

Coupled Quantum–Atomistic and Quantum–Continuum Mechanics Methods in Materials Research

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Abstract

The interface of quantum mechanics methods with classical atomistic simulation techniques, such as molecular dynamics and Monte Carlo, continues to be an area of considerable promise and interest. Such coupled quantum–atomistic approaches have been developed and employed, for example, to gain a comprehensive understanding of the energetics, kinetics, and dynamics of chemical processes involving surfaces and interfaces of hard materials. More recently, it has become possible to directly couple first-principles electronic structure techniques to continuum solid mechanics, either on the fly with feedback between length scales or by information passing between length scales. We discuss, with tutorial examples, the merging of quantum mechanics with molecular dynamics and Monte Carlo simulations, as well as quantum–continuum coupled techniques. We illustrate the opportunities offered by incorporation of information from quantum mechanics (reducing assumptions in higher length-scale models) and outline the challenges associated with achieving full predictive capability for the behavior of materials.

Introduction

Over the past few decades, theory/computation has firmly established itself as a partner to experiment in unraveling fundamental principles behind materials behavior. The ever-improving performance of computers and the development of accurate and efficient algorithms progressively bring predictive quantum mechanics models within reach. Nevertheless, full quantum mechanics treatments remain all but intractable at present for more than a few hundred atoms. Several schemes have been devised to couple quantum mechanics with less-expensive molecular mechanics or contin-

uum mechanics methods—conceptually, the molecular or continuum mechanics simulation region provides correct boundary conditions for the quantum mechanics region. While this coupling is motivated in part by necessity, the realization that it is unnecessary to use quantum mechanics to treat atoms that behave similarly provides further impetus for developing coupled methods.

This viewpoint presented may be thought of as a bottom-up approach to coupled models. One may also adopt the top-down point of view wherein the breakdown of continuum models at small

length scales necessitates the inclusion of additional physics from these smaller scales—this could be done by introducing microscopic parameters in the continuum model or, in cases where the coupling across scales is strong, by concurrent modeling at both scales. Whichever the point of view, coupled methods provide a powerful approach for *accurate* modeling of *realistic* situations with finite resources.

The building blocks of coupled schemes exist in well-honed numerical techniques at each length scale (Figure 1). At the quantum mechanics level, quantum chemistry approaches (e.g., configuration interaction or quantum Monte Carlo) provide the most accurate description of electronic structure. Unfortunately, their computational cost is still too high to be viable for quantum mechanics/molecular mechanics (QM/MM) coupling in the materials context. A more practical approach is density functional theory (DFT),^{1,2} which reduces the task of determining the many-electron wave function to a less-demanding problem of optimizing the electronic density. DFT is the method of choice for large systems, since it usually provides sufficient accuracy at a lower computational cost per atom. Traditionally, empirical potentials are used for molecular mechanics modeling. These potentials are typically fit to equilibrium properties and hence are less reliable far from equilibrium. *Ab initio* data are used increasingly to improve overall reliability, as will be discussed later. Nevertheless, processes such as bond formation, bond breaking, and charge transfer are best handled with quantum mechanics, leaving molecular mechanics to handle near-equilibrium situations. Finally, at the continuum level, the finite element method (FEM)³ continues to be the technique of choice, mostly due to the ease of modeling arbitrary geometries with wide-ranging boundary conditions. Defect kinetics (e.g., dislocation dynamics⁴⁻⁶) also can be included phenomenologically within FEM to produce mesoscopic-scale models.

This list of methods is by no means exhaustive. Computational materials science is an intersection of many disciplines, each of which has developed specialized tools at differing scales of interest. The challenge for coupling schemes lies in integrating these tools while making controllable approximations and without introducing spurious physics through *ad hoc* assumptions.

