

The Quantum Chemistry Group (Hättig Research Group)



Our group is working on a number of projects concerned with the accurate description of interactions between molecules and of molecules with surfaces, solvents and external (e.g. electric or magnetic) fields.

-

Solvation, Weak Molecular Interactions and Their Influence on Properties, Spectra and Reactivity

-

Electronic Excitations: Molecular Spectra and Structures of Excited States

-

The ricc2 Code: Correlated Ab Initio Methods for the Description of Electronic Excitations in Large Molecules

-

Heterogeneous Catalysis: Interactions of Molecules with Surfaces

-

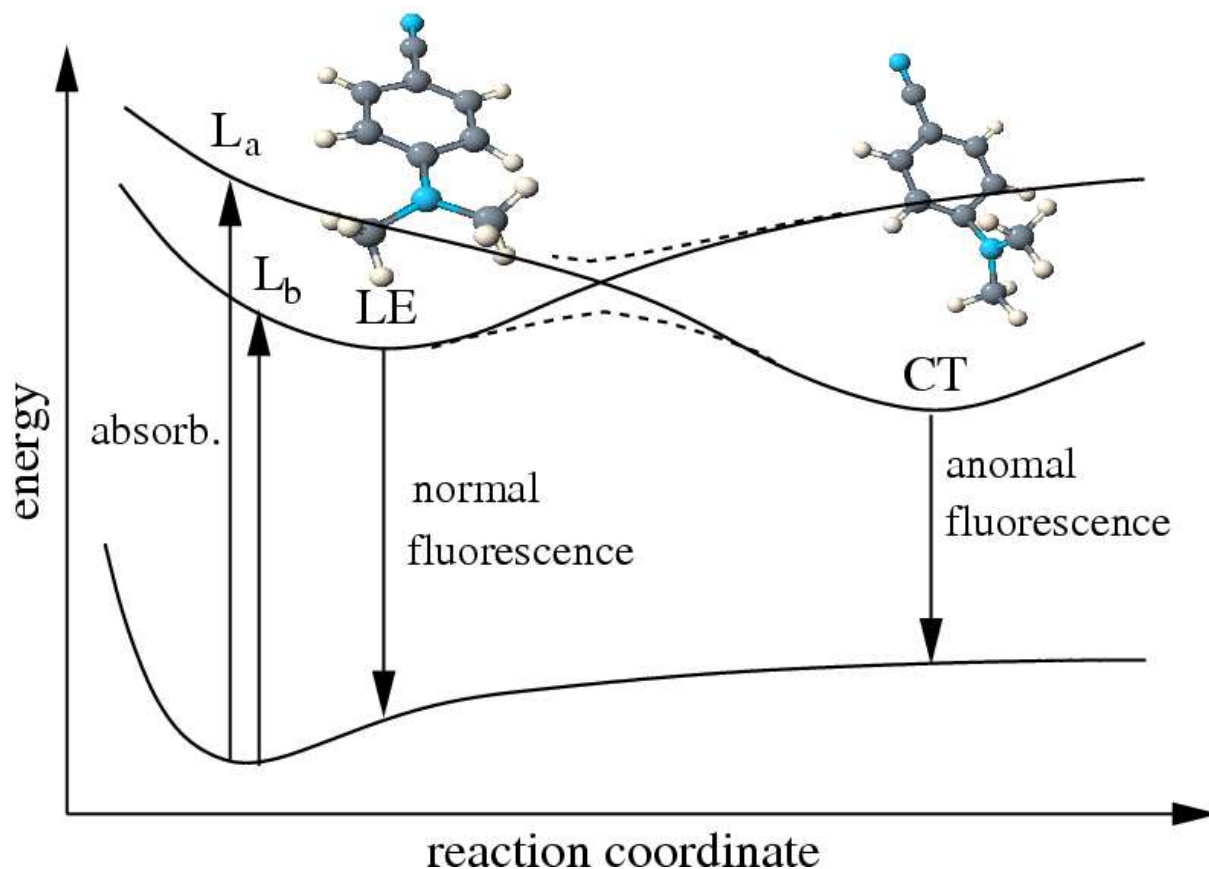
Interactions with Electromagnetic Fields: Linear and Nonlinear Optical Properties

-

Coupled-Cluster Response Theory: Ab Initio Methods for Frequency-dependent Molecular Properties

Our main tools for these investigations are the well-known quantum chemistry package TURBOMOLE, to which we also contribute as a development group, and the quantum chemistry packages DALTON, CFOUR, and Molpro.

