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Project Title: High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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Abstract

This project focused on developing high-performance software tools for First-Principles Molecular Dynamics (FPMD) simulations, and applying them in investigations of materials relevant to energy conversion processes. FPMD is an atomistic simulation method that combines a quantum-mechanical description of electronic structure with the statistical description provided by molecular dynamics (MD) simulations. This reliance on fundamental principles allows FPMD simulations to provide a consistent description of structural, dynamical and electronic properties of a material. This is particularly useful in systems for which reliable empirical models are lacking. FPMD simulations are increasingly used as a predictive tool for applications such as batteries, solar energy conversion, light-emitting devices, electro-chemical energy conversion devices and other materials. During the course of the project, several new features were developed and added to the open-source Qbox FPMD code. The code was further optimized for scalable operation of large-scale, Leadership-Class DOE computers. When combined with Many-Body Perturbation Theory (MBPT) calculations, this infrastructure was used to investigate structural and electronic properties of liquid water, ice, aqueous solutions, nanoparticles and solid-liquid interfaces. Computing both ionic trajectories and electronic structure in a consistent manner enabled the simulation of several spectroscopic properties, such as Raman spectra, infrared spectra, and sum-frequency generation spectra. The accuracy of the approximations used allowed for direct comparisons of results with experimental data such as optical spectra, X-ray and neutron diffraction spectra. The software infrastructure developed in this project, as applied to various investigations of solids, liquids and interfaces, demonstrates that FPMD simulations can provide a detailed, atomic-scale picture of structural, vibrational and electronic properties of complex systems relevant to energy conversion devices.

Publications

A total of 20 refereed publications acknowledge support from this Award and are listed at the end of this document.

Description of achievements

Algorithm development and implementation in the Qbox First-Principles Molecular Dynamics code

Several algorithmic improvements have been included in the Qbox FPMD code. Qbox is developed by the PI and is available in open-source form (http://qboxcode.org). We have redesigned numerically intensive algorithms to improve scalability on the BlueGene/Q architecture when using large partitions (>10k cores). We have demonstrated efficient MD simulations involving up to about 4000 atoms. Static electronic structure calculations and structure optimizations were demonstrated on systems including over 10,000 atoms on the ANL Mira platform. We have also developed scalable implementations of accurate hybrid density functional approximations of the exchange-correlation energy. This level of accuracy leads to a high computational cost. The highly scalable architecture of Qbox, combined with a recursive bisection algorithm, makes it possible to use hybrid density functionals in MD simulations of liquids and interfaces involving several hundred atoms. We have further optimized the hybrid DFT algorithm using with a new load-balancing algorithm for the parallel calculation of Hartree-Fock exchange based on an optimized scheduling strategy. The algorithm was published in the Proceedings of the Supercomputing 2014 Conference [Dawson2014]. We validated our numerical approximations in a detailed investigation of the accuracy of the recursive bisection method for acceleration of Hartree-Fock and hybrid DFT simulations. These results were published in the Journal of Chemical Theory and Computation [Dawson2015] and show that the recursive bisection method is applicable to a wide variety of systems, including semiconductors, metals and interfaces. A number of other features were added to the Qbox code, including the capability to compute the stress tensor when using hybrid density functionals. This enables constant-pressure molecular simulations of liquids.

Generation and validation of a new collection of optimized norm-conserving pseudopotentials

Pseudopotentials are a critical ingredient in first-principles simulations. Most importantly, pseudopotentials must be able to reproduce accurately the results of all-electron calculations. Systematic validation studies of available pseudopotentials are however lacking. Following the development of Optimized Norm-Conserving Vanderbilt (ONCV) potentials in 2013, we have implemented an optimization algorithm that selects optimal parameters in order to reproduce all-electron results in over 600 materials. The resulting collection of ONCV potentials (SG15) was made available for elements H to Bi under an open-source license at the http://quantum-simulation.org site managed by the PI. The ONCV optimization algorithm was published in Computer Physics Communications [Schlipf2015]. The pseudopotentials were then used in a cross-validation study in which several families of potentials were compared with multiple all-electron codes. The results of this study were published in Science [Lejaeghere2016], showing that recent pseudopotentials (including the SG15 collection) can accurately reproduce the results of all-electron codes.

Validation study of van der Waals exchange-correlation functionals

Van der Waals (vdW) interactions dominate intermolecular interactions in weakly bound molecular systems. Conventional DFT functional typically fail in describing correctly vdW interactions. The vdW density functionals implemented in the Qbox code were used in a validation study on 10 weakly bound molecules, comparing vdW-DFT with other quantum chemical methods. The results were published in the Journal of Chemical Physics [Taylor2016], and show that some recently developed density functionals (such as e.g. optB88) can rival much more costly quantum chemistry approach in their accuracy.

Ab initio simulations of the vibrational spectra of water and solid/water interfaces

We carried out the first ab initio simulations of the Raman spectra of liquid water, obtained by combining first principles molecular dynamics (FPMD) and density functional perturbation theory (DFPT). The algorithm combining FPMD and DFPT for arbitrary condensed systems (including ordered and disordered solids and liquids) was implemented in the Qbox code. Our computed Raman spectra of water are in good agreement with experiments, especially in the low frequency region. We also developed a systematic strategy to analyze the Raman intensities, which is of general applicability to molecular solids and liquids, and it is based on maximally localized Wannier functions and effective molecular polarizabilities. Our analysis revealed the presence of intermolecular charge fluctuations in liquid water, and highlighted the importance of taking into account electronic effects in interpreting the Raman spectra of liquid water. Our results were published in the Journal of Chemical Theory and Computation [Wan2013].

