Highly-excited electronic states of the lithium dimer

P. Jasik and J.E. Sienkiewicz

Department of Theoretical Physics and Quantum Informatics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland

Introduction

Homonuclear and heteronuclear alkali metal dimers and their ions have attracted attention of experimentalists and theoreticians for many years, mainly because they have got simple electronic structure (one or two valence-electron systems). It can serve as a convenient prototype for testing theoretical methods, which can be further applied to more complicated molecular systems. This poster is a complement of our previous reports in which we prsented twenty five the lowest lying adiabatic potential energy curves of the lithium dimer [1, 2, 3]. First useful theoretical calculations for highly-excited electronic states of the Li_2 molecule were presented by Poteau and Spiegelmann [4]. The most important experimental papers, where several Rydberg states of Li_2 molecule were presented, were performed by the group of Demtröder [5, 6, 7] and Jastrzębski and Kowalczyk [8, 9].

Computational method

All calculations reported in this poster were performed by means of the MOLPRO program package [10]. The core electrons of Li atoms are represented by pseudopotential ECP2SDF [11]. The basis for s and p orbitals, which comes with effective core potential ECP2SDF is enlarged by functions for d, f and g orbitals given by Feller [12] and assigned by CC-PV5Z. Additionally, our basis set was augmented by five s short range correlation functions (9996.402900, 1979.970927, 392.169555, 77.676373, 15.385230), five p functions (2290.589942, 470.456384, 96.625417, 19.845562, 4.076012), five d functions (13.495412, 7.115763, 3.751948, 1.978300, 1.043103) and three f functions (3.566932, 2.242072, 1.409302). Also, we added to the basis a set of fourteen diffused functions: three s functions (0.010159, 0.003894, 0.001493), three p functions (0.007058, 0.002598, 0.000956), three d functions (0.026579, 0.011581, 0.005046) and five f functions (0.885847, 0.556818, 0.055000, 0.027500). We checked the quality of our basis set performing the CI calculations for the ground and several excited states of isolated lithium atoms. The calculated Li_2 adiabatic potentials correlate to the $Li(2p) + Li(2p)$, $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$, $Li(2s) + Li(4s)$, $Li(2s) + Li(4p)$ and $Li(2s) + Li(4d)$ excited atomic asymptotes. The comparison of experimental and theoretical asymptotic energies for different states is shown in Table 1. We do not take into consideration in our calculations spin-orbit couplings (SO). 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.

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

Dissociation limit	Moore (exp.) [13]	Present work	Poteau (theory) [4]
$Li(2p) + Li(2p)$	**29808**	**29822**	
$Li(2s) + Li(3p)$	**30925**	**30931**	**30927**
$Li(2s) + Li(3d)$	**31283**	**31275**	**31291**
$Li(2s) + Li(4s)$	**35012**	**35014**	
$Li(2s) + Li(4p)$	**36470**	**36493**	
$Li(2s) + Li(4d)$	**36623**	**36618**	

Calculations of the adiabatic potential energy curves are performed for the internuclear separation R in the range from $3\ a_0$ to $90\ a_0$ with the various steps adjusted to the internuclear distance.

Results

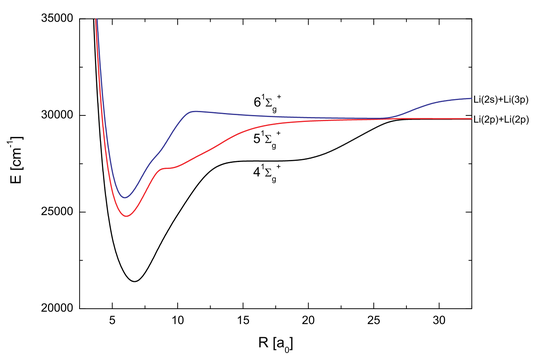

Fig. 1. Adiabatic potential energy curves for 3 excited states in the symmetry $^1\Sigma_g^+$ of the Li_2 molecule correlating to the $Li(2p) + Li(2p)$ and $Li(2s) + Li(3p)$ asymptotes.

