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Optimized Materials From First Principles Simulations: Are We There Yet?

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Optimized materials from first principles simulations: are we there yet?

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Abstract. In the past thirty years, the use of scientific computing has become pervasive in all disciplines: collection and interpretation of most experimental data is carried out using computers, and physical models in computable form, with various degrees of complexity and sophistication, are utilized in all fields of science. However, full prediction of physical and chemical phenomena based on the basic laws of Nature, using computer simulations, is a revolution still in the making, and it involves some formidable theoretical and computational challenges. We illustrate the progress and successes obtained in recent years in predicting fundamental properties of materials in condensed phases and at the nanoscale, using *ab-initio*, quantum simulations. We also discuss open issues related to the validation of the approximate, first principles theories used in large scale simulations, and the resulting complex interplay between computation and experiment. Finally, we describe some applications, with focus on nanostructures and liquids, both at ambient and under extreme conditions.

1. The challenge

In the last two decades, the coming of age of first principles theories of condensed and molecular systems, and the continuous increase in computer power have positioned scientists to address anew the complexity of matter at the microscopic level. Theoretical and algorithmic developments in *ab-initio* molecular dynamics [1], Quantum Chemistry [2] and Quantum Monte Carlo methods [3], together with optimized codes running on high-performance computers, have allowed numerous properties of matter to be inferred from the fundamental laws of quantum mechanics, without input from experiment.

In particular, quantum simulations are playing an increasingly important role in understanding and controlling matter at the nanoscale and in predicting with quantitative accuracy the novel and complex properties of materials (here the word ‘materials’ is used in a broad sense and it encompasses different thermodynamic states of matter). In the next few years, we expect quantum simulations to acquire a central role in materials science, as further theoretical and algorithmic developments will allow one to simulate a wide variety of condensed and molecular systems with specific, targeted properties. In turn this will open the possibility of designing optimized materials entirely from first principles.

Although the full accomplishment of this modeling revolution will be years in the making, its unprecedented benefits are already becoming clear. Indeed, *ab-initio* simulations are providing key contributions to the understanding of a rapidly growing body of measurements at the nanoscale, and of complex disordered systems, including liquids and solids under extreme conditions. In particular, they provide simultaneous access to numerous physical properties (e.g. electronic, thermal and vibrational), and in some cases they allow one to investigate properties which are not yet accessible to experiment. A microscopic, fundamental understanding is very much in demand for example in the field of nanoscience, as experimental investigations are often controversial and they cannot be explained on the basis of simple models.

Quantum simulations, whether using Density Functional Theory [4], Quantum Chemistry methods or QMC techniques, provide numerical solutions to equations representing the laws of quantum mechanics for interacting electrons and ions, in an approximate, non empirical manner. The challenge in providing meaningful predictions with quantum simulations consists in developing robust and efficient numerical techniques for the solution of these equations, while fully controlling the limit of validity of the underlying approximate theories. In this paper we will address the different aspects of this challenge, in particular we briefly describe the theoretical and numerical approximations involved in most quantum simulation (QS) tools utilized in condensed matter physics and physical chemistry (Section 2.), and then we give some examples of recent predictions of materials properties obtained using QS (Section 3.). Finally we present a perspective on future uses of QS in Section 4.

2. Quantum Simulations: theory, algorithms and numerical techniques.

2.1. Approximate, first principles theories

We restrict our attention to condensed and molecular systems whose equations of motion obey Newtonian dynamics, and we aim at a non empirical, quantum mechanical description of electron-electron and electron-ion interactions in these systems. Such a description is provided by equations which have been well known for about eight decades, the time dependent and time independent Schroedinger equations. However, as P.A.M. Dirac pointed out shortly after the principles of Quantum Mechanics were established, even for very simple systems containing few electrons, these equations are much too complicated to be soluble exactly. Therefore, one needs to resort to approximations. This is the first step a quantum simulation involves, i.e. the choice of an appropriate theoretical approximation to solve the Schroedinger equation of a system of interacting electrons. Let us further restrict our attention to the time independent Schoroedinger equation.

One of the most successful approximations to the solution of the time independent Schroedinger equation of interacting electrons has been provided by Density Functional Theory (DFT), a mean field theory containing specific approximations for the exchange and correlation energy of a many-body system of electrons (these are called local density approximations). This theory, developed in 1964-5 by Hohemberg and Kohn and Kohn and Sham [4], was originally applied in Solid State Physics to investigate zero temperature properties of solids. Starting in 1985 with the pioneering work of Car and Parrinello [1], the theory has then been used in conjunction with molecular dynamics (MD) techniques [5] to compute thermodynamic and dynamical properties of condensed systems, giving birth to the field of *ab-initio* molecular dynamics. In the 1990s, the development of sophisticated, local exchange-correlation energy functionals (so called, gradient corrected energy functionals [6]) has brought DFT into the Chemistry arena, with applications to molecular systems and eventually nanostructures; for certain classes of systems the usefulness of DFT is now being treated on a par with that of Quantum Chemistry methods, by the Chemistry community.