We also carried out ab initio MD simulations of the infrared spectra of water (IR) and of the alumina/water interface, which is a prototypical oxide/water interface. We used the generalized gradient approximation and the Qbox code. The computed structural properties of the interface are in good agreement with the results of synchrotron X-ray experiments. Detailed analysis of the computed infrared spectra revealed two types of bonding among water molecules at the hydrophilic oxide/water interface. Our results provide a molecular interpretation of the “ice-like” and “liquid-like” bands observed in sum-frequency vibrational spectroscopy experiments and underscore the significance of strong hydrogen-bonding interactions in determining the orientation of interfacial water molecules. Our results were published in J. Phys. Chem. C [Huang2014].

The properties of water at an interface depend on the hydrophobicity of the surface. In addition, the presence of molecular adsorbates at the surface can affect the structural and dynamical properties of water layers closest to the surface. We have investigated these effects by means of FPMD simulations of the Si/water interface in the presence of various adsorbates (including H, CH_3, CF_3 and COOH). The results, published in J. Phys. Chem. C [Lee2014], show that the dynamical properties of water are significantly influenced by the specific details of the adsorbates, in addition to the hydrophobic/hydrophilic character of the surface. Using MBPT to compute energy levels for a functionalized Si/water interface also provided a detailed picture of the position of Si band edges in relation to vacuum and water redox potentials [Pham2014_1].

The availability of both dipole moments and polarizabilities during FMPD simulations also allowed for the calculation of Sum-Frequency Generation spectra in semiconductors and insulators. The details of this computational procedure were published in Phys. Rev. Lett. [Wan2015].

Ab initio simulations of the electronic properties of water and aqueous solutions

We combined FPMD simulations and the calculation of electronic properties using many body perturbation theory (MBPT) and carried out the first ab initio calculation of the absolute position of the band edges of liquid water. These calculations were made possible by using Qbox to generate trajectories and optimized GW techniques that do not require the explicit calculations of single particle excited states. We showed that MBPT is crucial to obtain results that are in good agreement with experiment. We also found that the level of theory chosen to generate molecular dynamics trajectories may substantially affect the electronic structure of the liquid, in particular the relative position of its band edges and redox potentials. Our results represent an essential step in establishing a predictive framework for computing the relative position of water redox potentials and the band edges of semiconductors and insulators. Our results were published in Phys. Rev. B [Pham2014_1]**.**

We also carried out FPMD simulations of a dilute solution (1 M) of NaCl in water, using hybrid density functionals and a bisection technique to compute Hartree-Fock exchange, as implemented in the Qbox code. We showed that the structural and electronic properties of the solute and the solvent are the same as those obtained in the infinite dilution limit, i.e. for aqueous ions in the presence of a uniform compensating background. We found that irrespective of the functional used, the perturbation of the water structure by the ions is mostly localized to their first solvation shell, in agreement with recent experiments. Compared to semilocal density functionals (e.g. GGA), simulations with hybrid density functionals yield a less structured solution with a smaller number of hydrogen bonds and a larger coordination number for the Cl− anion. In addition, hybrid density functionals predict qualitatively correct positions of the energy levels of the ions with respect to the valence band of water. Our results were published in a Chem. Phys. Lett. Perspective Article [Gaiduk2014].

FPMD simulations of the solvated chloride anion using both DFT and hybrid DFT showed that a correct description of electronic states requires hybrid DFT trajectories. This study was published in J. Chem. Phys. [Zhang2013].

The ability to perform FPMD simulations using hybrid DFT also enabled a study of sulfuric acid, in conditions similar to electrolyte solutions used in photocatalytic water-splitting experiments. The results show that the PBE0 hybrid functional can provide a qualitatively correct description of the degree of dissociation of the HSO_4^- ion. A correct description of electronic states also requires the use of a hybrid functional. These results were published in J. Phys. Chem. Lett. [Wan2014].

Computations of the stress tensor within hybrid DFT were also used to investigate the equilibrium density and compressibility of water and ice. The results, published in J. Phys. Chem. Lett. [Gaiduk2015] show that the PBE0 hybrid functional does not properly describe

the relative density of water and ice, and that an approximate inclusion of dispersion interactions reduces this discrepancy.

In two further studies, we investigated the properties of solvated carbonates in extreme conditions. The ability of FPMD simulations to include arbitrary pressures enabled a study of the infrared spectrum of carbonates in conditions similar to those found in Earth's lower mantle. The combined theoretical and experimental study was published in Nature Communications [Boulard2015]. A further study of the solubility of carbon dioxide in extreme conditions showed that a majority of the carbon in water-rich geofluids is found in the form of ions rather than solvated CO_2. These findings were published in Science Advances [Pan2016].

Simulations of embedded nanoparticles

The methods developed in the project are applicable to the calculation of electronic properties and geometry optimization of complex structures. We used FPMD simulations in a study of silicon nanoparticles embedded in a ZnS amorphous matrix. The simulations show that the chemical composition of the matrix is modified near the nanoparticle/matrix interface. Combining DFT, hybrid DFT and MBPT calculations of the electronic structure shows that a type II heterojunction can be formed between the nanoparticle and the matrix, which favors complementary electron and hole transport in solar cell devices. These findings were published in Phys. Rev. Lett. [Wippermann2014].

Summary

The methods developed in this project have extended the size and accuracy of predictive simulations of materials. By developing high-performance, scalable software implementations of first-principles methods that make efficient use of large-scale supercomputers, we have demonstrated accurate, predictive calculations of structural and electronic properties in liquids, aqueous solutions, solid-liquid interfaces and nanoparticles. This project's results highlight the increasingly important role of FPMD simulations, coupled with MBPT methods, in investigations of atomic-scale properties of complex systems relevant to energy conversion devices.

Acknowledgement

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Refereed publications acknowledging Award DE-SC0008938

(listed in alphabetical order by first author)

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