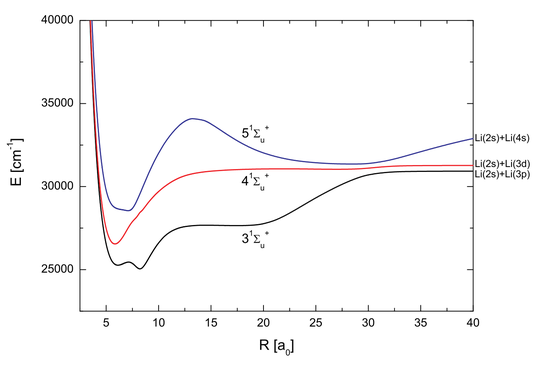

Fig. 2. Adiabatic potential energy curves for 3 excited states in the symmetry $^1\Sigma_u^+$ of the Li_2 molecule correlating to the $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4s)$ asymptotes.

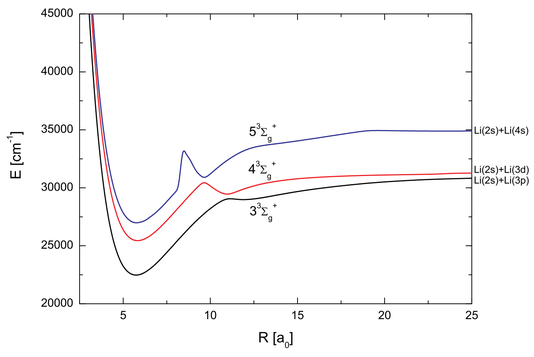

Fig. 3. Adiabatic potential energy curves for 3 excited states in the symmetry $^3\Sigma_g^+$ of the Li_2 molecule correlating to the $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4s)$ asymptotes.

Results

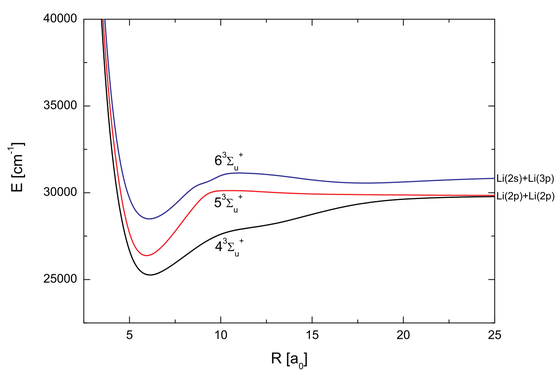

Fig. 4. Adiabatic potential energy curves for 3 excited states in the symmetry $^3\Sigma_u^+$ of the Li_2 molecule correlating to the $Li(2p) + Li(2p)$ and $Li(2s) + Li(3p)$ asymptotes.

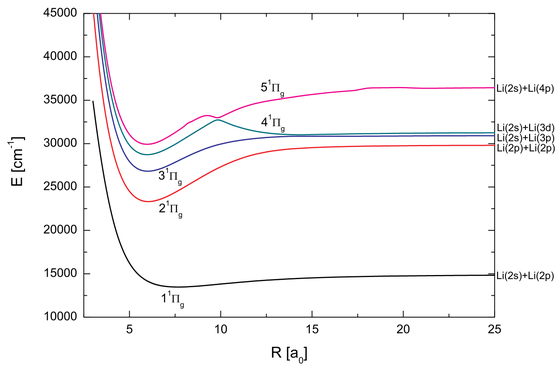

Fig. 5. Adiabatic potential energy curves for 5 excited states in the symmetry $^1\Pi_g$ of the Li_2 molecule correlating to the $Li(2s) + Li(2p)$, $Li(2p) + Li(2p)$, $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4p)$ asymptotes.