The central variable of DFT is the electronic charge density [$\rho(\mathbf{r})$], and a total energy functional of $\rho(\mathbf{r})$ is defined whose minimum with respect to the charge density represents the ground state of interacting electrons in the field of ions. The minimization of this functional can be cast into the solution of Schroedinger-like equations for single particle electronic wave-functions (orbitals). The DFT approach is rather different, in spirit, from Quantum Chemistry (QC) approaches: as mentioned, DFT is based on the electronic charge density and the minimization of an energy functional leading to the solution of non linear Schroedinger-like equations; on the other hand QC deals with perturbative solutions of the linear many-body Schroedinger equations of interacting electrons, and it is based on hierarchical approximations of the many-body electronic wavefunctions, starting from Hartree-Fock (exchange only) solutions. QC approaches, developed since the early days of Quantum Mechanics in the 1930s, have been mostly applied to molecules and finite systems and, since recently, to simple nanostuctures as well. While DFT is a ground state theory and its application to compute excited state properties, although rather widespread, has no robust theoretical foundation, QC approaches can be applied to the investigation of both ground and excited state properties.

The ability to compute a large variety of physical and chemical properties of molecules and solids, with direct comparisons with experimental data, using DFT and QC came at the end of the eighties and beginning of the nineties, as a result of key algorithmic and computational developments (including optimized computer codes, efficient basis sets expansions, novel correlation methods and the coupling of electronic structure methods with statistical mechanical techniques for the calculation of thermodynamic and dynamical properties of matter). Notably, in the DFT arena, the development of plane-wave techniques (for the expansion of the single particle orbitals) and the Car-Parrinello method [1] brought great advances to the field of QS.

At the same time as DFT and QC were applied to realistic systems, another approach to the solution of the many body Schroedinger equation was coming of age: Quantum Monte Carlo [3]. This is an explicitly many-body method which takes electron correlation into account from the outset, and utilizes a stochastic approach to solve the Schroedinger equation. Closer to QC in spirit (direct solution of the linear Schroedinger equation) than to DFT, QMC does not make use of perturbation theory to incorporate correlation effects into Hartree-Foch solutions, as most QC approaches. Almost all of QMC applications are based on the so-called fixed node approximation, where it is assumed that the nodal surface of the many-body electronic wavefunction is known from the start (e.g. from mean-field DFT or QC approximate calculations) and does not change during the stochastic optimization. Although capable of providing exact solutions to the Schroedinger equation in principle, in the case of interacting fermions, the so-called sign-problem has so far prevented applications of QMC methods to realistic systems without the fixed node approximation. Interesting attempts to the solution of the sign problem has been discussed in the recent literature [7].

It is worth noting the close link between DFT and QMC approaches. The application of DFT to study solids first and then molecules and nanostructures has been made possible by the definition of so called local energy functionals for the exchange correlation energy [4,6]; the parametrization of these functionals (and then their use in actual calculations) has in turn been made possible by data on the homogenous electron gas obtained using QMC techniques by D. Ceperly and B. Alder at the beginning of the eighties. These parametrizations are still used nowadays in modern DFT based electronic structure calculations and QS. On the other hand, trial wave-functions for stochastic optimizations within QMC are often derived from DFT calculations, and in particular from one determinant wavefunctions constructed from DFT single particle electronic orbitals.

In the next sections, we further restrict our attention to QS based on DFT, in particular on *ab-initio* MD, although we will briefly describe improvements on DFT solutions using QMC approaches, in particular for the description of excited states of nanostructures.

