EMSL Research and Capability Development Proposals

Accurate Embedded-Cluster Modeling of Insulators: Applications to Metal Oxide Surface Chemistry and Surface Excitation Processes

Project Duration: May 2008 – Sept 2010

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The accurate characterization of adsorbate reactivity and surface excitation processes at surfaces such as metal oxide interfaces is key to understanding, controlling, and designing molecular interactions and transformations for new energy sources. Electronic structure of defects and localized states and surface excitation processes are two recognized challenges in catalysis and interfacial chemical sciences that defy existing levels of theory and simulation. In this report, we present our progress toward developing theoretical approaches to address this problem using accurate quantum mechanical methods.

Implementing various embedding approaches allows us to tackle the electronic structure problem both in the ground and excited state using methods of increasing rigor beyond single determinant methods in a local region (QM) and in the presence of contributions of the host environment. Embedding models have a long history of development and can be broadly divided into the following groups: electrostatic, hybrid/quantum/classical force field (QM/MM), wave function, and density-based approaches. The applicability of these groups depends on the system of interest.

We have developed and implemented three different embedding approaches that can be applied to a wide array of ionic and semiconducting materials over the duration of the project, including:

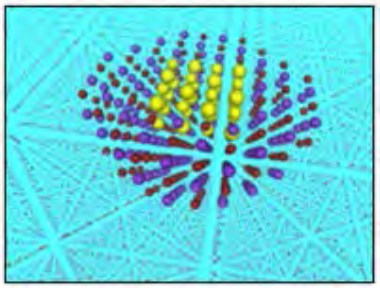
1) QM + Shell Model + Rigid Atom Model or GUESS approach
2) QM + Pseudosaturators
3) QM + Embedding charges derived using accurate Ewald motivated crystal potentials.

These methods are complementary and depend on the material of interest. All of the approaches have been implemented in a development version of NWChem. They are described in more detail as follows:

QM + Shell Model + Rigid Atom Model or GUESS approach: This approach broadly falls within the electrostatic embedding class where the quantum mechanical (QM) region is embedded within a surrounding host lattice. The embedding host lattice is divided into a region represented by a set of polarizable atoms and a region where the atoms are represented using an unpolarized rigid atom model. This approach is well suited for ionic systems such as alkali halides and ionic oxides. In this approach, the atoms closest to the quantum cluster are treated using a shell-model representation, while the far-field is represented using an unpolarized rigid atom model. In the shell-model representation, originally

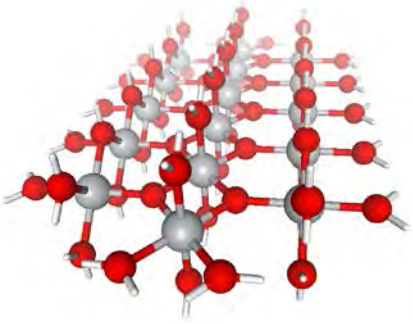
proposed by Dick and Overhauser (1958)[1], an atom is represented by two centers: a point core and a shell. The core typically has a positive charge, while the second center or shell, which can be loosely associated with the valence electrons, bears a negative charge and interacts with the core via a harmonic potential. The shell does not possess any mass and does not interact coulombically with its core. This two-component representation allows the core and shell of the atoms to respond in opposite directions when placed in an electric field and helps model the dipole polarizability of the atom. Therefore, the atoms described by the shell-model can respond to density changes in the system's quantum region. This approach was implemented in NWChem in collaboration with researchers at University College London (Sushko and Shluger).

We have used this embedding model to study the lowest electronic excitations in the alkali halide system (KBr). The figure (right) shows the quantum, shell-model and rigid-atom regions respectively. With this formulation, we were able to study the ground and excited states of the embedded cluster using quantum chemical methods of increasing rigor beyond single determinant methods. The excited states of the embedded cluster were systematically studied using time-dependent density functional theory, TDDFT(B3LYP), and high-level equation-of-motion coupled-cluster (EOMCC) methods. The embedded TDDFT(B3LYP) calculations systematically underestimate the lowest excitations in the bulk and surface consistent with B3LYP predictions. However, we are able to capture the bulk-surface exciton shift in reasonable agreement with experiment. Despite the weakness with the exchange-correlation functionals, DFT/TDDFT offers the best compromise between accuracy and computational performance.



We also performed calculations at a higher level of theory. The embedded surface EOMCCSD calculations are in good agreement with experiment. Of note, the embedded EOMCCSD calculations performed ($K_{16}B_{16}$ surface cluster) are some of the largest high-level correlated calculations to date.

