Challenges in Modeling Materials Properties Without Experimental Input

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study of function via so-called QM/MM methods. Again, the issue of time scales is relevant because the QM part of the system often dominates the computation. Unless approximate QM methods are employed, it becomes very challenging to run MD trajectories long enough to achieve adequate sampling, even with multiteraflop machines (*9*). Thus, new methods to enhance the sampling of rare events (such as the bond breaking in catalysis) are needed to help alleviate this problem (*24*). Another example of a multiscale method is the linking of electronic-structure methods to finite element-engineering approaches (*25*) to probe phenomena occurring at defects. Such methods are also likely to find application in the world of chemical biology.

With the predicted relentless increase in available computer resources, remaining issues that arise in the investigation of complex supramolecular organization and related phenomena in biological systems may be resolved via multiscale methods. However, for the near future, many aspects of the time-scale problem are likely to persist and remain beyond the scope of brute-force AA-MD simulations, even on petaflop machines. Thus, for the near term, CG and multiscale models will proliferate and yield exciting new data (*7*). The application of large-scale MD to chemical problems will be dominated by chemical biology, but the key to future progress will probably reside in new methods and algorithm development (*24*–*26*). Brute-force computation alone is going to be insufficient. Thus, the field is also poised to profit from future developments in the area of more refined methods for multiscale modeling to enable the efficient bridging between the QM, AA, CG, and finite element approaches. Finally, we have not discussed large-scale electronic structure calculations, which have been particularly successful in materials science, leading to the design of new catalysts (*27*). In the context of chemical biology, new functionals, and empirical corrections for van der Waals dispersion forces (*28*), are extending the range of validity of density functional theory to treat the interaction between large molecules such as DNA bases with high accuracy, which is likely to herald a new era for computational chemistry (*29*).

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PERSPECTIVE

Challenges in Modeling Materials Properties Without Experimental Input

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Simulations of materials behavior are an important component of materials science research, partly because measurements are indirect, requiring theoretical interpretation, and partly because often the ideal experiment simply cannot be performed (due to technological limitations). Empirical physical models used in this context often rely on parameters drawn from experiments on simpler systems, and so introduce various inaccuracies. In contrast, a quantum mechanical model can potentially offer an independent source of data more closely attuned to the complexities of the system at hand. This Perspective reviews current quantum mechanics–based materials modeling approaches and their successes and limitations, and offers a view to the future.

Imagine a day when we can invent new materials on demand just by entering into a computer the elements we want to use, the specific property we want to optimize, and our cost constraints. We are not there yet. Discovery and design of optimal, inexpensive materials will require both experimentalists and modelers working together to characterize the properties of new candidate materials. To this end, the theorist's role must be to develop and apply robust and accurate techniques that are first validated against well-characterized materials and then applied to new ones. This Perspective outlines the current state of quantum mechanics (QM)–based modeling of materials behavior and the frontier challenges that remain (*1*).

The first question to answer is, why focus on QM-based simulations? There is clearly much to be learned from atomistic, mesoscopic, and continuum-level modeling, but all such models require assumptions to be made about the physical laws governing the behavior of the material. Those assumptions can be good, but they are usually based on measurements taken from known, often simpler, materials, with unknown uncertainty as to their accuracy when applied to more complex materials. For instance, even one level less refined than QM, the classical mechanics or "atomistic" level, requires input of interatomic interaction potentials. Such potentials constrain the physics predicted via choice of functional form and fitted data, and do not exist for all combinations of elements. By contrast, in principle QM simply requires input of the atomic numbers of the elements, with no assumption made other than that the laws of QM hold.

