

Scientific Report

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Purpose of the visit

Dr. Bernd Nestmann deals with the R -matrix theory of electron-molecule collisions. He develops and maintains computer implementation of the R -matrix method. The purpose of this scientific stay was R -matrix calculation of the electron collision with the Li_2 molecule in the fixed-nuclei approximation and separation of the resonance states using the Feshbach-Fano R -matrix method developed by Bernd Nestmann.

Scientific group of Prof. Jiří Horáček at the Institute of Theoretical Physics (where I am a doctoral student) is dealing with nuclear dynamics of non-elastic electron collisions with diatomic molecules. The results obtained during my stay in Bonn are used in Prague to construct the non-local resonance model of the dissociative electron attachment (DEA) and vibrational excitation (VE) of the Li_2 molecule by electron impact.

Work carried out

During this stay I calculated low-energy elastic cross sections of the electron scattering off Li_2 molecule in the energy interval 0-3 eV as well as electronic excitation cross sections in this energy interval. All the calculations were carried out within the frame of the R -matrix method using implementation of Bernd Nestmann. Our calculation treats the excited electronic states of the neutral target correctly in the energy interval of interest (contrary to previous works). Special attention was paid to the correct inclusion of the electron correlation in the negative ion and neutral target state calculations, which plays an important role in the scattering calculations.

All the R -matrix calculations are performed in the irreducible representations of the group D_{2h} . Let us denote $|^1\Sigma_g\rangle$, $|^3\Sigma_g\rangle$, $|^1\Sigma_u\rangle$, $|^3\Sigma_u\rangle$, $|^1\Pi_u\rangle$, $|^3\Pi_u\rangle$ lowest eigenstates of the neutral target in corresponding symmetries and $|\sigma_g\rangle$, $|\sigma_u\rangle$, $|\pi_g\rangle$, $|\pi_u\rangle$ one-particle states of the electron in the MO (resp. CO) of the corresponding symmetry. Then one can combine them to construct the $(N + 1)$ -electron states providing the primary basis set of R -matrix eigenstates in symmetry $|^2\Sigma_g\rangle$. The Δ -states and Π_g -states of the target molecule are not included in the R -matrix calculations, because they do not appear in the CI expansions of $|\Psi_k\rangle$. Inclusion of all the excited target states listed above as scattering channels is necessary, because they appear in the expansion of $|\Psi_k\rangle$.

The implementation of the R -matrix method by Nestmann *et al.* [4, 2] enables the multi-reference, single and double excitation CI (MRD-CI) approach to calculation of $|\Phi_i\rangle$ and $|\Psi_k\rangle$. Since the lithium dimer contains 6 electrons, it is complicated to establish the set of correct references, in which the balanced correlation is introduced in the neutral target states and R -matrix eigenstates. In order to keep

the correlation balanced, the orbitals $1\sigma_g$ and $1\sigma_u$ are kept doubly occupied in all the calculations and no excitations from these orbitals are allowed. Using this approach the SD-MRDCI method with HF ground state of the neutral target as the only reference is equivalent to complete active space (CAS) CI calculation of $|\Phi_i\rangle$ with lowest four electrons excluded from the active space. It is possible to construct the set of references that single and double excitations from these references cover all the excitations of the negative ionic system with frozen 4 core electrons. Every reference configuration contains one electron in the virtual MO or in the CO and remaining 6 electrons in the lowest possible MOs of the corresponding symmetry. In this way it is possible to provide CAS CI calculation of the neutral target states $|\Phi_i\rangle$ as well as of the R -matrix eigenstates $|\Psi_k\rangle$ and avoid problems with balanced correlation. The occupation of the COs is restricted to one electron. Counts of configuration state functions (CSFs) generated from the reference sets in calculations of $|\Phi_i\rangle$ as well as of $|\Psi_k\rangle$ are listed in Table 1. The R -matrix poles E_k as well as transition density matrix used to calculate the

	References	CFS
$ \Sigma_g\rangle, \Sigma_g\rangle$	1	502
$ \Pi_u\rangle, \Pi_u\rangle$	2	420
$ \Sigma_u\rangle, \Sigma_u\rangle$	2	502
$ \Sigma_g\rangle$	85	21848

Table 1: Counts of references and CFS generated from them in CAS CI calculations of $|\Phi_i\rangle$ and $|\Psi_k\rangle$.

