Project closing report

This report summarizes the results and developments achieved during the grant period of my NKFIH grant titled “Development of Novel Methods in Quantum Molecular Dynamics” (grant No. PD124699). The report is organized into four main chapters providing information on the major topics of my research. The fifth chapter lists the review articles and book chapters I have coauthored during the grant period.

1. Permutation-inversion symmetry in quantum-dynamical computations

This part of my research has focused on the inclusion of permutation-inversion symmetries of molecules in the numerically exact and general variational nuclear-motion code GENIUSH (see Ref. [1] and references cited therein) which yields rovibrational energy levels and eigenstates for molecules of arbitrary composition. The exploitation of permutation-inversion can substantially reduce the computational cost and automatically labels the rovibrational eigenstates with the irreducible representations of the molecular symmetry (MS) group. Since GENIUSH employs direct-product discrete variable representation (DVR) vibrational basis functions, an algorithm had to be developed to generate symmetry-adapted DVR functions. This has been achieved by using the grand orthogonality theorem (GOT). The GOT-based projection of DVR functions results in linear combinations of DVR functions corresponding to different DVR points. Therefore, it has been necessary to develop an efficient matrix-vector multiplication algorithm that can multiply an arbitrary vector with the vibrational Hamiltonian represented in the symmetry-adapted DVR basis. The evaluation of matrix-vector products is required by the iterative Lanczos eigensolver algorithm used by GENIUSH. The new method is based on the assumption that each DVR point is mapped onto another DVR point (or onto itself in special cases) by the symmetry operations. This leads to a facile evaluation of group-theoretical projections, but at the same time it often limits the practically applicable symmetry group to a subgroup of the full MS group. It is important to stress that the symmetry-adaptation algorithm developed is applicable to molecules of arbitrary composition. The transformation of the DVR points by the symmetry operations and character table of the MS group for a given molecule must be supplied by the user.

The symmetry-adapted GENIUSH code has been first applied to study the intriguing quantum dynamics of the quasistructural protonated methane molecule (CH_5^+). The rovibrational energy level pattern of CH_5^+ consists of close-lying and often highly-degenerate levels that can not be interpreted based on the usual harmonic oscillator and rigid rotor models. The symmetry-adapted computations have resulted in vibrational and rovibrational energy levels for CH_5^+ using a seven-dimensional bend model. As contradictory predictions for the (ro)vibrational energy levels of CH_5^+ can be found in earlier papers, this work has been essential to assess former results. It has also been confirmed that the zeroth-order separation of rotations and vibrations completely breaks down in CH_5^+, as predicted by group-theoretical arguments. It has been concluded that neither tunneling nor free motion of the protons can explain the peculiar energy level pattern of CH_5^+. The symmetry-related methodological developments and the CH_5^+ results are described in Ref. [2] (selected as Editor’s pick article). This work started shortly after I had submitted my research proposal and Ref. [2] was accepted for publication before the beginning of the grant period. Another application of the symmetry-adapted GENIUSH code has focused on the vinyl radical [3].

As the originally-developed symmetry-adaptation algorithm is limited to the J=0 case (J is the angular momentum quantum number), an obvious development is to include the rotational degrees of freedom in the symmetry-adaptation procedure. The $J > 0$ algorithm relies on the factorization of the MS group elements as products of point-group symmetry elements and rotation operators. The symmetry-adapted rovibrational GENIUSH program has found its first application in combination with the ETC method [4] which is a general and semi-automatic technique for the variational computation of rovibrational resonance states. As the ETC method requires large-scale bound-state rovibrational computations performed beyond the dissociation limit, it is advantageous to exploit the rovibrational symmetries of the molecule. The manuscript describing the accurate computation of the rovibrational resonances of H_2O with the symmetry-adapted rovibrational GENIUSH program is currently under preparation.

