Quantum Simulations of Materials and Nanostructures (Q-SIMAN): Final Report

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Project Summary

The focus of this SciDAC SAP (Scientific Application) is the development and use of quantum simulations techniques to understand materials and nanostructures at the microscopic level, predict their physical and chemical properties, and eventually design integrated materials with targeted properties. (Here the word 'materials' is used in a broad sense and it encompasses different thermodynamic states of matter, including solid, liquids and nanostructures.) Therefore our overarching goal is to enable scientific discoveries in the field of condensed matter and advanced materials through high performance computing. Fig.1 summarizes the mission and goals of the project.

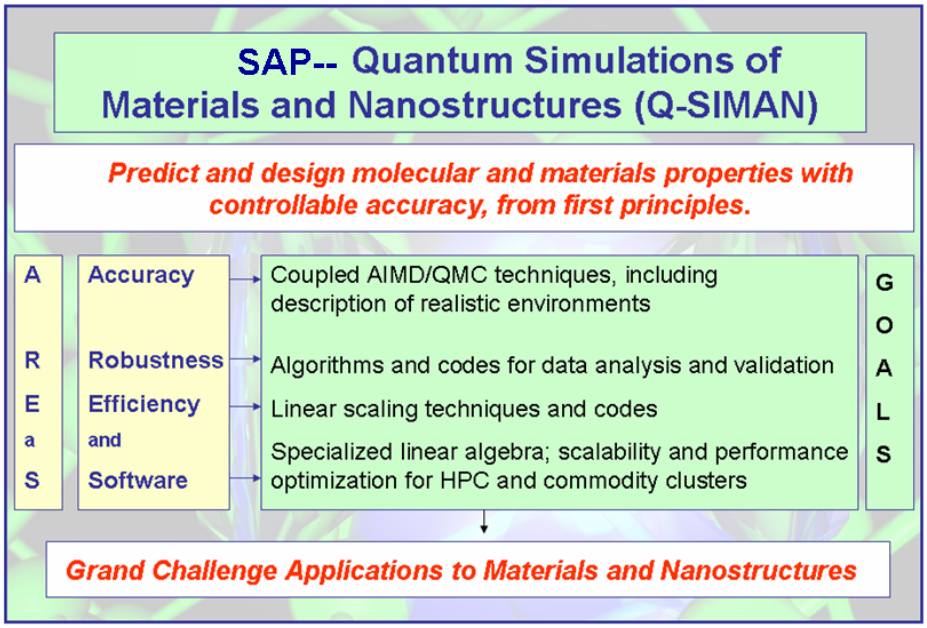

Fig.1: Our grand challenge (GC) : *predict and design molecular and materials properties with controllable accuracy, from first principles*. Major areas of work to address the GC: *accuracy* of quantum simulations (QS); *robustness* and reliability of data produced by QS; *efficiency* of algorithms and codes; *software* optimization and scalability on high performance computers (HPC). Our focus is on *ab-initio* molecular dynamics (AIMD) and Quantum Monte Carlo (QMC) .

The grand challenge addressed in this SAP has been relevant to several of the "most pressing scientific challenges" identified by DOE, for example: "…*expanding the frontiers of nanotechnology to develop materials with unprecedented properties for widespread potential*

scientific, energy and industrial application ..", and "…*using advanced computation, simulation, and modeling to understand and predict the behavior of complex systems beyond the reach of some of our most powerful experimental probes* …". In a way the investigations carried out in these project were similar, in spirit and technical developments, to the MGI announced much later, during the very end of the no-cost extension of the Institute,.

The specific activities carried out within our project are outlined in Fig.2.

Optimized Kohn-Sham solvers for electronic structure calculations and *ab-initio* molecular dynamics (MD) within Density Functional Theory (DFT), and Large Scale *ab-initio* MD simulations – Qbox and MGmol; Bai,Fattebert, Galli,Gygi,Schwegler

DFT-based quantum simulations in the presence of external magnetic and electric fields —Quantum Espresso and Qbox; Cai, Galli, Marzari, Schwegler, Spaldin

Electronic structure calculations beyond DFT: excited state properties and highly correlated systems —Quantum Espresso, FPLO; Galli,Gygi,Marzari,Pickett

Monte Carlo sampling techniques and coupling of ab-initio MD and Quantum Monte Carlo methods —QMCPack and Qbox; Ceperley,Galli,Gygi,Schwegler

Fig.2: The four main ongoing activities within this SAP are summarized, including the codes names (in blue) for each activity and the team members who was involved (in red). (See text).

The cornerstone of most modern quantum simulations (QS) of materials and nanostrcutures is Density Functional Theory (DFT), within various local and semi-local approximations for the exchange and correlation energy functional. The ground state properties of numerous classes of systems are well described within DFT; for other systems (e.g. highly correlated materials) or properties (e.g. excited state and spectroscopic quantities) for which this theory is inaccurate, DFT single particle wavefunctions are often used as input or as starting point to build improved theoretical treatments. It is therefore an essential prerequisite to the application of most QS tools to have accurate and efficient solvers of the basic equations of DFT: the Kohn-Sham (KS) equations. Part of this project was dedicated to developing **optimized KS solvers for electronic structure calculations and *ab-initio* molecular dynamics (MD) within DFT**, and related software. Our results in this area are described in Section I, which also contains examples of **large scale *ab-initio* MD simulations carried out on Leadership-class Computing Facilities.** Many phenomena of interest in condensed matter physics and materials science involve the presence of electric and magnetic fields, and we have developed and applied several **techniques enabling the description of materials**

and nanostructures in the presence of external fields. These techniques and related applications are described in Section II. Two major efforts in the description of properties and systems requiring **electronic structure formulations beyond DFT** were carried out in our SAP: development and applications of techniques to describe excited states and spectroscopic properties of materials from first principles, and calculations for highly correlated materials using Dynamical Mean Field Theory. These two efforts are described in Section III. Although MD sampling is appropriate to investigate several properties of materials at finite temperature and pressure, there are classes of systems (e.g. compressed fluids such as hydrogen) that require the use of more accurate and more efficient sampling techniques. Our effort in this area is focused on **path integral Monte Carlo (PIMC) and on coupled electron-ion Monte Carlo (MC) techniques**. These are described in Section IV, together with results in **coupling *ab-initio* MD and Quantum Monte Carlo (QMC) techniques** and calculations that are being carried out on DOE leadership-class computing facilities.