Coupled methods are broadly classifiable as either multiscale models seeking to couple two or more spatial and/or

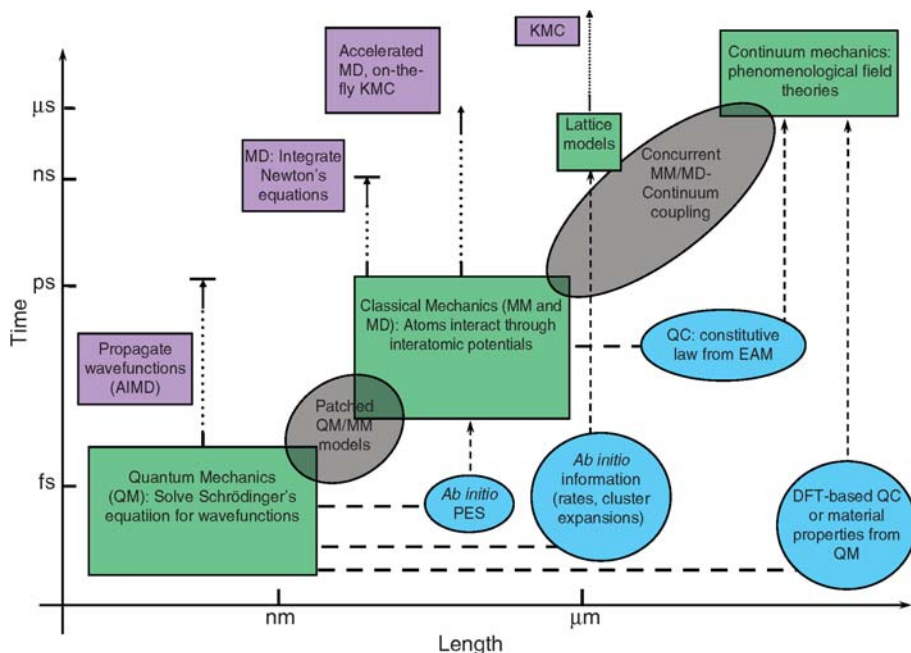


Figure 1. Schematic illustration of the coupling strategies discussed in this article. Representative length and time scales for each modeling strategy are indicated along the axes. Spatial modeling strategies are indicated in green boxes, time-stepping methods in purple boxes, direct coupling in gray ellipses, and sequential coupling (information-passing) in blue ellipses. Terminal points for time-stepping methods indicate the maximum time scales that are accessible in practice. Abbreviations used in this figure: AIMD, *ab initio* molecular dynamics; DFT, density functional theory; EAM, embedded atom method; KMC, kinetic Monte Carlo; MD, molecular dynamics; MM, molecular mechanics; PES, potential energy surface; QC, quasi-continuum; QM, quantum mechanics.

temporal scales; or multiphysics models where different physical descriptions, not necessarily at different scales, are coupled. In this article, we will focus attention on issues related to quantum-based multiscale methods. Our aim is not to provide a comprehensive review, which may be found in several excellent articles and proceedings,^{7–9} but rather to provide examples that address the twin issues of methodology and capability.

Improved Continuum Modeling through Quantum Mechanics Methods

Continuum theories have a well-established tradition within the engineering community. The limitations of continuum approaches in materials modeling are also well recognized—notable examples, among others, include the lack of a fundamental failure criterion and the inability to predict structural and dynamic aspects of defects (dislocations, grain boundaries, etc.). The solution to these problems typically involves the inclusion of additional physics, often in an *ad hoc* manner (e.g., cohesive zone models for fracture,^{10–12} regularization for dislocation cores,^{13,14} etc.).

Informed Continuum Models

The simplest remedy for the deficiencies of continuum models is to construct “informed” models (sequential multiscale models) where the material response is calibrated from a more fundamental model and propagated to higher length scales. Tadmor et al.’s¹⁵ characterization of the electromechanical response of a piezoelectric crystal (PbTiO_3) is illustrative. They built a quantum mechanical Hamiltonian—in essence, a constitutive model—for a finite element calculation. In this case, the Hamiltonian spanned the neighborhood of phases of interest and the barriers between these phases, which they deemed an adequate description of the energy landscape for their purposes. The model yielded qualitatively correct results for the highly nonlinear, hysteretic behavior of these materials and provided insight into the underlying microscopic mechanisms.

Another example of a continuum model informed by quantum mechanics is the work of Serebrinsky et al.¹⁶ on crack propagation in hydrogen-embrittled steels (Figure 2). Fracture is modeled within continuum approaches through an empirical “cohesive law” that allows for

the smooth decohesion of atomic planes at the crack tip, thereby enabling crack propagation. Hydrogen preferentially segregates to crack faces and the incipient fracture zone. The first-principles decohesion data^{17,18} and a renormalization procedure^{19,20} produced a realistic hydrogen-dependent cohesive law. Their findings on crack initiation times and dependence on applied stress intensity and yield strength were in agreement with experimental trends, as were their observations on intermittent crack growth. The main outcome was to demonstrate that hydrogen-induced decohesion could be a dominant fracture mechanism of steels in aqueous environments.

