	27200.28	29822.10	14891.71	27200.54	30930.78
52.00	−0.04	14928.41	27200.39	29822.15	14893.87	27200.59	30930.87
54.00	−0.04	14926.57	27200.46	29822.19	14895.72	27200.62	30930.94
56.00	−0.03	14924.98	27200.52	29822.22	14897.32	27200.65	30931.00
58.00	−0.03	14923.60	27200.57	29822.25	14898.70	27200.67	30931.04

(*continued on next page*)

Table 2 (*continued*)

$R(a_0)$	$1^1\Sigma_g^+$	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$	$1^1\Sigma_u^+$	$2^1\Sigma_u^+$	$3^1\Sigma_u^+$
60.00	−0.03	14922.40	27200.61	29822.27	14899.91	27200.69	30931.07
62.00	−0.03	14921.35	27200.64	29822.29	14900.97	27200.70	30931.10
64.00	−0.03	14920.42	27200.66	29822.30	14901.89	27200.71	30931.11
66.00	−0.03	14919.61	27200.68	29822.31	14902.71	27200.72	30931.13
68.00	−0.03	14918.89	27200.69	29822.32	14903.44	27200.73	30931.14
70.00	−0.03	14918.24	27200.70	29822.33	14904.08	27200.73	30931.15
72.00	−0.03	14917.67	27200.71	29822.37	14904.65	27200.74	30931.16
74.00	−0.03	14917.16	27200.72	29822.37	14905.17	27200.74	30931.17
76.00	−0.03	14916.70	27200.72	29822.37	14905.63	27200.75	30931.17
78.00	−0.03	14916.28	27200.73	29822.37	14906.05	27200.75	30931.18
80.00	−0.03	14915.91	27200.73	29822.37	14906.42	27200.75	30931.18
82.00	−0.03	14915.57	27200.74	29822.37	14906.76	27200.75	30931.18
84.00	−0.03	14915.26	27200.74	29822.36	14907.07	27200.75	30931.19
86.00	−0.03	14914.99	27200.74	29822.36	14907.35	27200.75	30931.19
88.00	−0.03	14914.73	27200.75	29822.36	14907.60	27200.75	30931.19

Energies are shown in cm^{-1} units.

Table 3
The Li_2 molecule adiabatic potential energy curves for $1^3\Sigma_u^+$, $2^3\Sigma_u^+$, $3^3\Sigma_u^+$, $4^3\Sigma_u^+$, $5^3\Sigma_u^+$, $1^3\Sigma_g^+$, $2^3\Sigma_g^+$ and $3^3\Sigma_g^+$ states

$R(a_0)$	$1^3\Sigma_u^+$	$2^3\Sigma_u^+$	$3^3\Sigma_u^+$	$4^3\Sigma_u^+$	$5^3\Sigma_u^+$	$1^3\Sigma_g^+$	$2^3\Sigma_g^+$	$3^3\Sigma_g^+$
3.20	18614.28	39539.21	44903.74	46180.63	47733.56	26768.74	37336.86	41348.13
3.40	15220.69	35578.15	40941.79	42286.27	43471.91	22450.56	33454.56	37235.96
3.60	12325.19	32280.65	37637.68	39032.05	39863.70	18944.63	30193.81	33830.75
3.80	9888.40	29573.41	34914.35	36317.32	36890.23	16133.01	27500.96	31054.29
4.00	7860.91	27377.86	32693.66	34032.97	34479.41	13903.37	25309.34	28821.74
4.20	6189.69	25618.25	30899.16	32093.77	32535.04	12155.91	23550.17	27051.27
4.40	4823.09	24225.63	29456.02	30468.32	30963.96	10805.34	22158.81	25668.83
4.60	3713.33	23139.25	28288.01	29138.88	29692.76	9779.72	21077.39	24609.73
4.80	2817.77	22306.78	27310.75	28084.03	28679.93	9018.96	20255.56	23818.56
5.00	2099.34	21683.63	26440.01	27287.72	27899.72	8473.24	19650.27	23248.54
5.20	1526.41	21232.21	25631.62	26713.55	27327.29	8101.53	19225.13	22860.53
5.40	1072.32	20920.97	24882.01	26306.22	26934.63	7870.21	18949.60	22621.99
5.60	714.85	20723.50	24193.44	26021.55	26692.34	7751.86	18798.25	22506.00
5.80	435.64	20617.53	23564.08	25831.08	26572.39	7724.11	18749.88	22490.31
6.00	219.51	20583.86	22990.12	25715.50	26550.21	7768.58	18786.78	22556.45
6.20	54.03	20604.97	22468.36	25660.12	26605.55	7870.17	18894.07	22688.99
6.40	−71.00	20661.94	21999.57	25652.86	26722.06	8016.36	19059.16	22875.00
6.60	−163.90	20723.64	21599.26	25683.60	26886.60	8196.80	19271.33	23103.59
6.80	−231.40	20704.47	21339.88	25743.95	27088.44	8402.92	19521.49	23365.57
7.00	−278.94	20495.35	21319.56	25827.09	27318.76	8627.69	19801.88	23653.24
7.25	−316.85	20108.86	21474.81	25955.01	27635.58	8926.12	20184.88	24039.12
7.50	−336.93	19713.34	21688.21	26102.36	27973.41	9235.62	20593.98	24444.51
7.75	−344.17	19337.42	21920.94	26263.37	28321.98	9549.13	21020.19	24860.83
8.00	−342.32	18986.23	22160.57	26433.52	28671.86	9861.22	21456.07	25281.10
8.25	−334.14	18660.34	22401.42	26608.73	29013.28	10167.75	21895.37	25699.56
8.50	−321.69	18359.20	22640.56	26784.90	29334.58	10465.62	22332.82	26111.46
8.75	−306.48	18081.92	22876.46	26957.81	29619.93	10752.59	22763.95	26512.85
9.00	−289.58	17827.46	23108.40	27123.21	29848.21	11027.08	23184.88	26900.42
9.50	−253.70	17382.36	23559.11	27416.28	29630.18	11534.96	23983.00	27623.46
10.00	−218.09	17013.92	23990.84	27642.77	29605.01	11985.51	24704.06	28263.03
10.50	−184.84	16711.40	24401.11	27801.53	29598.00	12379.25	25328.47	28802.14
11.00	−154.92	16464.07	24786.13	27910.07	29603.89	12719.34	25839.36	29137.83
11.50	−128.71	16261.99	25141.32	27992.84	29618.10	12874.97	25953.40	29223.78
12.00	−106.24	16096.38	25461.95	28071.00	29636.94	13030.58	26067.43	29309.71
12.50	−87.29	15959.83	25744.10	28158.45	29657.70	13186.18	26181.45	29395.64
13.00	−71.55	15846.31	25985.65	28262.02	29678.50	13341.78	26295.48	29481.57
13.50	−58.60	15750.95	26187.27	28382.69	29698.18	13497.39	26409.50	29567.50
14.00	−48.04	15669.95	26352.51	28517.27	29716.12	13652.99	26523.52	29653.43
14.50	−39.44	15600.34	26486.84	28660.25	29732.03	13808.60	26637.55	29739.36
15.00	−32.46	15539.84	26596.19	28805.45	29745.87	13964.20	26751.57	29825.30
16.00	−22.16	15439.78	26760.40	29081.20	29767.88	14275.52	26979.70	29997.22