QM + Pseudosaturators: In this approach, the dangling or unsatisfied bonds on the surface of the cluster are capped with pseudoatoms with appropriate charges so that there are no spurious states in the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap. The QM region is embedded in an array of suitably chosen pseudocharges based on physical principles. The optimization in this model is performed by keeping the atoms that are directly linked to the pseudoatoms fixed (along with the pseudoatoms) while all the remaining atoms are allowed to move. This procedure is effective in materials that have covalent character (for example, TiO_2)



We have used this embedding model (see figure on left) to shed light on the nature of the electronic states at play in N-doped TiO_2 nanoparticles. We performed detailed ground- and excited-state calculations on pure and N-doped TiO_2 rutile using an embedding model. The model was validated by comparing ground-state embedded results with those obtained from periodic DFT calculations. The results are consistent with periodic calculations. Using this embedding model, we have performed TDDFT(B3LYP) calculations of the excited-state spectrum and studied the lowest excitations using high-level EOMCC approaches involving all single- and inter-band double excitations. Using these calculations, the nature of the excitations for the pure and doped systems were compared and contrasted in detail. The calculations indicated a lowering of the bandgap and confirmed the role of the

[1] Dick Jr., B.G. and A.W. Overhauser. 1958. "Theory of the Dielectric Constants of Alkali Halide Crystals." *Physical Review* 112(1):90-103. DOI: 10.1103/PhysRev.112.90.

N^{3-} states on the UV/Vis spectrum of N-doped TiO_2 rutile supported by experimental findings. The figure (right) compares the calculated absorption spectra with results from experiment (inset).

QM + Embedding charges derived using accurate Ewald motivated crystal potentials: This approach also falls broadly within the electrostatic embedding class. Here, a set of embedding charges in the far-field are calculated to reproduce the exact Ewald potential of the crystal within the embedded QM cluster. The embedding calculation is performed in the presence of these charges. This procedure complements the GUESS approach in that it allows one to treat a broad class of ionic materials where shell model potentials are not available or validated.

Products and Output

These tools were developed within NWChem framework. The development version of the code is available for EMSL users through the user proposal system. The capability will be made to available to general users at a later date.

Publications

R. Van Ginhoven, S. Kerisit, F. Gao, L. Campbell, **N. Govind** "Ab Initio Calculations of Charge Carrier Properties and Excited-state Processes in Scintillator Materials: NaI and CsI" in preparation (2011)

H. Cho, W.A. de Jong, **N. Govind**, J. Autschbach, F. Aquino, S. A. Bryan, A.S. del Negro, S.E. hightower, C.Z. Soderquist, "Technetium-99 NMR and ab initio theoretical study of electronic structure of *trans*-Dioxotechnetium (V) complexes." in preparation (2011)

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K. Kowalski, J.R. Hammond, W.A. De Jong, P.D. Fan, M. Valiev, D. Wang, **N. Govind**. In press. "Coupled Cluster Calculations for Large Molecular and Extended Systems." In *Computational Methods for Large Systems: Electronic Structure Approaches for Biotechnology and Nanotechnology*, author J.R. Reimers, Wiley-Blackwell, Hoboken, New Jersey. ISBN: 978-0470487884.

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Presentations

R. Van Ginhoven, S. Kerisit, F. Gao, L. Campbell, **N. Govind. "**Ab Initio Calculations of Charge Carrier Properties and Excited-state Processes in Scintillator Materials: NaI and CsI" presented at the *Materials Research Society (MRS) Spring Meeting*, April 26, 2011, Symposium U, San Francisco, California.

N. Govind, R. Rousseau, K. Kowalski. 2010. "Visible-Light Photoresponse of Nitrogen-Doped TiO_2: Excited State Studies using Time-Dependent Density Functional Theory and Equation-of-Motion Coupled Cluster Methods." presented at the *Materials Research Society (MRS) Spring Meeting*, April 5-9, 2010, Symposium Y, San Francisco, California.

N. Govind. 2008. "Modeling electronic excitations in insulators using embedded time-dependent density functional theory and explicitly correlated electronic structure methods." presented at the *American Vacuum Society 55th International Symposium & Exhibition*, October 21-23, 2008, Boston, Massachusetts.

K. Kowalski. 2008. "Coupled cluster for modeling large molecular systems in various environments." presented at the *6th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VI)*, July 19-24, 2008, Vancouver, Canada.

Proposals

K. Kowalski, T. Bligaard, E.J. Bylaska, W.A. de Jong, **N. Govind**, M. Jarrell, M. Mavrikakis, J. Moreno, J.K. Norskov, R. Ramanujam, W.A. Shelton, T.P. Straatsma, K.A. Tomko, M. Valiev, J. Weare, 2011 "Electronic correlation studies in materials and complex emergent phenomena." *INCITE Proposal* (submitted).

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