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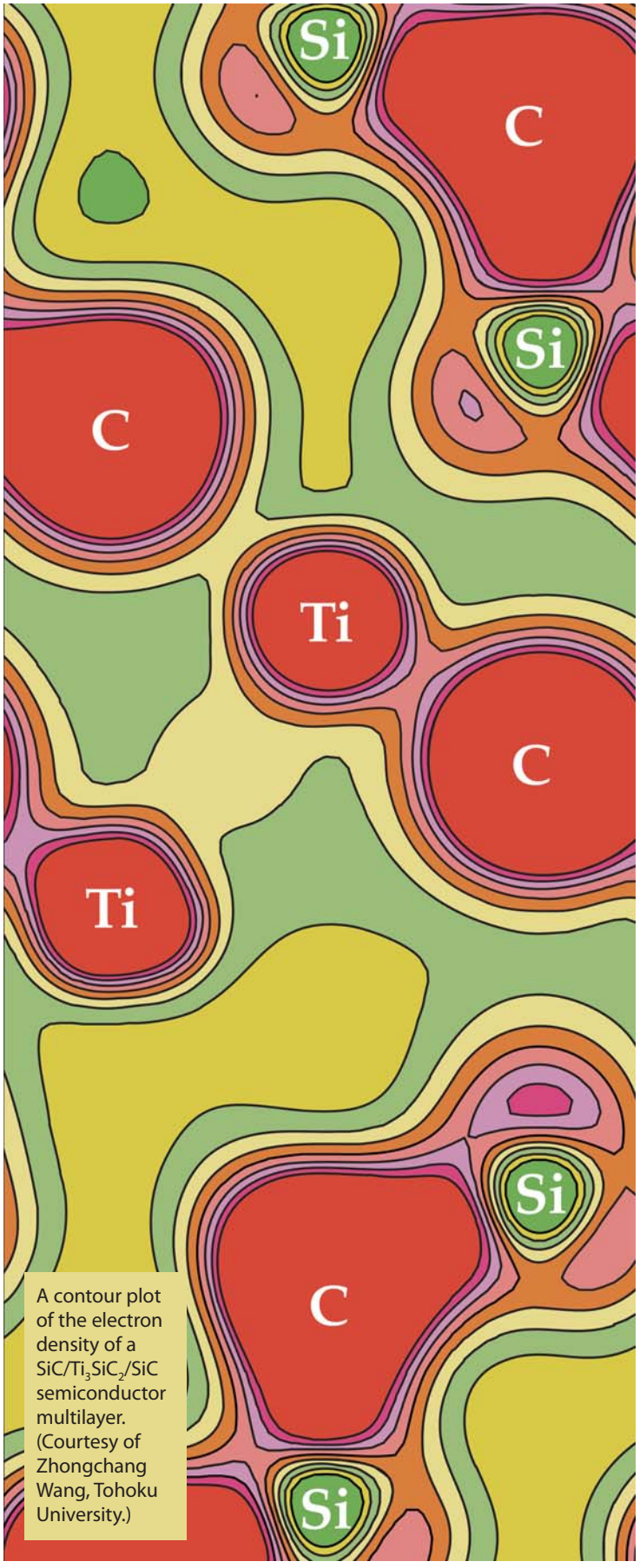

A contour plot of the electron density of a $SiC/Ti_3SiC_2/SiC$ semiconductor multilayer. (Courtesy of Zhongchang Wang, Tohoku University.)

A half century of density functional theory

Andrew Zangwill

Today's most popular method for calculating the electronic structure of atoms, molecules, liquids, solids, and plasmas began as a bold hypothesis: The electron density distribution completely characterizes the ground state of a many-electron system.

In 1929 Paul Dirac made a famous announcement:

> The general theory of quantum mechanics is now almost complete. . . . The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known. . . . It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.[1]

Beginning almost immediately, physicists and chemists rose to Dirac's challenge and developed the theoretical framework needed to calculate wavefunctions and energy eigenvalues for atoms, molecules, and solids.

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By the mid 1960s, computers had sufficient speed and memory to solve the Schrödinger equation for atoms and small molecules by using the Hartree–Fock approximation. That variational method makes a simple guess at the many-electron wavefunction and ensures that each electron interacts with the external potential from fixed nuclei, with the classical electrostatic potential produced by the other electrons, and with a nonlocal exchange potential, which provides short-range repulsion between parallel electron spins. Many-body correlation effects—principally short-range repulsion between antiparallel spins—not captured by the Hartree–Fock approximation were studied by atomic physicists and quantum chemists using more sophisticated choices for the many-electron wavefunction. As a matter of taste, physicists studying correlation effects in solids preferred to use analytic methods borrowed from quantum field theory to analyze model Hamiltonians constructed to capture the essential features of entire classes of materials.