Table 3 (*continued*)

$R(a_0)$	$1^3\Sigma_u^+$	$2^3\Sigma_u^+$	$3^3\Sigma_u^+$	$4^3\Sigma_u^+$	$5^3\Sigma_u^+$	$1^3\Sigma_g^+$	$2^3\Sigma_g^+$	$3^3\Sigma_g^+$
17.00	−15.34	15360.42	26875.76	29313.18	29783.62	14388.20	27028.52	30193.17
18.00	−10.79	15296.12	26959.43	29488.05	29794.70	14475.15	27069.25	30360.25
19.00	−7.72	15243.23	27021.08	29607.77	29802.47	14543.43	27101.78	30498.53
20.00	−5.61	15199.24	27066.71	29684.30	29807.93	14597.89	27126.93	30608.26
22.00	−3.11	15131.31	27125.37	29761.18	29814.55	14677.92	27160.06	30754.00
24.00	−1.82	15082.53	27157.28	29791.73	29817.99	14732.56	27178.01	30833.31
26.00	−1.12	15046.86	27174.76	29805.34	29819.83	14771.23	27187.58	30876.67
28.00	−0.72	15020.30	27184.59	29812.21	29820.87	14799.43	27192.78	30900.55
30.00	−0.48	15000.18	27190.31	29815.98	29821.46	14820.50	27195.71	30913.63
32.00	−0.33	14984.68	27193.78	29818.17	29821.81	14836.57	27197.42	30920.80
34.00	−0.24	14972.55	27195.95	29819.52	29822.02	14849.04	27198.48	30924.77
36.00	−0.17	14962.94	27197.36	29820.37	29822.15	14858.87	27199.15	30927.03
38.00	−0.13	14955.23	27198.30	29820.94	29822.23	14866.73	27199.59	30928.36
40.00	−0.10	14948.97	27198.95	29821.33	29822.28	14873.09	27199.90	30929.20
42.00	−0.08	14943.84	27199.41	29821.59	29822.31	14878.29	27200.11	30929.75
44.00	−0.07	14939.60	27199.74	29821.78	29822.33	14882.58	27200.27	30930.12
46.00	−0.06	14936.06	27199.98	29821.92	29822.35	14886.16	27200.38	30930.38
48.00	−0.05	14933.08	27200.15	29822.02	29822.36	14889.16	27200.47	30930.57
50.00	−0.05	14930.56	27200.28	29822.10	29822.36	14891.70	27200.53	30930.71
52.00	−0.04	14928.41	27200.39	29822.15	29822.37	14893.86	27200.58	30930.82
54.00	−0.04	14926.57	27200.47	29822.19	29822.37	14895.72	27200.62	30930.90
56.00	−0.03	14924.98	27200.53	29822.22	29822.37	14897.32	27200.65	30930.96
58.00	−0.03	14923.60	27200.57	29822.25	29822.37	14898.70	27200.67	30931.01
60.00	−0.03	14922.40	27200.61	29822.27	29822.37	14899.91	27200.69	30931.05
62.00	−0.03	14921.35	27200.64	29822.29	29822.37	14900.97	27200.70	30931.08
64.00	−0.03	14920.42	27200.66	29822.30	29822.37	14901.89	27200.71	30931.10
66.00	−0.03	14919.61	27200.68	29822.31	29822.37	14902.71	27200.72	30931.12
68.00	−0.03	14918.89	27200.69	29822.32	29822.37	14903.44	27200.73	30931.13
70.00	−0.03	14918.24	27200.70	29822.33	29822.37	14904.08	27200.73	30931.14
72.00	−0.03	14917.67	27200.71	29822.33	29822.37	14904.65	27200.74	30931.15
74.00	−0.03	14917.16	27200.72	29822.33	29822.37	14905.17	27200.74	30931.16
76.00	−0.03	14916.70	27200.72	29822.34	29822.37	14905.63	27200.74	30931.17
78.00	−0.03	14916.28	27200.73	29822.34	29822.37	14906.05	27200.75	30931.17
80.00	−0.03	14915.91	27200.73	29822.34	29822.37	14906.42	27200.75	30931.18
82.00	−0.03	14915.57	27200.74	29822.35	29822.37	14906.76	27200.75	30931.18
84.00	−0.03	14915.26	27200.74	29822.35	29822.36	14907.07	27200.75	30931.19
86.00	−0.03	14914.99	27200.74	29822.36	29822.37	14907.35	27200.75	30931.19
88.00	−0.03	14914.73	27200.75	29822.36	29822.37	14907.60	27200.75	30931.19

Energies are shown in cm^{-1} units.

Table 4
The Li_2 molecule adiabatic potential energy curves for $1^1\Pi_g$, $2^1\Pi_g$, $1^1\Pi_u$, $2^1\Pi_u$, $1^3\Pi_g$, $2^3\Pi_g$, $1^3\Pi_u$, $2^3\Pi_u$, $1^1\Delta_g$ and $1^3\Delta_u$ states

