PERSPECTIVES: DENSITY FUNCTIONAL THEORY

In Pursuit of the "Divine" Functional

Ann E. Mattsson

Paul Dirac reputedly said that the Schrödinger equation (SE) marked the end of chemistry: All answers could be calculated from the SE. The SE can indeed be solved exactly for some systems, such as the hydrogen atom, and numerically to arbitrary precision for systems with a small number of electrons. However, the many-body character of the SE sets a fundamental limit on the size of solvable systems (*1*).

In a seminal paper, Hohenberg and Kohn (*2*) showed in 1964 that the SE, formulated as an equation of an N-electron wave function of $3N$ variables, could be reformulated as an equation of the electron density with only three variables. Thanks to this tremendous simplification, density-functional theory (DFT) has become an invaluable alternative to the SE in most areas of physics and chemistry, as demonstrated at a recent workshop in Albuquerque, New Mexico (*3*).

An important step toward applying DFT to real systems was taken in 1965 when Kohn and Sham (*4*) published the Kohn-Sham (KS) equations, derived from the Hohenberg-Kohn theorem. The KS equations recast the SE problem of interacting electrons moving in an external ion potential into a problem of noninteracting electrons moving in an effective potential. The contributions to the total energy are divided into two main parts. The first part contains "easy-to-handle" terms—the kinetic energies, the potential energies, and the classical Coulomb energies of the noninteracting electrons.

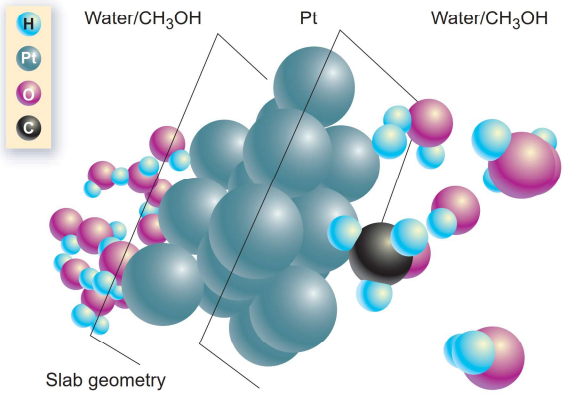
The second part, the exchange-correlation energy, consists of the remaining energies and thus incorporates many-body and quantum effects. It is customary to divide the exchange-correlation energy functional into an exchange part—for which there exists an exact expression (although computationally expensive to calculate)—and an unknown correlation part (*5*).

The only unknown part of the KS equations is then the exchange-correlation functional. If we knew this "divine" functional, all properties of a system could be calculated exactly, just as the properties of small systems can be calculated from the SE.

The first step toward the divine functional was the local density approximation (LDA), where only the electron density at a point in the system is used for determining this point's contribution to the total exchange-correlation energy of the system (*4, 6, 7*). LDA assumes a homogeneous electron gas but also works amazingly well for inhomogeneous systems. It is still used extensively.

Attempts to determine why the LDA worked so well led to an enhanced approximate functional, the generalized gradient approximation (GGA), where some nonlocal effects are incorporated by also using the gradient of the electron density for determining a point's contribution to the total exchange-correlation energy (*8*). In 1993, Becke proposed to mix GGA with exact exchange (*9*), resulting in a hybrid functional.

The GGAs and the hybrid functionals provided improved accuracy for molecular systems. Today, DFT is a popular tool not only in physics but also in chemistry. It is used, for example, to determine structural properties of surface reconstructions in semiconductors and of oxides with large unit cells. Diffusion and reaction barriers are calculated in a variety of many-ion systems. DFT is also extensively used in gas-phase catalysis, where the metallic character of the catalyst makes traditional SE methods inappropriate, and for determining phase diagrams (e.g., for steels).



DFT wins. A methanol molecule at the interface of water and platinum. Periodic boundary conditions are used, creating extended metallic surface states. Structural and energy information can be calculated with DFT, but this system is still beyond reach for high-level methods solving the SE. An improved approximation for the exchange-correlation functional would increase the accuracy of the DFT calculations.

In recognition of the importance of DFT, Walter Kohn was awarded half of the 1998 Nobel Prize in Chemistry (the other half was awarded to John Pople) (*10*). Today numerous approximate functionals are in use (*11*)—a sign of the method's utility but also an indication that none is suitable for all systems. As the complexity of systems investigated by DFT grows (see the figure), the task of choosing the right functional becomes increasingly difficult.

Although DFT is an invaluable tool in investigations of complicated systems, we cannot yet rely solely on this tool but need to combine it with, for example, some experimental data. Furthermore, recent studies involving surfaces have revealed unexpectedly poor and inconsistent energy results (*12, 13*). Errors are much harder to estimate for DFT than for SE contributions, making it difficult to know when DFT is likely not to give accurate results.

For many years, improved numerical techniques and faster algorithms have dominated efforts to improve the results of DFT calculations. Now a number of efficient DFT programs are available that, regardless of numerical method, give the same answer for a given functional. The remaining error stems from the exchange-correlation functional itself. To further improve the accuracy of DFT calculations, better functionals need to be developed.

To this end, a workshop was organized by Sandia National Laboratories in August of this year (*3*). Opening remarks by Walter Kohn (University of California, Santa Barbara) were followed by sessions on the deficiencies of present approximate functionals, chaired by Michael Teter (Cornell University), and strategies for developing improved functionals, chaired by John Perdew (Tulane University).