2.2. Algorithms

In an *ab-initio* MD, the time evolution of an ensemble of ions (describing a condensed or molecular system at finite temperature) is described using Newtonian dynamics, employing well established molecular dynamics techniques [5]. The self-consistent potential between ions, determined by electron-electron and electron-ions interactions, is computed within DFT by solving a set of N_{el} coupled, non linear partial differential equations (the Kohn-Sham equations) self-consistently, using iterative algorithms, subject to orthonormality constraints for the N_{el} electronic orbitals (ϕ_i)

$$\begin{cases} -\Delta\varphi_i + V(\rho,\mathbf{r})\varphi_i = \varepsilon_i\varphi_i \quad i = 1\ldots N_{\mathrm{el}} \\ V(\rho,\mathbf{r}) = V_{\mathrm{ion}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\mathrm{XC}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i(\mathbf{r})|^2 \\ \int \varphi_i^*(\mathbf{r})\,\varphi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij} \end{cases}$$

Here V is the self-consistent potential of interacting electrons in the field of ions and ϕ_i and ε_i denote electronic orbitals and single particle eigenvalues, respectively. V_{xc} is the exchange correlation potential which depends only on the charge density $\rho(\mathbf{r})$ in the local density approximation [4], while it depends also on the gradient of $\rho(\mathbf{r})$ in gradient corrected approximations [6].

The cost of solving the Kohn-Sham equations is dominated by orthogonality constraints and it grows as the third power of the number of electrons in the system. Most electronic structure and *ab-intio* MD simulations performed nowadays employs $O(N^3)$ iterative procedures, although many efforts have been devoted in the last ten years to achieve linear scaling, i.e. to solve the Kohn-Sham (KS) equations in O(N) operations [8-11]. Progress has been made based on one key concept, the so-called nearsightedness of matter [11] , i.e. by exploiting the local properties of the density matrix of electronic systems with an energy gap. The majority of linear scaling methods developed in the recent literature are based on localized electronic orbitals (representing the localized density matrix) leading to sparse Kohn-Sham Hamiltonians and overlap matrices. These localized orbitals are related to Maximally Localized Wannier Functions [12] and thus to the basic concepts of the modern theory of polarization [13]. Some open technical problems, especially in devising efficient iterative minimization procedures using localized orbitals, has so far prevented the use of linear scaling methods in *ab-initio* MD simulations of complex systems, although significant progress has been made in the last few years using, e.g. adaptive localization centers [10].

Algorithms similar to those developed within DFT to achieve linear scaling have been developed also in the context of QMC, in order to evaluate Slater determinants in nearly O(N) operations [14]; these algorithms have been successfully applied to the study of optical properties of nanostructures, as we will briefly describe in Section 3.

2.3. Numerical techniques

The most common approach to the solution of the KS equation consists in expanding solutions on an appropriate set of basis functions, converting the KS system of Partial Differential Equations (PDE) into an algebraic eigenvalue problem. This eigenvalue problem must be solved repeatedly in order to reach self-consistent electronic charge densities. Ideally, a Kohn-Sham solver must provide accurate solutions with maximal efficiency, i.e. using a limited number of basis functions, and the accuracy of the solutions depends primarily on the completeness of the basis set.

Electronic structure computations, including semi-empirical methods, have a 60-year history during which various types of basis sets were chosen, based on their ease of use and their ability to provide reasonably accurate answers with a limited number of basis functions. Among the most popular basis sets used by the Chemistry community are Gaussian functions, while plane waves (i.e. Fourier expansions) have been widely used within the Solid State Physics community. More recently, finite elements and wavelets have attracted some attention as well. Localized basis sets such as the Gaussian basis are very successful because atomic and molecular orbitals can often be adequately described using only a handful of basis functions. This leads to algebraic problems of tractable sizes, and thus to fast solvers. However, another important characteristic of a basis set is its ability to increase accuracy of the solutions in a systematic way. This property is displayed most naturally by the plane-wave basis, since the number of Fourier components used to describe solutions can be increased systematically, leading to more accurate solutions in a controlled manner.

Many other properties other than controllable accuracy and size of the algebraic problem, affect the choice of a basis set; some of them are related to the availability of efficient numerical algorithms for the calculation of various quantities (e.g. total energies and forces acting on ions) derived from the KS solutions. In that respect, the plane-wave basis again takes advantage of the efficiency of the fast Fourier transform algorithm, which allows for an efficient evaluation of the solutions on a real-space, three-dimensional grid starting from their Fourier coefficients. Plane waves also have the desirable property of being translationally invariant, i.e. they describe with equal accuracy solutions of the KS equations that are localized in different parts of the simulation domain. These properties of the plane-wave basis and its simplicity have contributed to make the plane-wave method the gold standard of first-principles molecular dynamics simulations.