$R(a_0)$	$1^1\Pi_g$	$2^1\Pi_g$	$1^1\Pi_u$	$2^1\Pi_u$	$1^3\Pi_g$	$2^3\Pi_g$	$1^3\Pi_u$	$2^3\Pi_u$	$1^1\Delta_g$	$1^3\Delta_u$
3.20	31693.55	41342.87	26364.14	37458.06	35180.66	37947.11	11248.38	38267.28	29252.64	50257.52
3.40	28814.78	37609.54	23321.78	34298.10	32500.84	34449.77	8892.35	34464.34	27501.14	47684.43
3.60	26251.45	34540.10	20690.58	31669.37	29625.86	32111.26	6998.49	31306.49	26026.99	45451.03
3.80	24003.14	32031.99	18488.62	29469.27	26966.24	30400.75	5519.10	28731.86	24787.17	43508.25
4.00	22066.05	29990.21	16697.36	27642.17	24712.23	29009.62	4403.12	26667.12	23754.14	41815.81
4.20	20424.10	28337.39	15277.02	26150.95	22855.57	27837.25	3599.88	25038.60	22910.11	40339.73
4.40	19050.60	27011.38	14179.94	24959.86	21348.36	26834.33	3062.04	23778.07	22241.37	39050.84
4.60	17913.54	25960.86	13357.98	24031.10	20138.32	25967.30	2746.67	22825.12	21734.45	37923.87
4.80	16979.96	25142.30	12766.18	23326.83	19177.12	25210.28	2615.66	22127.52	21374.56	36936.94
5.00	16218.71	24518.31	12364.45	22811.48	18422.33	24544.03	2635.93	21640.87	21145.73	36071.19
5.20	15601.78	24056.89	12118.01	22452.97	17837.53	23956.14	2779.10	21327.80	21031.60	35310.50
5.40	15104.77	23730.85	11997.20	22223.27	17391.81	23438.94	3021.14	21157.04	21016.23	34641.14
5.60	14706.91	23517.30	11976.98	22098.27	17059.00	22986.89	3341.75	21102.58	21084.77	34051.44
5.80	14390.72	23397.05	12036.27	22057.44	16816.90	22595.37	3723.91	21142.72	21223.71	33531.48
6.00	14141.63	23354.01	12157.32	22083.37	16646.56	22260.56	4153.32	21259.20	21420.99	33072.77
6.20	13947.53	23374.66	12325.03	22161.33	16531.69	21979.45	4617.93	21436.49	21665.96	32668.03
6.40	13798.44	23447.60	12526.52	22278.93	16458.22	21749.78	5107.56	21661.12	21949.31	32310.97
6.60	13686.10	23563.20	12750.76	22425.95	16414.06	21569.86	5613.59	21921.11	22262.87	31996.11

(*continued on next page*)

Table 4 (*continued*)

$R(a_0)$	$1^1\Pi_g$	$2^1\Pi_g$	$1^1\Pi_u$	$2^1\Pi_u$	$1^3\Pi_g$	$2^3\Pi_g$	$1^3\Pi_u$	$2^3\Pi_u$	$1^1\Delta_g$	$1^3\Delta_u$
6.80	13603.76	23713.32	12988.40	22594.23	16388.98	21438.30	6128.70	22205.34	22599.58	31718.66
7.00	13545.89	23891.11	13231.53	22777.54	16374.56	21353.71	6646.66	22502.85	22953.29	31474.41
7.25	13501.17	24143.54	13533.23	23021.24	16361.63	21311.39	7290.12	22875.14	23411.34	31210.13
7.50	13480.64	24420.86	13823.05	23276.41	16346.18	21335.28	7921.12	23221.07	23878.88	30985.57
7.75	13478.84	24715.44	14093.36	23540.74	16323.17	21419.32	8532.57	23505.04	24348.47	30795.21
8.00	13491.47	25021.04	14338.99	23813.69	16290.79	21556.19	9118.67	23697.08	24813.81	30634.27
8.25	13515.17	25332.49	14556.87	24095.46	16249.45	21737.83	9674.77	23800.94	25269.54	30498.59
8.50	13547.27	25645.51	14745.81	24386.08	16200.76	21956.23	10197.24	23852.81	25711.07	30384.55
8.75	13585.64	25956.51	14906.11	24685.04	16146.84	22203.88	10683.45	23889.46	26134.42	30288.97
9.00	13628.60	26262.42	15039.22	24991.02	16089.77	22474.11	11131.69	23933.98	26536.23	30209.11
9.50	13723.01	26848.89	15233.22	25615.56	15973.01	23060.36	11911.89	24088.17	27264.44	30087.26
10.00	13822.39	27387.79	15349.37	26238.51	15860.54	23679.57	12541.53	24348.75	27880.00	30003.50
10.50	13921.40	27866.27	15409.31	26836.07	15757.44	24307.58	13035.34	24708.06	28377.57	29946.43
11.00	14016.57	28275.57	15431.09	27385.96	15665.51	24928.10	13414.74	25143.59	28762.79	29907.85
11.50	14105.77	28611.94	15428.32	27869.99	15584.71	25530.08	13702.90	25628.97	29050.33	29881.93
12.00	14187.84	28877.65	15410.63	28276.32	15514.14	26106.06	13921.19	26139.54	29259.43	29864.60
12.50	14262.28	29080.68	15384.54	28602.17	15452.59	26650.80	14087.35	26654.71	29409.28	29853.02
13.00	14329.12	29232.64	15354.34	28854.65	15398.83	27160.26	14215.15	27158.28	29516.16	29845.27
13.50	14388.69	29345.79	15322.79	29047.51	15351.73	27630.72	14314.86	27637.46	29592.59	29840.04
14.00	14441.52	29430.82	15291.58	29195.56	15310.32	28058.11	14393.92	28081.67	29647.65	29836.45
14.50	14488.25	29495.98	15261.71	29310.98	15273.80	28437.65	14457.69	28480.99	29687.74	29833.96
15.00	14529.51	29547.12	15233.73	29402.49	15241.50	28763.99	14509.96	28825.24	29717.28	29832.18
16.00	14598.10	29621.94	15184.16	29535.75	15187.33	29242.05	14590.18	29315.15	29756.01	29829.89
17.00	14651.72	29673.69	15142.89	29624.42	15144.16	29507.73	14648.55	29559.54	29778.71	29828.49
18.00	14693.94	29710.84	15108.85	29684.10	15109.35	29639.94	14692.68	29668.12	29792.67	29827.51
19.00	14727.51	29737.92	15080.81	29724.44	15081.00	29707.63	14727.01	29721.27	29801.64	29826.74
20.00	14754.47	29757.78	15057.63	29751.85	15057.70	29745.34	14754.28	29751.09	29807.59	29826.11
22.00	14794.35	29783.36	15022.28	29783.86	15022.29	29782.82	14794.32	29782.22	29814.49	29825.12
24.00	14821.68	29797.77	14997.30	29799.97	14997.30	29799.79	14821.68	29797.57	29817.98	29824.39
26.00	14841.06	29806.24	14979.21	29808.66	14979.21	29808.63	14841.06	29806.20	29819.83	29823.86
28.00	14855.20	29811.44	14965.82	29813.64	14965.82	29813.63	14855.20	29811.43	29820.87	29823.48
30.00	14865.76	29814.74	14955.71	29816.62	14955.71	29816.62	14865.76	29814.74	29821.46	29823.20
32.00	14873.81	29816.91	14947.93	29818.48	14947.93	29818.48	14873.81	29816.91	29821.81	29823.00
34.00	14880.06	29818.38	14941.86	29819.67	14941.86	29819.67	14880.06	29818.38	29822.02	29822.85
36.00	14884.99	29819.39	14937.05	29820.45	14937.05	29820.45	14884.99	29819.39	29822.15	29822.75
38.00	14888.93	29820.11	14933.20	29820.98	14933.20	29820.98	14888.93	29820.11	29822.23	29822.66
40.00	14892.11	29820.63	14930.07	29821.35	14930.07	29821.35	14892.11	29820.63	29822.28	29822.60
42.00	14894.72	29821.01	14927.50	29821.60	14927.50	29821.60	14894.72	29821.01	29822.31	29822.55
44.00	14896.87	29821.30	14925.38	29821.79	14925.38	29821.79	14896.87	29821.30	29822.33	29822.52
46.00	14898.65	29821.51	14923.61	29821.92	14923.61	29821.92	14898.65	29821.51	29822.35	29822.49
48.00	14900.16	29821.68	14922.12	29822.02	14922.12	29822.02	14900.16	29821.68	29822.36	29822.46
50.00	14901.43	29821.80	14920.86	29822.09	14920.86	29822.09	14901.43	29821.81	29822.36	29822.45
52.00	14902.51	29821.90	14919.79	29822.15	14919.79	29822.15	14902.51	29821.90	29822.36	29822.43
54.00	14903.44	29821.99	14918.87	29822.19	14918.87	29822.19	14903.44	29821.99	29822.37	29822.42
56.00	14904.24	29822.05	14918.07	29822.22	14918.07	29822.22	14904.24	29822.05	29822.37	29822.41
58.00	14904.93	29822.10	14917.38	29822.25	14917.38	29822.25	14904.93	29822.10	29822.37	29822.40
60.00	14905.54	29822.14	14916.78	29822.27	14916.78	29822.27	14905.54	29822.14	29822.37	29822.39
62.00	14906.06	29822.17	14916.26	29822.28	14916.26	29822.28	14906.06	29822.17	29822.37	29822.39
64.00	14906.53	29822.20	14915.80	29822.30	14915.80	29822.30	14906.53	29822.20	29822.37	29822.39
66.00	14906.94	29822.23	14915.39	29822.31	14915.39	29822.31	14906.94	29822.23	29822.37	29822.38
68.00	14907.30	29822.24	14915.03	29822.32	14915.03	29822.32	14907.30	29822.24	29822.37	29822.38
70.00	14907.62	29822.26	14914.70	29822.32	14914.70	29822.32	14907.62	29822.26	29822.37	29822.37
72.00	14907.91	29822.27	14914.42	29822.33	14914.42	29822.33	14907.91	29822.27	29822.36	29822.37
74.00	14908.17	29822.28	14914.16	29822.33	14914.16	29822.33	14908.17	29822.28	29822.37	29822.37
76.00	14908.40	29822.29	14913.93	29822.33	14913.93	29822.33	14908.40	29822.29	29822.37	29822.37
78.00	14908.61	29822.30	14913.72	29822.35	14913.72	29822.34	14908.61	29822.30	29822.37	29822.37
80.00	14908.79	29822.31	14913.54	29822.35	14913.54	29822.35	14908.79	29822.31	29822.37	29822.37
82.00	14908.96	29822.31	14913.37	29822.35	14913.37	29822.35	14908.96	29822.31	29822.36	29822.37
84.00	14909.12	29822.32	14913.21	29822.35	14913.21	29822.35	14909.12	29822.32	29822.37	29822.37
86.00	14909.26	29822.32	14913.08	29822.35	14913.08	29822.35	14909.26	29822.32	29822.37	29822.37
88.00	14909.38	29822.33	14912.95	29822.35	14912.95	29822.35	14909.38	29822.33	29822.36	29822.36

