

Welcome to the Marx Group!

Scientific Interests of the Marx Group: A Short Overview

The **general theme** of our research consists in understanding structure, dynamics, and chemical reactions of **complex molecular many-body systems** - bridging the gap between chemistry and physics. Our aim is to capture nature as closely as possible by theoretical means - the basic entities being nuclei and electrons. This implies that we have to use **atomistic *ab initio* computer simulation techniques** which are capable of including dynamics and quantum mechanics - of course only approximatively. The notion "*ab initio*" or "first principles" means for us that we neither want to fit to experimental data nor do we want to adjust any parameters. The central working horse to turn these ideas into practical numerical tools are in particular the *ab initio* simulation methods going back to ideas of Car and Parrinello (1985).

The crucial idea of the **Car-Parrinello approach** to *ab initio* molecular dynamics consists in efficiently solving the electronic structure problem "on the fly" as the molecular dynamics trajectory is generated for a set of classical nuclei using Newtonian mechanics. Thus, within *ab initio* simulations it is neither required to compute a high-dimensional global potential energy surface prior to the simulation, nor is it necessary to reconstruct it approximately from local pair (or few-body) interactions.

This "classical" Car-Parrinello approach has been extended by Marx and Parrinello (1994) to include also the nuclei as quantum-mechanical degrees of freedom. In order to achieve this for "large systems" composed of the order of 100 nuclei or more, the **Feynman-Kac formulation** of quantum statistical mechanics in terms of path integrals is employed. This class of fully quantum-mechanical ***ab initio* path integral techniques** makes it possible to study - in a time-averaged sense - **zero-point motion** and **tunneling effects** for instance of protons in hydrogen-bonded or other complex environments.

More recently, another extension of the original Car-Parrinello method, which assumed the electrons to stay in the electronic ground state, was developed by Doltsinis and Marx (2002). The basic idea of this **nonadiabatic *ab initio* dynamics** technique is to use Tully's surface hopping algorithm in combination with the so-called restricted open-shell Kohn-Sham Ansatz. This efficient approach "beyond the Born-Oppenheimer approximation" allows us to study **photochemical reactions** with particular focus on laser-induced processes in solution.

We have developed a **multi-determinant Car-Parrinello propagation scheme**, which enables the description of the dynamics of electronic states that cannot be represented using a single Kohn-Sham determinant. Using this strategy, we have computed Heisenberg's **antiferromagnetic exchange coupling** obtained from a spin-projected, Hubbard-corrected, broken-symmetry ground state. Generating the time evolution of this quantity "on the fly" provides access to **magnetostructural dynamics**, which arise from the intricate coupling of molecular motion and magnetic properties.

A field pioneered in Bochum is the general theory and computer simulation of **covalent mechanochemistry**. In contrast to thermochemistry, photochemistry or electrochemistry (where temperature, light or electricity are used to trigger reactions), mechanochemistry utilises mechanical force to activate and control chemical reactions. Advances in this field impact on areas of application currently under investigation such as molecular nanomechanics of single-molecule junctions, functionalized surface coatings, and mechanoenzymes.

Among the most recent developments is a method that allows us to **solvate molecular complexes in superfluid helium droplets** at sub-Kelvin temperatures. It combines *ab initio* path integrals to treat chemically complex molecular solutes with a Monte Carlo sampling of the helium environment, in order to establish quantum mechanical indistinguishability - as required by the Bose-Einstein quantum statistics of liquid ^4He . This approach opens the doorway to the study of chemical reactivity in the absence of thermal energy, such as **aggregation-induced dissociation** phenomena and cryochemical reactions.

The ever-growing family of *ab initio* simulation techniques is ideally suited to the investigation of disordered systems at finite temperatures; **molecular liquids** being a prime example of this. As such, this set of methods provides the most direct insight into the structure and dynamics of **solvation shells**, the impact of hydrogen bonding on the properties of **aqueous solutions**, and, most importantly, the **influence of solvation on chemical reactivity**.