The second question is, what properties can QM actually predict? We're told that QM should be able to predict everything, but in practice, each QM technique has its own set of limitations, so it is important to consider what can be predicted correctly qualitatively, quantitatively,

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or not at all. Here's an undoubtedly incomplete list of material properties that can be obtained either directly from QM or by using the QM data in another theory: atomic-level structure of bulk crystals and interfaces; equations of state; phase diagrams; transition pressures; phase transition paths; melting points; elastic moduli; defect formation energies, including barriers to slip (dislocation nucleation); tensile and shear strengths at the nanoscale; fracture energies; phonon spectra; heat capacities; thermal expansion coefficients; thermal conductivity; electrical conductivity and conductance; magnetism; surface energies; and adsorption, desorption, diffusion, and reaction energetics, kinetics, and dynamics. Properties that QM cannot easily address are those that depend on complexities at larger length scales or integration over heterogeneities, such as plasticity in metals, and behavior of polycrystals or heterogeneous mixtures. For those, one must rely on multiscale modeling (*2*).

Unfortunately, no universal QM method exists that is appropriate for all materials and phenomena. Instead, we have a hierarchy of electronic structure techniques, all of which face a trade-off between accuracy and efficiency (Fig. 1). Ultimately, experimental validation of each theory is crucial, although it is difficult to design an experiment that measures exactly what was calculated (e.g., due to impurities and defects present in real samples).

We start with the most accurate: ab initio post-Hartree-Fock (HF) quantum chemistry (*3*) and quantum Monte Carlo (QMC) simulations (*4*). These methods incorporate the quantum mechanical effects of electron exchange (due to the Pauli exclusion principle) exactly and electron correlation (the motion of electrons is correlated to minimize repulsive forces) very accurately. No other physical approximations are made, both methods converge systematically toward exact solutions (within a fixed node approximation for QMC), and both provide properties of ground and excited electronic states. The fundamental difference between these two approaches is how observables are obtained. Ab initio post-HF quantum chemistry first solves for a many-electron wave function composed of the optimal linear combination of ground and excited state electron configurations expressed in terms of antisymmetrized products of orbitals, from which observables are then derived. QMC uses statistical sampling techniques to directly evaluate quantum mechanical observables, e.g., the energy. Ab initio quantum chemistry methods were developed initially to treat isolated molecules, whereas periodic QMC calculations on condensed matter came before applications to molecules. Three-dimensionally periodic post-HF methods are emerging, with second-order Møller-Plesset (MP2) perturbation theory as a first example (*5*). At present, other post-HF techniques have been used to study materials only via embedding schemes, in which a post-HF quantum chemistry calculation is performed on a cluster of atoms subjected to an embedding potential that accounts for the extended crystalline environment (*1*).

What are the main drawbacks of such methods? Foremost is computational expense. Post-HF quantum chemistry algorithms traditionally scale very poorly (where the required number of operations scale as N^5 or worse, for system size N) and QMC scales formally as $O(N^3)$ but with a large prefactor. Finite size effects turn out to be non-negligible in QMC, such that fairly large unit cells (at least tens of atoms) must be used to model a material, which adds to the cost. Encouragingly, the scaling of these methods has been reduced recently all the way to linear by the use of localized orbitals, local correlation, and integral screening techniques (*6*–*8*). On the other hand, these new methods calculate the wave function and energy but not forces on the nuclei in a linear scaling fashion. The latter is required to optimize structures and follow dynamics. Analytic gradients of post-HF energies have been available for decades, but such forces are very expensive. Only MP2 and various forms of multiconfigurational self-consistent field (MCSCF) forces are routinely used. QMC forces suffer not only from expense but also from the more fundamental problem of an infinite variance. However, recent clever renormalization and reweighting techniques have made accurate QMC forces available (*9*, *10*). A last challenge for QMC is treatment of transition metal–containing materials, which are problematic due to the highly oscillatory nature of the wave function; only a few examples of such calculations have appeared in the literature (*11*).

