

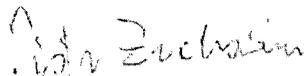
Dr hab. Piotr Żuchowski
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28 Oct 2016

Dear Sirs,

I gladly accept the report of Tijs Karman on his STSM. We had very fruitful time for exploring new ideas regarding new methods of calculationg the nonadiabatic couplings and did preliminary test calculations.

Sincerely yours,
Piotr Żuchowski

Piotr Żuchowski

Tijs Karman

2 Nov 2016

Report: Complexes of electronically excited O₂ molecules and atmospherically relevant collision partners

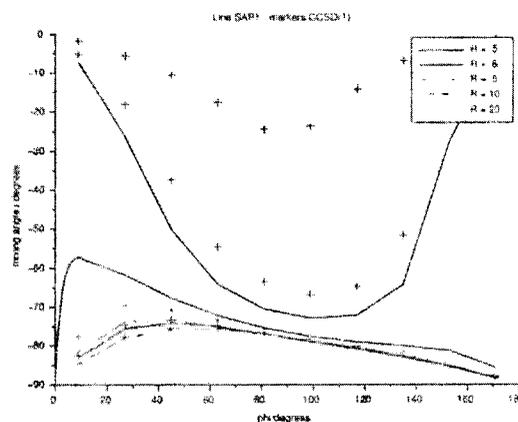
Final report of the STSM of Tijs Karman
in the laboratory of Piotr S. Żuchowski and Roman Ciuryło

October 27, 2016

The goal of this STSM was to study complexes of electronically excited O₂ molecules with atmospherically relevant collision partners, by treating non-adiabatic couplings in two complementary ways: One approach would be to compute adiabatic potentials using standard electronic structure approaches, and subsequently transform these to the diabatic representation. The second approach is to develop a generalized multi-state symmetry-adapted perturbation theory (SAPT), capable of treating systems with asymptotically degenerate or electronically excited states. During this STSM, we have focused on the latter approach.

In this STSM we have performed approximate SAPT calculations, in order to test the viability of this approach. We have calculated the first-order interaction only within the polarization approximation, which neglects inter-molecular exchange. This allowed us to directly compute the off-diagonal diabatic potential from one-electron reduced density matrices alone. These density matrices were obtained from configuration interaction calculations performed with the MOLPRO suite programs.

We have applied this approach to NO-H₂, a model system with an asymptotic spatial degeneracy. The attached figure shows the mixing angle, which describes the unitary transformation relating the adiabatic and diabatic representations, as a function of the dihedral angle of the complex, ϕ . For coplanar geometries, $\phi = 0$ or 180° , the mixing angle must equal a multiple of 90° on symmetry grounds, but for intermediate ϕ the states are mixed by non-adiabatic interactions. Lines are the results of approximate SAPT calculations, markers (+) represent CCSD(T) calculations in the super-molecular approach. Different colors correspond to different separations between the two molecules. For large separations, $R \geq 10 a_0$, the two approaches are in good agreement. At shorter separation, differences occur as exchange and higher order contributions to the off-diagonal potential, which are neglected, become important.



These results suggest that the extension of SAPT, including exchange and second order interactions, will be a useful tool to study systems with asymptotically degenerate or electronically excited states. In this situation, the SAPT approach could have additional advantages: Firstly, it provides a way to directly compute diabatic potentials, rather than to compute adiabatic potentials followed by a diabaticization step. Secondly, it directly computes the interaction between atoms and/or molecules. This avoids the "stabilization procedure", required in the super-molecular approach, when this approach is applied to systems undergoing Penning ionization.

Work is underway to include exchange and higher order contributions to the off-diagonal SAPT potentials. Another relevant direction is to employ SAPT to compute properties, such as transition dipole moments.


Tijs Karman 2 Nov 2016