The primary criticism of informed continuum models is the *a priori* assumption of “important” physics that invariably goes into the upscaling procedure. In the effective Hamiltonian approach, this occurs by restricting the functional dependence to certain parameters and to a particular region of the overall energy landscape. In the hydrogen embrittlement scenario, competing mechanisms (e.g., interaction of dislocations with crack tips, hydrogen trapping at dislocations) other than coverage-dependent decohesion are either ignored or treated approximately at best. Nevertheless, such models do have a role to play in imparting qualitative first insights into microscopic mechanisms underlying macroscopic observations. We are working on ways to incorporate mechanisms other than coverage-dependent decohesion to provide more sophisticated models of embrittlement.

Direct Ab Initio–Continuum Coupling

A more rigorous and conceptually appealing procedure to remedy the limitations of continuum models is to explicitly model the material at various requisite length scales with feedback between these scales. Relevant pioneering work by Ortiz, Phillips, and co-workers (see Reference 21 and references therein) focused on coupling FEM and atomistic calculations. Their technique, the quasi-continuum method, has found several applications and has undergone much refinement over the last decade or so. The original quasi-continuum method is based on constrained minimization of an atomistic energy, obtained from an empirical potential, with the ability to adapt the computational mesh to the deformation field. The latter feature enables a seamless transition from a fully atomically resolved material to a discretized continuum, as long as the empirical potential is short-ranged. We refer the reader to the companion article in