More recently, another criterion has become relevant in the choice of basis sets for electronic structure calculations. The availability of more powerful computers is related to parallel architectures, and the possibility of parallelizing an algorithm using a given basis set is becoming an important argument in the basis set choice. It would appear in a first analysis that the FFT algorithm is not easy to parallelize, and this would be a major impediment to the use of the plane-wave method on large parallel computers. Parallelization of the PW method on the order of 1024 CPUs has been achieved by several codes using global, parallel Fourier transforms. Such global transforms however do not scale well to very large numbers of nodes. A detailed investigation of all operations involved in a KS solver shows that many Fourier transforms can be performed in parallel on separate data. This property can be used to implement the plane-wave method on large parallel computers (beyond 1024 nodes), provided that a careful analysis of the data layout and of the data flow patterns is carried out.

The applications presented in Section 3. were carried out using Qbox, an implementation of *ab-initio* MD that was specifically designed for efficient use on large parallel platforms. In the Qbox code, the Fourier coefficients describing the solutions of the KS equations are distributed on a two-dimensional process grid. Each column of the process grid holds a subset of all electronic states. The plane wave basis set is evenly distributed among the processors of a column of the process grid. This data distribution leads to good load balancing and also lends itself well to the use of the ScaLAPACK library for the operations involving dense linear algebra on the Fourier coefficients of the solution.

This implementation strategy was used successfully on several large computers, including a 2k-CPU Linux/Xeon cluster (LLNL MCR), a 4k-CPU Linux/Itanium cluster (LLNL Thunder) and more recently, the 32k-node LLNL BlueGene/L platform. Figure 1 shows the scaling behavior of Qbox on the BlueGene/L platform when solving the KS equations for a 1000-atom molybdenum sample. A parallel efficiency of 86% can be obtained when scaling from 1024 to 32768 CPUs. The aggregate sustained floating-point performance when running on 32k CPUs is 22 TFlops, i.e. about 24% of the theoretical peak performance. Such high performance enables simulations of larger systems than were previously tractable, as well as longer simulation times.

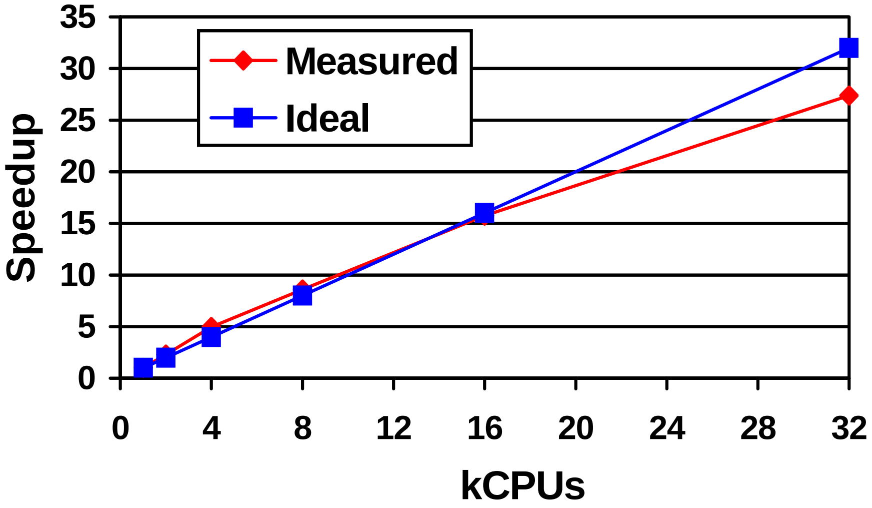

Figure 1: Strong scaling behavior measured on the BlueGene/L supercomputer using the Qbox first-principles molecular dynamics code for a simulation of 1000 atoms of molybdenum. A parallel efficiency of 86% is achieved between 1024 and 32768 CPUs. (From Ref. 15).

Obtaining good scalability of electronic structure simulation codes on large parallel platforms is challenging. New parallel architectures appear at regular intervals and force software developers to redesign their applications. In particular, data layouts adopted in some existing design often do not lead to good performance on a new architecture. This dependence of the efficiency on the details of the hardware is particularly damaging since it prevents software developers from building future codes on an infrastructure of reusable distributed objects. The development of efficient, reusable and parallel software components for electronic structure remains an important research topic to date.

3. Predictions: some examples

In the previous section, we have discussed the three key steps involved in performing quantum simulations: (i) choose theoretical approximations, (ii) devise algorithms to solve equations involved in the approximate, *ab-initio* theories; (iii) choose and control numerical integration techniques. Before describing some representative predictions, it is important to keep in mind that meaningful predictions relies on a thorough understanding and control of numerical accuracy. In addition, we note that when analyzing the results of QS, agreement with a well established set of experimental data is key for theory validation; however agreement with experiment is never a sufficient condition to judge simulation results, and in some cases it may be misleading, as we will illustrate with an example later in this Section. Finally, it is very important to always distinguish between performance of the theory and accuracy of numerical techniques; unfortunately this distinction-- essential to obtain meaningful predictions-- is often overlooked. As R.Laughlin writes in one of his paper on the limits of computations[16], "Simulations work in practice because they exploit higher-level organizing principles in nature. Good code writing requires faithfulness to these principles and the disciplines not to exceed their limit of validity".