R -matrix amplitudes[3] have been calculated using the MRD-CI program package DIESEL.[1] The R -matrix amplitudes, eigenphases and cross sections have been calculated using R -matrix program package by Nestmann *et al.*[4] The R -matrix expansion has been truncated and includes 50 lowest R -matrix states. Inclusion of additional states did not show observable influence on the cross sections and eigenphases.

Results

Our calculations of the electron collision with Li_2 in the fixed-nuclei approximation show clearly the $^2\Sigma_g$ resonance and provides its separation from the background scattering continuum. We have calculated the elastic scattering cross sections for several internuclear distances as well as electronic excitation cross sections. These data provide reasonable base for construction of the non-local resonance model and to describe the DEA and VE of the Li_2 molecule by the electron impact. Some preliminary examples of calculated results are showed in figures.

Publications

One publication dealing with the electron scattering off Li_2 fixed-nuclei approximation is in preparation.

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References

- [1] M. Hanrath and B. Engels. New algorithms for an individually selecting MR-CI program. *Chemical Physics*, 225:197–202, 1997.

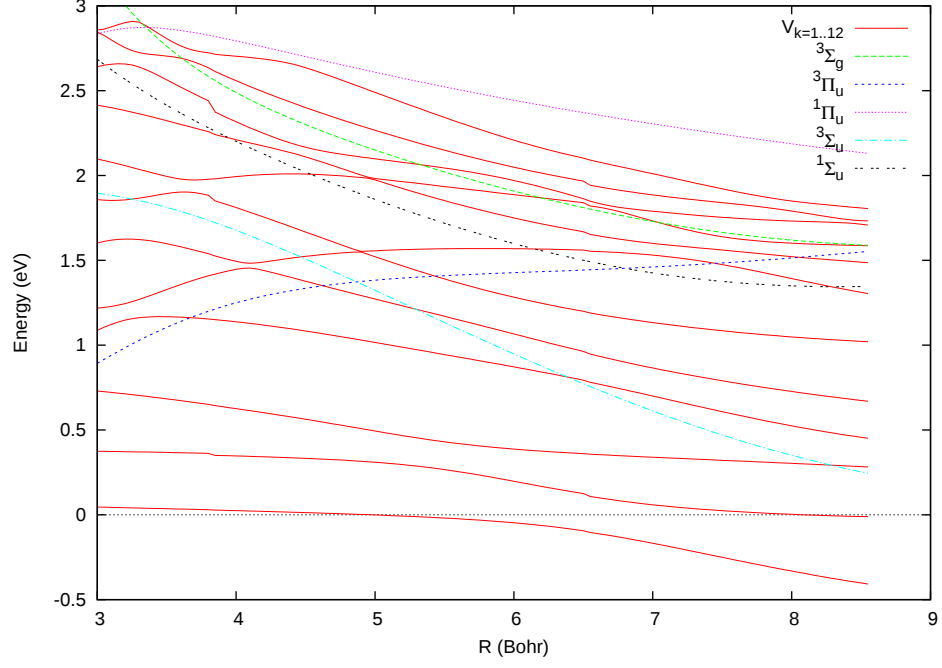


Figure 1: Lowest R -matrix poles V_k and excited neutral target states energies as function of the internuclear distance. All the values are relative with respect to the neutral target ground state energy curve.