That was the state of affairs in 1964–65 when density functional theory (DFT) appeared. A first paper by theoretical solid-state physicist Walter Kohn and his postdoctoral fellow Pierre Hohenberg proved that the electron density $n(\mathbf{r})$ at spatial point $\mathbf{r}$ is sufficient to completely characterize the ground state of an N-electron system—no many-electron wavefunction required.[2] A second paper by Kohn and postdoctoral fellow Lu Sham cast the exact many-body problem—calculating $n(\mathbf{r})$ and the total energy—in the form of a set of equations similar to, but simpler than, the Hartree–Fock equations.[3] An essential feature of the theory is the exchange-correlation energy $E_{xc}[n(\mathbf{r})]$. That formally exact but unknown quantity is a functional of the density. That is, it maps the electron density function $n(\mathbf{r})$ to the scalar energy E_{xc} associated with all exchange and correlation effects. An approximation to $E_{xc}[n(\mathbf{r})]$ is needed for practical work, and Kohn and Sham proposed one for that purpose.

Material-specific calculations performed throughout the 1970s and 1980s showed that the approximation proposed by Kohn and Sham could produce valuable information about electronic structure without appeal to experiment. A transformative event of the late 1980s was the development of significantly better approximations for $E_{xc}[n(\mathbf{r})]$. Commercial DFT codes soon appeared that allowed nonexperts with modest computational resources to perform calculations with great accuracy for many, if not all, systems of interest. The largest impact was felt for complex systems for which alternative computational methods were prohibitively expensive. DFT rapidly became the tool of choice for the vast majority of researchers interested in calculating the physical properties of specific atoms, molecules, liquids, solids, and plasmas.

Many types of problems have been tackled using DFT. Here's a sampling: Condensed-matter physicists predicted and then synthesized a new superconductor with a previously unknown crystal structure.[4] Physical chemists explored the relative reaction kinetics for the crystal growth of gallium nitride by using either trimethylgallium or triethylgallium as the precursor molecule.[5] Geoscientists predicted and then found a new crystalline phase of magnesium silicate whose calculated elastic properties explained several previously puzzling properties of the lowermost layer of Earth's mantle.[6] Theoretical biochemists combined DFT with classical molecular-dynamics simulations to identify the mechanistic reason why aspirin inhibits one form of the enzyme cyclooxygenase much more than a closely related form.[7] DFT also has made important contributions to materials-design projects intended to replace traditional trial-and-error experiments with carefully targeted experiments guided by theory and computation.[8]

In 1990 Hohenberg, Kohn, and Sham (shown in figure 1) published a lively reminiscence of their experiences creating DFT.[9] Less than a decade later, Kohn shared the Nobel Prize in Chemistry for his role in creating the theory (see PHYSICS TODAY, December 1998, page 20). In this article I commemorate the 50th birthday of DFT by looking back at its first 25 years with three questions in mind: What circumstances motivated the creation of DFT? How did theoretical physicists and quantum chemists react to DFT at first and as time went on? What will be the legacy of DFT?[10]

Figure 1. Creators of density functional theory. Walter Kohn (left, in 1962) and his two postdoctoral fellows, Pierre Hohenberg (middle, in 1965) and Lu Sham (right, undated), produced their theory in 1964 and 1965. (Photographs courtesy of Walter Kohn and the John Simon Guggenheim Memorial Foundation, Pierre Hohenberg, and Lu Sham.)

Alloys in Paris

In the summer of 1963, Kohn arrived in Paris to spend the fall with the research group of Philippe Nozières at the École Normale Supérieure. His plan was to study the effects of the electron–phonon interaction on the optical properties of metals. The topic was timely because experiments had just confirmed Kohn's prediction that the electron–phonon interaction produces anomalies in the vibrational