We shall describe three types of applications: first we comment on the study of apparently simple fluids, such as hydrogen and water-- the melting line as a function of pressure, in the case of hydrogen and the structural and electronic properties of the fluid under ambient conditions in the case of water; in addition we will discuss the investigation of semiconductor nanostructures, with one question in mind, i.e. how to use QS to help define the identity of nanoparticles and relate their structure to desired "functions".

In the last 15 years, first-principles methods based on DFT have been extensively used to complement and help interpret high-pressure experiments and, in some cases, to investigate properties not directly accessible to experiment, as we shall see below. These methods can provide a detailed description of the structural and bonding changes that a material undergoes under extreme conditions, as well as predictions of melting temperatures (T) as a function of pressure (P). However, given the high computational cost in determining phase boundaries, first-principles simulations have been used in only a few cases to compute melting temperatures, and mostly for elemental substances. Recently, a simple yet accurate approach for the determination of melting temperatures has been proposed, called two-phase simulation method, which is based on the direct comparison of liquid and solid free energies; this comparison is achieved by performing constant-pressure, constant-temperature (NPT) MD simulations of slabs containing the two phases separated by an interface. Until two years ago, this technique had been applied only in the context of MD simulations using empirical potentials. The generalization to *ab-initio*, quantum simulations was carried out by Ogitsu et al. [17], with a first application to the melting of LiH under pressure.

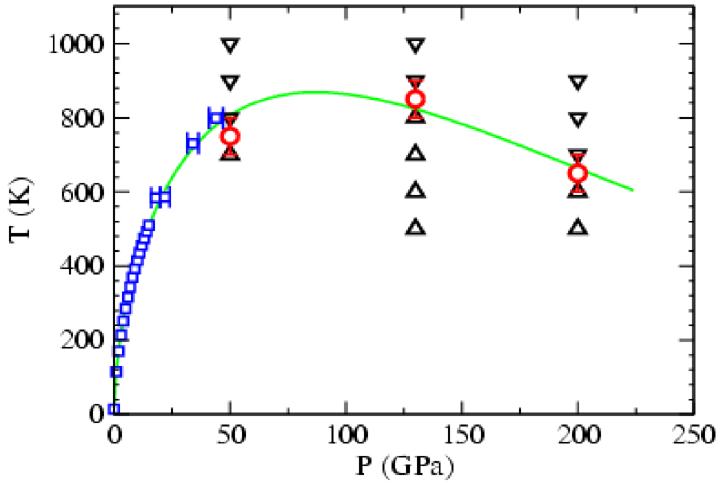

Figure 2: Melting temperature of hydrogen as a function of pressure. The blue dots represent experimental results and the red circles denote the results of *ab-initio* simulations [18]. The black triangles denote the two-phase simulations carried out in Ref. [18] to obtain the fluid melting temperature as a function of pressure. The green line is a fit to both experiment and theory to guide the eye.

Recently, Bonev et al. [18] applied the two-phase, *ab-initio* technique to the study of the melting line of hydrogen, predicting the melting temperature as a function of pressure up to compressions not yet reachable experimentally, and, in particular, predicting the existence of a maximum in the melting line of hydrogen (Fig.2). The existence of such a maximum further suggested that there could be a new phase of hydrogen at very low temperature and high pressure, a quantum fluid with possible super-fluid properties [19]. It has long been assumed that at high pressure solid hydrogen would transform directly to an alkali-like metal. However, some theoretical models suggest that compressed hydrogen may exhibit a liquid ground state or that it could be an unusual two-component (protons and electrons) low-temperature metallic fluid. The possibility of finding these new states of matter is conditional on the existence of a melting temperature maximum, as a function of pressure. To date, measurements of the hydrogen melt line up to 44~GPa have lead to controversial conclusions regarding the existence of this maximum. *Ab-initio* calculations [18] were able to establish the hydrogen melt line up to 200~GPa, and to predict that subtle changes in the intermolecular interactions as a function of pressure lead to a maximum in the melt line at about 90~GPa and 900 K. This implies that a transformation to a low-temperature quantum fluid may precede that to a monatomic crystal, as solid molecular hydrogen is compressed. The results of these simulations of hydrogen show that not only predictions about unknown portions of the phase diagram could be obtained using QS, but also suggestions, even if not proofs, of new states of matters could be evinced.