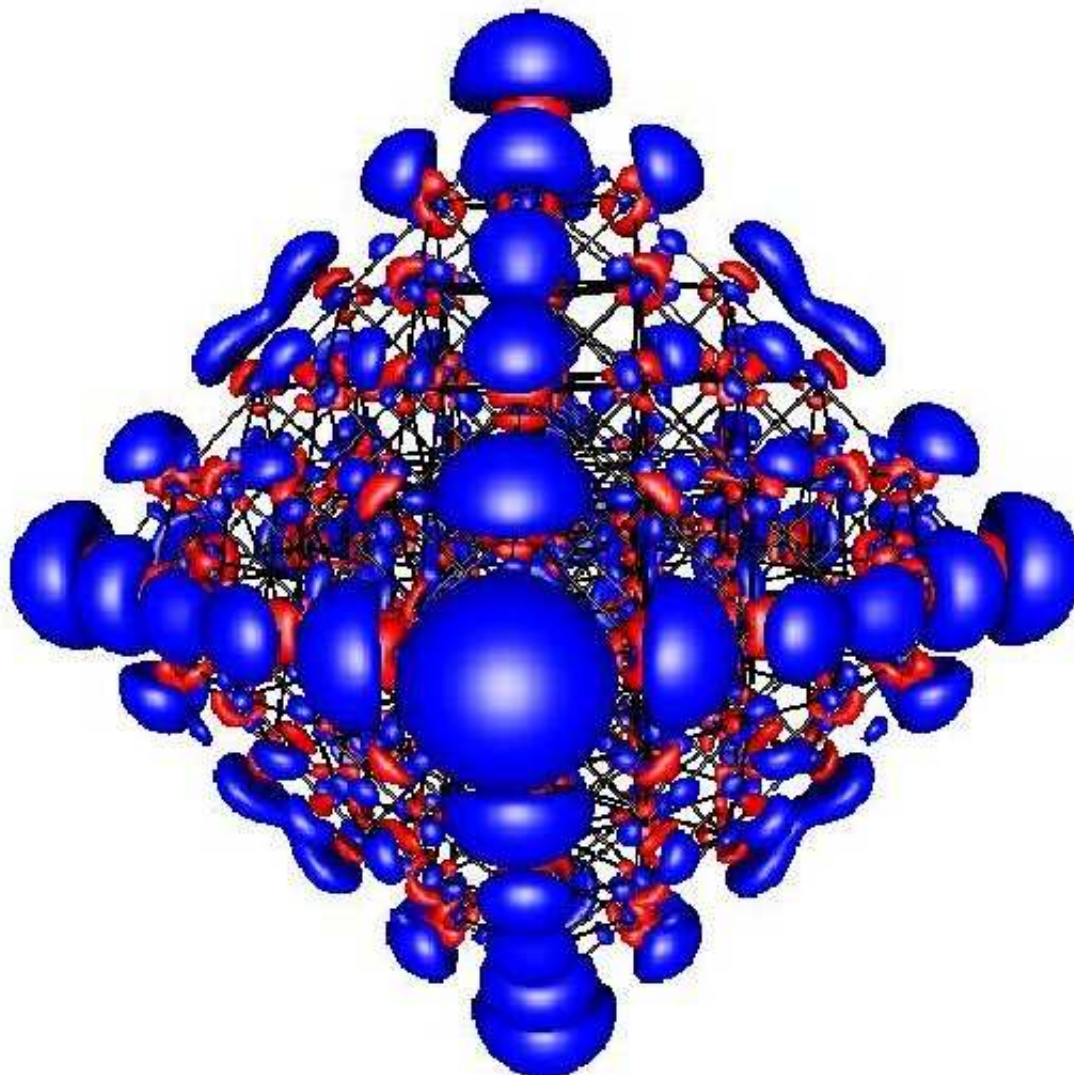
Electronic Excitations: Molecular Spectra and Structures of Excited States



