

MO 22: Theorie: Quantenchemie und Moleküldynamik

Zeit: Donnerstag 16:30–19:00

Raum: Poster C1

MO 22.1 Do 16:30 Poster C1

Approaches to Time-Dependent Multicomponent Dynamics — ●CHIRAG JHALA and MANFRED LEIN — Institute of Physics, Universitaet Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany.

Multicomponent density functional theory (MCDFT) for molecules treats electrons and nuclei on the same footing. Since practical functionals for time-dependent MCDFT are hardly available, we consider an H₂⁺ model system, where we can calculate the exact Kohn-Sham (KS) potentials by solving the time-dependent Schroedinger equation and inverting the time-dependent KS equations. As an alternative approach to MCDFT, we propose to use the stationary action principle in combination with an explicitly correlated ansatz for the full time-dependent wave function. By using an ansatz with orbitals depending on transformed coordinates, it is hoped that one needs less configurations than in the standard multi-configuration time-dependent Hartree method for accurate results.

MO 22.2 Do 16:30 Poster C1

Damping of vibrational dynamics in dimers attached to He nanodroplets — ●MARTIN SCHLESINGER and WALTER STRUNZ — Theoretische Quantendynamik, Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Femtosecond pump-probe spectroscopy is a well-established tool for studying vibrations in diatomic molecules [1]. Recent experiments investigate the evolution of vibrational wave packets excited in K₂ dimers attached to superfluid helium nanodroplets [2]. Deviations from gas-phase spectra are seen both in the time- and frequency domain. We simulate the pump-probe signal for the free molecule [3] and include different models to account for a possible damping of the wave packet due to the helium environment. For different damping constants, the effect is investigated by comparing with simulated gas-phase (no damping) and experimental spectra, for which we find good agreement. Our calculations show a shift of the central frequency of oscillations as also seen in the experiment.

[1] T. Baumert, V. Engel, C. Röttgermann, W. T. Strunz, and G. Gerber, *Chem. Phys. Lett.* **191**, 639 (1992).

[2] P. Claas, G. Droppelmann, C. P. Schulz, M. Mudrich, and F. Stienkemeier, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 1151 (2006).

[3] R. de Vivie-Riedle, B. Reischl, S. Rutz, and E. Schreiber, *J. Phys. Chem.* **99**, 16829 (1995).

MO 22.3 Do 16:30 Poster C1

Exact Wave-Packet Propagation for a Field Coupled Molecular System Employing a Perturbative Expansion — ●CIPRIAN PADURARIU¹, PHILIPP MARQUETAND², VOLKER ENGEL², and ULRICH KLEINEKATHÖFER¹ — ¹Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

A method for solving the time-dependent Schrödinger equation numerically for a field coupled two electronic state system is presented. In each state, wave packets are propagated using the established split-operator technique. However, the transitions between the electronic

surfaces are not treated within the standard generalization of this method to the two state problem which involves numerical evaluations of trigonometrical functions at each instant of time. In the proposed approach, the coupling is treated within time-dependent perturbation theory. The method relies on the observation that the perturbation wave function at time $t + dt$ can be obtained directly from the one at time t . A re-summation of the individual orders at each timestep dt is not necessary. Numerical results on a one-dimensional model system prove the robustness of the method, also exhibiting savings of approximately 35% in computation time compared to the standard split-operator technique for two surfaces. This is in particular important for higher dimensional systems where the computational effort is drastically reduced.

MO 22.4 Do 16:30 Poster C1

Circular Dichroism and absorption spectroscopy of merocyanine dimer aggregates: molecular properties and exciton transfer dynamics from time-dependent*quantum calculations — ●JOACHIM SEIBT¹, ANDREAS LOHR², FRANK WÜRTHNER², and VOLKER ENGEL¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

A wave packet approach to the calculation and interpretation of circular dichroism (CD) spectra is applied to the spectroscopy of aggregates of a merocyanine dye. A combined analysis of absorption and CD spectra allows for the extraction of geometric information and excited state electronic coupling. It is shown that in the case of dimer aggregates of a chiral merocyanine dye, it is possible to infer the dynamics of an exciton transfer directly from the CD spectrum. This relation is established via the Fourier relation to a time-dependent correlation function reflecting the quantum dynamics in the dye aggregate.

MO 22.5 Do 16:30 Poster C1

Absorption und Energietransfer von molekularen Aggregaten — ●JAN RODEN, GEORG SCHULZ, ALEXANDER EISFELD und JOHN BRIGGS — Theoretische Quantendynamik, Hermann-Herder-Str. 3, 79104 Freiburg

Unter Verwendung der CES-Näherung (Coherent Exciton Scattering) [1], bei der der exakte Greensoperator der Monomere durch ein Mittel über den Vibrationsgrundzustand ersetzt wird, können experimentelle Aggregat-Spektren mit sehr guter Übereinstimmung direkt aus dem gemessenen Monomer-Spektrum berechnet werden [2]. Es lassen sich die verschiedenen Linienformen des blauverschobenen H-Bandes und des extrem schmalen, rotverschobenen J-Bandes auf einfache Weise erklären. Insbesondere erhalten wir den exponentiellen Abfall der langwelligen Flanke des J-Bandes (Urbach-Martienssen Regel) analytisch aus der Form des Monomer-Spektrums in diesem Energie-Bereich [3].

Desweiteren untersuchen wir den Einfluss von Vibrationen auf den Energietransfer in molekularen Aggregaten.

[1] J.S. Briggs, A. Herzenberg *J. Phys. B* **3**, 1663 (1970) [2] A. Eisfeld and J.S. Briggs, *Chem. Phys.* **324**, 376 (2006) [3] A. Eisfeld and J.S. Briggs, *Chem. Phys. Lett.* **446**, 354 (2007)