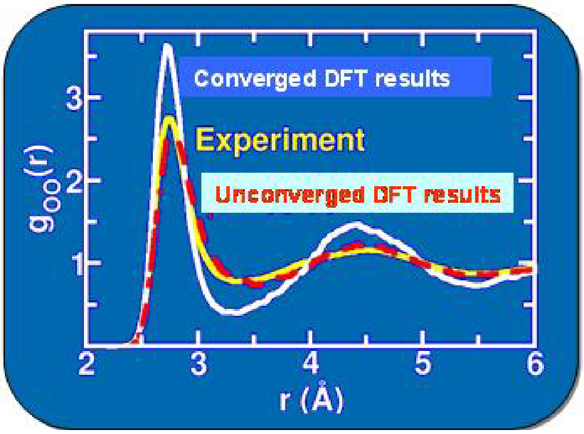

Figure 3: Oxygen-oxygen radial distribution function [goo] as a function of distance (r) for liquid water at the experimental equilibrium density and ~ 300 K, as obtained from experiment and in two different sets of simulations (see text and refs 20-21).

We now turn to the properties of another fluid, water, and we simply address the problem of determining its structure by *ab-initio* simulations. We will use this problem as an example of the importance of fully controlling numerical techniques, when performing simulations, and not to use comparison with experiment as the only way to judge the validity of the theoretical approximations used in the simulation. By performing a set of QS of water at ambient conditions (using either the Car-Parrinello method or direct minimization of the electronic ground state energy at each ionic step), Grossman et al. [20] and Schwegler et al. [21] could establish that in the absence of proton quantum effects, the agreement between DFT and experiment is only fair for the structural properties of water. This is at variance with numerous DFT results previously obtained for water with the same theoretical approximations but with numerical techniques which, unfortunately, were not properly converged. [The instances which led to a good agreement with experiment in the past are actually more complex than mere convergence issues; however, since it is not the scope of this work to report details, convergence issues are a good (although not precise) way to summarize the problem at hand in this case]. Fig.3 shows spatial distribution functions of oxygen in liquid water at the experimental density of 1. gr/cm^3 and about 300 K, illustrating the fortuitous agreement with experiment obtained with un-converged results. One of the implications of this agreement is, for example, that since classical Newtonian dynamics seemed to reproduce experiment rather well, proton quantum effects were expected not to be relevant in determining the structural properties of water at ambient conditions. This conclusion seems not to be holding any more, in light of Grossman's and Schwegler's results

[20-21], and of subsequent studies with path-integral simulations and classical potentials, indicating that proton quantum effects may be responsible for (part of) the disagreement found between DFT and experiment. Further studies to fully assess the performances of DFT in describing the structural properties of water and the relevance of proton quantum effects are underway. In the meantime, approximate but reliable [20-22] simulation protocols have been established to investigate solvation processes [23,24], water on surfaces [25,26] (see Fig.4), as well as confined states of the fluid.

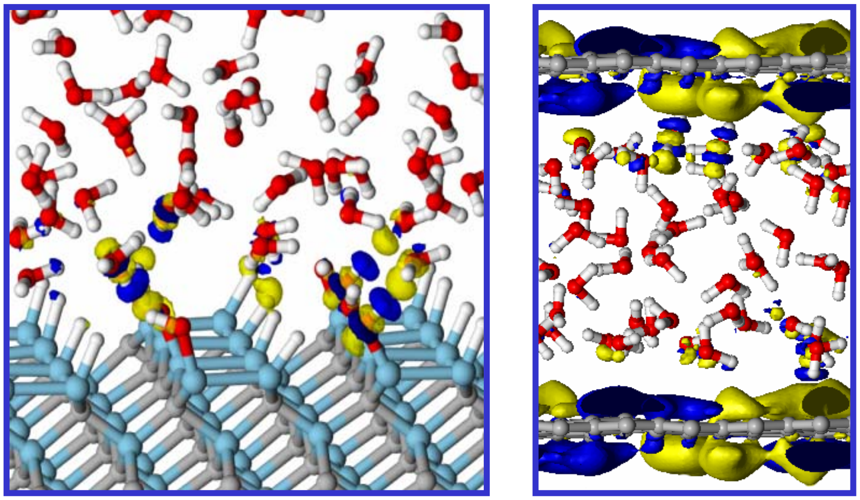

Figure 4: Ball and stick representations of snapshots of *ab-initio* simulations of water on a hydrophilic Silicon Carbide surface (right panel; ref. 25) and between two hydrophobic graphitic layers (left panel). Oxygen and hydrogen atoms are represented by red and white spheres, respectively; carbon and silicon by grey and light blue spheres. The iso-surfaces in gold and blue represent square moduli of selected electronic states.