Energies are shown in cm^{-1} units.

Table 5
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	Dissociation	Method	R_e	D_e	ω_e	T_e
$1^1\Sigma_g^+$	(2s + 2s)	Present work	2.658	8613	352.41	0
		Exp. [36]	2.673	8600	351.39	0
		Exp. [37]	2.673	8516.78		
		Exp. [40]		8615		
		Theory [9]	2.660	8510	353	0
		Theory [8]	2.675	8466	351.01	0
$1^3\Sigma_u^+$		Present work	4.134	344	65.95	8126
		Exp. [41]	4.127	336	67.58	8180.9
		Exp. [38]	4.171	333	65.13	8183.8
		Theory [9]	4.159	321	66.1	8189
		Theory [8]	4.182	322	63.73	8144
$2^1\Sigma_g^+$	(2s + 2p)	Present work	3.655	3274	129.94	20139
		Exp. [42]	3.651	3319	128.67	20101
		Theory [9]	3.667	3161	126.3	20253
		Theory [8]	3.655	3276	129.04	20128
$1^3\Sigma_g^+$		Present work	3.053	7184	253.19	16290
		Exp. [38]	3.068	7091.5	251.5	16328.8
		Theory [9]	3.055	7137	253.3	16277
		Theory [8]	3.067	7071	252.2	16333
$1^1\Sigma_u^+$		Present work	3.092	9483	257.54	13994
		Exp. [11]	3.108	9352.5	257.47	14068
		Theory [9]	3.094	9466	257.4	13948
		Theory [8]	3.108	9356	256.06	14048
$2^3\Sigma_u^+$		Present work	3.181	−5669	193.73	
		Theory [9]	3.185	−5712	213.1	
		Theory [8]	3.166	−5709		
$1^1\Pi_g$		Present work	4.048	1426	93.37	21968
		Exp. [43]	4.058	1422.5	93.35	21988.5
		Exp. [44]		1421.9	92.77	21998.8
		Theory [9]	4.063	1400	92.5	22013
		Theory [8]	4.073	1406	91.85	21998
$1^3\Pi_g$		Present work	repulsive			
$1^1\Pi_u$		Present work	2.934	2930	269.49	20553
		Exp. [25]		2984.42		
		Exp. [36]	2.936	2984.5	270.69	20436
		Theory [9]	2.939	2716	269.7	20698
		Theory [8]	2.942	2903	270.28	20501
$1^3\Pi_u$		Present work	2.577	12297	348.15	11225
		Exp. [45]	2.590	12145	345.6	
		Theory [9]	2.581	12178	348.7	11236
		Theory [8]	2.595	12148	345.88	11256
$3^1\Sigma_g^+$	(2s + 3s)	Present work	3.076	8333	246.62	27428
		Exp. [46]	3.086	8312.8	245.9	27410
		Theory [9]	3.074	8289	250.4	27434
		Theory [8]	3.085	8279	245.7	27396
$2^3\Sigma_g^+$		Present work	3.073	8451	270.07	27322
		Theory [9]	3.075	8428	270.4	27294
		Theory [8]	3.079	8379	270.68	27296
$2^1\Sigma_u^+$, inner well		Present work	3.081	5674	259.82	30094
		Exp. [21]	3.096		259.003	30101.407
		Exp. [47]	3.094		259.9	30100.3
		Theory [9]	3.083	5660	260.1	30062
		Theory [8]	3.089	5598	259.2	30077
$2^1\Sigma_u^+$, outer well		Present work	6.072	5413	119.05	30285
		Exp. [21]	6.037			30400.137
		Theory [9]	6.080	5453	117	30269
		Theory [8]	6.052	5329	121.96	