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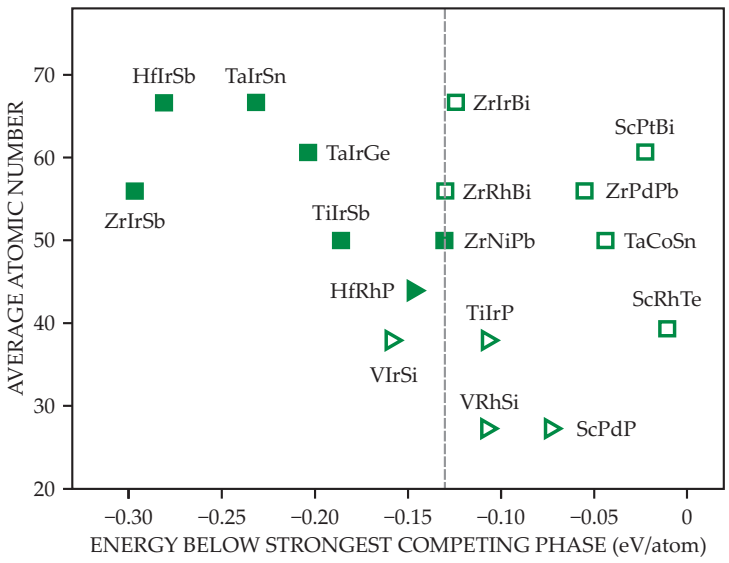

Figure 2. These previously unknown ternary compounds were predicted by density functional theory (DFT) to be thermodynamically stable and were later synthesized by experiment. The horizontal axis is the calculated energy "distance" from a compound's strongest competing phase. Square and triangular symbols designate cubic and noncubic crystal structures, respectively. DFT successfully predicted nearly all the compounds to the left of the dashed line as single phase (solid symbols) and compounds to the right of it as multiphase (open symbols). VIrSi is the only exception. DFT calculations also predicted the correct optical properties for the compounds.
(Figure adapted from ref. 16.)

spectrum of a metal. That prediction was part of the work for which he was awarded the 1961 Oliver E. Buckley Solid-State Physics Prize by the American Physical Society.

As it turned out, Kohn did not work on the electron–phonon problem in Paris. Instead, he began thinking about how to calculate the total energy of a disordered metal alloy. A likely trigger for the change of plan was the 1962 publication of an international symposium on metallic solid solutions in the *Journal de Physique et le Radium*. The contributors included many of Kohn's friends in the theoretical solid-state physics community: Nevill Mott, Sam Edwards, Jacques Friedel, and Pierre-Gilles de Gennes, among others. Kohn also had a long-standing interest in alloys because he had spent the years 1950–60 at the Carnegie Institute of Technology, where alloy physics was a specialty of the experimental solid-state physics faculty.

Disordered alloys are characterized by randomness in the chemical identity of the atoms located at the sites of an underlying periodic lattice. The electrostatic potential $v_{ext}(\mathbf{r})$ produced by the fixed ions and felt by the electrons thus varies randomly from site to site. Unfortunately, no method was known to solve the Schrödinger equation to find the many-electron wavefunction for such a situation. The wavefunction was required because the expectation values of the electron kinetic energy and the electron–electron Coulomb repulsion are important contributors to the total energy.

Kohn immersed himself in the metallurgical literature and studied the evidence that charge transfer occurs between the chemically different constituents of an alloy. As he related in his Nobel Prize lecture, "The electrostatic interaction energy of these charges is an important part of the total energy. Thus in considering the energetics of this system there was a natural emphasis on the electron density distribution $n(\mathbf{r})$." In the 1990 reminiscence paper with Hohenberg and Sham,[9] Kohn uses perturbation theory in reproducing a derivation of the total energy of a disordered alloy. The final expression involves only two quantities: the electron density averaged over the entire crystal and the actual, spatially varying electron density $n(\mathbf{r})$. At this point, he says, "the question occurred to [me] whether a knowledge of $n(\mathbf{r})$ alone determined—at least in principle—the total energy."

It is important to appreciate the revolutionary nature of that question. In the Schrödinger equation, the ionic potential $v_{ext}(\mathbf{r})$ is the only term that distinguishes one alloy from another. That potential determines the wavefunction, which in turn determines the electron density and the total energy. The energy is thus a functional of $v_{ext}(\mathbf{r})$. Kohn contemplated a radical inversion of that thinking. Is it possible that the total energy depends only on the electron density $n(\mathbf{r})$? Years earlier Llewellyn Thomas and Enrico Fermi had proposed approximate theories of the total energy where that was the case, but no one had seriously suggested that the exact total energy of any many-electron system could be a functional of the electron density alone. If it were true, knowledge of $n(\mathbf{r})$ was sufficient to determine the external potential, the many-particle wavefunction, and all the ground-state properties—even the Green functions of many-body theory! That was a very deep question. Kohn realized he wasn't doing alloy theory anymore.