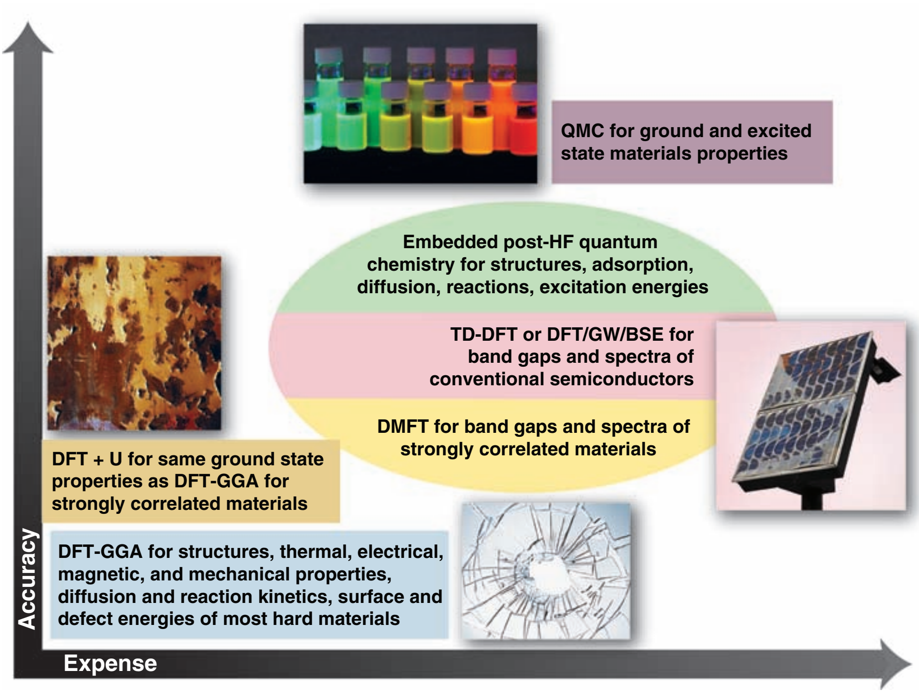

Fig. 1. Recommended quantum mechanics methods for various materials properties, distributed by accuracy and expense. The methods shown in the oval are comparable in cost and quality.

The more common family of methods for QM modeling of materials uses or builds upon density functional theory (DFT) (*12*), which is easily formulated with three-dimensional (3D) periodicity so that crystals can be simulated. It is much simpler and less costly than the methods above, solving either for a single-electron configuration in Kohn-Sham (KS) DFT (*13*) or, even simpler, solving for the density in orbital-free (OF) DFT (*14*). DFT is a formally exact ground state theory in which the material's energy is expressed as a functional of the electron density alone. However, two energy terms are usually approximated, because their exact density functional expressions remain unknown: the electron kinetic and exchange-correlation (XC) energies. Accurate electron kinetic energies require introduction of orbitals (*13*), which increases the algorithmic complexity from linear in OF-DFT to roughly cubic scaling in KS-DFT. However, for materials with a nonzero gap between occupied and unoccupied energy levels (the band gap), algorithms exist that recover linear scaling in KS-DFT above ~50 to 100 atoms (*15*). By contrast, OF-DFT can scale

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linearly for all sizes but presently is limited by available kinetic energy functionals to providing accurate structural predictions only for main-group metallic materials, such as sodium, aluminum, or magnesium alloys (*14*).

The primary disadvantage of current incarnations of DFT is the approximate XC functional. In contrast to post-HF and QMC methods, no systematic means to improve the XC functional exists. Much effort has been expended to derive approximate XC functionals, either by keeping the functional ab initio (obeying known sum rules, bounds, and other physical constraints), or by allowing the functional to become (semi)empirical (fitting parameters in a chosen functional to experimental data). For most ground state properties, the generalized gradient approximation (GGA) XC functionals, which come in both ab initio and semi-empirical flavors, provide sufficient accuracy (Fig. 1) (*16*).