2. Vibrational quantum-graph model

The variational computations of the (ro)vibrational energy levels of CH_5^+ has naturally led to the development of the simple and intuitive vibrational quantum-graph model. Although the quantum-graph model [5] has been applied in electronic structure theory and various fields of physics, it has never been employed to describe molecular vibrations before my work described here. The vertices of the quantum graph represent versions of the equilibrium structure with distinct atom numbering (5!=120 possibilities for CH_5^+), while the edges refer to collective nuclear motions (torsional and flip motions for CH_5^+, see Refs. [2] and [6]) that transform the versions of the equilibrium structure into one another. This construction allows the mapping of the complex vibrational quantum dynamics of CH_5^+ onto the one-dimensional motion of a particle that can move along the edges of the quantum graph. The vibrational energy levels are obtained by solving the one-dimensional time-independent Schrödinger equation on the quantum graph. As barriers hindering the torsional and flip motions of CH_5^+ are low, the one-dimensional motion along the edges of the quantum graph is assumed to be free. The energy levels are quantized by imposing appropriate boundary conditions on the plane-wave-like eigenstates of the free particle confined in the quantum graph. The quantum-graph model provides a qualitative understanding of the vibrational quantum dynamics of CH_5^+ and is able to reproduce the low-lying vibrational energy levels of CH_5^+ (and CD_5^+) with remarkable accuracy. A detailed description of the vibrational quantum-graph model is provided in Ref. [6] which was selected as part of the themed collection 2018 PCCP HOT Articles. Results were also presented at international conferences (poster at AMOC2018, Budapest, Hungary, http://kkrk.chem.elte.hu/amoc; invited lecture at the 3rd COST MOLIM General Meeting, Budapest, Hungary, http://kkrk.chem.elte.hu/gm3/; contributed talk at 73rd ISMS, Champaign-Urbana IL, USA, http://isms.illinois.edu/; invited lecture at the Mathematical Methods in Quantum Molecular Dynamics workshop, Mathematisches Forschungsinstitut Oberwolfach, Germany, https://www.mfo.de/occasion/1917; contributed talk at the Annual Meeting of the Working Committee on the Structure of Materials and Molecules of the Hungarian Academy of Sciences, Mátrafüred, Hungary, 2019). The poster presented at AMOC2018 was awarded a Molecular Physics poster prize.

My work on the vibrational quantum-graph model has caught the attention of Jonathan Rawlinson (Department of Applied Mathematics and Theoretical Physics, University of Cambridge, UK) who extended the vibration-only model to compute the rotational-vibrational energy levels and eigenstates of CH_5^+ [7]. An ongoing research project is the application of the quantum-graph model to another system, C_{60}^+, carried out in collaboration with Prof. Jeremy Richardson (ETH Zürich, Switzerland). C_{60}^+ has six equivalent equilibrium structures and can be described by a complete graph consisting of six vertices and fifteen edges. Each three-membered cycle in the C_{60}^+ quantum graph encircles a conical intersection (CI). As the adiabatic electronic wave function changes its sign when going around any closed path encircling a CI, the adiabatic electronic wave function must be multiplied by a phase factor which makes the electronic wave function single valued and continuous at the cost of introducing a vector potential in the nuclear motion Hamiltonian [8]. This implies that the magnetic Schrödinger equation must be solved for the quantum graph of C_{60}^+. In addition, potential energy functions along the edges can be included in the current algorithm that employs the finite-element method to solve the Schrödinger equation on the quantum graph.

3. Results and developments related to time-dependent quantum dynamics

This part of my research has been aimed at the accurate time-dependent quantum-dynamical description of molecules interacting with a time-dependent classical electromagnetic field under the assumption that the electric dipole moment approximation is valid. The time-dependent developments are based on the rovibrational energy levels and eigenstates provided by GENIUSH. Therefore, it was necessary to implement a new program module that is able to compute electric dipole moment matrix elements in the rovibrational eigenstate basis. The time-dependent wavepacket is represented in the basis of rovibrational eigenstates and the time-dependent Schrödinger equation is transformed into the interaction picture. The Chebyshev propagation method is utilized to solve the time-dependent Schrödinger equation.

The time-dependent version of GENIUSH has been applied to investigate the tunneling quantum dynamics (either field free or driven by an external time-dependent field) of ammonia isotopomers. The inversion motion of ammonia is a prototypical example of quantum tunneling and its accurate time-dependent quantum-dynamical treatment is amenable for GENIUSH. We have studied the time evolution of a superposition state which is initially localized in one of the potential wells and tunnels into the other potential well under field-free conditions. We have demonstrated that the tunneling process can be either accelerated or inhibited by appropriately-designed time-dependent electromagnetic fields. The quantum-dynamical schemes proposed rely heavily on the concept of light-dressed states and Floquet's theorem. It is important to stress that our computations, in contrast to previous studies, treat all rotational and vibrational degrees of freedom in a numerically exact way and assume neither the alignment nor the orientation of the molecule. Further insight into the tunneling dynamics is provided by our results on the nuclear-motion flux associated with the coherent tunneling process. The time-dependent methodological developments as well as results on the coherent control of tunnelling in ammonia isotopomers have been reported in Ref. [9]. Results were presented at international conferences (poster at AMOC2018, Budapest, Hungary, http://kkrk.chem.elte.hu/amoc; poster at the 3rd COST MOLIM General Meeting, Budapest, Hungary, http://kkrk.chem.elte.hu/gm3/; invited lecture at MOLIM2018 – Molecules in Motion, Athens, Greece, https://www.molim2018.ethz.ch; invited lecture at ISTCP-X, Tromsø, Norway, http://istcp-2019.org/). Further results on the role of the rotational degrees of freedom over the course of coherent infrared multiphoton excitation of ammonia isotopomers and the generation of the localized state from the delocalized vibrational ground state will be reported in a paper to be submitted later this year [10].