General questions require general solution methods, and Kohn was particularly well trained in one class of them: the variational methods of mathematical physics. Such methods were a particular specialty of the department of applied mathematics at the University of Toronto, where Kohn had earned his BA and MA degrees. The local experts there were chairperson John Lighton Synge and two of Kohn's mentors, Alexander Weinstein and Arthur Stevenson. Another virtuoso of variational methods, Julian Schwinger, supervised his Harvard PhD thesis, which introduces what is today called the Kohn variational principle. From the reminiscence paper,[9] or from any technical review of DFT, one can learn how variational methods are central to the proof of the Hohenberg–Kohn theorem and to the derivation of the Kohn–Sham equations.

The physicist's reaction

When it appeared in *Physical Review*, the elegant and austere Hohenberg–Kohn paper did not make a great impression on the physics community. A typical reaction came from one of Kohn's own postdocs, Vittorio Celli, who attended a seminar presented by Kohn when he returned to the US early in the spring of 1965:

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> I remember thinking that the theory with Hohenberg was cute but would not have many consequences. I certainly did not think it compared in significance with the many-body calculations for the electron gas that had been obtained by [Keith] Brueckner and his collaborators.[10]

In the late 1950s, physicists were beginning to apply the powerful methods of quantum field theory to many-body phenomena, and Lev Landau's theory of the Fermi liquid produced a natural focus on the excitation spectrum rather than on the ground-state properties that DFT was designed to address. Hohenberg began a long career at Bell Labs at the end of 1964, and he vividly remembers the reaction of the resident theorists when he spoke about his and Kohn's work: "Phil Anderson, Bill McMillan, and Phil Platzman were in the audience and there was no enthusiasm. They correctly understood that our results would not help them solve the difficult many-body problems they were struggling with."[10]

By contrast, the Kohn–Sham paper presented a set of Hartree-like equations that would appeal immediately to any physicist interested in calculating the electronic properties of specific crystalline solids. The equations in question are

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad (1)$$

where $\psi_i(\mathbf{r})$ is the ith single-electron wavefunction of a noninteracting electron system with the same density, $n(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$, as the interacting electron system of interest. The functional derivative $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n(\mathbf{r})]/\delta n(\mathbf{r})$ defines a local potential that takes exact account of both exchange and correlation. This is the deep achievement of the theory: If $E_{\text{xc}}[n(\mathbf{r})]$ was known, $v_{\text{xc}}(\mathbf{r})$ would be known, and one could exactly calculate $n(\mathbf{r})$ and the total energy of the ground state from the N solutions of equation 1.

Unfortunately, $E_{\text{xc}}[n(\mathbf{r})]$ is probably unknowable. So Kohn and Sham proposed a local density approximation (LDA) for $E_{\text{xc}}[n(\mathbf{r})]$, in which the exchange-correlation behavior of every tiny volume of an inhomogeneous system is taken to be the same as the behavior of a uniform electron gas with a density equal to the density of that volume. That gives

$$v_{\text{xc}}(\mathbf{r}) \approx \frac{d}{dn}\left[n\epsilon_{\text{xc}}(n)\right]_{n=n(\mathbf{r})} = v_{\text{x}}^{\text{LDA}}(\mathbf{r}) + v_{\text{c}}^{\text{LDA}}(\mathbf{r}), \quad (2)$$

where $\epsilon_{\text{xc}}(n)$ is the exchange–correlation energy per particle of an electron gas with uniform density n. The exchange part, $v_{\text{x}}^{\text{LDA}}(\mathbf{r}) = -[(3/\pi)n(\mathbf{r})]^{1/3}$, was known exactly, and the correlation part $v_{\text{c}}^{\text{LDA}}(\mathbf{r})$ was easily approximated from existing many-body calculations.

Materials-minded physicists concerned primarily with simple metals and semiconductors were respectful but not excited by the LDA because semiempirical methods already provided the information they wanted. But the LDA held real promise for those interested in more complex systems like transition metals, ordered compounds, and solid surfaces. Indeed, equations 1 and 2 were already being used to study those systems. Absent the correlation part, they had been proposed in 1951 by John Slater,[11] who replaced the nonlocal exchange potential in the Hartree–Fock equations by a local exchange potential, $v_{\text{x}}^{\text{Slater}}(\mathbf{r}) = -\frac{3}{2}[(3/\pi)n(\mathbf{r})]^{1/3}$. Because $v_{\text{x}}^{\text{LDA}} = \frac{2}{3}v_{\text{x}}^{\text{Slater}}$, the LDA was widely considered to provide theoretical justification for Slater's insight about the exchange part of the many-electron problem.

