Quantum Simulation of Materials at Micron Scales and Beyond
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The ability to perform quantum simulations of materials properties over length scales that are relevant to experiments represents a grand challenge in computational materials science. If one could treat multi-millions or billions of electrons *effectively* at micron scales, such first-principle quantum simulations could revolutionize materials research and pave the way to the computational design of advanced materials. There are two principal reasons why quantum simulations at relevant experimental scales are important. First of all, it allows a direct comparison between theory and experiment. Secondly, quantum simulations at larger scales are essential even for extended bulk crystals where periodic boundary conditions may be used. This is due to the fact that a real bulk solid always contains lattice defects (or impurities) whose interactions are long range - dislocations being the prominent example. An insufficiently large periodic unit cell would lead to unrealistically high concentrations of defects and/or impurities, rendering the results of such simulations questionable.

We propose a multiscale approach that is based *entirely* on density functional theory (DFT) and allows quantum simulations at the micron scale and beyond. The method, termed QCDFT, combines the coarse graining idea of the quasicontinuum (QC) approach and the coupling strategy of the quantum mechanics/molecular mechanics (QM/MM) method, and represents a major advance in the quantum simulation of materials properties. It should be stated at the outset that QCDFT is *not* a brute-force electronic structure method, but rather a multiscale approach that can treat large systems - effectively up to billions of electrons. Therefore, some of the electronic degrees of freedom are reduced to continuum degrees of freedom in QCDFT. On the other hand, although QCDFT utilizes the idea of QM/MM coupling, it does not involve any classical/empirical potentials (or force fields) in the formulation - the energy calculation of QCDFT is entirely based on orbital-free DFT (OFDFT). This is an important feature and advantage of QCDFT, which qualifies it as a bona fide quantum simulation method.

QCDFT is formulated within the framework of the QC method, which models an atomistic system without explicitly treating every atom in the problem [1, 2]. This is achieved by replacing the full set of N atoms with a small subset of N_r "representative atoms" or *repatoms* ($N_r \ll N$) that approximate the total energy through appropriate weighting. Atoms experiencing large variations in the deformation gradient field on an atomic scale are computed in the same way as in a standard atomistic method and these atoms are called *nonlocal* atoms to reflect the fact that their energy depends on the positions of their neighbors in addition to their own position. In contrast, the energies of atoms experiencing a smooth deformation field on the atomic scale are computed based on the deformation gradient $\{\mathbf{G}\}$ in their vicinity as befitting a continuum model. These atoms are called *local* atoms because their energy is based only on the deformation gradient

at the point where it is computed. The basic assumption employed is the Cauchy-Born rule, which relates the continuum deformation at a point to the motion of the atoms in the underlying lattice represented by this point.

The calculations of energy and stress in the continuum regions is based on OFDFT, which is the same energy formulation used in the nonlocal atomistic region. This makes the passage from the atomistic to continuum regions seamless since the same underlying material description is used in both. OFDFT is an efficient implementation of density functional theory which approximates the kinetic energy of noninteracting electrons in terms of their density, instead of the KS orbitals [3]. In OFDFT, the total energy is expressed as an explicit functional of electron density $\rho(\mathbf{r})$:

$$E_{\mathrm{OF}}[\rho] = T_{\mathrm{s}}[\rho] + E_{\mathrm{H}}[\rho] + E_{\mathrm{e-i}}[\rho] + E_{\mathrm{xc}}[\rho] + E_{\mathrm{i-i}}. \tag{1}$$

The various terms in Eq. (1) represent the non-interacting electronic kinetic energy, the Hartree electron repulsion energy, the electron-ion attraction energy, the electron exchange-correlation energy, and the ion-ion repulsion energy, respectively.