I. Optimized Kohn-Sham solvers for electronic structure calculations and ab-initio molecular dynamics

In this section we first describe our results in the development of algorithms to improve the efficiency of Kohn-Sham (KS) solvers (Section I.1), as implemented in two of the codes used in this SAP: Qbox and MGmol. The former code is a C++/MPI implementation of ab-initio Molecular Dynamics (MD), based on the plane-wave, pseudopotential formulation of DFT and makes use of a $O(N^3)$ algorithm, where N is the number of electrons in the system. The latter code is a C++/MPI implementation based on localized orbitals and uses an O(N) algorithm.

We then summarize software distribution and support, and simulation environments linking Qbox to another plane wave pseudopotential code used in this SAP: quantum espresso (Section I.2). Scalability and code performance are discussed as well. In Section I.3 examples of large scale simulations using Qbox are presented.

I.1 Algorithms' developments and implementation

In Qbox, trial wavefunctions are obtained by extrapolating from previous solutions and then applying orthonormalization. We have addressed the efficiency of both extrapolation and orthonormalization steps [(a)-(c)], as well as efficiency in computing unitary transformations of KS eigenfunctions, known as Wannier functions, that often provide useful physical interpretations of electronic and bonding properties of materials [(d)]. In addition a new algorithm for compressing electronic structure data produced by Qbox has been developed [(e)].

(a) The extrapolation step performed in Qbox uses Newton's method to compute the polar decomposition of a large matrix, for the subspace alignment during self-consistent iterations. The Newton's method is efficient since it is globally and asymptotically quadratic convergent. However, it has some drawbacks, including the use of explicit matrix inversion and possible numerical instabilities. The explicit matrix inversion is communication intensive due to pivoting. We have developed a **new algorithm** [Y. Nakatsukasa, Z. Bai and F. Gygi, Optimizing and Parallelizing Hally's iteration for computing the polar decomposition] which **replaces the explicit matrix inversion by a QR decomposition** (without pivoting). The QR-based algorithm is communication friendly [Demmel et al.]. Furthermore, we have devised a dynamical scaling for acceleration of the algorithm, and we have proven that the new method is globally and asymptotically cubic convergent. We consider this is as a breakthrough in our search for a communication-optimal algorithm for the computation of polar decompositions. We expect that

the implementation of this algorithm will critically improve the parallel performance of the Qbox code. [Bai,Gygi]

(b) The **Cholesky-QR (Gram-Schmidt) algorithm** is currently implemented in Qbox to orthonormalize wavefunctions. **Reducing communications** is critical to improving the performance of the algorithm. We have devised [Y. Nakatsukasa, F.Gygi and Z.Bai] an alternative implementation of the subspace alignment used by Qbox, where the computational kernel only involves the QR decomposition for a tall skinny matrix, referred to as the Tall Skinny QR (TSQR). The new subspace alignment algorithm can be optimized to avoid communication, both in terms of message passing between processors and of data movement between slow and fast memory. [Bai,Gygi]

(c) With the intent of improving further the efficiency of KS solvers, we have investigated numerical methods for large-scale linear and nonlinear eigenvalue problems, and we have devised [I. Yamazaki, Z. Bai, H. Simon, L.-W. Wang and K. Wu, Adaptive projection subspace dimension for the thick-restarted Lanczos method, submitted to ACM Transactions on Mathematical Software, September 2008] an **adaptive projection subspace dimension selection scheme**, and implemented it using the thick-restarted Lanczos method. This was done within a collaboration with the TOPS Scidac center (http://www.scidac.gov/math/TOPS.html, in particular with James Demmel and Sherry Li). The scheme we have developed is shown to be particular efficient when a relatively large number of eigenvalues are computed, as in the case of KS equations. We have also studied [X. Huang, Z. Bai and Y. Su, Nonlinear rank-one modification for the symmetric eigenvalue problem] the successive linear approximation method (SLAM) for solving a nonlinear eigenvalue problem. Finally we have proposed [Y. Su and Z. Bai, Solving rational eigenvalue problems via linearization] and implemented these algorithms for the KS problem [Bai]

(d) A **one-sided Jacobi method for the simultaneous diagonalization** of symmetric matrices was implemented **for the calculation of Maximally Localized Wanier Functions** (MLWFs) in the Qbox code. Performance measurements have been measured on BlueGene/L and then BG/Q at ANL. A slight superlinear scaling was found, due to cache effects, size-dependent MPI protocols and node mapping. The one-sided Jacobi method implementation opened the way to calculations of Wannier functions for very large systems, e.g. a ~ 7000 electrons crystal of gold nanoparticles. [Gygi]

(e) The size of electronic structure data grows as $O(N^2)$, and an important goal is compressing electronic structure data while preserving accuracy. **A Subspace Bisection Algorithm for Electronic Structure Data Compression** has been implemented that reduces I/O volume and restart file size of Qbox on large-scale parallel platforms. Our compression algorithm based on the CS decomposition was tested on (H2O)512 and a 304-atom Carbon Nanotubes (CNT). A compression ratio of 4.0 ((H2O)512) and 2.7 (CNT) was achieved. We are developing a recursive version of the algorithm to achieve even higher compression ratios [F.Gygi, Phys. Rev. Lett. 2009]. [Gygi]

In MGmol, a new algorithm for fully adaptive localization reqions has been implemented [(f)], together with the option to apply non-periodic boundary conditions [(g)]. In addition a new parallelization strategy to improve efficiency in calculations of the non local pseudopotential energy has been devised [(h)].