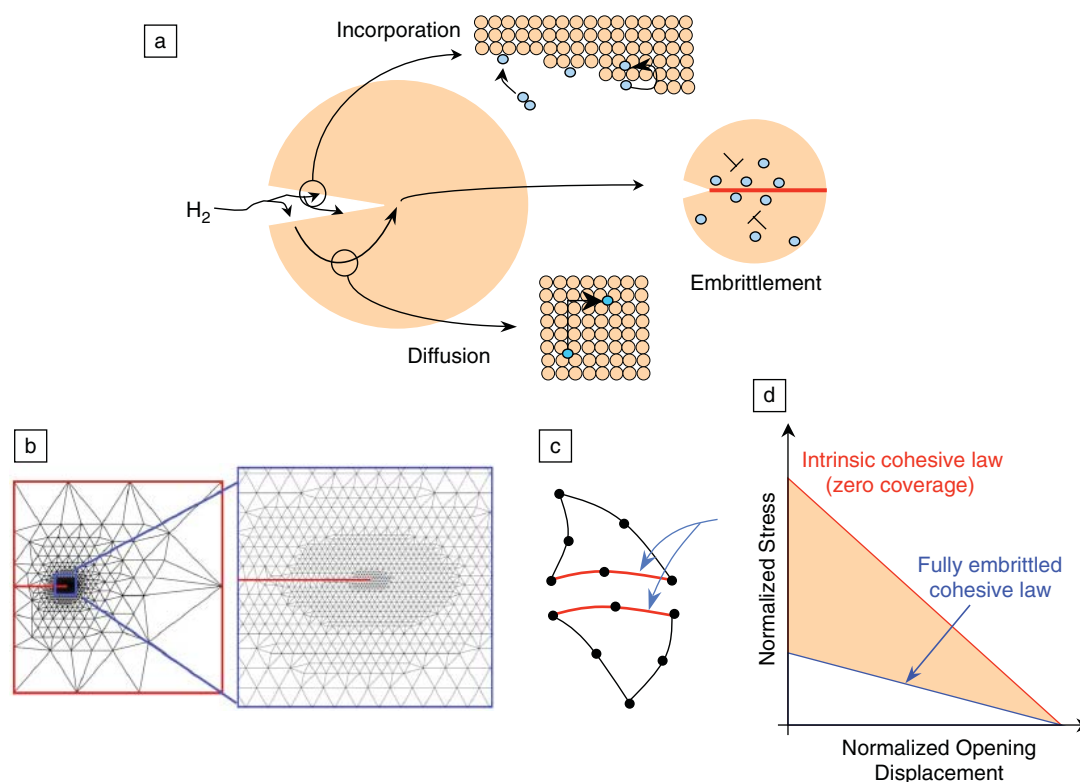


Figure 2. Schematic illustration of hydrogen embrittlement in metals. (a) Some individual processes involved in embrittlement: a preexisting crack is attacked by hydrogen from an external source, e.g., hydrogen molecules dissociate and adsorb on the crack flanks; some of the adsorbed atoms are absorbed in the bulk and can diffuse under stress gradients; accumulation of hydrogen near the crack tip lowers cohesion among host atoms near the crack tip and eventually leads to failure. (b) Finite element mesh with high resolution at crack tip. (c) Cohesive elements surrounding the crack tip. (d) The coverage-dependent traction–separation law that governs the behavior of the cohesive elements. The intrinsic cohesive law (no hydrogen) and the fully embrittled cohesive law (complete hydrogen coverage) are indicated; intermediate levels of coverage fall within the shaded region. (After Serebrinsky et al.¹⁶)

this *MRS Bulletin* issue by Tadmor and Miller for more details.

Another approach developed by Kaxiras, Abraham, and co-workers,^{22,23} dubbed “macroscopic atomistic *ab initio* dynamics” (MAAD), couples FEM with an atomistic region, which in turn is described by a combination of empirical potentials and quantum mechanics at the level of tight-binding. Different regions in the simulation interact with each other through interfaces or “handshake” regions. The construction of these handshake regions is not unique and requires special care to avoid discontinuities and wave reflections. MAAD was used successfully to simulate brittle crack propagation in silicon. The tight-binding region adaptively tracked the crack tip where increased accuracy, beyond the scope of empirical potentials, is required to describe bond breaking. At the time MAAD was presented, adaptive refinement of the continuum region or defect propagation between the atomistic and continuum region was not possible. Also,

the use of tight-binding at the crack tip (mostly appropriate for localized electronic densities) makes the extension to metallic systems problematic; recent work by Lu et al.²⁴ attempts to rectify this situation by replacing tight-binding with DFT (albeit within a quasi-continuum framework, rather than MAAD). On the other hand, the quasi-continuum method suffers from the lack of transferability of empirical potentials, especially in far-from-equilibrium situations. These shortcomings motivate direct coupling of quantum mechanics to FEM.

Nanoindentation tests are routinely used to evaluate the response of thin films and the onset of plastic flow in small volumes.^{25,26} Simulations can facilitate a deeper interpretation of these tests through analysis of individual events occurring during indentation. Computational challenges involve modeling realistic indenter and sample sizes, large deformations of the material, nucleation and interaction of dislocations below the indenter, and thermal effects, among others. Recently, Fago et al.²⁷

and Hayes et al.^{28,29} extended the quasi-continuum method to study nano-indentation of aluminum, and aluminum magnesium alloys (Al₃Mg), wherein the atomistic regions, normally described in the quasi-continuum method by empirical embedded-atom method (EAM) potentials, were replaced by quantum mechanics regions. To render the quantum mechanical calculations computationally affordable, they used orbital-free density functional theory (OFDFT),³⁰ which scales linearly with size, as opposed to traditional Kohn–Sham density functional theory (KSDFT), which scales cubically. For metals, OFDFT is 3–5 orders of magnitude faster than KSDFT. Their findings on the onset of dislocation emission—reported in terms of the nucleation site, indenter displacement, and load—were at significant variance with quasi-continuum calculations using EAM potentials (Figure 3). This is not surprising, since empirical potentials such as EAM potentials that are fitted to equilibrium properties cannot be expected to correctly capture behavior at large