Electronically excited states have usually a complicated electronic structure, and often also the molecular structure (geometry) is different from that in the ground state and difficult to predict. Chemical calculations are therefore an important tool for the understanding of the molecular spectra and the photochemical reactivity of molecules. Modern electronic structure methods, as e.g. density functional and coupled-cluster response methods allow today to investigate with first principles and ab initio methods excited states of relatively large molecules and to calculate quite accurately their spectra and to determine the equilibrium structures of excited states. In our group we apply for these investigations (in addition to TDDFT) mainly the RI-CC2 approach, which has been developed in our group and is well-suited for such applications on medium sized and large organic chromophores (up to ca. 100 atoms). Examples which have been studied with this approach in our group are:

- the transition energies to the lowest excited states in trans- and cis-azobenzene and their change on substitution in different positions with a variety of functional groups
- the equilibrium structures of the lowest excited states of 4-(dimethyl-amino)-benzotriole (DMABN) and the related NMC6 and NTC6, which are prototype molecules for the investigation and understanding of the so-called dual fluorescence phenomenon
- UV/VIS spectra of chlorophyll chromophores and their change with chemical modification and/or complexation

The ricc2 Code: Correlated Ab Initio Methods for the Description of Electronic Excitations in Large Molecules



The CC2 model is an approximated coupled-cluster singles-and-doubles (CCSD) method which has been proposed in 1996 by Christiansen, Jørgensen and Koch for response calculations on molecules which are out of reach for CCSD and higher correlated methods. It is one of the simplest correlated ab initio methods for excited states and yields energies for singly-excited states which are correct through second-order in the electron-electron interaction (dynamic electron correlation), as the well-known second-order Møller-Plesset perturbation theory (MP2) does for ground states. It is thus well-suited for the study of excited states of large closed-shell (or at least "single-reference") molecules. In difference to the perturbative doubles corrections CIS(D) to the widely used configuration interaction singles (CIS) method and similar perturbative approaches to excited states which use non-degenerate perturbation theory, CC2 is not limited to energetically isolated states. A feature, which is important in the search of excited state equilibrium structures. In several applications CC2 has been shown to be a viable tool for such studies.

As MP2 and other related methods based on a second-order treatment of electron correlation, CC2 can be implemented very efficiently with a so-called resolution of the identity approximation for the integrals which describe the electron-electron interaction and thereby made applicable to relatively large molecules, which have been intractable with conventional implementations. As demonstrated in the mid 1990's by Weigend and Häser for MP2, the computational costs and demands (CPU time, memory and disk space) are for most applications reduced by orders of magnitudes.

During the last years we have in our group developed the `ricc2` code of the Turbomole package, an implementation of CC2 with the resolution-of-the-identity approximation which includes

- ground and excitation energies
- transition matrix elements (e.g. oscillator or rotatory strength) and first-order properties (expectation values) of excited states
- analytic gradients for ground and excited states
- excitation energies and gradients for CIS(D_∞) and ADC(2)
- a distributed memory parallel implementation based on the MPI standard
- spin-component scaled SOS and SCS variants

As a side product the code includes a revised implementation of RI-MP2 for ground state energies and gradients and implementations of RI-CIS(D) and RI-ADC(2) (algebraic diagrammatic construction through second order, J. Schirmer 1981) for excitation energies. All functionalities at the MP2, CC2, CIS(D) and ADC(2) level are implemented for closed-shell and unrestricted Hartree-Fock references and most of them are parallelized for PC clusters using the Message Passing Interface (MPI) standard.