(f) We have developed a new algorithm which allows for an **automatic adaptation of the size of the localization regions** in which single particle wavefunctions are confined. This

algorithm extends a previously developed technique to automatically adapt the positions of the localization regions. It is based on the very simple idea of resizing on the fly the localization regions according to the spread of the orbitals they contain. This algorithm was implemented tested for various systems, e.g. a polyacethylene chain $C_{12}H_{12}$ including 30 occupied states and 12 unoccupied states, and (MgO)8 rings, and the exponential decay of the error with respect to the localization region average radius has been verified. We have also **revisited the iterative solver** used to search for the ground state of the DFT electronic structure problem **with localized orbitals** --- **preconditioned steepest descent with Anderson extrapolation**. We have reformulated the algorithm as a subspace accelerated inexact Newton scheme for eigenproblems with non-linear operator. This reformulation provides a clear interpretation of the Anderson extrapolation coefficients and allows for a more efficient tuning and faster convergence of the algorithm. This study also showed the relation between preconditioned steepest descent with Andersen extrapolation and the DIIS algorithm commonly used in quantum chemistry codes. [Fattebert]

(g) **The ability to deal with non-periodic boundary condition was added to the code MGmol.** When simulating a charged or very polar system, the dipole moment of the system is first computed in the non-periodic directions to evaluate the value of the potential at the cell boundaries. The Coulomb potential is then calculated by multigrid with Dirichlet boundary conditions. The method has been tested for the calculation of the dipole moment of a polar system such as Polyvinylidene Difluoride (PVDF) chain. This new capability combined with the O(N) algorithm in *MGmol* opens the way to calculating the electronic structure of large polar nanostructures. [Fattebert]

(h) The **parallelization of the part of MGmol computing the non local pseudopotential (PP) energy** was redesigned to reduce memory footprint and CPU time. This is a difficult problem since both so called Kleinman-Bylander projectors (involved in the calculation of the non local PP energy) and localized orbitals usually overlap only over a small subset of the processors and thus data can be neither fully distributed, nor duplicated on every processor. In addition, neither an all-to-all, nor a nearest neighbor communication pattern is appropriate to gather up results. Our new, mixed parallelization strategy has made possible large scale calculations, for example for silicon nanowires with up to 2500 atoms. Other ongoing large scale calculations involve simulations of a bio-chemical reactions facilitated by an enzyme active site. This calculation involves over 500 atoms embedded in an external electrostatic potential generated by the charged peptide groups surrounding the system but not included in the quantum calculation. Geometry relaxations of this system can be obtained in less than 8 hours using 640 CPUs on LLNL Linux clusters. [Fattebert, Schwegler]

I.2 Software distribution, support and scalability

We have contributed to the development of the **software package ASEF** (Algebraic Substructuring for Eigenvalue and Frequency response calculation). This was a **joint effort with other SciDAC teams**, in particular with researchers supported under the SciDAC TOPS grant. ASEF is based on an algebraic multi-level sub-structuring (AMLS) method. AMLS divides a large sparse matrix into smaller sub-matrices from which a subset of eigenvalues and eigenvectors are extracted and combined to form approximate solutions to the original problems. [Bai]

New features have been added to the Qbox code and Qbox has been adapted for operations on several HPC platforms, [Gygi]

- The calculation of Maximally Localized Wannier Functions (MLWFs) used to compute electric polarization has been included. This has enabled large molecular dynamics simulations of infrared spectra discussed below.
- An MPI-IO based parallel I/O interface has also been designed and included into Qbox to accelerate the process of reading and writing simulation restart files.
- A client-server interface has been developed in order to allow other simulation codes to use Qbox as part of another calculation. In this mode, Qbox acts as a server and reads a stream of commands issued by another code (the client). The output produced by Qbox is then read by the client code. This procedure has enabled efficient calculations of free energies in DFT simulations while completely eliminating software dependencies between client and server programs. In one example, a client written in Fortran90 was used to drive Qbox. This feature will be used to extend the applications of Qbox to hybrid quantum-classical simulation schemes.
- The capability to compute electronic structure with arbitrary sets of k-points has been added.

The **scalability of the Qbox code** was demonstrated on leadership-class DOE platforms as well as on other large-scale platforms.

I.3 Large scale ab-initio MD simulations on Leadership-class Computing Facilities

In the following we briefly describe some of the large scale *ab-initio* MD simulations carried out using Qbox on DOE high performance architectures. Part of the calculations where carried out at LLNL and part at ANL and greatly benefited from INCITE awards.

Ab-inito simulations of hydrophobic solutes: The hydrophobic effect plays a central role in processes spanning numerous scientific and technological disciplines, from protein folding to the formation of natural gas hydrates in oil and gas pipelines. We have used a combination of classical and ab-initio MD simulations to probe the impact of small hydrophobic solutes on the local structure of water. In particular, we have carried out long time scale ab-initio and classical simulations of benzene and hexafluorobenzene molecules in water. The solvation of these solutes represent interesting test cases for MD because they both involve two quite different interfaces when it is surrounded by water. For example, the equatorial region around the benzene ring resembles a typical hydrophobic solute, whereas the axial regions near the center of the benzene ring can interact with neighboring water molecules by forming weak π-hydrogen bonds. Three papers have been published on this topic [Galli,Schwegler, Gygi]

Ab-initio simulation of water at interfaces: We have computed infrared (IR) spectra of heavy water (D2O) confined between graphene and deuterium-terminated (D-terminated) diamond(111) surfaces using ab-initio MD. The analysis of these spectra reveal clear signatures of electronic charge fluctuations at the interfaces, occurring even in the case of highly hydrophobic substrates. Our results point at a complex electro-dynamical interaction of liquid water and the surfaces, and highlight the key role played by the surface electronic structure in determining interfacial interactions. The computed spectra also exhibit blue shifts of stretching modes under confinement, and red shifts of the hindered translational

modes, that arise mostly from the modifed hydrogen bonded network at the interface. Two papers have been published [Galli, Schwegler]

Our calculations on water and water-related systems are summarized in Fig. 3.