- [2] B. M. Nestmann and T. Beyer. A study of the threshold behavior in $e^- + \text{HF}$ scattering based on R -matrix theory. *Chemical Physics*, 2007.
- [3] B.M. Nestmann, R.K. Nesbet, and S.D. Peyerimhoff. A concept for improving the efficiency of R -matrix calculations for electron-molecule scattering. *J. Phys. B: At. Mol. Opt. Phys.*, 24:5133–5149, 1991.
- [4] K. Pfingst, B.M. Nestmann, and S.D. Peyerimhoff. An R -matrix approach for electron scattering off polyatomic molecules. *J. Phys. B: At. Mol. Opt. Phys.*, 27:2283–2296, 1994.

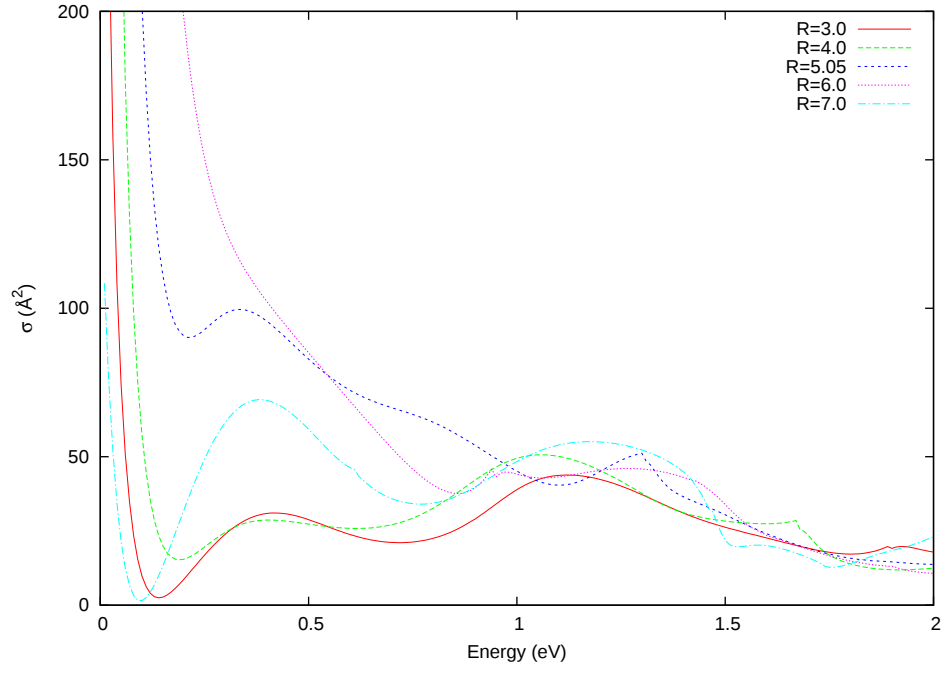


Figure 2: Elastic scattering cross sections in the $^2\Sigma_g$ symmetry as a function of E for several internuclear distance R (Bohr).