We turn to the last example of this Section, e.g. prediction of nanostructure properties, with focus on small semiconductor nanoparticles of group IV. The upper part of Fig.5 shows structural models of bare nanodiamonds as obtained using *ab-initio* MD simulations [27]. These calculations have shown that, in the 1-4 nm size range, nanodiamond has a fullerene-like surface and, unlike silicon and germanium, exhibits very weak quantum confinement effects. These carbon nanoparticles characterized by a diamond core and a fullerene-like surface reconstruction have been called bucky diamonds. The proposed microscopic structure of bucky diamonds has been experimentally verified by a series of X-ray absorption and EELS measurements. In addition, *ab-initio* calculations of bare and hydrogenated nanodiamonds [28] have shown that at about 3 nm, and in a broad range of pressure and temperature, particles with bare, reconstructed surfaces become thermodynamically more stable than those with hydrogenated surfaces. These findings provided an explanation of the size distribution of extra-terrestrial nanodiamond found in meteorites and in outer space (e.g. proto-planetary nebulae) and of terrestrial nanodiamond found in ultradispersed and ultra-crystalline diamond films.

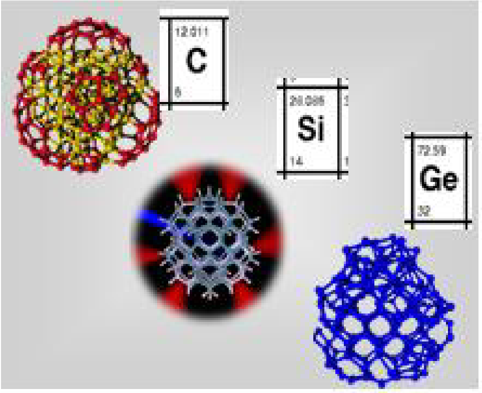

Figure 5: Carbon, Silicon and Germanium nanoparticles of ~ 1-2 nm diameter (see text) investigated using quantum simulations.

Carbon is unique among group IV elements in exhibiting very weak quantum confinement effects at the nanoscale, as recently studied in detail by a combination of DFT and QMC calculations [29]. Both Si and Ge (pictorially represented at the nanoscale in the middle and right hand side of Fig. 5) are known to present stronger quantum confinement (below 5-6 nm), although experimentally it has been difficult to understand the interplay between mere size reduction of the crystalline nanoparticle core and surface reconstruction effects. Using a combination of quantum Monte Carlo (QMC) and *ab-initio* MD techniques, the relative stability of Si nanoparticles (up to 2 nm) with reconstructed and unreconstructed surfaces has been predicted [30,31]. Interestingly, these simulations have permitted to identify reconstructions which are unique to the highly curved surfaces of nanostructured materials and could not be guessed by a simple knowledge of the structure of solid surfaces. In addition, a clear connection between structure and function has been established: for example, these calculations have shown that reconstructions of surface steps dramatically reduce the optical gap of hydrogenated Si dots, and decrease excitonic lifetimes, by localizing the band edge electronic states on the surface of the clusters. These predictions provided an explanation of both measured photoluminescence spectra of colloidally synthesized nanoparticles and observed deep gap levels in porous silicon. While surface reconstruction and some surface passivation (e.g. by oxygen) have been found to greatly influence the optical properties of Si dots, *ab-initio* MD simulations of solvation of oxygenated Si clusters in water [32] have shown no observable impact of the solvent. This is in contrast with blue shifts observed for several organic molecules in polar solvents and indicates that the vacuum optical properties of Si dots are preserved in the presence of water. This information is extremely important for possible applications of Si dots as sensors in aqueous environments.

The need for quantum simulations in investigations of group IV nanostructures is apparent, given current experimental difficulties encountered in synthesizing and characterizing most of these nanoparticles. In addition, QS play a very important role in understanding other systems (such as e.g. CdSe dots) which are better characterized experimentally. For example, *ab-initio* calculations [33] of the structural and electronic properties of CdSe nanoparticles (see Fig.6) have shown significant geometrical rearrangements of the nanoparticle surface while the wurtzite core is maintained. Remarkably these reconstructions, which are very different from those of group IV dots, are similar in vacuo and in the presence of ligands used in colloidal synthesis. Surface rearrangements lead to the opening of an optical gap even in the absence of passivating ligands, thus “self-healing” the surface electronic structure. These calculations provided microscopic models which opened the way to study the growth of both spheres and wires and eventually the surface functionalization of CdSe nanostructures [34].