The energy and force of each local repatom can be obtained from the strain energy density and the stress tensor of the finite elements that share the same repatom. More specifically, according to the Cauchy-Born rule, the deformation gradient $\mathbf{G}$ is uniform within a finite element, therefore the local energy density ε and the stress tensor for each finite element can be calculated as a perfect infinite crystal undergoing a uniform deformation specified by $\mathbf{G}$. In other words, one could perform an OFDFT-based energy/stress calculation for an infinite crystal by using periodic boundary conditions with the primitive lattice vectors of the deformed crystal. Once the strain energy density $\varepsilon(\mathbf{G}_k)$ is determined, the energy contribution of the jth local repatom is given as

$$E_j^{\mathrm{loc}}(\{\mathbf{G}\}) = \sum_{k=1}^{M_j} w_k \varepsilon(\mathbf{G}_k) \Omega_0, \tag{2}$$

where M_j is the total number of finite elements represented by the jth repatom, and w_k is the weight assigned to the kth finite element. The force on the jth local repatom is defined as the gradient of the total energy with respect to its coordinate $\mathbf{R}_j^{\mathrm{loc}}$.

For the energy/force calculation in the nonlocal region, we resort to a novel QM/MM approach that was developed recently for metals [4]. The coupling between the QM and MM regions is achieved quantum mechanically within an OFDFT formulation. We wish to stress two important points here: (1) The original QC formulation assumes that the total energy can be written as a sum over individual atomic energies. This condition is not satisfied by quantum mechanical models. The total energy of QCDFT should be expressed as:

$$E_{\mathrm{tot}}^{\mathrm{QCDFT}} = E^{\mathrm{nl}}[\rho^{\mathrm{tot}}] + \sum_{j=1}^{N^{\mathrm{loc}}} n_j E_j^{\mathrm{loc}}(\{\mathbf{G}\}). \tag{3}$$
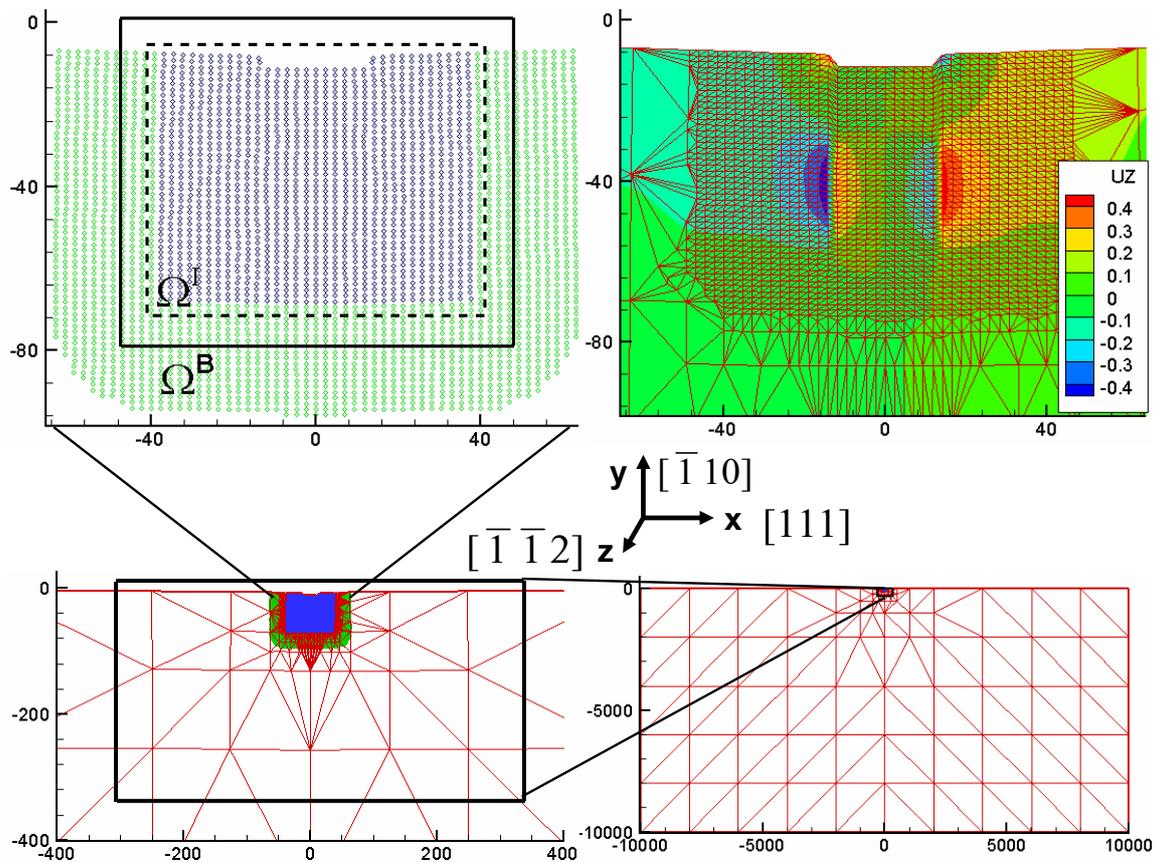
Figure 1: (Color online) The overview of the entire system and domain partition in QCDFT with nanoindentation as an example. The x, y and z axes are along [111],[$\bar{1}$10], and [$\bar{1}\bar{1}$2], respectively. Ω^{I} and Ω^{B} are 2.8 Å and 8 Å beyond the non-local region in $\pm x$ and $\pm y$ directions, respectively [4]. The colors indicate u_z, the out-of-plane displacement of atoms in the z-direction.