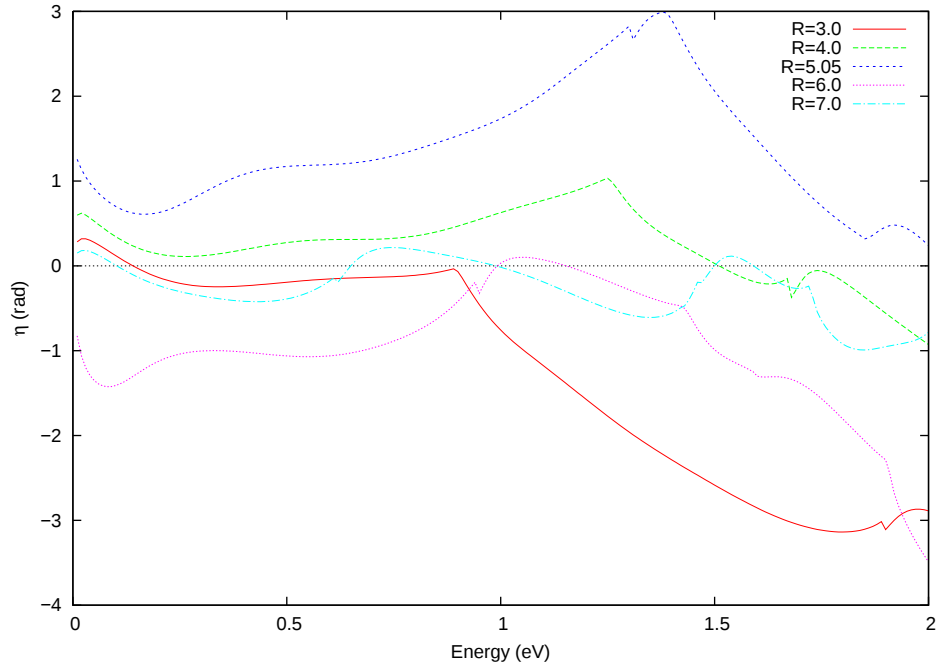


Figure 3: Elastic scattering eigenphase sum in the $^2\Sigma_g$ symmetry as a function of E for several internuclear distance R (Bohr).

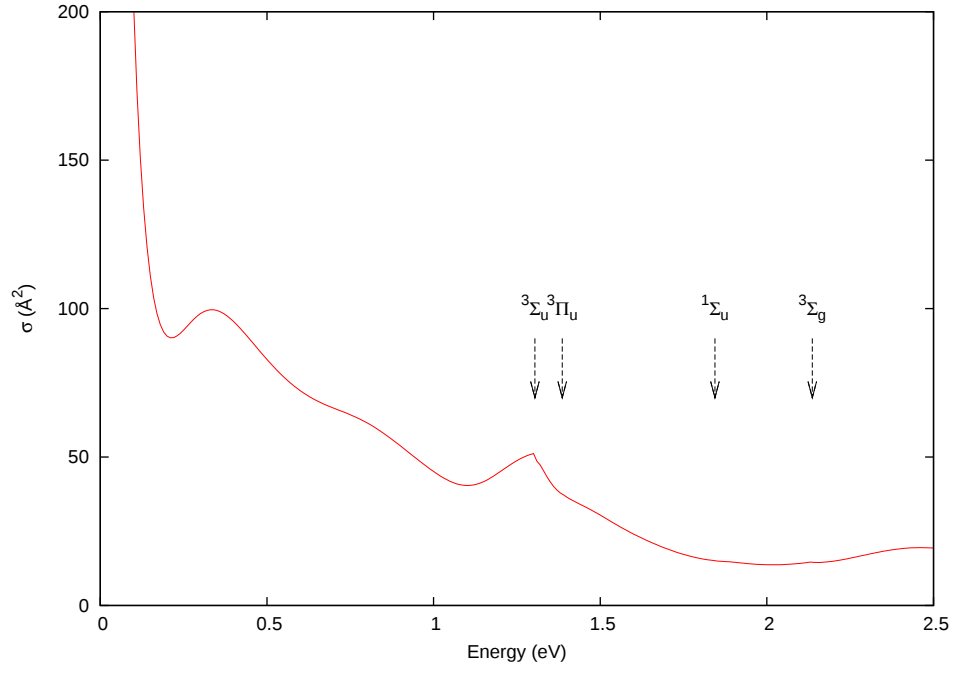


Figure 4: Elastic scattering cross section in the ${}^2\Sigma_g$ symmetry as a function of E for the equilibrium internuclear separation $R=5.05$ Bohr and its comparison with previous results (to be done).