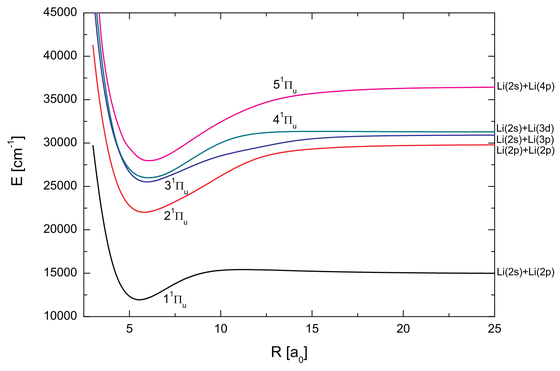

Fig. 6. Adiabatic potential energy curves for 5 excited states in the symmetry $^1\Pi_u$ of the Li_2 molecule correlating to the $Li(2s) + Li(2p)$, $Li(2p) + Li(2p)$, $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4p)$ asymptotes.

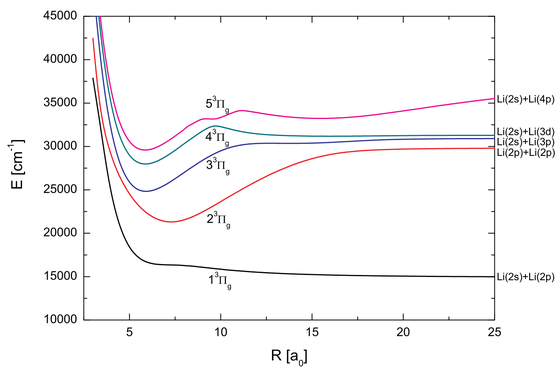

Fig. 7. Adiabatic potential energy curves for 5 excited states in the symmetry $^3\Pi_g$ of the Li_2 molecule correlating to the $Li(2s) + Li(2p)$, $Li(2p) + Li(2p)$, $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4p)$ asymptotes.

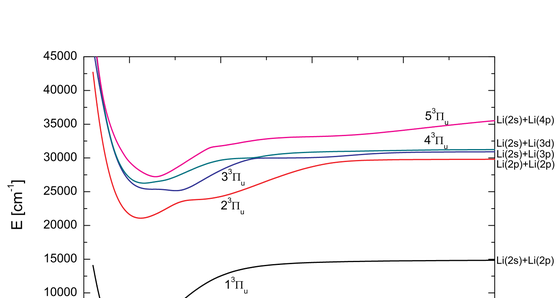

Fig. 8. Adiabatic potential energy curves for 5 excited states in the symmetry $^3\Pi_u$ of the Li_2 molecule correlating to the $Li(2s) + Li(2p)$, $Li(2p) + Li(2p)$, $Li(2s) + Li(3p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4p)$ asymptotes.

Results

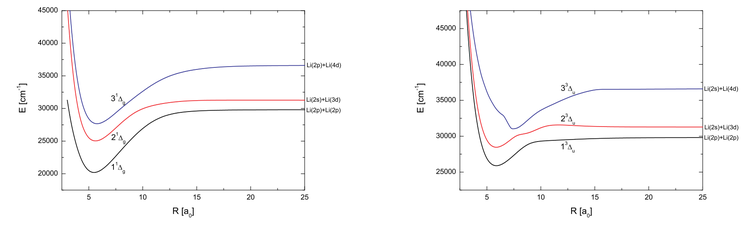

Fig. 9. Adiabatic potential energy curves for 6 excited states in the symmetry $^1\Delta_g$ and $^3\Delta_u$ of the Li_2 molecule correlating to the $Li(2p) + Li(2p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4d)$ asymptotes.

