Scientific Report
Application of the FFR method to diatomic molecules

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30. 10. – 17. 12. 2004

Purpose of the visit

This project was aimed at the extension and application of a novel method designed for the treatment of nuclear dynamics of negative transient molecular ions (resonances). Many theories describe resonances by poles of appropriate operators such as S-matrix or Green operator for energies in the lower complex plane. However, in study of dissociative electron attachment (DEA) to molecules it has been shown that the trajectory of the pole corresponding to the resonance, which is responsible for the energy transfer between the electronic and nuclear motion, does not necessarily turn into the potential curve of the stabilized anionic state. In that case the adiabatic description is no longer possible and the diabatic basis has to be introduced.

The diabatic description of a resonance is given by the discrete component of the Hilbert space corresponding to the metastable molecular anionic state. The concept of discrete states is essential for understanding of the DEA process. The molecule is able to capture electron temporarily and the weakened bond in the charged complex may cause its dissociation. The decay of the metastable anionic state due to its interaction with the electronic background continuum is represented by the resonance width, which depends on the energy of the free electron. In the process of DEA the energy dependence of the resonance width becomes highly important due to the energy transfer from the scattered electron into the nuclear motion.

General concept for the construction of the discrete components of the resonances does not exist and adequate numerical description of these states is still a subject of recent research. The FFR method of B. M. Nestmann [1] extracts the discrete component, its decay width and the background scattering phase shifts from the solution of the entire scattering problem within the R-matrix formalism. The discretization of the scattering continuum provided by this formalism allows to apply the concept of diabatization as commonly used in cases of avoided curve crossing in electronic bound state calculations.

Very stable and accurate methods of the consequent treatment of the nuclear dynamics of the DEA process were developed in the group of J. Horáček at the Charles University in Prague. A combination of these techniques with the FFR method seems to be very appealing.

The collaboration in this particular field between the two groups has started in December 2003 after the visit of V. Brems in Prague. The codes developed recently by P. Kolorenč were adapted to enable application of the FFR method to the spherically symmetric potential scattering problem. The analysis of the method on simple systems was aimed at obtaining better understanding of the procedure and improving the FFR method. One of the two tasks of the visit of P. Kolorenč in Bonn was to work on a common paper concerning this topic. Second task was to construct a fully *ab-initio* model of the lowest $^2\Sigma_u^+$ resonance, which governs the process of DEA in low-energy collisions of electrons with chlorine molecules. The Cl_2^- system was recently investigated experimentally and the results were compared with semi-empirical R-matrix calculations [2].

Description of the work carried out during the visit

First step in construction of the model of the Cl_2^- system was to perform MRD-CI calculations of the potential curves of the ground state of neutral Cl_2 molecule and the lowest state of the Cl_2^- of the $^2\Sigma_u$ symmetry. We have used the correlation consistent polarized valence (cc-pVTZ) basis set [3]. This basis was chosen with respect to the subsequent R-matrix calculations which require the target wave function to be completely contained within the R-matrix sphere. Impact of inclusion of additional diffuse functions on electron affinity was investigated. For the MRD-CI calculations the basis was augmented with diffuse (exponent 0.049) p function. Potential curves of the ground state of neutral Cl_2 molecule and the lowest $^2\Sigma_u$ state of Cl_2^- was evaluated on the large range of the internuclear distances from 1.5 to 20 a.u.

The R-matrix calculations were carried out using the same basis without the additional diffuse p function. For description of the scattering wave function diffuse functions optimized for the sphere with radius $r_\Omega = 10$ a.u. were added. Present FFR codes do not allow to perform calculations at the MRD-CI level. The actual calculations were carried out at the static exchange (SE) and static exchange plus polarization level (SEP). For the electronic structure of the ground state of the neutral Cl_2 molecule the SE level is equivalent to the self-consistent field (SCF) level. SE level of the $^2\Sigma_u$ state of the Cl_2^-

anion consists in expanding this state in the set of configurations defined by adding one electron to the each unoccupied σ_u orbital in the neutral ground state configuration. The SEP level of calculations consists of adding to the SE configurations all configurations defined by exciting one electron from orbital occupied at the SE level to any unoccupied compact orbital.

SCF Cl_2 ground state calculations and R-matrix fixed nuclei scattering calculations at SEP level were carried out for 64 internuclear distances between 2.8 and 6 Bohr. Separation of the lowest resonance from the scattering phase shift was performed using the FFR method, resulting in smooth discrete state potential curve and energy-dependent discrete state-continuum coupling. The data were used to construct nonlocal resonance model of the Cl_2^- system via spline interpolation. Preliminary results for the DEA cross section were obtained using the Franck-Condon reflection principle.

