PHYSICS

A benchmark for materials simulation

Material properties can now be predicted reliably from first-principles calculations

By **Chris-Kriton Skylaris**

Density functional theory (DFT) stands out from all first-principles quantum mechanical methods for the simulation of materials, as it enables very good approximations for the complicated components of electronic motion called exchange and correlation. DFT is the method of choice for many materials simulations because of the availability of general-purpose programs that can perform calculations on any material. Results obtained with one DFT program need to be reproducible by any of the other DFT programs, and this has not been straightforward up to now. On page 1415 of this issue, Lejaeghere et al. (1) describe an extensive effort by developers of the major solid-state DFT codes to provide a unified and reproducible benchmark of precision for their calculations based on a reliable criterion, the so-called Δ gauge. Using the Δ gauge, the authors found that the level of precision that can be achieved today in DFT calculations of elemental crystalline solids is comparable to the precision of the most advanced techniques for experimental measurement of the properties of materials. The work leads to the conclusion that the DFT simulation of elemental crystalline solids is a (computationally) solved problem, but also poses the question of whether we can achieve the same levels of validation and reproducibility for more complex simulations of materials involving several elements and/or several methods.
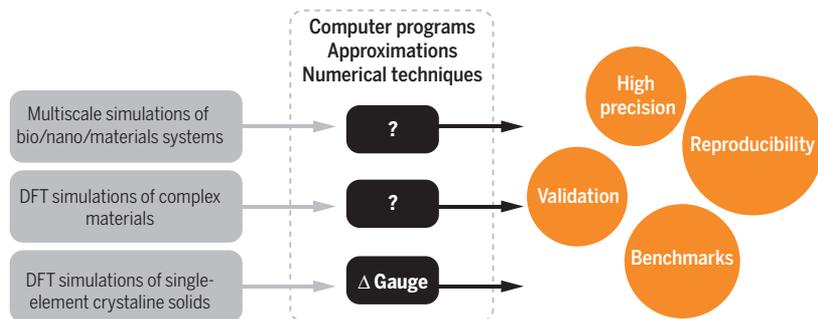
First-principles quantum mechanical calculations use the fundamental equations of quantum theory that govern the behavior of electrons, atoms, and molecules. In principle, quantum theory allows us to compute any observable property of materials with extremely high accuracy. However, this capability can only be realized at the expense of appreciable computational effort; for

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most cases, the quantum mechanical equations cannot be solved analytically and must be approximated numerically. A variety of implementations exist that are based on different numerical approximations, and at the theoretical limit of infinite computational power, they are expected to produce the same answers. However, in real calculations it is difficult to know how the numerical approximations used by each program affect its results. Lejaeghere et al. demonstrate this by comparing published calculations of the lattice constant of crystalline silicon and

How the calculations measure up. The Δ gauge approach described by Lejaeghere et al. allows us to validate calculations between different DFT programs. Can an equivalent criterion be derived for DFT simulations of complex materials and eventually for multiscale simulations?

showing that in the early years of development of such programs, the error in precision was larger than the difference from the value measured in experiments.

The development of DFT by Kohn (2) was a major breakthrough in first-principles calculations. DFT is an alternative formulation of quantum theory in which the electronic density is the central quantity rather than the wave function. This is a dramatic simplification, as the electronic density is a mathematical function of only three geometrical variables x, y, and z, whereas the wave function is a function of $3N$ variables, that is, three variables for each of the N particles simulated. As a result, DFT, in the form developed by Kohn and Sham (3), has found extensive use in simulations of materials. Although DFT is formally an exact theory, there is no explicit expression for the so-called exchange and correlation energy that describes interactions between the electrons, so this term has to be approximated. Over the past few decades, a hierarchy of increasingly accurate approximations of the term has been developed (4).

DFT has proved its value in calculations in an impressive range of applications such as drug design (5), catalysis (6), crystal structure prediction (7), nanoelectronics (8), and geophysics (9), to name just a few.

The tremendous success of DFT has been enabled by the development of highly sophisticated programs that are general-purpose and can perform calculations on any material or molecule. These computational tools have a high level of complexity, as a consequence of the fact that a host of numerical techniques are required to solve the DFT equations (10). As a result of this complexity, DFT programs had to be developed over many years by dedicated communities, and each such community has acquired expertise on how to set up calculations with their code to achieve the required level of precision for each application. These codes have now matured and become established, and because they were developed according to a "black-box" philosophy that allows the user to control the approximations via a small set of input parameters, they are now available as tools for research by non-experts. As this transition from "community products" to general-purpose research tools is taking place, it is imperative to be able to compare and tune the quality of calculations between different codes. Results obtained with one code can only be credible if they can be reproducible by any of the other codes at the same level of DFT theory (that is, the DFT exchange-correlation functional).

Lejaeghere et al. outline the extensive efforts by developers of the major solid-state DFT codes to provide a unified and reproducible benchmark of precision for DFT calculations. This multinational consortium evaluated the major codes against each other using a reliable criterion, the Δ gauge (see the figure). DFT calculations of the equation of state of elemental crystalline solids have been compared among all the codes in the study. An outcome of this work is that all the DFT codes were able to produce results at the same level of precision as the most advanced experimental techniques for mea-

suring structural and electronic properties of materials. Thus, "computer experiments" can be used on a par with experimental investigation. Users of DFT codes now have a dependable estimate for the level of precision of their results and a confidence of reproducibility by other DFT codes. This work has far-reaching implications, as it affects the entire community of DFT users, in fields as diverse as metallurgy and biochemistry.