These simulation algorithms together with the required computer hardware constitute what we like to call a "**Virtual Laboratory**". In this theoretician's version of a real laboratory chemical reactions of molecules can take place at finite temperature in liquids or on surfaces - solely governed by the basic laws of physics. This makes it possible to investigate "**chemically complex**" **molecular systems** - possibly in close contact with experimentalists. To foster this, the Marx Group is or has been involved in several large-scale collaborative research projects such as SFB 558 ("Heterogeneous Catalysis"), FOR 436 ("Water at Interfaces"), FOR 618 ("Molecular Aggregation") and various Projects of the Volkswagen-Stiftung ("Stress-Controlled Molecular Electronics", "Multiscale Modelling"). In particular, key research of the Marx Group is carried out in the framework of the Research Department "Interfacial Systems Chemistry" (RD IFSC) and the Research Consortium "Solvation Science@RUB" supplemented by the Koselleck Focus Group on "Covalent Mechanochemistry and Molecular Nanomechanics".

Much more detail on this topic can be found in the monograph
"Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods"
written by Dominik Marx and Jürg Hutter
(Cambridge University Press, Cambridge 2009)

The **research group** itself consists (as a time average) of physicists, chemists, and biochemists and it is characterized by **trans-disciplinarity**. The spectral range of our interests is rather broad and covers **applications** to molecules, clusters, liquids, solids, surfaces, as well as to biologically relevant species. In order to be able to achieve these goals, we are constantly developing **novel techniques** and/or we are improving existing methods.

Some of our current and recent **projects** are:

- **Covalent Mechanochemistry and Molecular Nanomechanics**
 - Basic Theory: Force (Legendre-) Transformed Potential Energy Surfaces
 - Biasing Reaction Mechanisms with Force
 - Force Transduction to Mechanophores along Polymer Chains
 - Towards Understanding Mechanoenzymology
 - Mechanical, Optical, and Opto-Mechanical Switching of Anchored Dithioazobenzene Bridges
 - Molecular Mechanochemistry Understood at the Nanoscale
 - Mechanochemistry and Thermochemistry are Different: Stress-Induced Strengthening of Chemical Bonds
- **Ab Initio Path Integrals**
 - Basic Techniques - Quasiclassical Dynamics: *Ab Initio* Centroid MD
 - Trotter Discretization Errors: Simple "*A Priori*" Estimates
 - *Ab initio* path integral Monte Carlo simulations
 - Bosonic Exchange: Superfluid Helium
 - Quantum Fluctuation Effects on Photoabsorption Spectra
 - Scrutinizing Centroid and Ring Polymer Path Integral Molecular Dynamics
 - Quantum Effects on Vibrational and Electronic Spectra of Hydrazine
- **Generalizing Ab Initio Simulation Technology**
 - Surface Hopping "on the fly": Review Article
 - Linear-Response Time-Dependent DFT: Gradients and Nonadiabatic Couplings
 - Targeted *Ab Initio* Molecular Dynamics
 - Multi-Determinant States: Antiferromagnetic Exchange in [2Fe-2S] Proteins
 - Multi-Determinant States: Computing Antiferromagnetic Exchange Couplings
 - Nonadiabatic QM/MM Molecular Dynamics: Photoswitching in Condensed Matter
 - Coupling QM/MM Approaches to Coarse-Grain Mesoscale Modeling for Materials Science