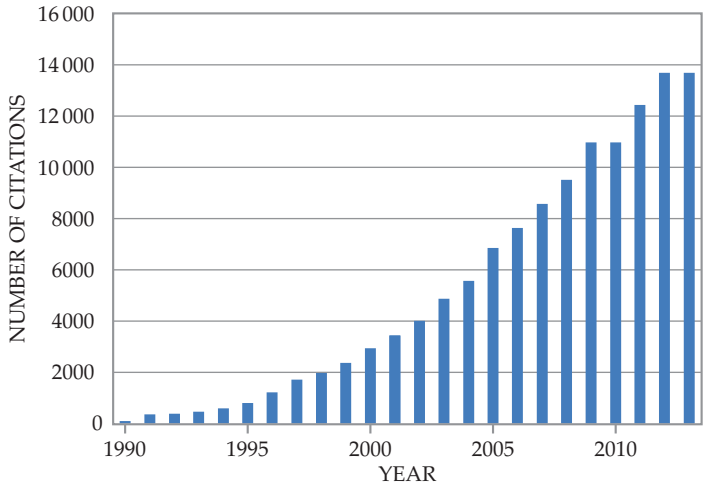

Figure 3. The number of annual citations to one or both of the foundational papers (references 2 and 3) of density functional theory (DFT). Both papers are among the most highly cited in the history of *Physical Review*, a fact that reflects the increasingly widespread adoption of DFT as a method to compute electronic structures. (Data from the Web of Science.)

LDA calculations performed through the decade of the 1970s yielded ground-state properties of solids to within 1–10% of their experimental value. That track record led Michael Schlüter and Sham to argue in their February 1982 PHYSICS TODAY article (page 36) that the LDA version of DFT was the most reliable method to predict crystal structures, equilibrium lattice constants, phonon spectra, cohesive energies, and work functions. In some cases, practitioners had success interpreting the quantities ϵ_i and $\psi_i(\mathbf{r})$ in equation 1 as one-electron energy eigenvalues and eigenfunctions of the *interacting* electron system being studied, despite the lack of any formal justification from Kohn–Sham theory to do so. The remarkable impact of the LDA on physics by the end of the 1980s can be judged from the contents of *Physical Review B*, the leading archival journal of condensed-matter physics. Of the 112 articles published in the 15 December 1990 issue, 32 either reported new LDA calculations or compared new experimental results with previously published LDA calculations.

In parallel with researchers who performed LDA calculations, a small but dedicated group examined the foundations of DFT itself. Some plumbed the depths of the Hohenberg–Kohn theorem; others discovered exact properties of the exchange–correlation energy and used them to

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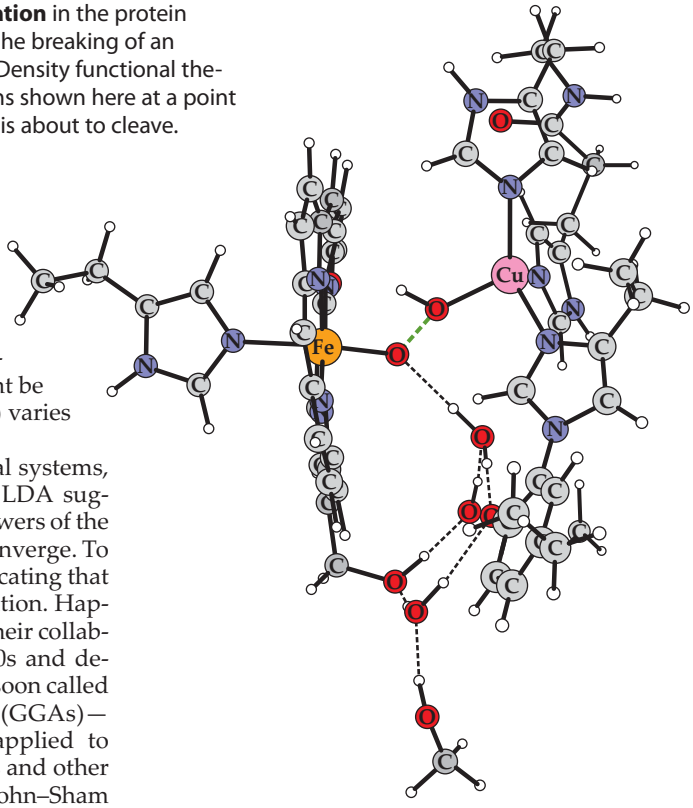