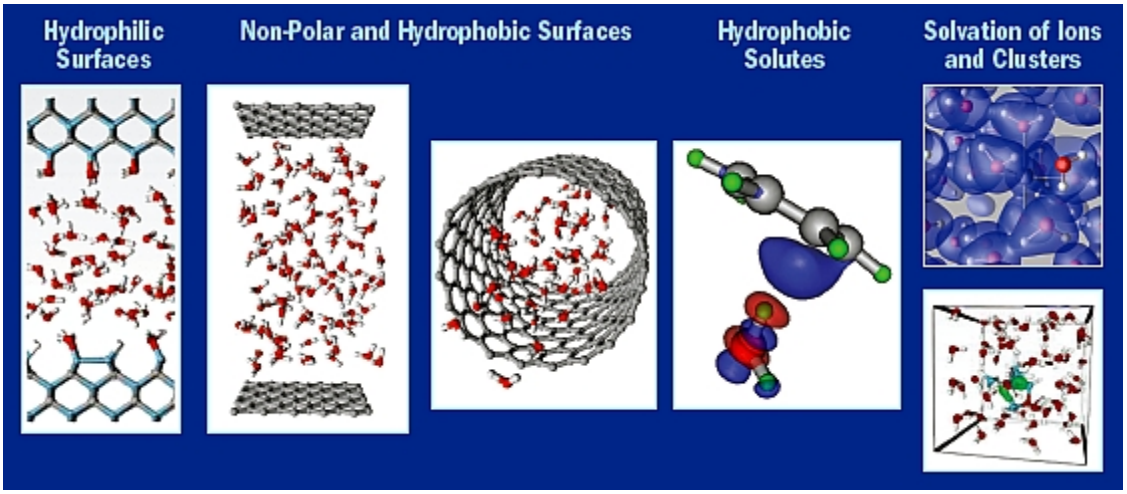

Fig. 3 Snapshots from *ab initio* simulations of water in contact with surfaces, clusters, and molecules, representative of state-of-the-art calculations of the interaction of liquid water with (from left to right) hydrophilic substrates (hydroxylated SiC), hydrophobic substrates (graphite and carbon nanotubes), and hydrophobic solutes such as benzene and small ions (for example, Mg and Ca ions and small silicon clusters.

Ab-initio computation of phase boundaries: As part of a broad effort to investigate equilibrium phase boundaries in materials under high-pressure conditions, we have used the two-phase coexistence approach to determine the melting temperature of water as a function of pressure. In particular, we used a two-phase approach to determine the melting temperature of the ice-VII phase of water in the range of 10–50 GPa. Our computed melting temperatures are consistent with existing diamond anvil cell experiments. We find that for pressures between 10 and 40 GPa, ice melts as a molecular solid. For pressures above ≈45 Gpa, there is a sharp increase in the slope of the melting curve because of the presence of molecular dissociation and proton diffusion in the solid before melting. The onset of significant proton diffusion in ice-VII as a function of increasing temperature is found to be gradual and bears many similarities to that of a type-II superionic solid. A manuscript describing this work was published in the Proceeding of the National Academy of Sciences. [Galli, Gygi, Schwegler].

While for some systems it is possible to describe phase boundaries from first principles, as described above in the case of water, there are many cases of interest to materials science where *ab-initio* simulations are not yet feasible and thus classical simulations are being explored, with the goal of coupling them to *ab-initio* methods, if and when needed, in the future. One of such investigations is the **study of the melting point of Si and Au using the MEAM potential model**: We have determined melting points of pure Si and Au from the MEAM potential (with error bar ~ 1K). We found that for MEAM potentials and using the latest implementation of MD algorithms, computing the melting point from the free energies of the solid and liquid phases is by far the most efficient way. Molecular Dynamics simulation of the co-existence of liquid and solid phase (with an interface) can easily give a rough estimate of melting point (error bar ~100 K) but becomes very time consuming if we want to reduce the error bar to below 10 K. This finding can be used to

compute melting point from first principles, where the only extra calculation required is the free energy difference between MEAM and ab initio models. We have also developed an empirical Au-Si potential fitted to the binary phase diagram. The model is constructed based on the modified embedded-atom method (MEAM) formalism and its binary phase diagram is computed by efficient free energy methods. The eutectic temperature and eutectic composition of the model match well with the experimental values. [Cai].

II. Quantum simulations in the presence of external fields

Several techniques to describe materials in the presence of magnetic fields have been developed and explored in this project, some based on perturbation theory and one based on a direct approach. They are summarized in *II.1*, together with related theoretical developments. Calculations in the presence of external electric fields are presented in *II.2*, and results of specific applications are outlined.

II.1 Magnetic field

We have extended our previously published method for **including a magnetic field in ab initio simulation with periodic boundary conditions** (Cai, Galli, Phys.Rev.Lett. 2004) so that arbitrarily tilted supercells and non-zero k-points are treatable. This allowed us to compute the magnetic band structure (requiring non-zero k-points) and change of band structure with the orientation of the magnetic field (requiring tilted supercell).

In order to enable large scale MD simulations in the presence of a magnetic field, we **implemented in the Qbox code** the algorithms mentioned above. We can now use Qbox to relax the electronic wave functions to the ground state for isolated molecules or nano-clusters under magnetic field (an example is given in Fig. 4). [Cai, Galli]