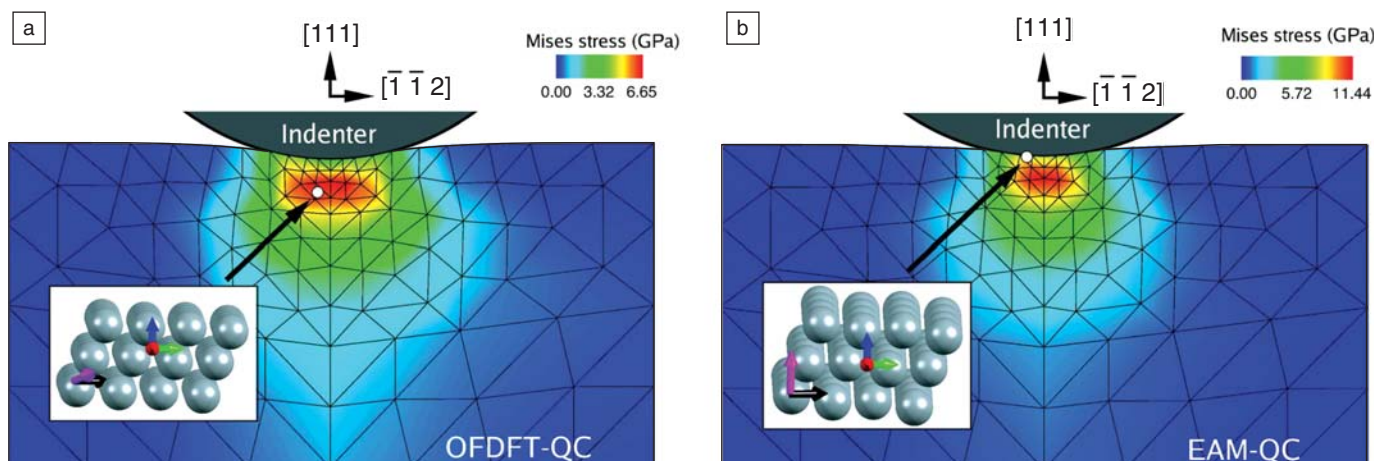


Figure 3. Nanoindentation along the $[111]$ direction of a $2\ \mu\text{m} \times 1\ \mu\text{m} \times 1\ \mu\text{m}$ Al sample using both (a) OFDFT- and (b) EAM-based quasi-continuum methods. The OFDFT calculation predicts nucleation of a dislocation at 50 nm indentation at a distance of $0.15\ \mu\text{m}$ below the indenter, whereas EAM predicts nucleation at 35 nm indentation and at $0.04\ \mu\text{m}$ below the indenter. The magenta and black arrows in the insets indicate the slip plane normal and Burgers vectors, respectively—both EAM and OFDFT predict the formation of $[0\bar{1}1]$ dislocations, but the slip planes are (111) for the former and $(\bar{1}11)$ for the latter.²⁷

deformations. However, the DFT-based quasi-continuum method is not yet developed to the point where the EAM-based approach is obsolete. Chief among the present limitations is the restriction to periodic OFDFT calculations. Consequently, the finite element mesh cannot be resolved down to individual atoms, which would then need to be handled as nonperiodic clusters. Also, at present, only metals are well described by OFDFT, and transferability to other materials (through improved pseudopotentials^{31,32} and kinetic energy functionals³³) remains a matter of current research.

Finally, we mention briefly the work of Woodward and co-workers,^{34–36} who have employed Green's functions in conjunction with quantum mechanics methods to simulate isolated dislocations in bulk metals and alloys. While there is no explicit coupling of continuum and quantum mechanics regions, the Green's functions in effect mimic the continuum by providing appropriate boundary conditions to the quantum mechanics region. This approach eliminates the overhead of a finite element calculation. Reference 36 provides an interesting application of this method to solid-solution softening in bcc metals.

Coupled Quantum Mechanics/Molecular Mechanics Approaches: Extending Length and Time Scales

Quantum mechanics provides high accuracy in materials models, albeit at a high computational price per atom. This naturally leads to a limit on system sizes amenable to quantum mechanics

treatment. A more serious restriction arises in dynamics simulations (e.g., the Car–Parrinello³⁷ or Born–Oppenheimer^{38–40} methods) from the inherently small time steps required to stably integrate the equations of motion, not to mention the expense of frequent quantum mechanics force evaluations. Hence, from a practical perspective, *ab initio* molecular dynamics (AIMD) can be used only for studying short-time-scale phenomena (e.g., picoseconds). Also, it is still beyond the reach of AIMD to gather reliable statistics, which require hundreds to thousands of trajectories. Accordingly, AIMD trajectories should be treated as anecdotal rather than definitive. Nevertheless, AIMD, with its accuracy and predictive capability, has come to be an important addition to the arsenal. In particular, DFT-based AIMD enjoys greater applicability, due to its lower cost, and has been applied to a wide spectrum of problems such as surface and interface chemistry, catalysis, chemical reactions, reactions in solution, solvation of proteins, and proton transfer in biomolecules. A recent comprehensive review on the theory and applications of AIMD may be found in Reference 41. The interested reader might also wish to peruse reviews on surface chemistry⁴² and applications to molecules.⁴³ Here, we focus only on examples that seek to extend the length and time scales of *ab initio* methods.

