

2.6 Getting meaningful results fast: Semiempirical methods with orthogonalization corrections

Theoretical Chemistry Emeritus Group by Walter Thiel

Prof. Thiel passed away on August 23rd, 2019. His activities were reviewed by Axel Koslowski and Frank Neese

ABSTRACT The activities of the Thiel Emeritus group are centered around the development and application of semiempirical methods, especially those with orthogonalization corrections. These methods are computationally cheap and yet they provide a realistic and well-balanced description of the potential energy surfaces in the ground state as well as in the low-lying excited states that are dominated by valence transitions. This makes these models ideally suited for the large number of energy and gradient evaluations that occur in non-adiabatic molecular dynamics simulations. Combination with molecular mechanics methods allows studies of chromophores in condensed phases (solvent, protein matrices etc.). Other quantum mechanical methods like density functional and *ab initio* methods are also applied, especially for studies in organometallic catalysis.

1. Method development and evaluation

1.1 Semiempirical models

The advancement of semiempirical methods is one of the central topics of the Theoretical Chemistry Emeritus group. The corresponding work has been funded by the European Research Council with an ERC Advanced Grant till the end of 2018. The focus is on models including orthogonalization corrections, which in the past have proven to be instrumental for obtained more accurate energies and geometries. This strategy has led to the ODM2 and ODM3 models,¹ which are based on the older models OM2 and OM3 methods. The principal improvement is the incorporation of Grimme-type D3 orthogonalization corrections.

Other yet unpublished work concerns the integration of *d* orbitals for the parameterization of biochemically important second-row elements (sulfur, phosphorus), of heavier halogenes and of first-row transition metals. To further develop the model Hamiltonian beyond the established neglect of diatomic differential overlap (NDO) approximation, the multi-center integrals that appear in *ab initio* calculations have been subjected to a statistical analysis and a new model has been proposed in which the largest terms neglected so far are considered.²

The uniform quality of the potential energy surfaces in the ground state and in excited states is a strength of semiempirical methods with orthogonalization corrections. In order to be able to apply these to larger systems and to improve the potential energy surfaces in case of mixing between active and inactive orbitals, configuration interaction (CI) methods based on single excitations have been implemented to complement the existing GUGA-based multi-reference CI module.^{3,4}

1.2 Other methods

The new semiempirical models have been combined with molecular mechanics (MM) methods that take into account the polarization of the MM atoms by the QM region.^{5,6} Unfortunately, it has been found that in order to be able to compete with pure MM methods, the QM and MM components need to be very well adjusted to each other. MM polarization improves the results only marginally.

In order to speed up the computation of potential energy surfaces for MD simulations and rotation-vibration spectra, machine learning methods have been employed to reduce the number of points needed for training these methods to a fraction of the usual number required for interpolation.^{7,8}

Finally, two methods for obtaining the free energy from MD simulations have been comparatively evaluated.⁹

2. Applications

2.1 Photochemical and photophysical processes

A major focus has been the study of non-adiabatic MD on the basis of the new semi-empirical models. Examples are the photoisomerization of urocanic acid¹⁰ which is a natural UV filter found in human skin, and of tetraphenylethylene.¹¹ To determine the quantum yield, 6000 and 1000 trajectories have been computed, respectively.

Combined with a MM method, chromophores in a condensed-matter environment may also be studied. Examples are the photoisomerization of a green fluorescent protein mutant¹² and of azobenzene attached to a DNA duplex replacing one of the bases.¹³

A number of different methods (DFT or *ab initio*) have also been used in applications.¹⁴⁻¹⁸

2.2 Elucidation of mechanisms of catalytic reactions

Chemical catalysis in all variants (homogeneous, heterogeneous and biocatalysis) has been pursued in close collaboration with experimental departments at the institute. For the description of the biological activity of enzymes again combined QM/MM procedures are employed.¹⁹⁻²⁵

The description of processes in homogeneous catalysis is done mainly with DFT methods and occasionally employing wavefunction based *ab initio* procedures. All work in this field is the result of in-house cooperations, namely with Alois Fürstner^{26, 27} and with the junior group leaders Manuel Alcarazo²⁸⁻³⁰ and Bill Morandi.^{31, 32}

Applications in heterogeneous catalysis include the photocatalytic reduction of nitrogen to ammonia on a rutile surface that was modelled using periodic DFT calculations.³³

Interactions of a solute with the solvent have been examined in two papers.^{34, 35}

2.3 Highly accurate calculations on small molecules

Highly accurate equilibrium structures for nitrogen aromates³⁶ and phosphorous halogenes³⁷ have been computed using coupled cluster (CC) methods. By employing an incremental procedure, the following contributions have been taken into account such that results very close to the complete basis set limit (CBS) have been obtained: explicit electron correlation, iterative single, double and triple and perturbative quadruple excitations, core-valence correlations and scalar relativistic effects. Vibrational frequencies have been anharmonically corrected using analytical second and numerical fourth derivatives.

Nine-dimensional potential and dipole surfaces of methyl fluoride have been computed at a similarly high CC level for the variational calculation of the rotation-vibration spectrum.³⁸ The six fundamental frequencies have been obtained with a root mean square error of only 0.69 cm⁻¹ which represents the most precise computation of a rotation-vibration spectrum of this molecule to date.

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