Solvation, Weak Molecular Interactions and Their Influence on Properties, Spectra and Reactivity

SOLVATION@RUB Apart from laboratory measurements carried out in ultra high vacuum (and the interstellar space) molecules don't appear as isolated species but in a chemical environment where the interaction with other molecules influences their properties, structure and reactivity. The interaction between molecules is of electric nature, governed by the simple Coulomb law $V(r) = Z_1 Z_2 / (4\pi\epsilon_0 r)$ for the interaction between charged particles. But because of the many possible ways how the electric interaction can become apparent, e.g. as interaction between static electric (e.g. dipole) moments, or between static moments and (through the polarizabilities and hyperpolarizabilities) induced moments, or as van der Waals dispersion interaction the detailed description of intermolecular interactions in terms of molecular properties is usually rather complex. Together with the weakness of these interactions, this makes the determination, understanding and prediction of the potential energy surfaces and the structures and spectra of van der Waals complexes and the influence of intermolecular interactions on the chemical and physical properties and chemical reactions a rich and challenging field. Because of their electric nature intermolecular interactions are intimately connected with the electric or optical molecular properties and response theory. Some problems which have been studied by us in collaboration with various partners are:

- Photochemistry of DNA basis pairs
- Prediction of the optical rotation of molecules in gas phase and solution by ab initio calculations

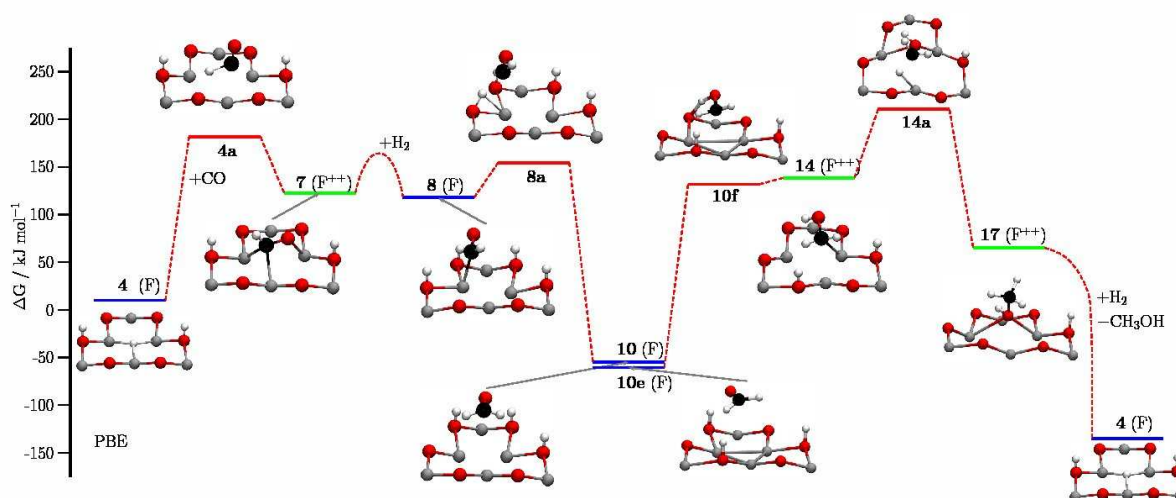
- Theoretical prediction of nonlinear optical properties of molecular crystals

- accurate ab initio calculations of van der Waals dispersion coefficients

- The description of intermolecular interactions between polyatomic molecules through distributed multipole moments, polarizabilities and van der Waals dispersion coefficients

- Pressure-dependence of linear and nonlinear optical properties of rare gases

Heterogenous Catalysis: Interactions of Molecules with Surfaces



The synthesis of methanol from CO and H₂ by heterogenous catalysis, is one of the most important processes in chemical industry. A large quantity of methanol is produced annually using the multicomponent Cu/ZnO/Al₂O₃ catalyst and CO₂/CO/H₂ as the feed gas. Our goal, as part of the collaborative research center (SFB 558), is to find a closed reaction pathway for the methanol synthesis at oxygen vacancies at the polar 000-1 ZnO surface. Starting from optimized structures for educts and products, we performed Growing-String Newton-Trajectory calculations, in the framework of the embed cluster approach, to obtain initial guesses for possible reaction pathways. To refine this reaction pathways, we did subsequent Nedged Elastic Band calculations. The structures with the highest energy along the "elastic band" give a first approximation for the transition state structures, which we are refine using a Trust-Region-Image-Minimization algorithm. The optimized structures for the transition state as well as the sturctures for products and educts are check by evaluating the forces constant (Hessian) matrices. From latter we also calculate the zero point vibrational energies within the harmonic approximation. In this way we also obtain IR-Spectra for the possible intermediates and free enthalpies. By comparison of such "simulated" vibrational spectra and enthalpies with experimental IR and HR-EELS data (obtained within the collaborative research center) we are able to identify and characterize intermediates and adsorbates on the surface and gain insight into reaction and adsorbtion processes.