Ab Initio–Derived Molecular Dynamics

We first consider the approach of *ab-initio*-derived potentials. This is the atomistic analogue of an informed continuum

model. The basic idea is to produce an analytical expression for the potential energy surface, whose parameters are fit to data obtained from *ab initio* calculations, in distinct contrast to the empirical approach of using experimental material properties. Experimental observables represent a thermal sampling of a limited set of configurations within the experimentally accessible phase space. Hence, empirical potentials typically suffer from a lack of transferability; that is, they can only be relied upon to accurately reproduce regions of the potential energy surface to which they were fit. Situations often arise where experimental data are not available or cannot be produced (e.g., for oxides in the Earth's mantle or radioactive waste); *ab initio* calculations provide the only viable route for designing potentials under these circumstances. The main challenge lies in designing a potential that is accurate, transferable, and, if possible, computationally inexpensive—fitting a good potential is as much an art as it is a science. Thereafter, the well-honed machinery of molecular dynamics can be brought to bear upon the problem.

An early example of *ab initio* potentials used with molecular dynamics examined fluorine reactions with silicon surfaces.^{44,45} The parameters of the classical Stillinger–Weber potential were refit for *ab initio* data on Si–F interactions. The new potential accurately captured the initial stages of etching silicon. Additionally, new phenomena were predicted, such as local-heating-induced disorder at the silicon surface caused by the reaction's high exothermicity, which was subsequently

verified experimentally. The key point of this example is that even refitting an empirical potential to accurate *ab initio* data can lead to a much improved potential energy surface and enhanced modeling capability.

Other instances exist of increasingly sophisticated interatomic potentials derived from *ab initio* methods. For example, Madden and co-workers⁴⁶ developed techniques for ionic materials. Their potentials account for many-body effects via multipole expansions and coordination-dependent parameters such as ionic radii. Potential fitting is achieved via molecular dynamics and quantum mechanics calculations across a range of states and fitting parameters to minimize discrepancies between the two methods, thus ensuring transferability. The availability of quantum mechanical information for various states allows one to increase or decrease the complexity of a potential and thereby ascertain the importance of different physical effects. For covalently bonded materials, Goddard and co-workers^{47,48} developed reactive potentials (dubbed ReaxFF for “reactive force field”) fit to data sets derived from *ab initio* calculations on clusters and condensed phases. The key ingredient is the notion of a “bond-order” parameter updated continuously from instantaneous interatomic positions, which allows for bond creation and dissociation. The ability to handle bond formation and breaking, albeit more approximately than true *ab initio* methods, greatly enhances an interatomic potential’s capability to simulate surface reactions, interfaces in materials, and proteins in solution, among others. An application to dynamic fracture is found in Buehler et al.’s work.⁴⁹

Finally, in the context of potential fitting, Csányi et al.^{50,51} recently presented a “learn-on-the-fly” strategy. The idea is to use *ab initio* methods as a “black box” from which information can be gleaned during the course of a simulation. The algorithm starts by using a simple empirical potential to evolve a short molecular dynamics trajectory (“predictor phase”). The validity of the potential is then tested, particularly in defective regions of the crystal, with respect to a more accurate method (tight-binding or DFT), and the parameters are refitted locally to minimize errors in the forces. The molecular dynamics trajectory is then rerun (“corrector phase”) with an interpolation of the potentials between the initial and new values. The approach’s efficacy has been demonstrated thus far for defects in silicon; localized covalent bonds in silicon allow the use of small cluster models in

the *ab initio* calculations. The extension to metals, which has not yet been done, is more delicate, since the delocalized electron distribution would necessitate a more elaborate embedding scheme.⁵² Also, varying the interatomic potential amounts to using a time-varying Hamiltonian that does not conserve energy. Hence, simulations must be run in the canonical (constant NVT, where N is the number of particles, V is their volume, and T is their temperature) ensemble with a thermostat. Nevertheless, the method’s advantage lies in eliminating the need for patching through handshake regions or, alternatively, the need for elaborate interatomic potentials that will be less accurate than the parent *ab initio* method. On the other hand, the on-the-fly potential, as with all analytical potentials, is forever limited by choice of functional form, which will constrain behavior that can be observed.