(*continued on next page*)

Table 5 (*continued*)

State	Dissociation	Method	R_e	D_e	ω_e	T_e
$3^3\Sigma_u^+$		Present work	3.658	5903	373.15	29922
		Theory [9]	3.667	5866	356.4	29853
		Theory [8]	3.695	5839	392.69	29836
$4^1\Sigma_g^+$, inner well	(2p + 2p)	Present work	3.545	8388	229.19	29985
		Exp. [48]	3.548	8349.3	227.3	29975
		Theory [9]	3.543	8377	231.1	29941
		Theory [8]	3.551	8319	229.55	30023
$4^1\Sigma_g^+$, outer well		Present work	9.107	2159	19.38	36110
		Theory [9]	8.750	2158	17	36160
		Theory [8]	8.940	2166		
$4^3\Sigma_u^+$		Present work	3.351	4157	187.36	34195
		Theory [9]	3.267	4395	206.4	33923
		Theory [8]	3.371	4075	186.17	34267
$5^3\Sigma_u^+$		Present work	3.149	3260	265.39	35132
		Theory [9]	3.126	3079	264.9	35240
$2^1\Pi_g$		Present work	3.191	6469	230.70	31905
		Exp. [49]	3.2014	6455	229.26	31868.4
		Theory [9]	3.201	6398	229.1	31920
$2^3\Pi_g$		Present work	3.853	8511	189.83	29842
		Exp. [50]	3.816	8484	189.1	29840.5
		Theory [9]	3.851	8435	191.3	29883
$2^1\Pi_u$		Present work	3.077	7751	236.47	30627
		Exp. [51]	3.074	7648.4	239.1	30549
		Theory [9]	3.089	7641	231.3	30677
$2^3\Pi_u$		Present work	2.968	8720	283.82	29681
		Theory [9]	2.965	8671	284.1	29647
$1^1\Delta_g$		Present work	2.822	8811	276.30	29586
		Exp. [52]		9579	271.44	
		Theory [9]	2.919	9368	273.1	28950
$1^3\Delta_u$		Present work	repulsive			
		Theory [9]	3.126	3430	251.6	34888
$3^3\Sigma_g^+$	(2s + 3p)	Present work	3.034	8446	274.49	31060
		Exp. [50]	3.081	8401	273.3	31041.7
		Theory [9]	3.034	8346	274.4	31091
		Theory [8]	3.030	8396	278.89	31149
$3^1\Sigma_u^+$		Present work	4.369	5848	295.30	33668
		Theory [9]	4.340	5839	258	33594
		Theory [8]	4.315	5875	256.16	33670

3. Computational method

All calculations reported in this paper were performed by means of the MOLPRO program package [34]. The core electrons of Li atoms are represented by pseudopotential ECP2SDF [27], which was formed from the uncontracted (9s 9p 8d 3f) basis set. The basis for the s and p orbitals, which comes with this potential is enlarged by functions for d and f orbitals given by P. Feller [35] and assigned by CC-PV5Z. Additionally, our basis set was augmented by three s short range correlation functions (392.169555, 77.676373, 15.38523), three p functions (96.625417, 19.845562, 4.076012) and three d functions (3.751948, 1.9783, 1.043103). Also, we added to the basis a set of five diffused functions: two s functions (0.010159, 0.003894), two p functions (0.007058, 0.002598) and one d function (0.026579). 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 potentials correlate to the (2s + 2s) ground atomic asymptote and (2s + 2p), (2s + 3s), (2p + 2p), (2s + 3p) 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. The corresponding active space in the D_{2h} point group involved the molecular counterparts of the 2s, 2p, 3s, 3p and 3d valence orbitals of the Li atom.

4. Results and discussion

Calculations of the adiabatic energy curves are performed for the internuclear separation R in the range from $3.2a_0$ to $88a_0$ with the various steps adjusted to the internuclear distance. Numerical values of the calculated potential energies are shown in Tables 2–4. 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 5. As it is seen, overall agreement of all our spectroscopic constants and other theoretical and experimental data is very reasonable. Particularly, what is worth noting, there is a good agreement for the spectroscopic constants in the case of double wells for two states $2^1\Sigma_u^+$ and $4^1\Sigma_g^+$. Present results for all singlet and triplet states are plotted relative to the corresponding experimental values of the atomic terms in Figs. 1–3. The states $5^3\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$ are calculated for the second time (besides Poteau and Spiegelmann [9]). All our states are calculated for the first time, for large internuclear separations R (up to $88a_0$). We obtain asymptotic energies for ground and excited states, which are in very good agreement with experimental and other theoretical values (Table 1.) We also present almost all states corresponding to the 2p + 2p asymptote (Fig. 3), except $1^1\Sigma_u^-$ and $1^3\Sigma_g^-$ states, which are not available by methods of the MOLPRO program package [34]. In Fig. 4, we

