COMPUTATIONAL MATERIALS SCIENCE

Predicting Properties from Scratch

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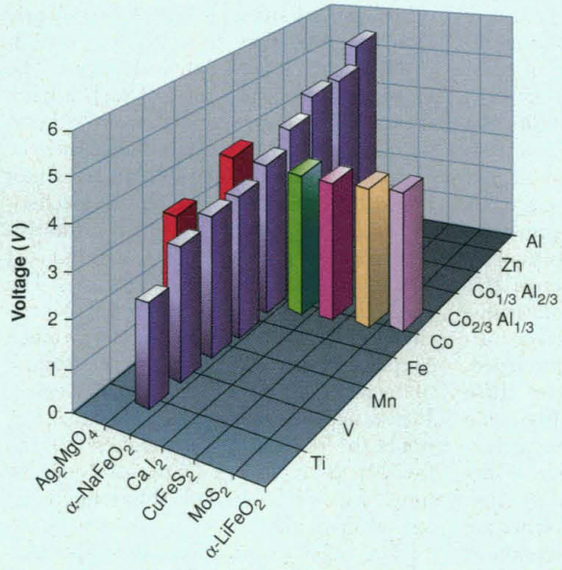
TECH VIEW

It has always been a dream of materials researchers to design a new material completely on paper, optimizing the composition and processing steps in order to achieve the properties required for a given application. In principle, this should be possible, because all the properties of a material are determined by the constituent atoms and the basic laws of physics. This approach of using only knowledge of the composition of a material to predict properties is referred to as a first-principles or ab initio calculation. Successful first-principles methods can bring obvious advantages to materials research because no experimental input is needed, and the behavior of a material can be predicted before it is synthesized, making it possible to quickly focus on promising systems when designing new materials. Besides the search for novel materials with optimized properties, first-principles methods also have benefits for studying well-known systems. Because of the detailed perspective they offer into the behavior of atoms and electrons, we can often significantly enhance and deepen our understanding of how materials function. A large collection of examples of this type can be found on the World Wide Web (*1*).

Although still in its infancy, the field of computational materials science, or "computational alchemy" as it is sometimes referred to, has become one of the most promising developments in materials research. Sixty-five years after the first ab initio calculation on a material (*2*), first-principles modeling is starting to pay off in a dramatic way. Researchers in this field have acquired enough confidence in their arsenal of computational methods to make bold predictions that have run ahead of experiments or, in some cases, even corrected them. The table shows a small selection of materials predictions made solely on the basis of first-principles calculations. Several of these have been confirmed experimentally.

With the increasing capabilities of first-principles methods, some researchers have started to think about computer-based design of materials. Because first-principles calculations are not limited to physically realizable states of a material, they can be used to conduct "what-if" experiments. In a calculation, it is reasonably simple to change the crystal structure of the material, move or substitute an atom, change the applied pressure, and so forth, and then to evaluate the effect of these modifications on the properties of interest. Although it may seem futuristic to completely design a material sitting in front of a computer screen, two examples from last year indicate that we have arrived at the brink of this fascinating possibility.



Designer batteries. Independent effect of host crystal structure and composition on the average lithium intercalation potential (vertical axis) in oxides (between MO_2 and $LiMO_2$ composition) for use as battery cathodes.

Researchers from Eastman Kodak (*3*) recently used first-principles calculations to arrive at novel high-performance magneto-optic recording media. In such thin-film media, light from a laser is reflected differently depending on the state of magnetization of the material. By calculating the magneto-optical properties of modulated materials, they predicted that Tb/Bi/FeCo and Tb/Pb/FeCo superlattices could have higher Kerr rotation than the more traditional TbFeCo alloys. As a result, higher figures of merit and signal-to-noise ratios have since been verified experimentally for these materials (*3*). In this example, first-principles calculations clearly guided the way, allowing fewer and more focused experiments.

In recent research, the "what-if" capability of first-principles modeling was used to design a new cathode material for rechargeable lithium batteries (*4*). Owing to their high energy density, lithium batteries are rapidly becoming the energy-storage technology of choice for applications where weight or volume are important (such as portable electronics). Li_xCoO_2, which is currently used as a cathode (*5*), is prohibitively expensive, creating a need for inexpensive replacement materials. One of the important factors in battery applications is the voltage at which lithium can be inserted in the cathode. Traditionally, determining the voltage for a newly proposed material requires first the development of a synthesis route to make the material, after which its structure and electrochemical characteristics have to be characterized. This process must be repeated for every new composition to be tested. First-principles computations offer a far superior way to identify compounds with high energy density. Starting with Li_xCoO_2 it is possible to substitute other less expensive metals for Co and recalculate the battery voltage. The figure shows the results for a variety of metals substitutions on one axis and the effect of changing the structure on the other. Traditionally, the search for replacements to Li_xCoO_2 has focused on transition-metal oxides. This figure indicates that most transition metal-oxides will have a lower voltage than Li_xCoO_2, but that a nontransition metal such as aluminum, previously thought to be nonactive in battery oxides, may actually be most potent in raising cell voltage. This result has recently been confirmed experimentally (*4*). Detailed studies of calculated electron densities showed that the increase in voltage is the result of the increased electrochemical activity of the oxygen ions in aluminum-substituted systems (*4*).