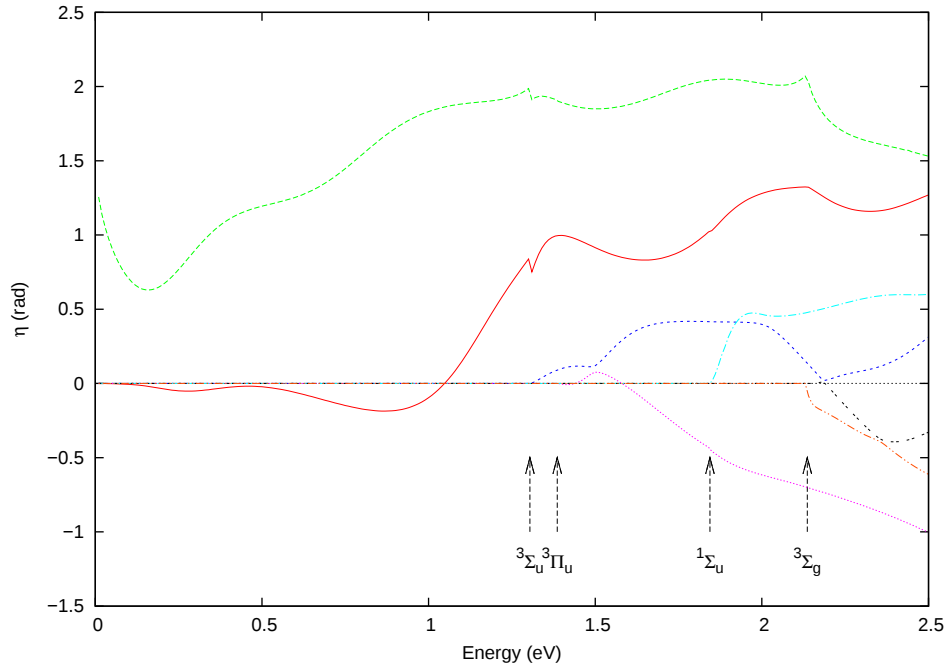


Figure 5: Elastic scattering eigenphasees in the ${}^2\Sigma_g$ symmetry as a function of E for the equilibrium internuclear separation $R=5.05$ Bohr.

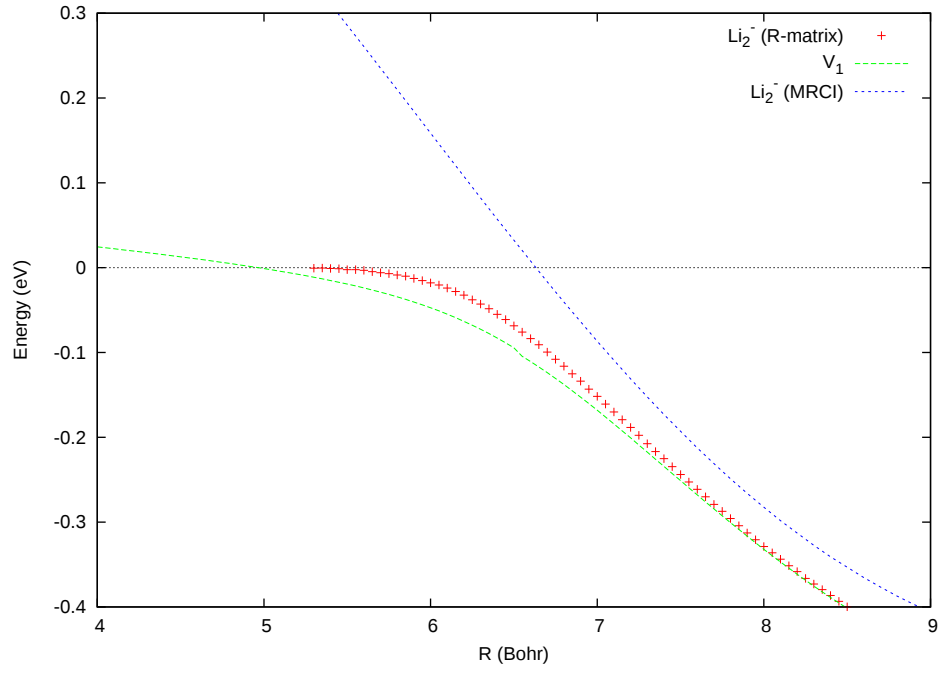


Figure 6: Potential curve of the Li_2^- ground state near its crossing with the potential curve of the neutral target calculated using R -matrix in closed channels and its comparison with full CI calculation in the basis of the neutral target and lowest R -matrix pole potential curve V_1 . All the values are relative with respect to the neutral target ground state energy.