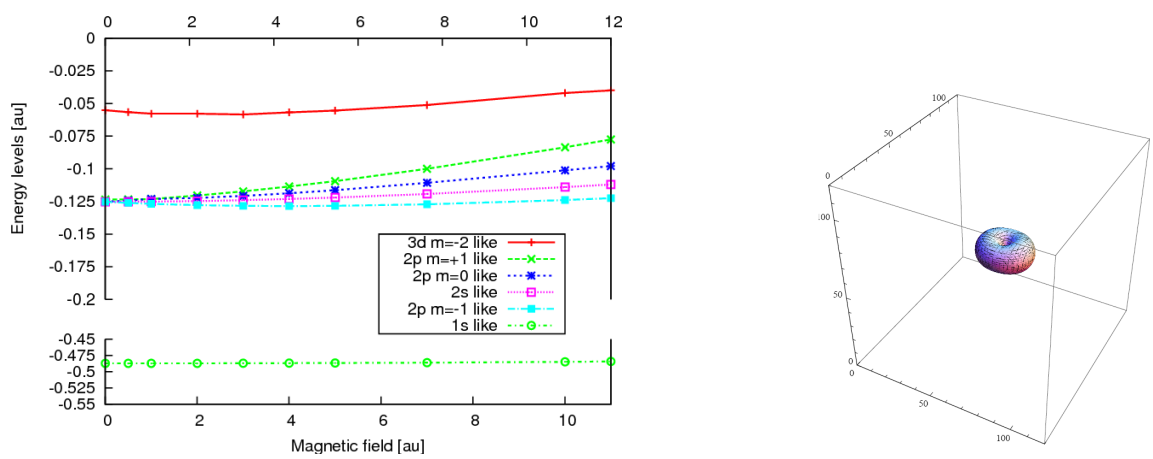

Fig. 4. (left) Energy levels of hydrogen atoms in magnetic field computed by Qbox. (right) Electron density of the first excited state of a hydrogen atom in magnetic field. The supercell size is 50x50x50 au. Energy cut-off is 20 Ry.

We have also developed an **algorithm for computing Berry's phase contribution to the effective Lorenz force on atomic nuclei moving in a magnetic field**. This force is superimposed on the electrostatic (Feymann-Hellman) force and the Lorenz force due to the applied magnetic field and affects the nuclei trajectory. The MPBC method has the advantage that only one calculation is needed in which a uniform magnetic field is applied to all atoms, as opposed to one independent calculation needed to compute the NMR shift for each nucleus in the technique by Marzari et al. However limitations in the magnitude of the field one can use are still present in the MPBC approach. [Cai, Galli]

We have **reformulated the problem of computing NMR shielding tensors** in such a way that the need for a linear-response framework is circumvented. (T. Thonhauser, Arash A. Mostofi, Nicola Marzari, R. Resta, and David Vanderbilt, "A converse approach to the calculation of NMR shielding tensors", submitted to Phys. Rev. Lett. (2007). Previous methods to calculate NMR shifts can be summarized as "direct" approaches, in that a magnetic field is applied and the local field at the nucleus is computed. Our alternative, "converse" approach obtains the NMR shifts instead from the macroscopic magnetization induced by magnetic point dipoles placed at the nuclear sites of interest. The method has been implemented in the Quantum Espresso Package (http://www.quantum-espresso.org) and improvements on parallelization are underway. As a first benchmark we have calculated the NMR chemical shifts for some small organic molecules, large polycyclic aromatic hydrocarbons and in solids (diamond, SiO_2 polymorphs). Our results are in very good agreement with experiments and with previous theoretical results. [Marzari]

We have **applied DFT-based linear response theory to compute NMR chemical shieldings**, in particular ^{1}H-NMR chemical shieldings of water confined in carbon nanotubes (CNTs). In this investigation, the shieldings were sampled from trajectories generated via first-principles molecular dynamics simulations at ambient conditions, for water confined in (14,0) and (19,0) CNTs with diameters of d = 11 Å and 14.9 Å, respectively. We have found that the confined water resonance is shifted upfield relative to free, bulk liquid water. In particular, for the liquid-filled CNTs that we have examined, we find the magnitude of the upfield shift can be as large as ~-23 ppm relative to unconfined liquid water. The shift is a consequence of strongly anisotropic magnetic fields induced in the CNT by an applied magnetic field. [Galli, Schwegler].

II.2 Electric field

We have first developed a **method** [Ab initio theory of metal-insulator interfaces in a finite electric field, M. Stengel and N. A. Spaldin, Phys. Rev. B 75, 205121 (2007)] **to apply finite electric fields to metal-insulator heterostructures within first-principles DFT**. This involved the extension of recently developed finite-field techniques for insulators, (which break down if the system is metallic in any direction) and exploited the maximally localized Wannier functions methodology developed by co-PI Marzari. The development was originally implemented and tested in an in-house code, and is currently being transferred to the public electronic structure code ABINIT. This new tool allowed us to solve the long-standing problem of the origin of the dielectric dead layer in nanoscale capacitors. [Spaldin]

We have then implemented a **spin-polarized extension** to the **finite-electric field method** described above. The extension allowed us **to study the electric field response of magnetic systems**, and in particular to calculate magnetoelectric response – that is the magnetic response to an applied electric field and vice versa. We then applied the method to design of novel systems with enhanced magnetoelectric response. In particular, we demonstrated a previously un-identified linear magnetoelectric effect that arises from a novel carrier-mediated mechanism, and is a universal feature of the interface between dielectrics and spin-polarized metals. Using our new first-principles method, we illustrated the effect at the $SrRuO_3/SrTiO_3$ interface (see Fig. 5) and determined its origin. [J.M. Rondinelli, M. Stengel and N.A. Spaldin, Carrier mediated magnetoelectricity in complex oxide heterostructrures, Nature Nanotechnology 3, 46 (2008)], Experimental verification of the effect is underway.

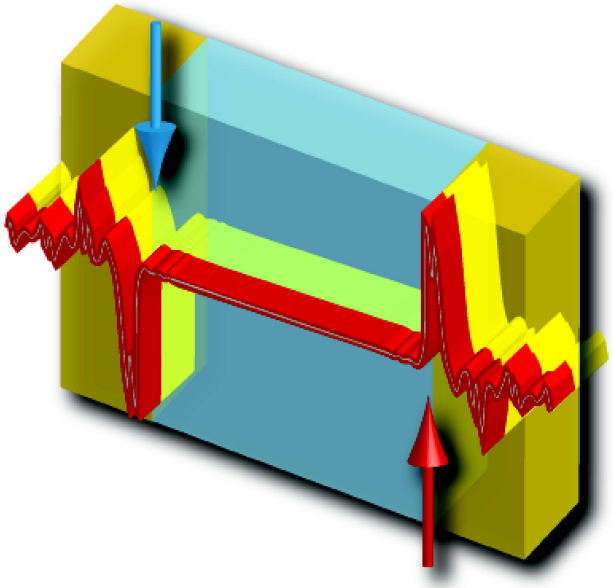

Fig. 5 Calculated change in magnetization under an applied electric field at the SrTiO3 (blue) / SrRuO3 (gold) interface