Being able to do such accurate quantum calculations is insufficient when the goal is to solve complex problems of technological relevance. Molecules, biomolecules, and materials are neither isolated nor at a temperature of 0 K. On the contrary, they interact heavily with each other and their environment (for example, a solvent) and are in constant thermal motion. To make an impact in grand challenges such as understanding the function of a living cell or a nanodevice, we will need to tackle much larger (thousands to millions of atoms) length scales than can be approached with conventional DFT. Part of the answer to this challenge will be provided by linear-scaling DFT approaches (11), which can treat much larger numbers of atoms. Inevitably, however, multiscale methods that couple DFT with coarser descriptions such as classical atomistic force fields (12), and eventually continuum models, will be needed. These multiscale simulations will also need to describe how the materials evolve in time, so the choice of a configurational sampling problem that can be tackled with methods such as molecular dynamics (13), with implementations able to take advantage of the largest supercomputers (14), is equally important. Thus, a new, greater challenge is posed for the field of materials simulation: Can we have the same confidence in the reproducibility and precision of multiscale simulations as we have now for simple DFT calculations? Only time will tell. ∎

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IONIC TRANSPORT

Two-dimensional nanofluidics

Restacked exfoliated sheets create interconnected nanofluidic channels for ion transport

By Andrew R. Koltonow and Jiaxing Huang

The remarkable electronic properties of graphene and related two-dimensional (2D) materials result from the confinement of electrons within the material. Similarly, the interstitial space between 2D materials can enable the 2D confinement of ions and electrolytes and alter their transport. Many different 2D sheets can be obtained by exfoliation of natural layered materials (1), and an exfoliation-reconstruction strategy can convert powders of layered materials into continuous, robust bulk forms in which lamellar nanochannels occupy a substantial volume fraction (up to several tens of percent). Nanofluidics, which enables the manipulation of confined ions and electrolytes, has applications in electrochemical energy conversion and storage, biosensing, and water purification.

Electrolytes exhibit drastically different properties when confined in nanochannels.
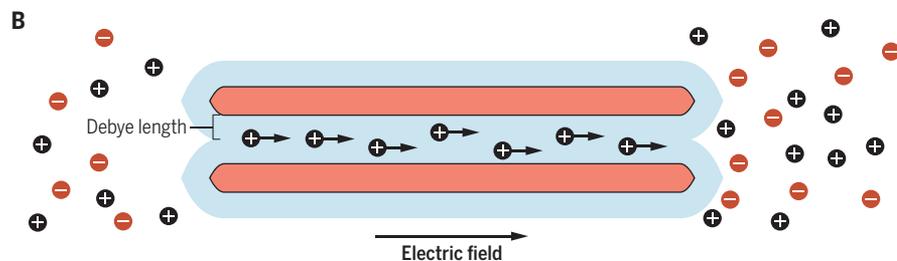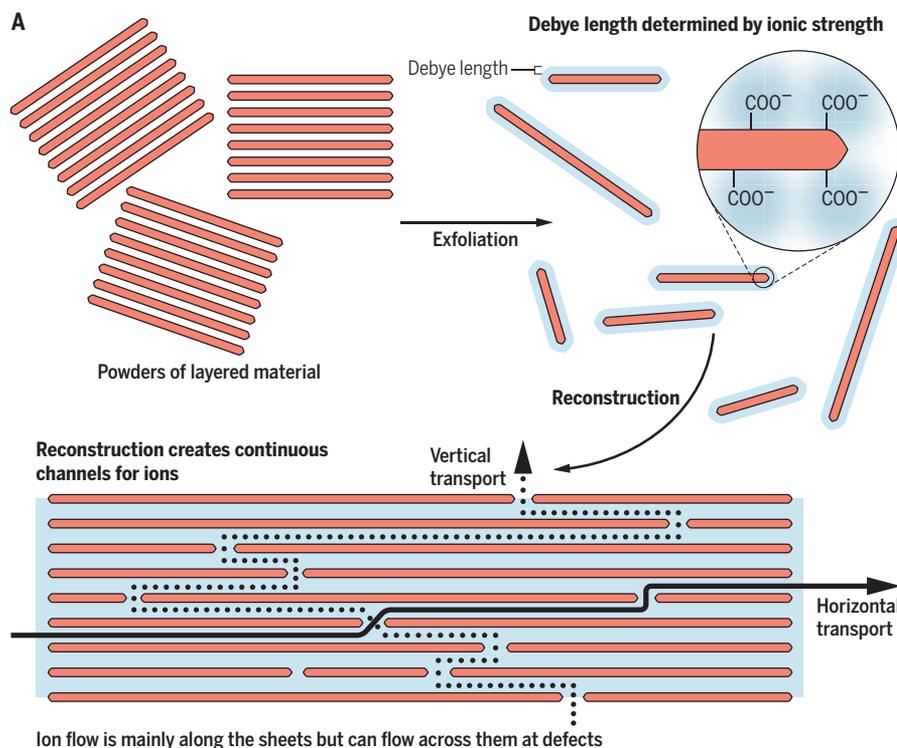
Confining ion flow. (A) Lamellar film with massive arrays of 2D nanofluidic channels can be made by the exfoliation-reconstruction approach, as illustrated with models of graphene oxide (GO) sheets that are terminated with negatively charged carboxyl groups. (B) Debye layers of neighboring sheets overlap to create unipolar 2D ion channels with greatly enhanced cation conductivity.

Editor's Summary

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