Here ρ^{tot} is the total electron density in the nonlocal region as well as the coupling nonlocal/local region i.e., the buffer region in the following discussion. (2) The nonlocal energy, E^{nl} should be calculated with appropriate boundary conditions; that is to say, it should include the interaction energy between the nonlocal atoms and neighboring local atoms. In the original QC framework, this requirement is realized by including dummy atoms in the energy/force calculation of a given nonlocal repatom. These dummy atoms are in the local region and within the cut-off radius of the given nonlocal repatom. The dummy atoms are not independent degrees of freedom in the local region, but rather slaves to the local repatoms. In this way, the nonlocal calculation is carried out with the appropriate boundary conditions, and at the same time, the energy of the dummy atoms is still treated with the Cauchy-Born rule, consistent with their status. In the QCDFT approach, a buffer region including the dummy atoms and local repatoms that are adjacent to the nonlocal repatoms is selected as the "MM" region, and the nonlocal

atoms constitute the QM region. The nonlocal atoms are treated by OFDFT, and the coupling between the "MM" and QM region is also formulated within OFDFT. Therefore the entire system is formulated with one energy functional, OFDFT. Note that "MM" here is actually a misnomer: the local atoms are treated by OFDFT with the Cauchy-Born rule as mentioned earlier, and we retain the designation "MM" solely to indicate the similarity to the earlier coupling scheme [4].

The present QCDFT approach is applied to nanoindentation of an Al thin film resting on a rigid substrate with a rigid knife-like indenter. The crystallographic orientation of the system is displayed in Fig. (1). The size of the entire system is $2\,\mu m \times 1\,\mu m \times 4.9385$ Å along the [111] (x direction), the [$\bar{1}$10] (y direction), and the [$\bar{1}\bar{1}$2] (z direction), respectively. The system is periodic in the z-dimension, has Dirichlet boundary conditions in the other two directions, and contains over 60 million Al atoms - a size that is well beyond the reach of any full-blown brute-force quantum calculation. The simulation is performed quasistatically with a displacement control where the indentation depth (d) is increased by 0.2 Å at each loading step. The final configurations were achieved by the relaxation of all repatoms using a conjugate gradient method until the maximum force on any repatom is less than 0.03 eV/Å.

The QCDFT results are validated by comparing against conventional QC with a OFDFT-refined EAM potential. The results suggest that QCDFT is an excellent method which represents a new direction for quantum simulation of materials properties at length scales relevant to experiments.

<div align="center">REFERENCES</div>

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Continuum approximation of the Peach-Koehler force on dislocations in a slip plane

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We derive a continuum model for the Peach-Koehler force on dislocations in a slip plane. To represent the dislocations, we use the disregistry across the slip plane, whose gradient gives the density and direction of the dislocations. The continuum model is derived rigorously from the Peach-Koehler force on dislocations in a region that contains many dislocations. The resulting continuum model can be written as the variation of an elastic energy that consists of the contribution from the long-range elastic interaction of dislocations and a correction due to the line tension effect.

We consider dislocations γ_j, $j = ..., -2, -1, 0, 1, 2, ...$ in the xy plane with the same Burgers vector **b**. Without loss of generality, assume that the Burgers vector