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2007 J. Phys.: Condens. Matter 19 266001

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Surface passivation for tight-binding calculations of covalent solids

N Bernstein

Center for Computational Material Science, Naval Research Laboratory, Washington, DC, USA

E-mail: noam.bernstein@nrl.navy.mil

Received 20 February 2007, in final form 30 April 2007

Published 24 May 2007

Online at stacks.iop.org/JPhysCM/19/266001

Abstract

Simulation of a cluster representing a finite portion of a larger covalently bonded system requires the passivation of the cluster surface. We compute the effects of an explicit hybrid orbital passivation (EHOP) on the atomic structure in a model bulk, three-dimensional, narrow gap semiconductor, which is very different from the wide gap, quasi-one-dimensional organic molecules where most passivation schemes have been studied in detail. The EHOP approach is directly applicable to minimal atomic orbital basis methods such as tight-binding. Each broken bond is passivated by a hybrid created from an explicitly expressed linear combination of basis orbitals, chosen to represent the contribution of the missing neighbour, e.g. a sp^3 hybrid for a single bond. The method is tested by computing the forces on atoms near a point defect as a function of cluster geometry. We show that, compared to alternatives such as pseudo-hydrogen passivation, the force on an atom converges to the correct bulk limit more quickly as a function of cluster radius, and that the force is more stable with respect to perturbations in the position of the cluster centre. The EHOP method also obviates the need for parameterizing the interactions between the system atoms and the passivating atoms. The method is useful for cluster calculations of non-periodic defects in large systems and for hybrid schemes that simulate large systems by treating finite regions with a quantum-mechanical model, coupled to an interatomic potential description of the rest of the system.

1. Introduction

Quantum-mechanical calculations of materials require careful treatment of boundary conditions. To simulate extended systems, either periodic or free boundaries can be used. Periodic boundary conditions eliminate any free surfaces at the ends of the region simulated, but they require that the geometry of interest be periodic. Free boundaries enable simulations of non-periodic systems, but they entail free surfaces that are essentially unphysical, resulting from the cutting of a finite cluster from the extended system. Especially in covalent systems,

these fictitious surfaces must be passivated to prevent the formation of surface states that can dramatically alter atomic behaviour throughout the cluster. The most commonly used approach is hydrogen passivation, where each broken bond is saturated with a hydrogen atom. Another technique for passivating the fictitious surfaces, closely related to the method presented here, is to use hybrid orbitals [1–5]. Cluster approaches have become even more important with the development of hybrid methods that couple a quantum-mechanical (QM) calculation in a small region, where its reliability is essential, to an interatomic potential calculation for the rest of the system [6–11]. For these sorts of calculations there is often no practical way of constructing a periodic supercell representing the geometry of the QM region.

Passivation with hydrogen atoms, or with pseudo-hydrogens that are designed explicitly for such passivation [7], has several drawbacks. One is that parameters that describe the interactions between the system atoms and the passivating atoms need to be determined. For tight-binding (TB) models [12–14], where developing parameters can be time consuming, this is a significant limitation. Another issue is that the passivation is not perfect, and atoms near the passivation layer feel forces that can be quite different from the forces they would feel in the full system. This leads to a requirement for a buffer region around the part of the cluster where the QM accuracy is desired. The atoms in this buffer region are included in the QM calculation and add to the computational expense, but forces on them are incorrect and must therefore be discarded or accepted as an inevitable inaccuracy. The perturbation caused by the passivation layer is particularly important for solid-state systems, where gaps are typically smaller and the non-locality of the electrons (as embodied in the localization of the density matrix) is typically greater than in molecular systems.

Here we present an explicit hybrid orbital passivation (EHOP) method that uses analytically constructed hybrid orbitals to passivate fictitious surfaces created when representing a portion of an extended system by a free-standing cluster. The approach is applicable to methods that use atomic-orbital-like basis functions to simulate covalently bonded systems, where broken bonds can be identified. It is particularly well suited to minimal basis methods such as TB [15, 16]. It causes minimal perturbation of atoms near the passivation layer, and requires no additional parameters to describe the interaction between the system atoms and passivation orbitals. While the idea behind the method is closely related to earlier work [1–5], the details and application are quite different. Most significantly, we test the method on a solid-state system with a narrower gap than the molecules where hybrid orbital passivation has traditionally been applied.

