

Multiscale Modeling of Small Molecules in Zeolite-4A

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Motivation—Confinement within the nanoscale pores of a zeolite strongly modifies the physical and chemical behavior of small molecules such as water, ammonia, and carbon dioxide. Realistic modeling of such phenomena requires simultaneously capturing the detailed behavior of chemical bonds and the possibility of collective dynamics occurring in a complex unit cell (672 atoms in the case of Zeolite-4A). Classical simulations alone cannot reliably model the breaking and formation of chemical bonds, while quantum methods alone are incapable of treating the extended length and time scales characteristic of complex dynamics. Therefore, we have taken a mixed quantum/classical approach in which we embed a small region treated with the Kohn-Sham density functional theory (DFT) within a larger system represented by classical potentials.

Accomplishment—A key ingredient of an efficient and accurate quantum-to-classical coupling is the reformulation of the DFT in terms of a spatially localized set of electronic state functions. In order to obtain such a localized representation of the electronic structure, we have implemented and compared two alternative approaches, one based on Green's function techniques and the other using the Grassmann Conjugate Gradient algorithm. We have found that these approaches have complementary strengths, and are currently engaged in developing a hybrid approach that we believe will combine the advantages of both. These approaches are implemented in fully functional software, and we have integrated the Socorro *ab initio* electronic structure code with the LAMMPS classical molecular dynamics

code in order to obtain an initial length-scale-bridging dynamic model. On the materials science front, we have investigated ion rearrangements, modifications of the cage structure, and the absorption of three molecules (water, ammonia, and the ammonium ion) in Zeolite-4A. Unlike previously studied systems, we have found that these molecules prefer to absorb into the 8-oxygen rings of the zeolite structure, where crowding effects between the absorbed molecules and the native ions are important. Based on these observations, we are investigating a possible explanation for the irreversible aging observed in zeolite-based weapons desiccants. In order to perform these studies, we have developed a hierarchy of models for the Zeolite-4A system including one-eighth cell and one-half cell models. These models capture many of the important features of Zeolite-4A, but the strict Si-O-Al alternation of the cage is interrupted. We are currently systematically evaluating the accuracy of this hierarchy of models.

Significance—This project provides the basic principles and techniques to understand the aging of Zeolite-based desiccants (used in most modern weapons systems) and to predict the effects of environmental changes following refurbishment. The scientific understanding and approaches developed in this project will serve as a prototype for studying other complex materials involving the interplay of chemistry and collective phenomena. The software developed in this project will provide a flexible, efficient, production-level tool for materials science research.

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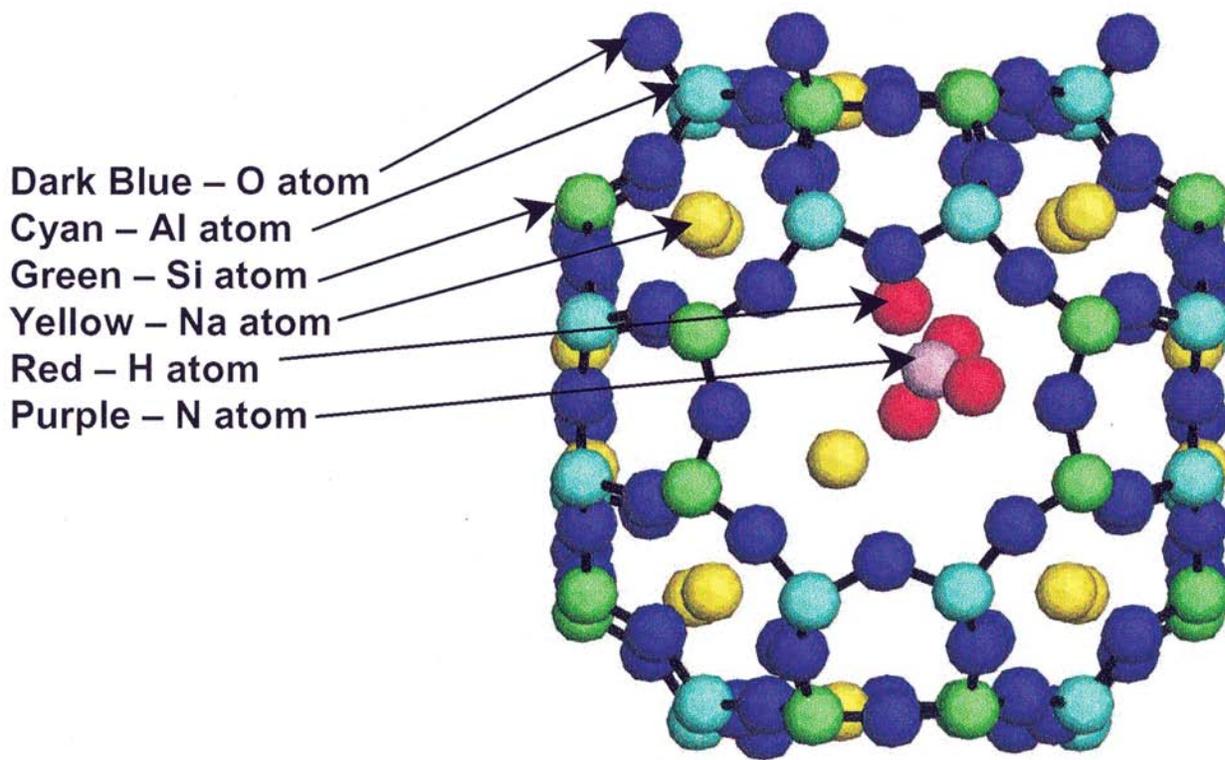


Figure 1. Low energy configuration of an ammonium ion absorbed in our one-eighth cell model of Zeolite-4A. The ammonium ion may block the movement of water through the 8-oxygen ring, reducing the ability of zeolite-based desiccants to absorb water.

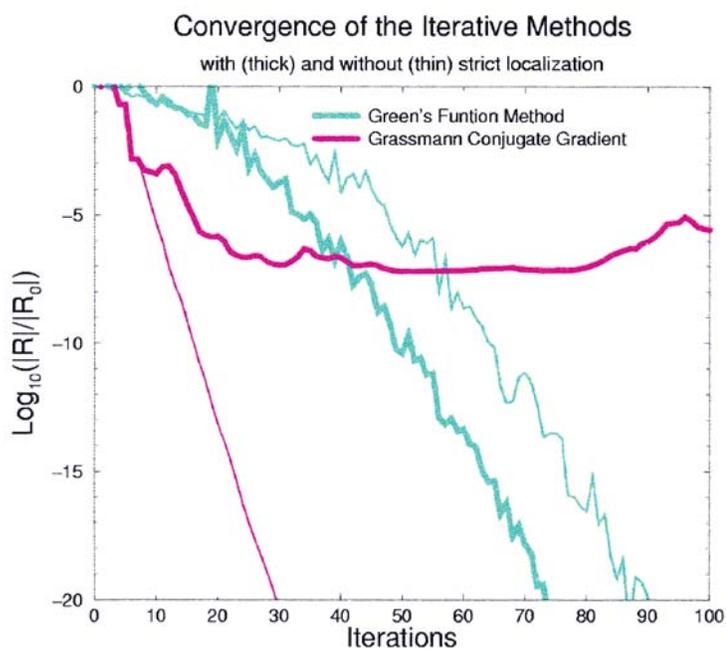


Figure 2. The Green's function method converges rapidly when the orbitals are not strictly localized (forced to be zero outside some radius), but it fails to converge with strict localization. The Grassmann Conjugate Gradient algorithm converges more slowly, but it is also more robust.