

DÓRA PAPP

**Variational determination of  
resonance states of weakly-bound  
molecular complexes**

Theses of PhD dissertation

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## Introduction and aims

The primary aim of my PhD research was the development of a general variational tool, which can be used to determine resonance, or quasi-bound, rovibrational states of flexible, polyatomic molecules by solving the time-independent nuclear Schrödinger-equation. Resonance states of a system can be defined as metastable states that have sufficient energy to break up the molecule into subsystems. Resonance states have finite lifetimes. Such states play an important role in molecular spectroscopy, in scattering processes, and they are also closely related to reaction dynamics. A further goal of my PhD work was to apply the newly-developed code to interesting chemical systems, including van der Waals complexes.

There are several strategies to compute resonance states, for example, the indirect methods of scattering theory, where resonances are reflected by peaks in collisional cross sections, and variational nuclear motion procedures, resulting directly in the energies and lifetimes of resonance states. The latter group includes either conventional Hermitian techniques, such as the so-called stabilization method, or effective non-Hermitian protocols, which involve complex Hamiltonians, whose complex eigenvalues can be associated with resonance energies and lifetimes. Examples to the non-Hermitian treatment of resonances are the complex coordinate scaling (CCS) and the complex absorbing potential (CAP) methods. Since the CCS technique requires the modification of an analytic Hamiltonian, it is less suitable to be linked to general codes utilizing numerical representations of the Hamiltonian, such as GENIUSH, a quasi-variational rovibrational bound-state-computing program developed previously in our group. Therefore, I have implemented the more straightforwardly generalizable CAP technique, linked it to GENIUSH, and applied it successfully on the weakly-bound systems of  $\text{Ar}\cdot\text{NO}^+$ ,  $\text{H}_2\text{He}^+$ , and  $\text{H}_2\cdot\text{CO}$ .<sup>1,2,3</sup> Such complexes are perfect subjects for studying interesting resonance phenomena due to their relatively low dissociation energies, low

number of bound states, and the weak coupling between their intra- and intermonomer motions. Moreover, some of these systems are also of wide astrophysical interest.

## Methods applied

During my work on method developments and on the interpretation of the results obtained I employed the C++, Mathematica and Fortran programming languages, and the LAPACK++ and BLAS libraries. For applications on weakly-bound systems, I used the GENIUSH bound-state-computing program and the GENIUSH-CAP code I developed for resonance computations.

## Results and discussion

### Method developments

- 1 During the course of my PhD work, I have implemented the CAP technique and linked it to the GENIUSH protocol. The new code, named GENIUSH-CAP, is capable of computing rovibrational resonance states of molecules or complexes of, in principle, arbitrary size, using arbitrary coordinate systems, while treating the nuclear-motion problem both in full and in reduced dimensions. GENIUSH-CAP is a new variational tool for investigating resonance states, which can also be used for the study of flexible polyatomic molecules.<sup>2</sup>
- 2 I have developed a series of codes which make possible the automatic visualization of the complex rovibrational resonance wave functions computed with GENIUSH-CAP. The visualization tools plot the absolute values of the resonance wave functions along two selected internal coordinates.<sup>2</sup>

**3** I have compared the resonance energies and lifetimes of the  $\text{H}_2\text{He}^+$  system computed with GENUSH-CAP with those obtained from complex coordinate scaling computations (the latter employed the in-house  $\text{D}^2\text{FOPI-CCS}$  code). This comparison between the results of the two different procedures show remarkable agreement, *i.e.*, resonance energies agree within a few  $0.1 \text{ cm}^{-1}$ , and the lifetimes are always in the same order of magnitude.<sup>2</sup>

## Applications

**4** I have carried out stabilization and GENIUSH-CAP computations on the  $\text{H}_2\text{He}^+$  system, which, supported also by  $\text{D}^2\text{FOPI-CCS}$  results, revealed the interesting resonance structure of this molecule, related to openings of new dissociation channels corresponding to the rotational excitations of the  $\text{H}_2^+$  unit. I have further identified long-lived resonances corresponding to strong intramonomer-stretching and intermonomer-bending coupling.<sup>3</sup>