More costly hybrid XC DFT-GGA techniques include some exact HF exchange, which improves the description of any material with a band gap (*17*), but is not appropriate for metals, because HF band energies exhibit an unphysical logarithmic singularity at the Fermi level (the energy level separating occupied from unoccupied states). Because metals have occupied states around the Fermi level, this artifact manifests itself by producing fictitious charge and spin density waves in metals (*18*). Use of hybrid XC for metals, and attendant claims of accuracy, is thus a case of getting the right answer for the wrong reason. DFT+U is a more refined yet far less costly version of hybrid XC that also introduces exact X, but only for localized open-shell electrons for which the "self-interaction error" (due to approximate X) is greatest, instead of for all electrons as in hybrid XC. The delocalized electrons are treated with standard XC density functionals (*19*). DFT+U theory greatly improves the description of materials with this mixed type of electron distribution. This materials class includes mid-to-late first row transition metal oxides and sulfides, because the self-interaction error is largest for such multiply charged (i.e., +2 or higher) open-shell metal ions. DFT+U theory does require selection of one parameter, U-J, the difference between intra-atomic Coulomb and exchange energies. Recently, a means to systematically calculate U-J was proposed that uses exact exchange within ab initio HF theory, to render DFT+U theory non-empirical and free from any self-interaction error in the determination of U-J (*20*, *21*).

To calculate electronic or optical spectra of materials, one must have methods that can accurately predict excited states in condensed matter. Time-dependent DFT (TD-DFT) provides excitation energies, electron energy loss spectra, and absorption spectra, albeit within linear response theory (and therefore is limited to single-electron excitations). TD-DFT calculations on crystals have been rare, although new, more accurate XC functionals accounting for long-range interactions may encourage its use (*1*, *22*). Ionization energies and electron affinities, photoemission and inverse photoemission spectra, and band structures and band gaps can be obtained by using the many-body Green's function method within the GW approximation (*23*). The GW method takes DFT orbitals and energies as input and solves DFT-like equations in which the usual XC potential is replaced with the "self-energy," which is the product of a single-particle Green's function G and a dynamically screened Coulomb potential W. Neutral single-electron excitation energies and optical spectra can be obtained from the Bethe-Salpeter equation (BSE) (*23*), which takes DFT and GW data as input and accounts for electron-hole interactions. The GW/BSE and TD-DFT methods rely on ground state DFT being a good starting point. For strongly correlated electron materials such as first row late transition metal oxides, DFT with standard XC fails badly, and the GW approximation also breaks down. In this case, either QMC, embedded ab initio post-HF methods, or dynamical mean field theory (DMFT) (*24*) may be useful for predicting excitation energies, all of which should be able to describe strong electron correlations properly.

With these details in mind, I consider the appropriate methods to use in order to predict a given property for a given materials class as a function of accuracy and expense (Fig. 1). DFT-GGA is the workhorse, usually delivering qualitatively correct results at reasonable cost for chemical properties (molecular and crystal structures, bonding, molecular adsorption and diffusion on surfaces, bulk diffusion of atoms, and reaction energetics) of most hard materials, including metal alloys and semiconductors. Embedded ab initio post-HF methods correct qualitative and quantitative errors in structure and energetics engendered by DFT-GGA, but at additional complexity and expense (*1*). Therefore, DFT-GGA or embedded post-HF quantum chemistry would be the method of choice, e.g., for optimization of a heterogeneous catalyst. DFT-GGA also can estimate intrinsic mechanical properties [adhesion and fracture energies, tensile strengths when properly rescaled (*25*)] of brittle materials such as ceramics, as long as they are not strongly correlated materials like the transition metal oxides discussed earlier. For the latter, ab initio DFT+U theory may provide the best estimates of such chemical and mechanical properties at the nanoscale. Therefore, if kinetics of rust formation in a steel pipe or magnetic properties of Cr and Fe oxides for memory devices are of interest, ab initio DFT+U theory is a good choice.