Description of the main results obtained

The paper concerning the application of the FFR method to potential scattering is nearly prepared for publication. The analysis of the model scattering problems demonstrated the properties of the FFR separations and revealed some limitations of the present implementation of the method. Significant improvement was proposed and demonstrated on the studied problems.

Nonlocal resonance model of the Cl_2^- system was constructed at the static exchange plus polarization level. Obtained potential curve of the Cl_2 ground state and the diabatic $^2\Sigma_u^+$ discrete state potential obtained by the FFR method are plotted in Fig. 1. Fig. 2 shows energy dependent resonance widths and level shift functions for several internuclear distances. Preliminary results for the DEA cross section obtained from these data via Franck-Condon reflection principle are compared with semi-empirical one-pole R-matrix calculations of Fabrikant [2] in Fig. 3. Full nuclear dynamics calculation have not been performed yet. Present reflection principle DEA cross section has maximum at about 100 meV, which is somewhat higher than shows the relative measurements of Ruf et al. (50 – 60 meV) [2]. The magnitude of the cross section is by a factor of 1.3 smaller than results from the calculations of Fabrikant. It is difficult to predict how the results will change when the nuclear dynamics is fully included, but we expect the cross section maximum to move towards the lower energies for the following reasons. When the possibility of autodetachment of the captured electron is taken into account, the DEA cross section should be suppressed at the higher energies compared to the lower energies. The probability of the autodetachment raises with increasing distance of the system from the stabilization point (crossing of the neutral and anionic curves) and this distance raises with increasing energy of the captured electron.

Projected publications

The results of the application of the FFR method to both the potential scattering as well as to the electron-Cl_2 scattering will be published in the PhD. thesis of P. Kolorenč. We plan to publish two papers. One will be devoted to the potential scattering and the improvement of the FFR method and the second to the electron-Cl_2 scattering.

References

[1] Bernd M. Nestmann. Characterization of metastable anionic states within the R-matrix approach. *J. Phys. B*, 31:3929–3929, 1998.

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[3] David E. Woon and Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. III. the atoms aluminium through argon. *J. Chem. Phys.*, 98(2):1358–1371, 1993.

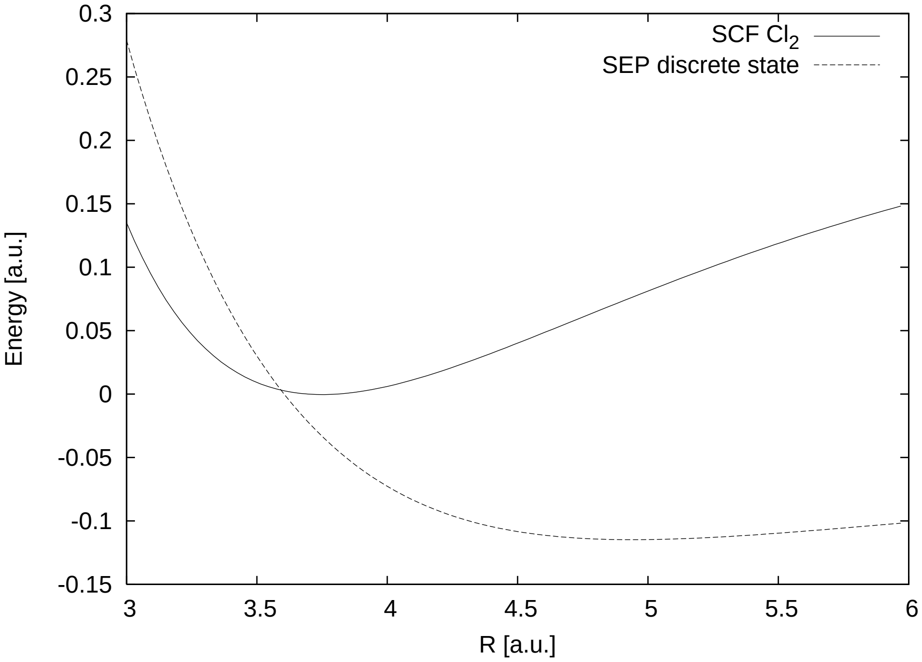

Figure 1: Potential energy curves of the Cl_2 and the $^2\Sigma_u^+$ discrete state at the SEP level of theory.