We have **developed and implemented a formalism to carry out calculations at a fixed value of the dielectric displacement D** [M. Stengel, N. A. Spaldin and D. Vanderbilt, First-principles calculations at constant dielectric displacement, Nature Physics 5, 304 (2009)]. We then investigated ferroelectric capacitors based on $BaTiO_3$ and $PbTiO_3$. Using these model systems, we determined the intrinsic interfacial effects that are responsible for the destabilization of the ferroelectric state in thin-film devices. We showed that the interfacial capacitance depends crucially on the local chemical environment of the interface through the force constants of the metal-oxide bonds, and is not necessarily related to the bulk screening properties of the electrode material. In particular, in the case of interfaces between AO-terminated perovskites and simple metals, we demonstrated a novel mechanism of interfacial ferroelectricity that produces an overall *enhancement* of the ferroelectric instability of the film, rather than a suppression as is usually assumed. [Spaldin]

A fully-featured implementation of the **electric-enthalpy approach** (non perturbative calculations in the presence of an electric field) has been coded in the two quantum engines (PWscf and CP) of the open-source public distribution Quantum-ESPRESSO. For the case of Car-Parrinello CP code a direct minimization of the electric enthalpy as a functional of the wavefunctions is performed; for PWscf (an iterative DFT code) an operator is added to the Hamiltonian such that the ground state of the modified Hamiltonian coincides with the minimum of the electric enthalpy, thus allowing for an interative path to selfconsistency. This latter idea, generalized by Marzari et al. to the many body case and implemented in the QMC code Casino, has allowed us to determine for the first time **higher-order susceptibilities and polarizabilities using quantum Monte Carlo** [Marzari]

III Electronic structure calculations beyond DFT

As mentioned in the Project Summary, while ground state properties of numerous materials are well described by DFT, there are properties, notably excited states', for which DFT performs poorly. Therefore we are developing theoretical and computational frameworks to understand and predict dielectric and spectroscopic properties of materials beyond mean field theory (*III.1*). In particular we have developed techniques to efficiently compute dielectric matrices of complex systems [(a)]; dielectric matrices appear in all formulation of excited state properties based on many body perturbation theory (MBPT). We have applied such techniques to investigate dielectric and excited state properties of water and ice [(b)]; to develop tools to describe van der Waals bonded molecular crystals [(c)] and to propose a method to solve Bethe-Salpeter equations, necessary to account for excitonic effects in materials and nanostructures [(d)]. We have also co-developed (in collaboration with a group at SISSA, in Italy) and applied [(e)] a new formulation of MBPT at the so-called GW level [G denotes Green Function and W screened Coulonb interaction]. All of our excited state effort is based on quantum espresso.

In some cases DFT not only describes poorly certain properties, such as excitations of materials, but is unable to account for ground state properties as well. This is the case for so called highly correlated systems. Our effort to describe these systems within Dynamical Mean Field Theory (DMFT) is described in *III.2*. Our DMFT effort is based on the FLPO code, also briefly described in *III.2*.

III.1 Excited states

(a) We have developed an **iterative method for the calculation of the eigenvectors of dielectric matrices of materials and nanostructures,** based on Density Functional Theory, within a linear response framework. We have shown [H.Wilson, F.Gygi, G.Galli, PRB 2008; H.Wilson, D.Lu, F.Gygi and G.Galli 2009-2011] that by computing a relatively small number of eigenvectors and eigenvalues via iterative dielectric response calculations, one may reconstruct the full dielectric matrix of a given system to high accuracy. The proposed method bypasses the need for the calculation of a large number of excited states required by earlier dielectric matrix computations based on the Random Phase Approximation. The scaling of the algorithm and the efficiency of the approach have been demonstrated by the calculation of the static dielectric properties of several silicon-based nanostructures. This method opens the way to efficient calculations of optical and excitonic properties in materials. Some applications are given below [Galli, Gygi]

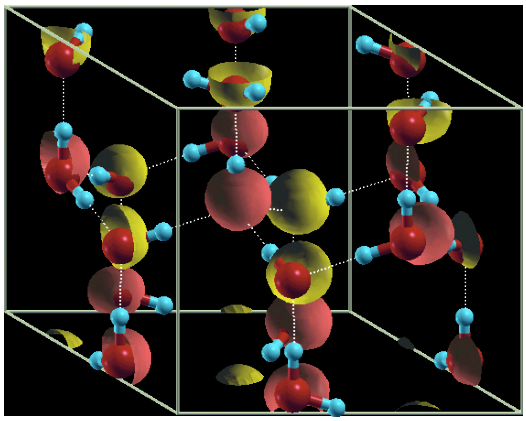

Fig. 6 Isosurface (yellow and pink) of the highest dielectric eigenmode in an ice crystal. (Ohygen and hydrogen are represented by red and turquoise sheres, respectively; see text).

(b) We have carried out a **first-principle study of the static dielectric properties of ice and liquid water**. The eigenmodes of the dielectric matrix were analyzed in terms of maximally localized dielectric functions (see Fig. 6) similar, in their definition, to maximally localized Wannier orbitals obtained from Bloch eigenstates of the electronic Hamiltonian. We have shown that the lowest eigenmodes of the inverse dielectric matrix are localized in real space and can be separated into groups related to the screening of lone-pairs, intra-, and inter-molecular bonds, respectively. The local properties of the dielectric matrix were conveniently exploited to build approximate dielectric matrices for efficient, yet accurate calculations of quasiparticle energies at the GW level. (D.Lu, F.Gygi, G.Galli, PRL 2008)

(c) We have also used the algorithm described in (a) above **to improve the efficiency of the calculation of van der Waals interactions within the random phase approximation.** In particular we combined exact exchange energy calculations with those of correlation energies defined within adiabatic connection fluctuation dissipation theorem under the random phase approximation. We then applied our approach to the study of a prototypical vdW bonded system, the benzene crystal. Our study yields structural and bonding properties in very good agreement with experiment (D.Lu, Y.Li, D.Rocca and G.Galli, PRL 2009) and opens the way for calculations of vdW forces in complex systems.