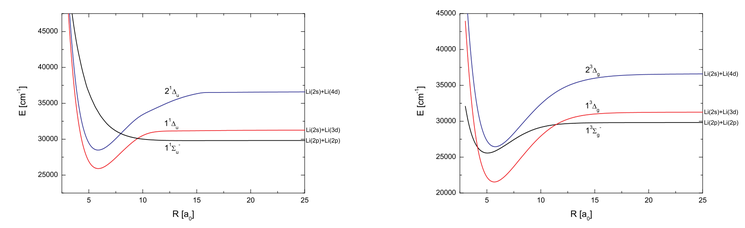

Fig. 10. Adiabatic potential energy curves for 6 excited states in the symmetry $^1\Sigma_u^-$, $^3\Sigma_g^-$, $^1\Delta_u$ and $^3\Delta_g$ of the Li_2 molecule correlating to the $Li(2p) + Li(2p)$, $Li(2s) + Li(3d)$ and $Li(2s) + Li(4d)$ asymptotes.

Comparisons

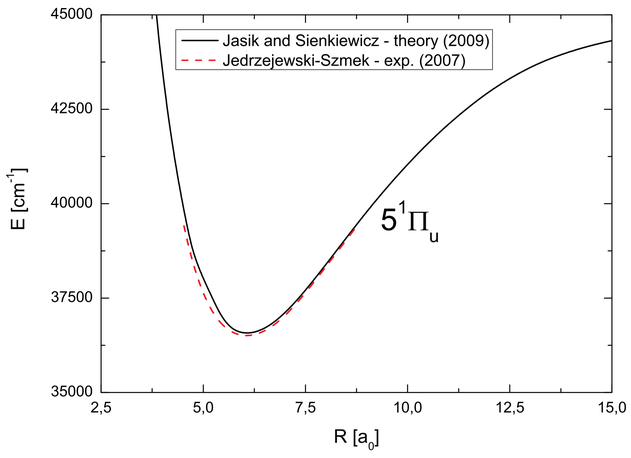

Fig. 7. Comparison of the $5^1\Pi_u$ state correlating to $Li(2s) + Li(4p)$ asymptote with experimental result obtained by Jędrzejewski-Szmek *et al.* [9].

References

References

[1] P. Jasik and J. E. Sienkiewicz, *Chem. Phys.* 323, 563 (2006).

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

[3] P. Jasik, PhD Thesis (2008).

[4] R. Poteau, F. Spiegelmann, *J. Mol. Spectrosc.* 171, 299 (1995).

[5] S.B. Rai, B. Hemmerling, W. Demtröder, *Chem. Phys.* 97, 127 (1985).

[6] W. Theiss, H.J. Müschenborn, W. Demtröder, *Chem. Phys. Lett.* 174, 126 (1990).

[7] Th. Weyh, S. Lokai, W. Demtröder, *Chem. Phys. Lett.* 257, 453 (1996).

[8] M. K. Kubkowska, A. Grochola, W. Jastrzbski, P. Kowalczyk, *Chem. Phys.* 333, 214 (2007).

[9] Z. Jędrzejewski-Szmek, A. Grochola, W. Jastrzębski, P. Kowalczyk, *Chem. Phys. Lett.* 444, 229 (2007).

[10] MOLPRO is a package of *ab initio* programs written by H. J. Werner and 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 and T. Thorsteinsson.

[11] P. Fuentealba, H. Preuss, H Stoll and L. Von Szentply, *Chem. Phys. Lett.* 89, 418 (1982).

[12] Private communications, as cited in MOLPRO manual (http://www.molpro.net).

[13] Ch. E. Moore, *Atomic energy levels as derived from the analyses of optical spectra. Volume I*, Circular of the National Bureau of Standards 467, U. S. Government Printing Office, Washington, 1949.

Acknowledgments

This scientific work is partially financed by the COST Action CM0702 - Chemistry with Ultrashort Pulses and Free-Electron Lasers: Looking for Control Strategies Through Exact Computations (CUSPFEL).

Contact with authors

Patryk Jasik e-mail: p.jasik@mif.pg.gda.pl

Józef E. Sienkiewicz e-mail: jes@mif.pg.gda.pl