Mechanical properties of metals will not be predicted properly by any QM method, as these properties are governed by plasticity, i.e., the motion of higher length-scale defects such as dislocations and grain boundaries. However, atomic-scale processes involved in the creation of these defects, such as barriers to slip (to create a dislocation), can be calculated reliably. Dislocation and grain boundary motion in main-group metals can be simulated reliably with OF-DFT, which gives insight into plastic deformation of simple metals (*26*). Thus, understanding how precipitates in an Al alloy affect its hardness or formability for use in a car door or airplane wing could be examined with OF-DFT.

Band gaps, photoemission and inverse photoemission spectra, and optical spectra are best calculated via GW/BSE for most semiconductors except those that are strongly correlated, for which DMFT is the current method of choice. TD-DFT and GW/BSE can be used to calculate qualitatively reasonable optical and electronic spectra of semiconducting nanostructures. Thus, the development of new infrared detectors or new solar cell materials might make use of these methods. Electrical conductivity and conductance, as well as thermal properties, can be calculated by using DFT as input; discussion of these methods is beyond the scope of this article.

Predicting the behavior of molecular, soft, amorphous, or heterogeneous materials poses notable challenges. Interactions in soft materials or molecular crystals are determined in large part by van der Waals forces, which are not described properly by standard XC functionals in DFT. Recent work applying specialized XC functionals (*27*), GW (*28*), and periodic local MP2 (*5*, *29*) have the correct physics and show great promise for treating such dispersion forces. With such techniques, properties of materials composed of, e.g., polymers, colloids, and proteins, will be accessible with QM.

Amorphous structures are difficult to model with QM for two reasons: The usual 3D periodic boundary conditions introduce correlation length artifacts, and it is never certain that a random amorphous structure generated, e.g., by quenching a dynamics trajectory, will be a representative one, due to the huge mismatch in time scales associated with molecular dynamics (MD) simulations versus actual laboratory quench times. Applying accelerated MD methods that bridge time scales may resolve the latter issue (*30*); the former is best addressed by the continued development of ever more efficient linear scaling QM methods to treat larger periodic unit cells. Heterogeneous mixtures of materials offer perhaps the most severe challenge for future materials modeling: The large numbers of constituent atoms require linear scaling algorithms and the presence of multiple types of materials may require different methods to be used simultaneously.

Simulation of complex materials motivates the recent strategy in materials simulation of multiscale modeling (*2*), which aims to bridge length and/or time scales to make overarching predictions of materials behavior, e.g., the mechanical response of a macroscopic-sized polycrystal subjected to shock or evaluating the thermal or electrical conductivity of a heterostructure. The methods include coupled QM-MD/MC and QM-(quasi)continuum methods, coupled atomistic-mesoscale techniques (e.g., MD coupled to dislocation dynamics/grain boundary motion), phase field/level set descriptions of microstructure, and continuum models informed by data passed from smaller length scales. Major unsolved issues in this area include how to transfer heat and mass across all scales; how best to bridge time scales and to coarsen or refine representations seamlessly and adaptively, without introducing additional physical assumptions; how to quantify uncertainties in this mixed representation; and ultimately, how to extract new concepts and new nonempirical physical laws from such simulations.

So where are we now, regarding modeling materials properties without experimental input? Admittedly, we still typically start with guidance from experiment regarding approximate initial structure (e.g., crystal symmetry, coordination number) and composition (e.g., elements, stoichiometry) before beginning to make predictions (*31*). But given such guidance, the strength of QM is that we can provide insight into how properties will change as we change the composition and structure, thereby furthering atomic-scale manipulation of the design of materials. We can suggest ways to improve catalysts for fuel production or coatings to inhibit corrosion and to protect against extreme heat. We can characterize optoelectronic, magnetic, and mechanical properties of materials important for designing the next solar cell, iPod, or fuel-efficient vehicle. Among the remaining challenges is how to move QM from characterizing a homogeneous material to doing the same for heterostructures: Real devices and macroscopic objects use multiple materials that may require multiple QM methods and higher length-scale theories operating in concert to predict an overall signal from a device, be it a mechanical, electrical, optical, or thermal signature. This challenge, of heterogeneity and integration of information, is the next frontier.

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