2. Passivation method

To construct the passivation, bonds that are broken by the formation of the cluster must be identified. Since cluster calculations typically assume that nothing interesting is happening except near the centre of the cluster, interatomic positions and angles at the edge should be near equilibrium values. Broken bonds can then be identified through a geometric criterion, where pairs of atoms within some cutoff distance are assumed to be bonded. The assumption that atoms at the edges of the cluster are near equilibrium often breaks down for hybrid simulations that couple QM and interatomic potentials (whether because of thermal motion or because the QM region is treated by breaking it down into many smaller subclusters with edges that might intersect with the region of interest). Nevertheless, we have found that the geometrical criterion for identifying bonds is usually still applicable in practice. The type of bond (single or double, for example) can be identified through the bond order or related quantities [17, 18].

Given the cluster and the list of bonds broken when the cluster is extracted from the extended system, the passivation can be constructed straightforwardly. If atom i at position

\mathbf{r}_i has a broken bond with atom j at position \mathbf{r}_j (which is not part of the cluster), we create one or more hybrid orbitals to passivate that broken bond. For each single bond constructed from sp^3 hybrids, we create a hybrid orbital (similar to the definition used in [2] and [3]) centred around \mathbf{r}_j :

$$\phi = \frac{1}{2} \left[\phi_s + \sqrt{3} (\hat{r}_x \phi_{px} + \hat{r}_y \phi_{py} + \hat{r}_z \phi_{pz}) \right] \quad (1)$$

where ϕ_s is an s orbital, $\phi_{p\alpha}$ are p orbitals aligned along the Cartesian axes, and $\hat{\mathbf{r}}$ is the unit vector parallel to $\mathbf{r}_j - \mathbf{r}_i$. The factor of $\sqrt{3}$ multiplied by the magnitudes of the $\hat{\mathbf{r}}$ components yields a sp^3 hybrid, and the constant prefactor is chosen to normalize the hybrid orbital. Our formula for the coefficients of the hybrid orbital is different from that used in previous work [2, 3, 5]. In [2] and [5] the orientation of the passivating hybrid is normal to the plane defined by the three neighbouring atoms that are outside the cluster. Here we assume that the hybrid is pointed directly from the passivation atom to the cluster atom with the dangling bond. Our definition is simpler to implement, especially for the Pulay-like terms in the forces that come from derivatives of the hybrid orbital with respect to atomic positions [3]. In [3], the orientation of the hybrid is the same as here, but the weight of s versus p orbitals are precomputed for the particular bond, or taken to be optimization parameters.

To implement the passivation, we compute the Hamiltonian and overlap matrices for the cluster that includes the nearest neighbours of the boundary atoms. The hybrid orbitals are created by a change of basis, where the coefficients in the transformation matrix are simply the coefficients of the atomic orbitals in equation (1). The change of basis is applied by a transformation matrix with $N + M$ rows, where N is the number of atomic orbitals for atoms in the QM region and M is the number of passivating hybrid orbitals, and $N + M'$ columns, where M' is the number of atomic orbitals on atoms adjacent to the QM region. All of the normal tools to solve the electronic structure problem can be applied to the transformed matrices. The number of electrons in the system is the number expected for the cluster atoms, plus one for each passivation orbital. As noted by Gao *et al*, the computational expense of the change of basis is small because non-diagonal elements occur only for surface atoms [5]. Since the transformation matrix is explicitly dependent on atomic positions, derivatives of the transformed Hamiltonian and overlap matrices have additional corresponding terms [3]. The way our method uses the hybrid orbital differs from [2] and [5]. This first of these earlier methods used a large number of parameters optimized specifically for the hybrid orbital, and used the hybrid in the context of a single valence-bond description embedded in a large molecular mechanics system. The second also optimized parameters for the passivation atom that is transformed into the hybrid orbital, and modified its effective core potential based on the excluded basis orbitals corresponding to that atom. The optimization of parameters is efficient when focusing on one class of systems, e.g. organic molecules where one can hope to cut only one type of C–C bonds. However, we want to apply our method to covalently bonded systems with various atomic species present in different bulk materials, so we avoid the optimization of special passivation parameters by simply applying the orbital transformation to the regular basis function interactions. Our use of the hybrid orbital also differs from [3], where the hybrid is used to manually construct a parameterized bond orbital between the dangling bond atom and the passivation atom, rather than letting the eigensolver determine the coefficients of the occupied states.