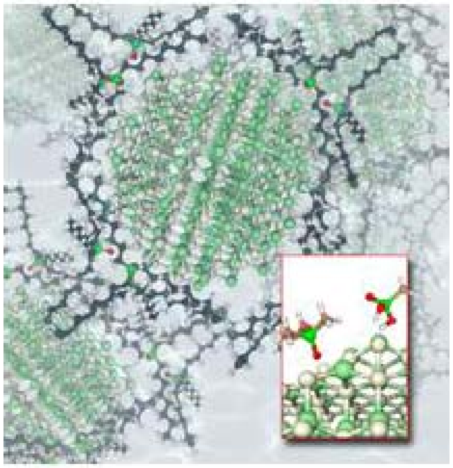

Figure 6: Ball and stick representation of CdSe nanoparticles (green and grey spheres) in a colloidal solutions (grey and black chain-like molecules). The inset shows a model ligand interacting with the surface of the nanoparticle. (See refs. 33 and 34).

One common and important point shown by the three examples on nanoparticles reported above is the unique ability of quantum simulations to separate different physical effects and assess their quantitative relevance in determining various properties (e.g. the relative importance of quantum confinement and surface structure in determining stability and optical gaps of semiconductor nanoparticles, or the relative importance of thermal disorder and solvation effects in determining electronic properties). This ability to discern between various physical effects is a unique feature of quantum simulations and it is an essential prerequisite to the development of materials design tools.

The nanostructures discussed above contain between 100 and 500 atoms and they are representative of what can be dealt with today with *ab-initio* MD and QMC tools. At present, state-of-the-art *ab-initio* molecular dynamics can treat systems with a few hundred atoms (200-500 depending on the number of electrons and the accuracy required to describe the electronic wave-functions) and simulation times of 10-100 ps (depending on the size of the systems involved). State-of-the-art Quantum Monte Carlo (QMC) codes using newly developed linear scaling algorithms [6] can now enable the calculation of the energy and optical gaps of sp-bonded systems with up to 100-300 atoms, as illustrated above in the case of Si clusters.

4. Quo vadis ?

It is now natural to ask about the future of Quantum Simulations. We estimate that in the next few years algorithmic developments (e.g. linear scaling methods [8-11]) along with an anticipated surge in computational power will enable *ab-initio* simulations of systems comprising 3000-4000 atoms for several picoseconds, as well as of systems comprising 200-300 atoms in the nanosecond range. In addition nearly linear scaling QMC calculations [14] of systems containing several thousand atoms, will be made possible with unprecedented levels of accuracy. This will permit realistic simulations of e.g., organic/inorganic interfaces found in nanoscale devices for bio-detection, transport properties of single-molecule electronic devices and semiconductor nanowires, the properties of magnetic systems at the nanoscale and in general of advanced materials.

Finally, the application of *ab-initio* MD and QMC techniques may extend beyond the traditional fields of condensed matter physics and physical chemistry into biochemistry and biology. In the next decade we expect quantum simulations to effectively enter the realm of biology and to tackle problems such as microscopic modeling of DNA repair mechanisms and drug/DNA interactions. In particular nearly exact QMC results may provide invaluable theoretical benchmarks that may help overcome some of the current limitations of experimental biology.

Although promising, quantum simulations still require important improvements, in order to provide tools that theoreticians and experimentally alike can use to design new materials, and many challenging problems remain to be solved. Besides the clear need for theoretical and algorithmic developments and complex code optimizations to adapt to new and changing platform architectures, new strategies need to be developed to best use these techniques in a way fully complementary to experiment. In particular, novel approaches to control the limit of validity of the theoretical approximations in a systematic way need to be developed, as well as ways to analyze, store and use data obtained from quantum simulations (including meaningful visualization tools and simulation data bases) need to be devised.

Progress in all of these areas will bring quantum simulations to be robust predictive tools for the design of new materials with targeted properties. In particular, large increases in computer power— together with efficient coupled classical/quantum-mechanical techniques (e.g. classical and *ab-initio* molecular dynamics and quantum Monte Carlo)— may enable the design of new materials, by generating a vast amount of accurate data to be used in configurational-expansion searches [35]. The creation of easily accessible libraries of *ab-initio* data for quantum design of materials will then allow one to predict systems with desired properties and quantities which are amenable to experimental validation.

Coming back to the title of this paper, we can safely say we are not there yet; as a matter of fact we have just started, and there are many, exciting challenges ahead of us.

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