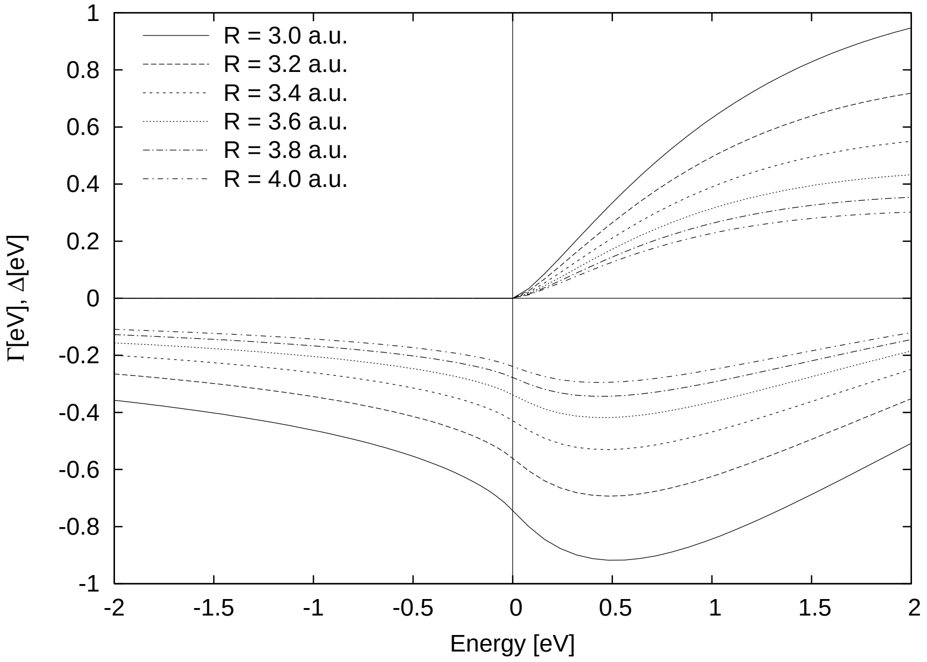

Figure 2: Energy-dependent resonance widths (upper curves) and level shift functions (lower curves) for the range of internuclear distances from 3.0 to 4.0 a.u.

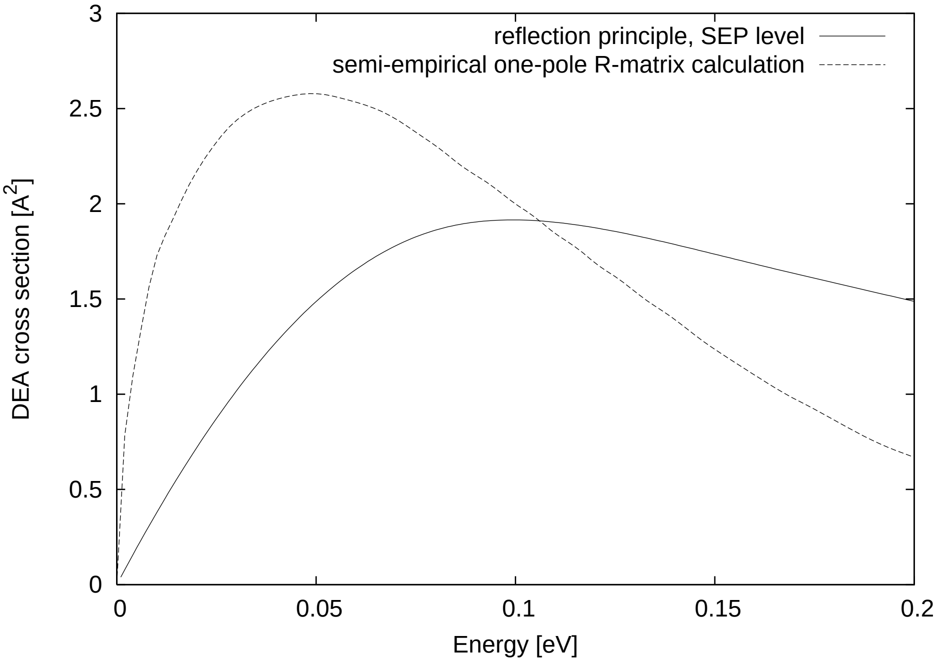

Figure 3: Dissociative electron attachment cross section obtained from present data via reflection principle. Results are compared to the results of Fabrikant [2].