**5** By means of a series of stabilization computations I have revealed an interesting repetitive pattern of resonance states of the  $\text{Ar}\cdot\text{NO}^+$  complex, even up to energies much above the first dissociation limit. These states are long-lived Feshbach resonances, in which the intermonomer stretching and bending motions are augmented with the vibrational excitations of the  $\text{NO}^+$  moiety. This observation, along with reduced-dimensional computations with GENIUSH, supports the view that in the case of  $\text{Ar}\cdot\text{NO}^+$  the large-amplitude intermonomer motions can almost perfectly be separated adiabatically from the small-amplitude intramonomer vibration.<sup>1</sup>

**6** With GENIUSH-CAP I have also identified several shorter-lived low-lying resonance states of  $\text{Ar}\cdot\text{NO}^+$ , and compared them with close-coupling scattering results. The comparison showed good agreement

between the two conceptionally completely different methods.<sup>1</sup>

**7** I have determined, using GENIUSH-CAP, several resonance states of the H<sub>2</sub>·CO complex, which is the first system containing more than 3 atoms and subjected to non-Hermitian variational resonance computations. I found that the *ortho*-H<sub>2</sub>·CO bound states, lying well above the first dissociation threshold of the complex, can be identified as extremely long-lived resonances.<sup>2</sup> This finding is also supported by the experimental IR spectrum of H<sub>2</sub>·CO.

**8** I have identified and assigned numerous additional resonance states of both the *para*- and the *ortho*-H<sub>2</sub>·CO complexes, corresponding to the openings of new dissociation channels and simultaneous rotational excitations of the monomers.<sup>2</sup>

## Publications

### Scientific papers related to the PhD research

**1** Complex rovibrational dynamics of the Ar·NO<sup>+</sup> complex

**D. Papp**, J. Sarka, T. Szidarovszky, A. G. Császár, E. Mátyus, M. Hochlaf, T. Stoecklin, *Phys. Chem. Chem. Phys.*, **2017**, *19(12)*, 8123–8622.

**2** A general variational approach for computing rovibrational resonances of polyatomic molecules. Application to the weakly bound H<sub>2</sub>He<sup>+</sup> and H<sub>2</sub>·CO systems

**D. Papp**, T. Szidarovszky, A. G. Császár, *J. Chem. Phys.*, **2017**, accepted for publication

**3** Intriguing resonance structure of the H<sub>2</sub>He<sup>+</sup> system

**D. Papp**, A. G. Császár, K. Yamanouchi, T. Szidarovszky, **2017**, in preparation

## Additional scientific papers

- 4 Four faces of the interaction between ions and aromatic rings  
**D. Papp**, P. Rovó, I. Jákli, A. G. Császár, A. Perczel, *J. Comp. Chem.*, **2017**, DOI: 10.1002/jcc.24816
- 5 The role of entropy in initializing the aggregation of peptides: A first principle study on oligopeptide oligomerization  
G. Pohl, I. Jákli, I. G. Csizmadia, **D. Papp**, G. F. Matías, A. Perczel, *Phys. Chem. Chem. Phys.*, **2012**, *14*(4), 1507-1516.

## Lectures presented during the time of the PhD work

- Computation of unbound states of van der Waals complexes (in Hungarian)  
**D. Papp**, T. Szidarovszky, T. Stoecklin, A. G. Császár, *AMMB meeting*, Mátrafüred, Hungary, **2016**
- Computation of unbound states of van der Waals complexes  
**D. Papp**, T. Szidarovszky, T. Stoecklin, A. G. Császár, *Graduate Conference on Theoretical Chemistry*, Keszthely, Hungary, **2016**
- Rovibrational states of Ar·NO<sup>+</sup> below and above dissociation  
**D. Papp**, T. Szidarovszky, J. Sarka, T. Stoecklin, M. Hochlaf, A. G. Császár, *The 14-th Central European Symposium on Theoretical Chemistry*, Banská Bystrica, Slovakia, **2015**

## Posters presented during the time of the PhD work

- Bound and unbound rovibrational states of Ar·NO<sup>+</sup>  
**D. Papp**, T. Szidarovszky, J. Sarka, T. Stoecklin, M. Hochlaf, A. G. Császár, *AMOC: Anharmonicity in medium-sized molecules and clusters*, Madrid, Spain, **2015**

- Computing resonance states of polyatomic molecules: Vibrational resonance states of the Ne trimer

**D. Papp**, T. Szidarovszky, A. G. Császár, *The 23rd International Conference on High Resolution Molecular Spectroscopy*, Bologna, Italy, **2014**