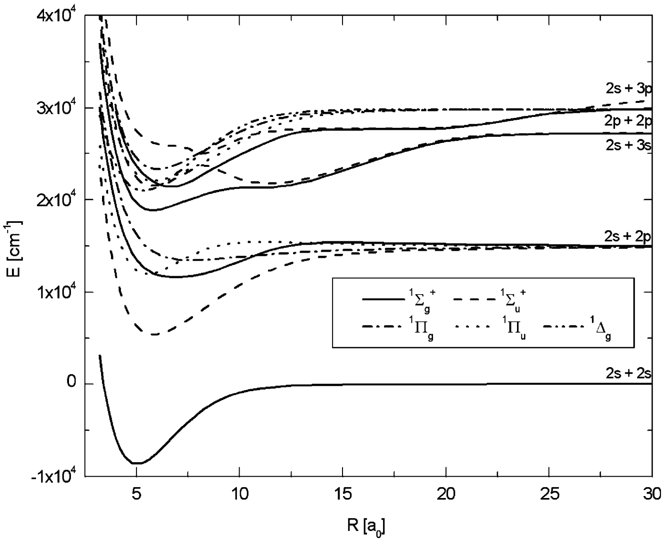

Fig. 1. Adiabatic potential energy curves for the ground and excited singlet states of the Li_2 molecule correlating to the 2s + 2s, 2s + 2p, 2s + 3s, 2p + 2p and 2s + 3p asymptotes.

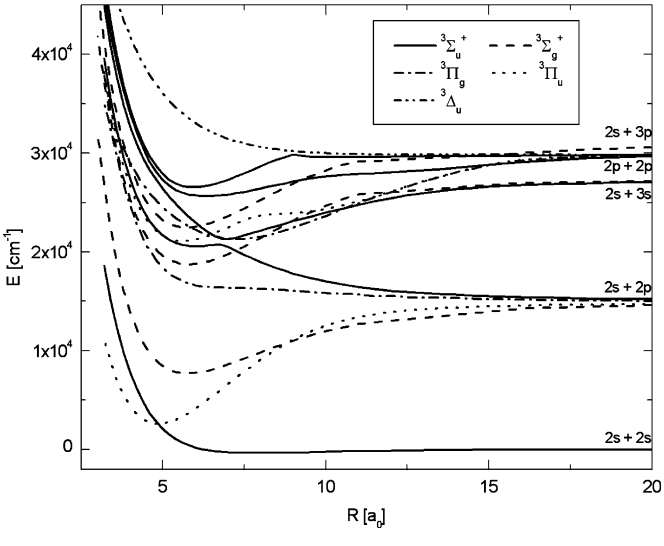

Fig. 2. Adiabatic potential energy curves for excited triplet states of the Li_2 molecule correlating to the 2s + 2s, 2s + 2p, 2s + 3s, 2p + 2p and 2s + 3p asymptotes.

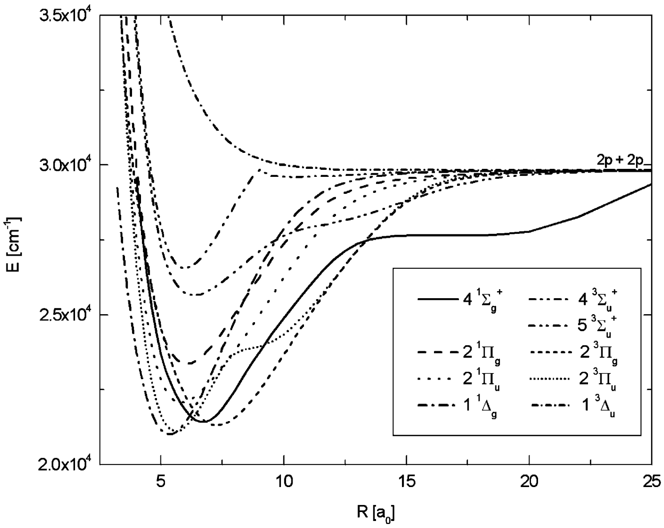

Fig. 3. Adiabatic potential energy curves for excited states of the Li_2 molecule correlating to the 2p + 2p asymptote.

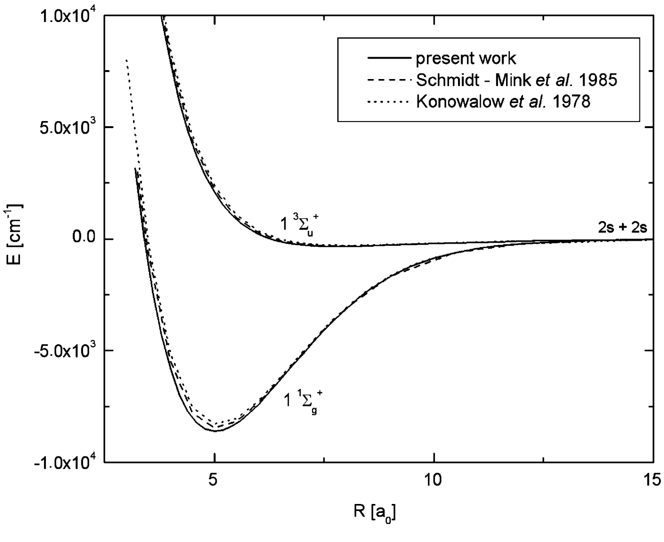

Fig. 4. Comparison of the ground and the first excited molecular state correlating to 2s + 2s asymptote with the theoretical results of Olson and Konowalow [3,4] and Schmidt-Mink et al. [8].

compare our ground and the first excited molecular state correlating to ground state of lithium atoms along with the theoretical results of Olson and Konowalow [3,4] and Schmidt-Mink et al. [8]. As one may see, the agreement is very good. In Fig. 5. we compare present results of the ground state $X(1)^1\Sigma_g^+$ with two curves derived from experiments by Hessel and Vidal [36] and Barakat et al. [37]. In the vicinity of the potential well we note better agreement with the curve of Hessel and Vidal [36], but for larger distances we note the perfect fit with the curve of Barakat et al. [37]. In Fig. 6, the comparison for $a(1)^3\Sigma_u^+$ with the curve derived from experiment by Linton et al. [38] shows some discrepancy for the repulsive part of potential curve. Also our theoretical curve displays a deeper well of about 11 cm^{-1}. In Fig. 7 we show our results along with the experimental curve given by Bouloufa et al. [25] and theoretical results of Schmidt-Mink et al. [8]. Here, we underline the good agreement in the distinctive hump shape which appears around 10–13a_0. In turn, in the Fig. 8, we display the comparison with two $^1\Sigma_g^+$ states derived form experiment. 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 [22,23] we find a disagreement for small internuclear distance.

