

Computational Materials Design with First-Principles Quantum Mechanics

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The ultimate goal of computational materials design is the reliable prediction of the entire life cycle of a material and the feedback of these simulated results into the choices of chemical composition of the material itself. Of all the aspects relevant to materials design, the atomistic architecture of a material stands out as a cornerstone for any rational development approach—as it does for molecular biology and drug design. Progress in first-principles quantum mechanical calculations has culminated now in an unprecedented capability to predict atomistic structures, even when subtle energy changes are involved. This is a remarkable accomplishment, and therefore it is worthwhile to put the current capabilities in perspective.

An example of the sensitivity of current approaches is the investigation of the site-selective adsorption of carbon atoms on Al(111) surfaces (1). Carbon is a common contaminant of aluminum surfaces, but the exact adsorption geometry and binding mechanism are not clearly understood. Carbon atoms can be adsorbed on an Al(111) surface in two possible geometries: a fourfold-coordinated site slightly below the surface and a sixfold-coordinated site halfway between the first and second Al layers. The sixfold-coordinated site is calculated to be more stable by 0.1 ± 0.05 eV per atom, but the energy hypersurface is shaped such that in a deposition process the near-surface site is kinetically preferred (1).

These results (1) are based on first-principles density functional theory with the local density approximation (LDA) and a pseudopotential plane wave method (2). A “density functional” relates the total electron density and the total energy. From this, one can derive effective one-particle Schrödinger equations, which can be solved iteratively to give the electronic states, the charge density and the total energy. In the LDA it is assumed that the quantum mechanical many-body interactions (the ex-

change and correlation effects) experienced by an electron at a given point only depend on the electron density at that point. Pseudopotentials are used to simplify the one-electron equations by replacing the inner electrons of each atom by effective potentials acting on the valence electrons. The electronic wave functions of the valence electrons can then be expanded in terms of computationally convenient exponential functions (plane waves). None of these theoretical or computational aspects is particularly new: Density functional theory and the LDA were formulated more than 30 years ago, the use of pseudopotentials goes

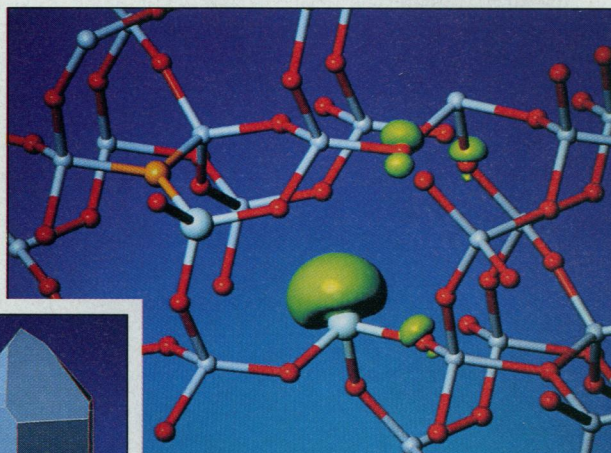
a large body of density functional calculations on bulk solids, surfaces, and molecules. Accurate LDA calculations give equilibrium bond distances typically within about 0.02 Å compared with experimental results, except for weakly bonded systems such as those involving hydrogen bonds or van der Waals complexes, where computed bond lengths tend to be too short. Relative energies, for example, between two similar adsorption sites of an atom on a surface, are significant to within ~0.1 eV or even better on the LDA level; current gradient-corrected density functionals give absolute binding energies typically within ~0.1 eV and often result in better geometries for weakly bonded systems.

The computational efficiency is the result of the development of methods such as the pseudopotential plane wave approach that uses conjugate-gradient techniques for obtaining the LDA eigenstates. Additional approximations as those introduced by the pseudopotentials and truncations in basis sets have been validated by comparison

with accurate all-electron approaches such as the full-potential linearized augmented plane wave (FLAPW) method and are thus very well controlled.

The inclusion of dynamical aspects is made possible by the accurate calculation of forces acting on each atom. This is particularly efficient in the framework of pseudopotentials and plane waves, but it is also possible for all-electron localized-basis methods. This capability has opened the field of ab initio molecular dynamics. Since the original paper by Car and Parrinello (4), progress on this frontier has been steady, but two major obstacles have now become clear: one practical and the other fundamental. The practical obstacle is that only short time intervals of the order of several picoseconds and fairly small systems containing about 50 atoms

per unit cell are currently accessible to ab initio molecular dynamics within a reasonable computational effort. Progress in computer hardware and algorithms can be expected to push this frontier continuously back. The other, fundamental obstacle is that ab initio molecular dynamics methods can simulate the formation and breaking of chemical bonds, and one should be able to follow chemical reactions across barriers. However, there is increasing evidence that



Relaxation of the atoms around an oxygen defect in α -quartz as obtained from first-principles quantum mechanical calculations (6).

After the elimination of an oxygen atom, one of the adjacent silicon atoms seeks an environment with fourfold coordination which involves an unusual oxygen coordination of three (note orange-colored oxygen atom). The other silicon atom is left with a dangling bond that corresponds to an electronic wave function in the optical gap (the green mushroomlike structure). The inset shows the unit cell of α -quartz and a macroscopic crystal morphology that can be obtained from the atomistic knowledge of surface energies and growth rates, thus connecting atomistic phenomena with macroscopic properties.

back to the early days of band theory, and plane waves have gone hand in hand with pseudopotentials since then. Furthermore, the first density functional total energy calculations on surfaces had already been performed by around 1980. However, present calculations (3) are distinguished in at least three major aspects: the level of confidence, the computational efficiency, and the inclusion of dynamical aspects.