We have also demonstrated that m-D-phenol can be used as a molecular quantum switch. m-D-phenol exhibits a double-well potential along the torsional coordinate. The two torsional potential wells are not equivalent due to the different vibrational zero-point energies of the syn and anti isomers. This gives rise to localized low-energy and delocalized high-energy torsional eigenstates, i.e., tunneling switching occurs. In the tunneling switching regime with localized low-energy states and delocalized high-energy states the molecular quantum switch can be operated in two different ways: (i) a quasiclassical switching by coherent infrared radiation between the syn and anti isomeric structures, and (ii) a highly-nonclassical switching based on bistructural quantum superposition states of the syn and anti structures. As m-D-phenol was not amenable to GENIUSH due to its size, the reaction path Hamiltonian method was used to obtain vibrational energy levels and eigenstates, needed by the solution of the time-dependent Schrödinger equation. Results were reported in Ref. [11] which became part of the themed collection 2018 PCCP HOT Articles.

4. Studies on nonadiabaticity induced by classical and quantum light

It was demonstrated a decade ago that conical intersections (CIs) can be induced in diatomic molecules by light [12,13]. Such CIs are called light-induced CIs (LICIs) whose position, in contrast to natural CIs, can be controlled by the frequency of the laser. My work on time-dependent quantum dynamics and discussions with Prof. Ágnes Vibók (University of Debrecen) at a conference have resulted in a collaboration on investigating LICI-related effects in polyatomic molecules with Ágnes Vibók and Gábor Halász (Debrecen), as well as Benjamin Lasorne (Montpellier) and Lorenz S. Cederbaum (Heidelberg). Our fruitful collaboration has led to an interesting excursion into the realms of nonadiabatic quantum dynamics. The main focus of our work has been the identification of light-induced nonadiabatic effects in the absorption spectrum of molecules dressed with light [14].

We have studied the absorption spectrum of H_2CO dressed by classical light. The singlet electronic ground state (X) and a singlet excited electronic state (A) corresponding to the HOMO-LUMO excitation have been considered and all the six vibrational degrees of freedom of H_2CO have been taken into account by our highly-accurate computations. We assume that the molecule interacts with a time-dependent periodic electric field (called dressing field) whose frequency is in near resonance with the X-A electronic transition, which gives rise to so-called light-dressed states and light-induced potentials (Floquet approach). Moreover, LICIs are created between the light-induced potentials by the dressing field. We have investigated the absorption spectrum of the light-dressed H_2CO molecule and successfully identified fingerprints of the LICI in the spectrum region where vibrational transitions of the field-free molecule occur in the electronic ground state. A striking fingerprint of the LICI in the dressed spectrum is the emergence of several peaks that are missing from the field-free vibrational spectrum (intensity borrowing phenomenon). This is the first study of light-induced nonadiabatic effects in polyatomic molecules, our results have been published in Ref. [15].

We have examined the absorption spectrum of H_2CO coupled to a quantized mode of an optical cavity. Due to the coupling between the molecule and the quantized cavity mode so-called polaritonic (hybrid light-matter) states emerge [16]. The polaritonic states can be described as superpositions of molecular electronic states multiplied by eigenstates of the cavity mode (Fock states). In Ref. [16] it has been concluded for larger organic molecules that nonadiabatic couplings between the polaritonic potential surfaces can be neglected (called Born-Oppenheimer approximation or BOA in Ref. [16]), at least for stronger molecule-cavity couplings. We have investigated H_2CO in this context and calculated the absorption spectrum of H_2CO coupled to a quantized cavity mode using full-dimensional and different reduced-dimensional quantum-dynamical models. Our results contradict the main conclusion of Ref. [16]. For H_2CO we have managed to prove that the nonadiabatic coupling between polaritonic potential surfaces can not be neglected and the BOA breaks down due to avoided crossings or CIs induced by the quantum light. This important finding is true irrespective of the molecule-cavity coupling strength and the dimensionality of the quantum-dynamical model used. Numerical results along with analytical considerations are reported in Ref. [17]. Another paper dedicated to the spectroscopy of H_2CO dressed with quantum light will be submitted to a Journal of Chemical Physics special issue [18] in the forthcoming weeks.

Work on the quantum calculation of reaction rate coefficients by the flux-flux autocorrelation formalism is currently in progress. This development is expected to find applications in the field of polaritonic chemistry. Results published in Ref. [19] and more recent papers imply that chemical reactions can be accelerated or inhibited if the molecules involved in the reaction are placed in a cavity. We plan to combine the work outlined in this section with the quantum calculation of rate coefficients to investigate chemical reactions in cavities. We hope that the planned work can contribute to this rapidly-developing and novel field.

5. Review articles and book chapters

I have coauthored a review article and two book chapters during the grant period. My work on vibrational quantum graphs and the vibrational quantum dynamics of CH_5^+ forms an integral part of a recent review article on quasistructural molecules [20]. Results on CH_5^+ and the handling of permutation-inversion symmetries in DVR-based variational nuclear motion codes are also presented in a book chapter [21], while another book chapter [22] briefly describes the results obtained for the coherent control of tunneling in ammonia isotopomers.

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