Although voltage is not the only property of importance for battery applications, and other properties need to be investigated, it is obvious that in the early development stage of these cathodes, computational modeling is a far more superior way to screen new candidates.

What has caused this remarkable progress of first-principles materials science? It can be argued that two factors have contributed sig-

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CASE	REF	STATUS
$YBa_2Cu_3O_2$	(11)	Prediction of several new compounds (confirmed)
Pd-Pt and Rh-Pt phase diagrams	(12)	Correction of published phase diagrams
Pd_8V	(13)	Prediction of new compound
Cu_7Pt	(14)	Prediction of new compound
$Li_{0.2}CoO_2$	(15)	Identification of compound
Si	(16)	Prediction of high-pressure phases (confirmed)
Ag_2Al	(17)	Prediction of order/disorder reaction in precipitates
III-V semiconductors	(18)	Explanation/prediction of surface ordering (confirmed)
β-C_3N_4	(7)	Prediction that material will be harder than diamond
GaN co-doped with Mg and Si	(19)	Prediction that material will be low-resistivity p-type, useful for blue-lasers
$Li(Co,Al)O_2$	(20)	Prediction that Al raises the lithiation voltage (confirmed)

Computational scorecard. Some predictions that were made on the basis of first-principles calculations. Several of these have been confirmed.

nificantly to its emerging importance. Most obvious is the sheer increase in computer speed over the last two decades. The number of multiplications a computer can perform per second per dollar spent on the machine—a reasonable indicator of the performance-to-cost ratio—has increased by almost 4 orders of magnitude in the last 15 years. Few other research tools in materials research can boast such a dramatic improvement. Developments in condensed matter theory constitute the other factor. The specific milestones that have brought us to accurate first-principles calculations have recently been discussed by Zunger (6). In essence, all first-principles methods require the solution to a many-particle Schrödinger equation. Although this equation is not exactly solvable for any realistic problem, in recent years very good quantitative approximations have been developed. Computer programs to implement these methods for real materials are now becoming readily available for any materials researcher.

Experimentalists do not yet have to fear the unemployment line, however. The successes of computational materials science are concentrated on a fairly small selection of properties, most of them electronic or thermodynamic. There is still a wide gap between the type of information that first-principles calculations can produce and many of the properties materials engineers want. The direct output of first-principles calculations are energies, band structure, charge density, crystal constants, bond lengths, and so forth. Although these are important properties, they are often difficult to relate to more macroscopic (but technologically relevant) properties, such as strength, corrosion resistance, creep, crystal structure, microstructure, transformation temperature, and kinetics, among others. Building this link between electronic structure methods and macroscopic "engineering" information, remains one of the foremost challenges of computational materials science. This road from first-principles methods to quantum engineering is littered with potholes. Lack of a good theory for properties can lead to misguided predictions, as has been illustrated by the search for a material that is harder than diamond. In what was probably the earliest attempt to develop a superior material from quantum mechanics, Liu and Cohen (7) predicted in 1989 that the C_3N_4 analog to β-Si_3N_4 might be harder than diamond. The large application potential of such a hard, inexpensive material set off a worldwide experimental effort to validate the prediction. However, a property such as hardness cannot be directly evaluated from quantum mechanics, and there is currently no quantitative theory that even relates it to anything that can be calculated from first-principles. The prediction of super hardness for β-C_3N_4 was therefore based on the bulk modulus, a much simpler property that represents the stiffness of the material, and can be calculated easily. It now appears that the bulk modulus may not be the best indicator of hardness (8), and β-C_3N_4, even if ever synthesized successfully, will probably fail the scratch-test against diamond.

The other major challenge of computational materials science is the prediction of crystal structure (9). While the properties of a material in a given structure can sometimes be predicted, it is still very difficult to demonstrate that the particular structure chosen will be stable, or can at least be synthesized metastably. The fact that there have been no reproducible sightings of β-C_3N_4 indicates that it is probably not very stable. For all the sophistication of first principles theory, structure prediction is still approached with brute (but ineffective) force. To "predict" the structure of a compound, researchers compute, at best, the energy of a few "reasonable" candidate arrangements and then proclaim the one with lowest energy to be the stable one. While such an approach may be reasonable when working on well-known systems, it is of little benefit when dealing with novel or complex multicomponent materials. The prediction of structure for compounds and mixtures is therefore one of the still missing cornerstones on which the success of computational materials science needs to be built. Fortunately, significant advances are being made in this area (10) and phase stability in binary systems can now be reasonably well predicted.

All in all, the future is bright for computational materials science, because it will undoubtedly continue to gain importance for materials research and development. The stage is set: Traditional materials research is time-consuming and expensive, while computing becomes faster and less costly. In the 21st century, competitiveness in materials research and development is therefore likely to require experimental programs that are well integrated with computational modeling.

With computing power becoming less of an obstacle, computational materials science must focus on the need for quantitative materials theories in order to apply what is found from atoms and electrons to macroscopic properties. This requires replacing the qualitative theories that are now common in materials science. Ironically, this is an area in which first-principles modeling can probably get a lot of help from experimentalists.

References and Notes

1. A list of examples can be found at www.msi.com/info/applications/
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