The confidence in the results is based on

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present density functional calculations with gradient corrections give energy barriers of chemical reactions that are too low. A qualitative step forward is called for, similar to the step from the LDA to current gradient-corrected density functionals (5).

For these reasons, the design and optimization of high-performance electronic, optical, and magnetic materials benefits perhaps the most from the capabilities of first-principles quantum mechanical methods, because in these systems the key aspect is typically the relation between a static geometric structure and the corresponding electronic structure. A good example is related to the design of high-performance optical fibers, in which any impurity or defect is a potential source of scattering that can degrade performance. One such defect is caused by oxygen vacancies within the SiO₂ network. Starting from a crystal of α -quartz (see figure), the removal of an oxygen atom leaves two silicon atoms in the lattice with unsaturated bonds. It is not obvious how these atoms relax to minimize the total energy of the system. One possibility is that an internal Si-Si dimer forms, thus closing the microvoid created by the oxygen vacancy. Local density functional calculations (6) reveal that on removal of one oxygen atom the adjacent Si atoms spontaneously dimerize.

However, a puckered conformation is found as another possible metastable conformation (see figure). For this structure, the calculations give a highly localized electronic state (see figure). The energy of this state falls into the optical gap of the perfect silica and thus may be a cause for light absorption. A key finding, which is being further investigated, is the fact that the puckered structure is stabilized by the trapping of a positive charge. In fact, with this detailed knowledge of the nature of the oxygen impurity and its sensitivity to the charge state, it is possible to design improved materials and processes that avoid this type of defect, thus leading to better high-performance silica materials for applications such as optical fibers.

These two examples demonstrate that current quantum mechanical methods allow the prediction of subtle structural features that can have significant effects on the properties of a material, such as its optical characteristics. Equipped with this type of predictive structural tool, materials scientists are now in a position to explore the "materials design space" in a much more creative and productive way than with a purely experimental approach. A large part of all possible combinations of atoms is still unknown, as can be seen from an analysis of the documented materials and phases.

Whereas 83% of all possible binary systems have been experimentally characterized, less than 10% of all ternaries and less than 1% of quaternary systems are known (7). The majority of materials have yet to be synthesized and characterized. An important tool to this end is the reliable prediction of atomic structures, now possible with first-principles quantum mechanical approaches even when very subtle effects and dynamical aspects are involved.

References and Notes

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Digging into Caveolae

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Eukaryotic cells use stringent sorting mechanisms to maintain the lipid and protein composition of their intracellular organelles. This sorting process is best understood for the recruitment of certain transmembrane proteins into pits in the plasma membrane (defined by their coats of the protein clathrin). Concentration of these proteins generates heterogeneity within the plane of the membrane. The cell uses a different strategy to maintain other distinctive plasma membrane structures, the caveolae, a strategy that makes use of the biophysical properties of lipids rather than protein-protein interactions. A new purification technique for caveolae, reported in this issue of *Science*, demonstrates this in a striking way (1).

Caveolae ("small caves"), flask-shaped invaginations of the plasma membrane, are a prominent feature of many mammalian cells (2, 3). They were originally defined by

electron microscopy and are particularly abundant in adipocytes, smooth muscle, and endothelia. In the past 5 years, progress on the biochemistry of caveolae has been greatly facilitated by the characterization of VIP21-caveolin, a 21-kilodalton integral membrane protein proposed to be part of the "caveolar coat" (4, 5). This unusual protein forms a hairpin structure in the membrane, with both the amino and carboxyl termini facing the cytoplasm (6). VIP21-caveolin is also present in the trans-Golgi network (TGN) and in both apical and basolateral exocytic vesicles of epithelial cells. It was isolated from such epithelial cells on the basis of its presence in low-density, detergent-insoluble complexes (7), which also contain glycosyl phosphatidylinositol (GPI)-linked proteins and other proteins implicated in signal transduction, including Src-family kinases and heterotrimeric guanosine triphosphate-binding proteins (G proteins) (8). The complexes are enriched in glycosphingolipids (GSLs), sphingomyelin, and cholesterol, but are de-

pleted of phospholipids (9). These results suggested a link to earlier observations in lymphocytes showing that cross-linking of GPI-anchored proteins caused activation of Src-family kinase-mediated signaling pathways dependent both on the GPI-anchor and on the lipid modification (palmitoylation) of the Src kinase (10-12). Moreover, detergent treatment of lymphocytes extracted complexes enriched in GPI-anchored proteins and Src kinases (13). These findings led to the idea of microdomains of distinct lipid composition that mediate signal transduction.

However, the equivalence of detergent-insoluble complexes and caveolae has now been questioned (14), and it appears that at least in lymphocytes and neuroblastoma cells detergent-insoluble complexes can exist in the absence of caveolae, as shown by morphological criteria and by the absence of VIP21-caveolin (15, 16). Clearly, signal transduction in these cells does not require VIP21-caveolin or caveolar invaginations. In addition, GPI-anchored proteins may not be greatly enriched in caveolae under steady-state conditions (17, 18) and hence their detergent insolubility would not correlate with their presence in caveolae. Nevertheless, these points remain controversial. We therefore propose that the term "caveolae" be used for the classical morphological entity as originally defined and that these structures be differentiated from the de-

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