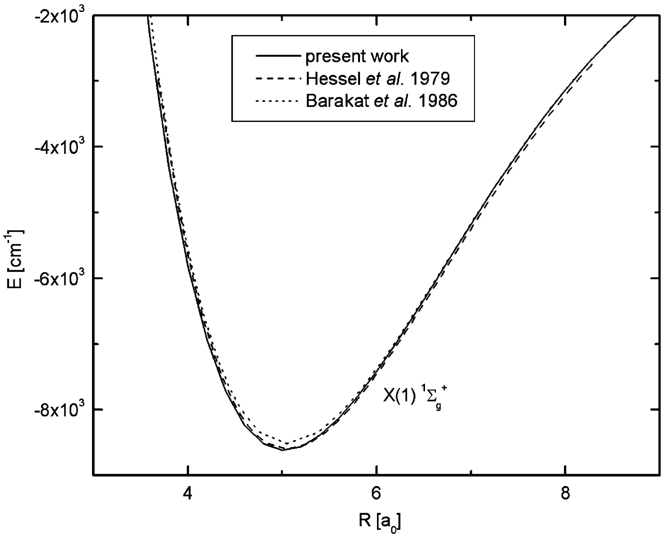

Fig. 5. Comparison of the ground state with the experimental results of Hessel and Vidal [36] and Barakat et al. [37].

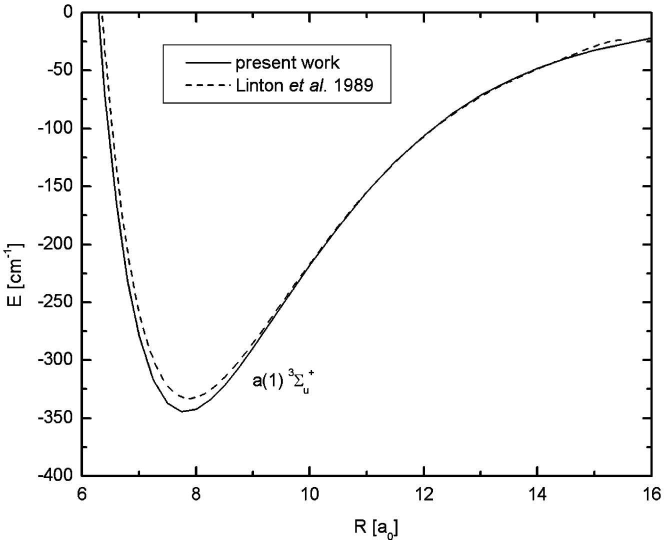

Fig. 6. Comparison of the first excited molecular state correlating to 2s + 2s asymptote with the experimental result of Linton et al. [38].

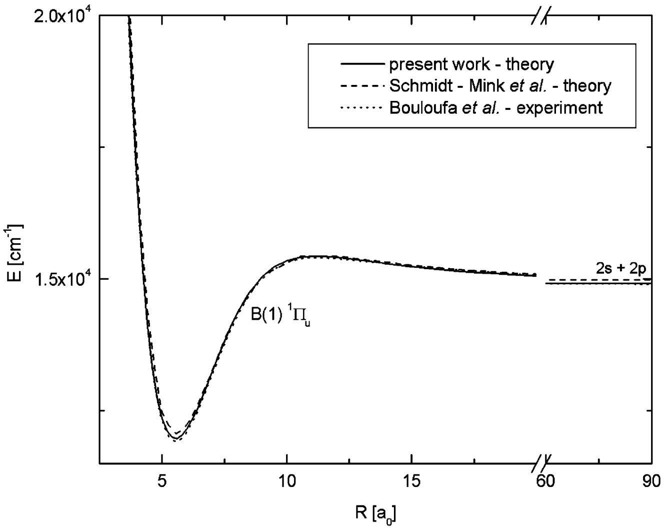

Fig. 7. Comparison of the $B(1)^1\Pi_u$ state correlating to 2s + 2p asymptote with results derived from experiment by Bouloufa et al. [25] and theoretical results of Schmidt-Mink et al. [8].

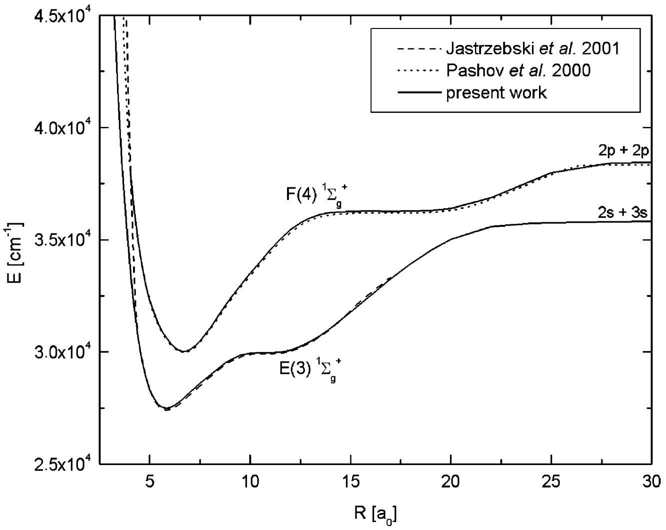

Fig. 8. Comparison of the $E(3)^1\Sigma_g^+$ and $F(4)^1\Sigma_g^+$ states correlating, respectively, to 2s + 3s and 2p + 2p asymptotes with potential curves derived from experiment by Jastrzebski et al. [22] and Pashov et al. [23].

5. Conclusion

We have calculated the adiabatic potential energy curves of the lithium dimer using CASSCF/MRCI method. Several curves correlated to the excited atomic states are presented for the second time (besides Poteau and Spiegelmann [9]): $5^3\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$. Comparisons with available lowly-lying theoretical and experimental curves provide almost perfect agreement. Only in the case of the repulsive part of the $3^1\Sigma_g^+$ state, we note certain disagreement. In the near future, we plan to calculate adiabatic potential energy curves for heavier alkali dimers.

Acknowledgements

The authors gratefully acknowledge fruitful and helpful discussions with prof. E. Czuchaj. This research is partially supported by ESF Network – CATS (Collisions in Atom Traps).