- **Associated Liquids**
 - Theoretical THz Spectroscopy: Analyzing Solvation in Aqueous Media
 - Aqueous Basic Solutions: Hydroxide Solvation via Dynamical Hypercoordination
 - Theory of Structural Diffusion based on Population Correlation Functions
 - Connecting Solvation Shell Structure to Proton Transport Kinetics
 - Amino Acids in Aqueous Solution: Zwitterionic Solvation and IR Spectroscopy
 - Peptide Synthesis in Aqueous Environments: The Role of Extreme Temperature and Pressure
 - Influence of Extreme Conditions and Pyrite Surfaces on Peptide Synthesis in Aqueous Media
 - Microsolvation of Hydronium and Zundel Cations: IR Messenger Spectroscopy
 - Characterizing Pt-Derived Anticancer Drugs: Oxaliplatin in Aqueous Solution
 - Explaining Asymmetric Solvation of Pt(II) versus Pd(II) in Aqueous Solution
 - Revealing Anionic Hydration of Cations: Pt(II) versus Pd(II)
 - MRI Contrast Agents in Aqueous Solution: Interfacial Water around Gadolinium
 - The Nature and Mechanism of Diffusion in Basic Solutions
(See also Nature Highlight, RUB, and NYU press releases.)
 - Hydrophobic Diffusion in Water: Some Surprises
 - Charge Defects in Water: Grothuss Structural Diffusion
 - Hydrogen Bonding in Liquid Ammonia and Lithium/Ammonia Solutions
- **Molecular Solids, Surfaces, Chemisorption, and Materials**
 - Glycine at the Pyrite-Water Interface: The Role of Surface Defects
 - Hydrogen Coverage, Charge State of Oxygen Vacancies, and Chemical Reactivity of ZnO
 - Composition, Structure, and Stability of Rutile Surfaces
 - F-Centers versus Dimer Vacancies on ZnO Surfaces: STM and STS Calculations
 - Superstructures by Water Auto-Dissociation on ZnO Surfaces
 - Ice at Ultrahigh Pressures: Phase Transitions and Proton Shapes
 - Solid Hydrogen: Atoms out of Molecules and Metallization?
 - Heterogeneous Catalysis: Methanol Synthesis on ZnO (see SFB 558)
 - Dynamical Water Autodissociation on an Oxide Surface
 - Heterogeneous Catalysis: First Principles Surface Phase Diagrams
- **Isolated Molecules and Clusters**
 - Quantum-Induced Symmetry Breaking Explains Infrared Spectra of CH₅⁺ Isotopologues
 - Enhancing Photoswitching by Constraining: Bridged Azobenzene
 - Microsolvation of Protonated Methane
 - Microsolvation of HCl by Water: Connecting Structures to Infrared Spectra
 - Fluxionality of CH₅⁺: Pseudorotation and IR Spectra
 - Intramolecular Proton Transfer: Malonaldehyde
 - Gold Clusters and Surfaces Interacting with Methanol and Thiols
 - Excited State Proton Transfer along Intramolecular Hydrogen Bonds: OHBA
- **Chemical Reactions and Bonding in Complex Environments**
 - Aggregation-Induced Reaction Yields the Smallest Droplet of Acid
 - Peptide Synthesis in Aqueous Environments: Amino Acid Activation
 - Nonadiabatic QM/MM Dynamics of Azobenzene Photoswitching in Bulk Liquid Environment
 - Breaking and Symmetrizing Hydrogen Bonds by Compression
(See also RUB press release)
 - Solid Hydrogen: Atoms out of Molecules and Metallization?
 - Three-Center Bonding and Fluctuations in CH₅⁺
 - Lithium: From Molecules to Clusters and Bulk
- **Biobusiness**
 - Conformational Dynamics of Minimal Elastin-Like Polypeptides
 - Potential Proton-Release Channels in Bacteriorhodopsin
 - Spectral Signatures of the Pentagonal Water Cluster in Bacteriorhodopsin
 - Structures and IR Spectra of Protonated Water Networks in bR
 - Hydration and Conformational Transitions of Elastins (see FOR 436)
 - Proton Transduction in Bacteriorhodopsin (see FOR 436)
 - Catalysis on Pyrite Surfaces and the "Iron/Sulfur World" Scenario
 - DNA Bases in Gas and Liquid Phases: Photochemical and Photophysical Properties

- Formation of the "Glycosidic Bond" that Holds together Oligomeric Sugars

- **Codes**

- CPMD

- CP2K

- Check also the Media Gallery

If you want to know more about the various *ab initio* simulation techniques used and developed in the Marx group and applications of these methods we recommend to have a look at our local collection of books and review articles on the subject.

The **publication lists of Dominik Marx and the Marx Group** can be obtained as a pdf file (CV of Professor Marx). Note that it is illegal to download most of the articles listed there: please contact us at theochem@theochem.rub.de and you will receive legal reprints as soon as possible.