Quantum-Based Kinetic Monte Carlo Methods

Kinetic Monte Carlo (KMC) methods^{53,54} are a stochastic way of extending time scales in simulations. When combined with a spatial coarse-graining procedure, this additionally leads to a method of bridging length scales. Examples of applications of KMC to materials modeling abound—one that encompasses several modeling techniques is the recent work of Reuter and co-workers,^{55,56} who used KMC to study oxidation of CO to CO₂ on RuO₂. The relevant processes, such as molecular adsorption and recombinative desorption, are thermally activated rare events, not easily accessible to direct simulation. DFT was used in combination with transition-state theory to obtain process rates. Surface binding sites were modeled as a simplified lattice, since these were clearly identifiable, and KMC was performed. A similar approach, employing configuration interaction instead of DFT to obtain rates, was used earlier⁵⁷ for studying hydrogen desorption from silicon. The key outcome of the DFT KMC work was the ability to predict phase diagrams and pressure-dependent turnover frequencies (a measure of catalytic performance), which agreed with experiments over wide ranges of temperature and pressure.

The main drawback of KMC is the lack of true time evolution, in contrast to molecular dynamics. Accordingly, interest abounds in developing accelerated methods that extend molecular dynamics to long times—the review by Voter et al.⁵⁸ provides seminal details. Also, restricting myriad processes to predetermined events is fraught with danger, as important non-

intuitive processes may be overlooked. Feibelman⁵⁹ provided the cautionary tale: the commonly assumed surface diffusion mechanism for metals (direct hops) is incorrect; instead, diffusion occurs by concerted motion of two atoms. The most reliable way to overcome this serious deficiency is to employ on-the-fly KMC methods that only utilize information about the current state and then exhaustively determine connected transition states.^{60,61} The high computational cost of on-the-fly KMC, however, makes it impractical for use with *ab initio* methods. The use of *ab-initio*-derived potentials, possibly in conjunction with a self-learning procedure,⁶² may render such methods very effective.

Concluding Remarks

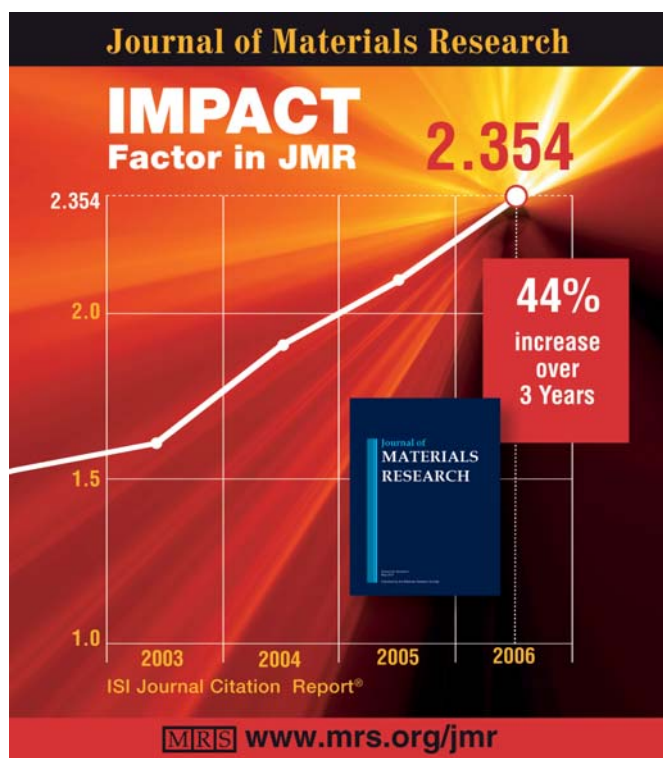
In this short review, we attempted to give a flavor of quantum-based multiscale/multiphysics methods. It is by no means comprehensive; most glaringly, we omitted discussion of patched quantum mechanics and molecular mechanics (QM/MM) methods.^{63–65} We also limited our attention to hard materials, which is a small subset of materials research.

In conclusion, much work remains to extend quantum-based multiscale/multiphysics methods to full realism and accuracy. We believe the solutions lie not just in greater computing power (always at a premium), but primarily in theoretical and algorithmic work that spans disciplines.

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