(d) We have developed a **first principle approach to solve the Bethe-Salpeter equation** (BSE), and thus predict the absorption spectra of materials with different dimensionalities at a high level of accuracy. Our approach built on the development in time-dependent density functional perturbation theory [D. Rocca, R. Gebauer, Y Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008 and PRB 2010) and uses the eigenvalue decomposition representation of the dielectric matrix described in (a) above. Compared to standard BSE implementations, which usually can only access a narrow energy window in the absorption spectra, our approach does not require the explicit calculation of single particle unoccupied states, making it suitable for calculations involving large basis sets and/or a large number of transitions. Furthermore, full spectra can be obtained in our approach from a single calculation, which largely enhances the predicting power of the theory. The efficiency and accuracy of the new approach were demonstrated by calculating the optical properties of silicon nanoclusters.

(e) We have **improved the memory requirements and the computational efficiency**) of the recently developed quasiparticle GW-Wannier (**GWW**) **technique** [P. Umari,G. Stenuit, and S. Baroni, cond-mat/0811.1453].This is a MBPT theory technique at the GW level, based on the use of Wannier Functions to reduce the computational cost of polarizabilities. We have then applied this GWW method to explore the quasiparticle properties of different DNA bases and base-pairs (Fig. 12), finding results greatly improved over those obtained with local or semilocal approximations to DFT. For example HOMO-LUMO gap and the peak position and shapes of photoemission spectrum and the calculated ionization potential agree with experimental data within 7%. We have also applied this method to calculate band gaps of various semiconductors and insulators with both norm-conserving and ultrasoft pseudopotentials. The nice quantitative agreement between the calculated band gaps and experimental data demonstrates the reliability of the GWW method.

III.2 Calculations for highly correlated materials

Strongly correlated materials (viz. transition metal oxides, lanthanide and actinide compounds) are not treated properly by standard DFT approaches, which fail because they lack adequate treatment of the strong interactions and associated quantum fluctuations. The simplest method which extends DFT to treat correlated systems with itinerant and localized electrons is the LDA+U (correlated band theory) method; however this technique does not treat dynamic fluctuations and has limitations in treating e.g. non-integer occupations.

Advanced many-body technique methods such as determinant quantum Monte Carlo (DQMC) can properly treat the strong interactions and resulting quantum fluctuations, but many such techniques have only been applied to model systems so far. Dynamical mean field theory (DMFT) is an excellent approach which allows one to use an advanced many-body treatment for a subset of the orbitals on an atom, and all other orbitals can be treated via any other static method, such as LDA. For the weakly correlated electrons, LDA works very well, and therefore it is important to have a technique like DMFT which can be merged with LDA. One of our efforts in focused on the **DMFT treatment of strongly correlated systems and the coupling of LDA with DMFT.**

Several challenges are involved in the implementation of the so-called (LDA+DMFT) technique: (i) both LDA and DMFT are self-consistent techniques, but the "large loop" of making the output charge densities of LDA and DMFT self-consistent (hereafter termed charge self-consistency) has not yet been successfully exploited. (ii) both LDA and DMFT parts treat the Coulomb interaction of the correlated electrons, so an extra correction term is required in both the global energy functional and in the orbital potential entering the Kohn-Sham equation and the Dyson equation, in order to avoid double-counting. Within this project both challenges are addressed.

To integrate DMFT together with an established general purpose LDA code, we have chosen the FPLO (full potential local orbital) code. It has a local ('atomic orbital') basis set, it is open-source and well supported, and it is relatively easy to modify. In our LDA+DMFT code, we first implemented the computationally efficient Hubbard I (atomic-like self-energy) impurity solver. Hubbard I allows us to use an analytic pole expansion of the local self-energy in the Green function G_{loc}, and we have implemented an additional algorithm that allows us to greatly speed up the computation. With a modest increase in the dimension of the problem being solved, the pole expansion allows one to linearize the computation of G_{loc} in frequency. Then rather than calculating G_{loc} by inverting a matrix at each Matsubara frequency, one can instead diagonalize a single matrix and analytically sum over frequency. This pair of algorithms gives a straightforward means of calculating a new density from DMFT but within the FPLO representation of density, and thereby to complete the charge self-consistency cycle. This procedure gives an order of magnitude speed-up over using a purely numerical self-energy, since typically one uses between 50 and 500 Matsubara frequencies depending on the temperature of the simulation.

We have developed a charge self-consistent implementation of LDA+DMFT which is now integrated into the source code of FPLO and is undergoing testing. We close this

loop by taking the output local Green's function G_{loc} of our DMFT calculation and computing a new density to update the single-particle LDA Hamiltonians, which then goes into the next DMFT and G_{loc} calculation.

For our first application, we have calculated the valence transition $f^{14} \rightarrow f^{13}$ in elemental Yb under pressure. Neither LDA nor LDA+U obtains any valence change. In this study, we have used the Hirsch-Fye QMC finite temperature algorithm extensively. It requires that imaginary time (related to temperature) be discretized into *L* time slices, which introduces some error into the calculation that can be eliminated by extrapolating quantities of interest to the $L \rightarrow \infty$ limit. The QMC algorithm scales as $O(L^3)$, and it turns out as *L* gets large, (non)ergodic behavior in the algorithm can make convergence very difficult to reach (the system can get caught in f^{14} or f^{13} regions of phase phase). To solve this problem **we parallelized our Hirsch-Fye code** and thereby increased statistics substantially. For our final calculations, at each volume we required roughly 30,000 CPU-hours which illustrates the necessity of a parallelized version of the code.