The two main strategies for developing improved functionals are the "Jacob's ladder" (*14*) and hybrid functionals (*9*). The Jacob's ladder scheme, advanced by Perdew and coworkers, is the traditional strategy in the physics community and is an extension of the strategy that led to the GGAs. The philosophy is to keep everything that works in old functionals while adding capability. The strategy can be viewed as a ladder with five rungs, leading up to the divine functional, the ultimate goal in functional development.

The first rung is the LDA, using only the electron density. The next rung holds the GGAs, where the gradient of the density

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adds refinement. The community is now working on the third rung, the meta-GGAs, where the kinetic energy density is introduced. The fourth rung approaches the divine functional by treating exchange exactly. For this to work, the exact exchange must be combined with a compatible correlation (*14*). The last rung retains the exact exchange and refines correlation by evaluating part of it exactly. The divine functional must have both exact exchange and exact correlation.

The main strategy in the chemistry community is to refine the use of hybrid functionals. The mix of exact exchange and GGA is usually determined by fitting to selected properties of certain groups of molecules. Anne Chaka (NIST) showed that different mixings are optimal for different properties. Varying the mixing throughout a system was proposed to circumvent this problem. Other speakers explored more radical routes, such as the subsystem functional scheme that divides a system into subsystems and uses different, highly specialized, functionals in these subsystems (*15*). Others include DFT for the Hubbard model (*16*) and phase-space functions and energy densities (*17*).

As usual, the workshop raised more questions than it answered. Is it possible to reach the divine functional? Is any one path more promising than another? To be able to go further, do we need an approach radically different from the two main strategies? There was consensus that at least another order of magnitude improvement in calculated energy differences could be expected from DFT. This would tremendously expand the usefulness of DFT calculations and would enable predictive quantitative results for systems from nanotubes to biopolymers.

References and Notes

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18. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the Department of Energy under contract DE-AC04-94AL85000.

PERSPECTIVES: QUANTUM MECHANICS

To Condense or Not to Condense

T. M. Rice

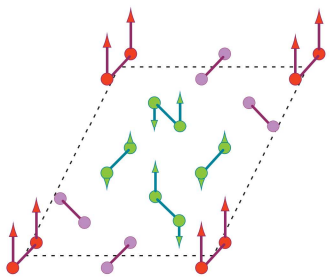
In quantum mechanics, particles are divided into two classes: bosons with integer spin and fermions with half-integer spins. As the temperature is lowered, an ideal gas of bosons undergoes a transition to a phase with a macroscopic occupation of the lowest single-particle state. This Bose-Einstein condensation was recently realized in specially prepared dilute atomic gas clouds cooled to very low temperatures (*1*). But under normal circumstances, bosonic atoms form classical crystals, with the exception of ^{4}He, whose light mass keeps it liquid to the lowest temperatures. Its superfluid transition can be viewed as a Bose-Einstein condensation among strongly interacting bosons. Much less attention has been paid to quantum magnets, where the competition between the classical crystalline and the quantum Bose-Einstein condensed ground states of bosons can be observed in another guise.

The starting point is a crystalline array of dimers—pairs of ions with spin $S = 1/2$ that are coupled antiferromagnetically. Dimers made from two Cu^{2+} ions are ideal for this purpose. The ground state of each dimer is a singlet (a state with paired spins) ($S = 0$). The three excited states form a triplet (with parallel spins) ($S = 1$; $S_z = +1, 0, -1$). A triplet excited on one dimer can hop to a neighboring dimer; as a result, the triplet delocalizes in a way similar to electrons that become delocalized in crystals. The ground state of the dimer crystal is a singlet spin liquid with short-range correlations between spins.

Consider now what happens when an external magnetic field, H_z, is switched on. The field does not alter the singlet ground states but leads to a splitting of the triplets, with the component that is parallel to the field lowered linearly with the field. The minimum energy needed to excite this component will be lowered too, and this energy will reach zero at a critical field strength, H_{crit}.

The triplet components with $S_z = +1$ can be regarded as bosons with a hard core repulsion, which prevents more than one boson from being present on a single dimer. The coupling to the magnetic field, which is proportional to the total magnetization, controls the boson density. The z-component of the exchange interactions generates a repulsion between neighboring bosons. The result is a system of interacting bosons whose ground state is determined by the balance between the kinetic energy and the repulsive interactions.

Consider first the case where the repulsive interactions dominate. Here, the bosons will try to minimize the repulsive interactions. This will work best when the boson density per dimer is a simple rational fraction, because the bosons can then form a simple superlattice. In this case there will be a finite energy cost to creating a separated interstitial-vacancy pair in the bosonic superlattice. This causes a jump in the chemical potential versus boson number, which translates as a plateau in the magnetization versus magnetic-field strength at a rational fraction of the saturation magnetization (*2*).



Complex order. In the magnetization plateau of $SrCu_2(BO_3)_2$, with a net magnetization of 1/8 of the saturation value, the spins of the Cu^{2+} ions form a complex pattern: one in eight of the dimers are strongly polarized parallel to the magnetic field, whereas the remaining dimers have a weaker staggered polarization.

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Such plateaus have been observed in a number of systems for some years (*3*, *4*). However, a direct measurement of the magnetic superlattice has only recently been achieved by Kodama *et al.* (*5*), who used a high-field nuclear magnetic resonance (NMR) technique on $SrCu_2(BO_3)_2$. This material is a frustrated two-dimensional lattice of Cu^{2+} dimers and is a realization of a spin model that was solved in zero field by Shastry and Sutherland (*6*).

The frustrated form of the dimer lattice leads to a narrow bandwidth for the triplet ex-

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Science, 298 (5594), • DOI: 10.1126/science.1077710