Interactions with Electromagnetic Fields: Linear and Nonlinear Optical Properties

The interaction of molecules with electromagnetic fields (homogenous or inhomogeneous, static or time-dependent) are related to a large variety of important molecular properties. The most well-known ones are the permanent dipole moment and the dipole polarizability, which describe the change of the energy in an homogenous electric field through first- and second-order in the field strength: $E = f \cdot \hat{I}/4 + f^2 \cdot \hat{I}^2 + \hat{a}'$. In higher orders the interaction with electric fields is described by hyperpolarizabilities and \hat{a} if magnetic fields are involved \hat{a} magnetizabilities and hypermagnetizabilities, which are responsible for various nonlinear (magneto-) optical effects

-
- Kerr effect
-
- Pockels effect
-
- second and higher harmonic generation
-
- intensity-dependent refractive index
-
- Verdet effect
-
- Faraday effect
-
- Buckingham effect
- Cotton-Mouton effect \hat{a}'

With the availability of strong lasers and magnets, the accurate knowledge of these nonlinear (magneto-) optical properties became essential for the understanding and the prediction of the behavior of molecules in strong fields. For some of these effects, however, accurate quantitative measurements are difficult and/or only possible relative to a reference substance. Quantum chemical calculations are here of great help for a better understanding of these properties and for the validation of experimental results. Highly accurate ab initio calculations can serve for calibration of measurements. This has been the motivation for a number of investigations we have carried out in collaboration with international partners, in particular the Theoretical Chemistry Group at Århus University, Denmark:

-
- accurate calculation of frequency-dependent polarizabilities and hyperpolarizabilities
-
- calibration of ab initio methods for the calculation of static and frequency-dependent hyperpolarizabilities
-
- highly accurate calculations on the electric field induced second harmonic generation (ESHG) hyperpolarizability of the Ne atom
- validation and calibration of coupled-cluster response methods for the calculation of nonlinear magneto-optical properties

Many of these properties are related to intermolecular interactions (which are also of electric or electromagnetic nature) and their influence on molecular properties. E.g. the well-known van der Waals C_6 dispersion coefficients can be obtained from the frequency-dependent dipole polarizability.

Coupled-Cluster Response Theory: Ab Initio Methods for Frequency-dependent Molecular Properties

Driven by the interest in frequency-dependent molecular properties, theoretical spectroscopy and intermolecular interactions, the development of ab initio, in particular coupled-cluster, methods for the theoretical description of the interaction of molecules with oscillating (i.e. time-dependent) fields has become a central topic of our research. The basis of this work is a modern formulation of response theory based on a time-dependent Lagrangian, which provides a general handle for the description of a physical system interacting with time-dependent external fields in approximate wavefunction models. Most of our work in this field has been carried out in collaboration with the group of Poul Jørgensen at Århus University and other developers of the Dalton program and is included in the coupled-cluster response code which is part of Dalton. Our recent work in this field has been concerned with

-

the implementation of the approximate coupled-cluster singles, doubles and triples model CC3 for frequency-dependent first and second hyperpolarizabilities, which allows now highly accurate calculations of these nonlinear optical properties

- the development of a coupled-cluster response program which employs an explicitly correlated R12 or F12 ansatz for the wavefunction to increase the accuracy and/or reduce the computational costs for such calculations. This work is carried out in collaboration with Wim Klopper and coworkers (Institute of Physical Chemistry, University of Karlsruhe and Institute of Nanotechnology, Forschungszentrum Karlsruhe) as a project of the DFG priority program 1145 "Modern and universal *first-principles* methods for many-electron systems in chemistry and physics".
-