References

[1] M.L. Olson, D.D. Konowalow, Chem. Phys. Lett. 39 (1976) 281.
[2] M.L. Olson, D.D. Konowalow, Chem. Phys. 22 (1977) 29.
[3] M.L. Olson, D.D. Konowalow, Chem. Phys. 21 (1977) 393.
[4] D.D. Konowalow, M.L. Olson, J. Chem. Phys. 71 (1979) 450.
[5] D.D. Konowalow, J.L. Fish, Chem. Phys. 77 (1983) 435.
[6] C. He, L.P. Gold, R.A. Bernheim, J. Chem. Phys. 95 (1991) 7947.
[7] W. Müller, W. Meyer, J. Chem. Phys. 80 (1984) 3311.
[8] I. Schmidt-Mink, W. Müller, W. Meyer, Chem. Phys. 92 (1985) 263.
[9] R. Poteau, F. Spiegelmann, J. Mol. Spectrosc. 171 (1995) 299.
[10] M. Song, P. Yi, X. Dai, Y. Liu, Li Li, G.H. Jeung, J. Mol. Spectrosc. 215 (2002) 251.
[11] P. Kusch, M.M. Hessel, J. Chem. Phys. 67 (1977) 586.
[12] R. Uberna, Z. Amitay, C.X.W. Qian, S.R. Leone, J. Chem. Phys. 114 (2001) 10311.
[13] S. Antonova, K. Urbanski, A.M. Lyyra, F.C. Spano, Li Li, Chem. Phys. Lett. 267 (1997) 158.
[14] P. Cacciani, V. Kokoouline, N. Bouloufa, F. Masnou-Seeuws, R. Vetter, Phys. Rev. A 68 (2003) 042506.
[15] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, P. Pillet, Phys. Rev. Lett. 80 (1998) 4402.
[16] E.R.I. Abraham, W.I. McAlexander, C.A. Sackett, R.G. Hulet, Phys. Rev. Lett. 74 (1995) 1315.
[17] E.R.I. Abraham, N.W.M. Ritchie, W.I. McAlexander, R.G. Hulet, J. Chem. Phys. 103 (1995) 7773.
[18] I.D. Prodan, M. Pichler, M. Junker, R.G. Hulet, Phys. Rev. Lett. 91 (2003) 080402.
[19] S. Jochim, M. Bartenstein, A. Altmeyer, G. Hendl, S. Riedl, C. Chin, J. Hecker Denschlag, R. Grimm, Science 302 (2003) 2101.
[20] C. Chin, M. Bartenstein, A. Altmeyer, S. Riedl, S. Jochim, J. Hecker Denschlag, R. Grimm, Science 305 (2004) 1128.
[21] S. Kasahara, P. Kowalczyk, M.H. Kabir, M. Baba, H. Kato, J. Chem. Phys. 113 (2000) 6227.
[22] W. Jastrzębski, A. Pashov, P. Kowalczyk, J. Chem. Phys. 114 (2001) 10725.
[23] A. Pashov, W. Jastrzębski, P. Kowalczyk, J. Chem. Phys. 113 (2000) 6624.
[24] A. Pashov, W. Jastrzębski, P. Kowalczyk, Comp. Phys. Commun. 128 (1999) 622.
[25] N. Bouloufa, P. Cacciani, R. Vetter, A. Yiannopoulou, F. Martin, A.J. Ross, J. Chem. Phys. 114 (2001) 8445.
[26] P. Jasik, J.E. Sienkiewicz, SPIE Proc. 5849 (2005) 82.
[27] P. Fuentealba, H. Preuss, H. Stoll, L. Von Szentply, Chem. Phys. Lett. 89 (1982) 418.
[28] E. Czuchaj, M. Krośnicki, H. Stoll, Chem. Phys. 265 (2001) 291.
[29] E. Czuchaj, M. Krośnicki, H. Stoll, Chem. Phys. 292 (2003) 101.
[30] E. Czuchaj, M. Krośnicki, H. Stoll, Theor. Chem. Acc. 107 (2001) 27.
[31] E. Czuchaj, M. Krosnicki, H. Stoll, Chem. Phys. Lett. 371 (2003) 401.
[32] E. Czuchaj, M. Krosnicki, H. Stoll, Theor. Chem. Acc. 110 (2003) 28.
[33] E. Czuchaj, F. Rebentrost, H. Stoll, H. Preuss, Theor. Chem. Acc. 100 (1998) 117.
[34] MOLPRO is a package of ab initio programs written by H.J. Werner and P.J. Knowles with contributions from R.D. Amos, et al.
[35] Private communications, as cited in MOLPRO manual.
[36] M.M. Hessel, C.R. Vidal, J. Chem. Phys. 70 (1979) 4439.
[37] B. Barakat, R. Bacis, F. Carrot, S. Churassy, P. Crozet, F. Martin, J. Verges, Chem. Phys. 102 (1986) 215.
[38] C. Linton, T.L. Murphy, F. Martin, R. Bacis, J. Verges, J. Chem. Phys. 91 (1989) 6036.
[39] S. Bashkin, J.O. Stoner Jr.Atomic Energy Levels and Grotrian Diagrams, vol. 1, North-Holland, Amsterdam, 1975.
[40] W.C. Stwalley, J. Chem. Phys. 65 (1976) 2038.
[41] X. Xie, R.W. Field, J. Chem. Phys. 83 (1985) 6193.
[42] B. Barakat, R. Bacis, S. Churassy, R.W. Field, J. Ho, C. Linton, S. Mc Donald, F. Martin, J. Verges, J. Mol. Spectrosc. 116 (1986) 271.
[43] D.A. Miller, L.P. Gold, P.D. Tripodi, R.A. Bernheim, J. Chem. Phys. 92 (1990) 5822.
[44] C. Linton, F. Martin, R. Bacis, J. Mol. Spectrosc. 142 (1990) 340.
[45] F. Engelke, H. Hage, Chem. Phys. Lett. 103 (1983) 98.
[46] R.A. Bernheim, L.P. Gold, P.B. Kelly, T. Tipton, D.K Veirs, J. Chem. Phys. 76 (1982) 57.
[47] C. Linton, F. Martin, R. Bacis, J. Verges, J. Mol. Spectrosc. 137 (1989) 235.
[48] R.A. Bernheim, L.P. Gold, P.B. Kelly, C. Tomczyk, D.K. Veirs, J. Chem. Phys. 74 (1981) 3249.
[49] R.A. Bernheim, L.P. Gold, P.B. Kelly, T. Tipton, D.K. Veirs, J. Chem. Phys. 74 (1981) 2749.
[50] X. Xie, R.W. Field, J. Mol. Spectrosc. 117 (1986) 228.
[51] K. Ishikawa, S. Kubo, H. Kato, J. Chem. Phys. 95 (1991) 8803.
[52] C. Linton, F. Martin, P. Crozet, A.J. Ross, R. Bacis, J. Mol. Spectrosc. 158 (1993) 445.