For double bonds constructed from sp^2 orbitals, this procedure is more complex. The orbital coefficients are changed to

$$\phi = \frac{1}{\sqrt{3}} \left[\phi_s + \sqrt{2} (\hat{\mathbf{r}}_x \phi_{px} + \hat{\mathbf{r}}_y \phi_{py} + \hat{\mathbf{r}}_z \phi_{pz}) \right] \quad (2)$$

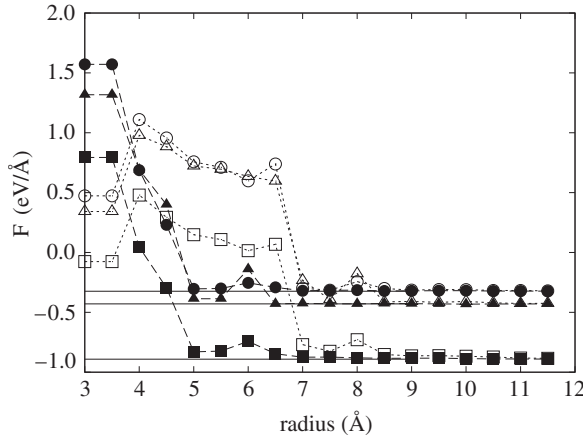


Figure 1. Cartesian components of the force on an atom adjacent to a vacancy as a function of passivated cluster radius. Solid lines show reference full system calculation values, dashed lines and solid symbols show passivation orbitals, and dotted lines and open symbols show hydrogen passivation.

and a second passivation orbital

$$\phi = (\hat{\mathbf{p}}_x \phi_{px} + \hat{\mathbf{p}}_y \phi_{py} + \hat{\mathbf{p}}_z \phi_{pz}) \quad (3)$$

is added. Again, the constant factors are chosen to form a normalized sp^2 hybrid. The coefficients of the second passivation orbital are dependent on the geometry of the atom that the orbital is replacing. If the geometry is near equilibrium, it is expected that the missing atom will have two single bonds in addition to the broken double bond to be passivated, and $\hat{\mathbf{p}}$ is a unit vector normal to the plane defined by the three bonds. If the broken bond to be passivated is a triple bond, the passivation orbitals comprise an sp hybrid and two orthogonal p orbitals.

3. Tests

We test the passivation orbitals on a simple but representative model system: crystalline silicon with a vacancy. This system is fundamentally different from organic molecules, where cluster and hybrid approaches are normally used. Organic systems are typically heterogeneous, one-dimensional, and have a large band gap, leading to greatly enhanced localization of bonding compared to a homogeneous, three-dimensional and relatively small-gap bulk semiconductor such as silicon. We use a non-orthogonal sp basis TB model where parameters for pseudo-hydrogen atoms, optimized for passivation, have been determined [13, 7]. The full system consists of a 1000-atom diamond structure cube with one atom removed. The atoms are then perturbed by 0.1 Å in random directions. Reference forces on the atoms are computed in the full system with periodic boundary conditions, sampling the Brillouin zone at the Γ point. The forces are then computed for different clusters passivated with the pseudo-hydrogen parameters in equation (21) of [7] and with the passivation orbitals presented here. We test the convergence of the forces on an atom adjacent to the vacancy as a function of radius for a cluster centred around the atom. We also test the stability of the force on one atom in a moderately large cluster as a function of displacement of the cluster centre away from the atom.

The first test is the convergence of the forces as a function of cluster radius. The Cartesian components of the force on an atom adjacent to the vacancy are plotted in figure 1. The plot clearly shows that EHOP is more effective than the pseudo-hydrogen passivation, which shows