We have computed LDA+DMFT results for the 4f occupation for Yb under pressure without charge self-consistency as a basis for comparison with experiment. LDA+DMFT, even with the simplest impurity solver (Hubbard I), gets the correct qualitative behavior, and is not far off quantitatively (see Fig.7). The results for the *4f* orbital occupation are shown in Fig. 1 for three impurity solvers, Hubbard I (HI), continuous time quantum Monte Carlo (CTQMC, a distinct quantum Monte Carlo method) and Hirsch-Fye QMC (HFQMC). The error of about 0.1 electrons at low volumes may be due to the lack of charge self-consistency, but the correspondence to experiment is still impressive. Charge self-consistency is expected to be more important for the equation of state, and energy functional for DMFT are currently being tested. A paper on the Yb work has been submissed to PRL. [Pickett]

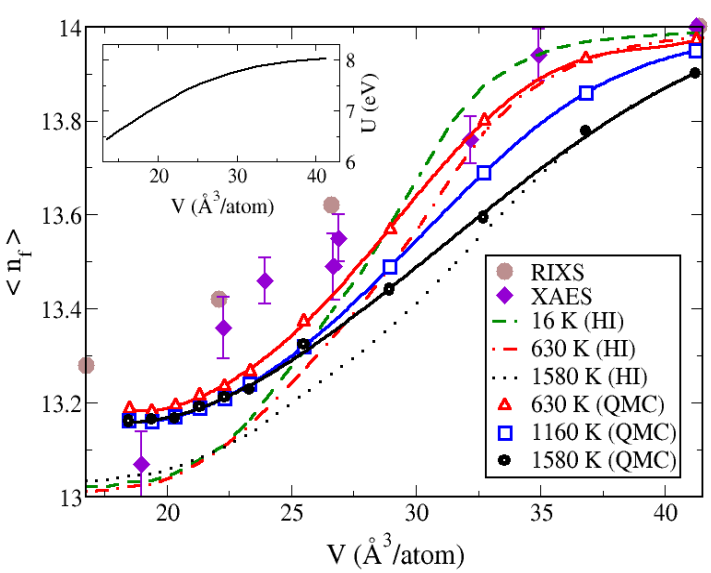

Fig. 7 The 4f shell occupation of Yb vs pressure at various temperatures compared to the experimental data (closed symbols). Open symbols are QMC data; the 630 K and 1160 K curves were obtained with CTQMC, and the 1580 K curve with HFQMC with 80 imaginary time slices. Inset shows the interaction parameter U vs. volume, calculated from constrained LDA.

IV Monte Carlo sampling techniques and coupling of ab-initio MD and Quantum Monte Carlo methods

Within this SAP, a cooperative effort between UCD, Livermore and UIUC has been working on testing and improving simulations of liquid water with respect to those presented in Section I. Obtaining an accurate microscopic description of water structure and dynamics is of great interest to molecular biology researchers and in the physics and quantum chemistry simulation communities. After decades of effort, accurate first principles simulation of liquid water remains an active area of research and an elusive goal; we still do not have a fully quantitative description of the microscopic physics, including hydrogen bonding phenomena. We addressed questions of the accuracy of the intermolecular potential, the efficiency of simulation and the effects of proton zero point motion. To this end we developed and tested several techniques, summarized below.

(a) We developed **a hybrid simulation technique in which path integral Monte Carlo (PIMC) is coupled with electronic structure calculations from density functional theory (DFT),** such that a PIMC simulation of the ions samples the Born-Oppenheimer potential energy surface. [Ceperley]

(b) We tested the use of the **Coupled Electron Ion Monte Carlo (CEIMC) to perform first principles simulation of liquid water**. CEIMC uses Path Integral Monte Carlo (PIMC) to sample molecular configurations; the path integral representation rigorously captures proton zero point motion. Molecular configurations are accepted or rejected based on energy differences obtained from a projector-based ground state Quantum Monte Carlo (QMC) method, which samples the Born Oppenheimer potential energy surface. The group at UIUC is working on the first phase of this project. We have prepared of the order of 1000 statistically independent molecular configurations generated from a Monte Carlo simulation whose energies were computed from a DFT-GGA electronic structure calculation (using Qbox) or from an empirical model potential. Preliminary results are reported in Fig. 8. For each configuration, we are in the process of performing parallel diffusion Monte Carlo (DMC) calculations. By comparing the ab initio QMC energies with DFT and with model potential energies for each configuration, we will determine the accuracy of the assumed potential energy surface. Using re-weighting techniques and perturbation theory, we estimate observables, such as the pair correlation function and melting temperature, yielding the first ab initio calculations of these quantities for a bulk system to mHa accuracy. The configurations and QMC determined energies and ionic forces will be made available to other researchers, e.g. to constrain empirical potentials for bulk water.

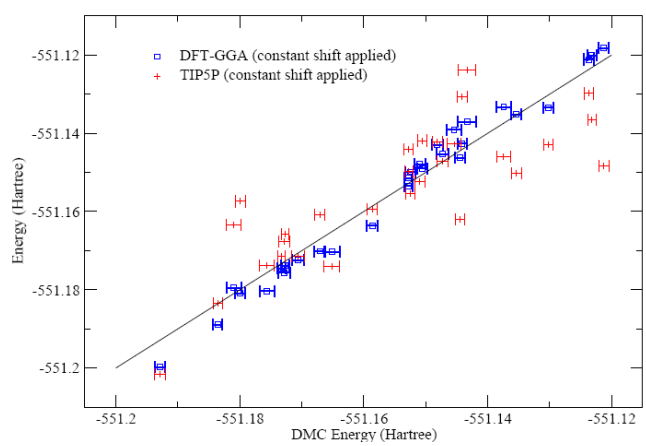

Fig. 8: Comparison between total energies of a 32 molecule water sample as obtained using DFT-GGA, Diffusion Monte Carlo (DMC) and an empirical potential (TIP5P)

(c) **We have integrated two standalone codes: Qbox and PIMC++** (an open-source path integral Monte Carlo code) to compute energy differences using the results of a Qbox DFT calculation. By performing a series of Metropolis MC moves using a fast potential and accepting or rejecting the whole series according to the ab initio DFT potential, the system evolves in configuration space more rapidly, and the expensive DFT calculation need only be performed after many particles have been updated.

(d) We have **improved the performance of QMCPACK on Leadership class computing facilities**; QMCPACK is a high performance, open source quantum Monte Carlo code in C++ developed at UIUC and used for our production runs. Using efficient in-house libraries for data structures, linear algebra, and splines, QMCPACK uses MPI to distribute walkers across nodes and perform load balancing, and multiple threads on a single node are supported using OpenMP..

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