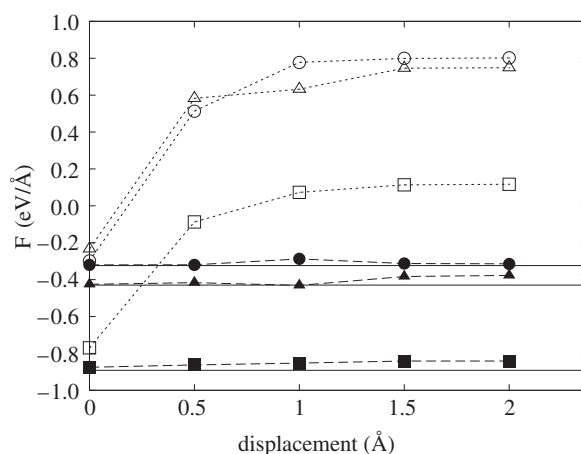


Figure 2. Cartesian components of the force on an atom adjacent to a vacancy as a function of passivated cluster centre offset. Solid lines show reference full system calculation values, dashed lines and solid symbols show passivation orbitals, and dotted lines and open symbols show hydrogen passivation.

slower convergence and qualitative errors for radii below 7 Å. The convergence of the forces is not monotonic, because the smaller clusters truncate the longer-range parts of the density matrix. While these matrix elements decay with distance, they do not do so monotonically and they may be of either sign, so neglecting them can lead to errors of substantial magnitude in either direction. The difference in sufficient radius translates to a large change in computational time, because the time scales as the cube of the total number of basis functions. The 5 Å radius cluster has 64 cluster atoms including 36 passivation atoms, while the 7 Å radius cluster has 154 cluster atoms including 80 passivation atoms. Since sp basis models often use s and p orbitals for the hydrogen or pseudo-hydrogen atoms, the savings for EHOP can be even more pronounced, with each four-orbital hydrogen replaced by a single passivation orbital (for sp^3 hybrid single bonds, as in this example). The total number of orbitals, even assuming the same 7 Å radius cluster, is reduced from 616 to 376, or a reduction in computation time by a factor of 4.4.

The large forces that occur when the atom is within 5–7 Å of the boundary reflect the difference between bulk silicon and organic molecules where hybrid methods are typically used. In organic systems, where the gap, heterogeneity, and one-dimensional nature of bonding lead to strong localization, the effects of the surface are short ranged and can be compensated for by modifying the interatomic potential at the boundary of the non-QM region. No reasonable modification of silicon interatomic potentials [19, 20], which are very short ranged, could correct for the long-range effects of the QM region boundary.

The second test is the stability of the forces with respect to small changes in the construction of the cluster. As an example, we test the forces on an atom near a vacancy as a function of displacement of the centre of a 7 Å radius cluster away from the atom of interest. The results are plotted in figure 2. While for zero offset (cluster centred around the atom of interest) the pseudo-hydrogen passivated forces are in reasonable agreement with full system results, they quickly diverge when the cluster centre is moved. Even for a 0.5 Å displacement, the forces are qualitatively wrong. The EHOP cluster forces, on the other hand, are quite stable. Moving the cluster centre by as much as 2 Å does not change them significantly. These results demonstrate the sensitivity of hydrogen passivation, even for moderately large clusters, to details of the surface.

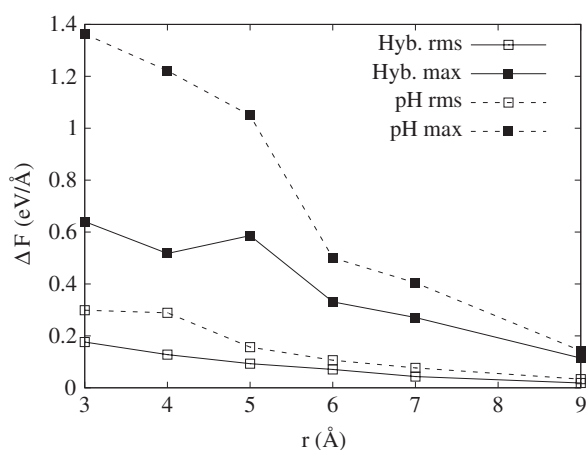


Figure 3. Deviations between exact tight-binding forces and calculation where the force on each atom is computed from a cluster centred around that atom, as a function of cluster radius. Root-mean-squared (open symbols) and maximum (filled symbols) force deviations are plotted for EHOP clusters (solid lines) and pseudo-hydrogen passivated clusters (dashed lines).

A more physically relevant system related to the vacancy configuration is high-temperature molecular dynamics simulation, where many atoms experience a large deviation from equilibrium, and the vacancy can migrate. We compute the forces on each atom in a configuration from a Stillinger–Weber interatomic potential [19] simulation of a 215-atom system with a vacancy at $T = 1100$ K, at an instant when the vacancy is migrating. Reference forces for each atom are computed using TB for the full periodic system. The forces are then computed separately for each atom from a spherical passivated cluster centred around that atom. Only the force on the central atom of each cluster is used, and all other forces from each cluster calculation are discarded. This approach, used by Csanyi *et al* [10] and also potentially useful as a linear-scaling method, tests the passivation scheme in a wide range of geometries, both in the core of the cluster and near the cluster edges. The root-mean-squared and maximum force deviations as a function of the radius of the passivated clusters are plotted in figure 3. We see that EHOP is more effective than the pseudo-hydrogen passivation, with average and maximum force deviations that are smaller at each cluster radius.

While covalent bonding is fairly localized, non-local effects do extend beyond the nearest neighbours. The extent of localization depends on details of the electronic structure [21]. Any passivation scheme that uses a real potential to saturate broken bonds will perturb electronic states, and therefore atomic properties, within some distance from the passivation layer. The EHOP method presented here attempts to minimize these perturbations while maintaining a simple implementation. As we have shown, it perturbs interatomic forces within a much thinner layer near the surface as compared with pseudo-hydrogen passivation. While the fraction of the system where forces are affected will go down with increasing cluster size, it is significant even for fairly large clusters. For a 12 Å radius, 357-atom sphere, a 5 Å buffer region includes about 700 atoms while a 7 Å buffer region includes over 1050 atoms. It is clear that a smaller buffer region can lead to great savings in computational cost. The effects of the passivation are also seen in local charges, where EHOP produces substantial ($>1\%$) perturbations within only 2 Å of the surface, as compared with the pseudo-hydrogen passivation where large perturbations occur up to 5 Å from the surface. These differences suggest that electronic and optical properties that depend on charge transfer and polarization are likely to be more accurate for the EHOP method compared with pseudo-hydrogen passivation.

4. Extensions of the method

We have applied EHOP to non-self-consistent minimal-basis TB models. However, EHOP is also applicable to more sophisticated electronic structure methods. Self-consistent TB models (e.g. density-functional TB [22]) can be used without much difficulty, within the general limitations of the cluster approach (neglected or approximated electrostatic interactions with the rest of the extended system, for example). Hybrid orbitals associated with each missing atom can be treated as a charge centre with the same U parameter as the corresponding atom and a core charge equal to the number of hybrids. Methods that use a larger basis require more significant changes, which we briefly describe here for two cases. Tight-binding methods that use the larger basis simply to improve conduction band properties can be handled directly, by simply setting the hybrid orbital coefficients for the additional basis functions to zero. First-principles methods that use an atomic-orbital-like basis [23] typically use several angular momentum states and radial functions in their basis. For such methods, one would need to construct a minimal basis that approximately spans the occupied space in the perfectly bonded material. For example, one could fit the parameters of a single s and a single p radial function to reproduce the energy and charge density for a bulk system computed with a converged calculation. This would define a minimal basis (which may not be transferable) that could be transformed into hybrid orbitals using the formulas presented here. As in related approaches [1, 4, 5], electrostatic interactions can be handled by embedding the cluster in a potential created by the charges associated with the interatomic potential, and vice versa, but this does not change the way the passivation orbitals are defined or used.

5. Conclusions

We have presented the EHOP method for passivating the boundary of a cluster used to represent a finite portion of a larger covalently bonded system in an electronic structure simulation, and tested its effects on the atomic structure of a model semiconductor. The EHOP method uses hybrid orbitals constructed to mimic the effects of the missing atoms outside the explicitly simulated cluster. It is particularly well suited to minimal basis methods such as tight-binding, and does not require the development of new parameters for the passivating orbitals. Tests on bulk silicon with a vacancy show that surface effects are substantial due to the size of the band gap and the three-dimensional nature of bonding, but that EHOP results in more accurate forces (for a given size cluster) than pseudo-hydrogen passivation. This improvement leads to more accurate and computationally efficient calculations, especially for methods that couple a finite region treated with the quantum-mechanical model to a larger system treated with interatomic potentials.

Acknowledgments

This work was supported by the US Office of Naval Research and the Naval Research Laboratory. I would like to thank G Csanyi for helpful suggestions.

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