Figure 4. The process of cellular respiration in the protein complex cytochrome c oxidase involves the breaking of an oxygen–oxygen bond (shown in green). Density functional theory determined the arrangement of atoms shown here at a point in the reaction pathway when that bond is about to cleave. (Adapted from ref. 17.)

explain why the eigenvalues of the Kohn–Sham equations do not correctly predict the energy bandgap in a semiconductor. Other aspects of $E_{xc}[n(\mathbf{r})]$ helped explain why the LDA succeeds so often in situations where it might be expected to fail—for example, where $n(\mathbf{r})$ varies rapidly in space.

Density gradients can be large in real systems, and early studies of corrections to the LDA suggested that an expansion of $E_{xc}[n(\mathbf{r})]$ in powers of the dimensionless ratio $|\nabla n|^2/n^{8/3}$ might not converge. To some researchers, that was a red flag indicating that the LDA was an uncontrolled approximation. Happily, David Langreth, John Perdew, and their collaborators reexamined the issue in the 1980s and derived new approximations for $E_{xc}[n(\mathbf{r})]$—soon called generalized gradient approximations (GGAs)—which outperformed the LDA when applied to atoms, solids, and surfaces. Today, GGAs and other post-LDA functionals for solving the Kohn–Sham equations are the standard for solid-state work in which quantitative, material-specific information is desired. (Figure 2 shows one example.) The ubiquity helps explain why the Kohn–Sham article is one of the most highly cited papers in all of physics. The number of citations to it per year has increased nearly every year since it was published (see figure 3 and the article by Sid Redner, PHYSICS TODAY, June 2005, page 49).

The chemist's reaction

Chemists grapple daily with the small energy differences that drive the diversity of their subject. Theoretical chemist E. Bright Wilson made that point in 1983 when he discussed the contributions of quantum mechanics to chemistry:

> One thinks perhaps first of the thousands of quantitative calculations of electronic energies from which values of interatomic distances, heats of reaction, barriers to internal rotation, reaction rates, etc. have been obtained. I believe that ultimately this will be the most important type of contribution.[12]

Computational chemistry is judged by its ability to calculate energies accurately, and the standard of less than 0.1 eV needed for most chemical problems is much more severe than the accuracy needed for most solid-state physics problems. For that reason, chemists largely ignored DFT throughout the entire LDA era.

A quantum chemist typically solves the Schrödinger equation for an N-electron molecule by using a trial-wavefunction method:

- Create a set of orbitals for each atom by superposing analytic basis functions with adjustable weight factors.
- Create a set of molecular orbitals by superposing different groups of atomic orbitals with adjustable weight factors.
- Choose groups of N molecular orbitals and organize each group into fully antisymmetric one-electron wavefunctions called Slater determinants.
- Use adjustable weight factors to superpose all the determinants into a single many-electron wavefunction.

The computational task is to vary the weight factors until the calculated ground-state energy is minimized.

Two papers published in the summer of 1972, both about the water molecule, demonstrated that a first-generation molecular LDA calculation could not compete with a high-quality wavefunction calculation.[13] The wavefunction calculation superposed more than 2000 Slater determinants and obtained a total energy within 0.25% of the experimental value. The LDA calculation, by contrast, incorrectly found that the ground-state geometry of the molecule was linear rather than bent. Years later, LDA practitioners realized that the principal source of error in the calculation was not its use of a local exchange potential, but rather its use of an additional simplification of the total potential function introduced to facilitate the numerical solution to equation 1. Nevertheless, the damage was done, and many quantum chemists simply refused to take LDA calculations seriously.

Robert O. Jones is one of several scientists who developed methods to solve the Kohn–Sham equa-

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tions for molecules without making any simplifying approximations beyond the LDA. In a recent reminiscence,[14] Jones describes the disbelief of quantum chemists when his 1979 calculation predicted that the beryllium dimer would have a very short bond length. Up to that time, all wavefunction calculations had predicted that Be_2 was either unbound or had a very long bond. The subsequent experimental confirmation of the LDA prediction did not change many minds. To his dismay, Jones learned later from the editor of the *Journal of Chemical Physics* that "despite the large number of manuscripts published [in this journal using DFT], many chemists remain to be convinced of its value."

By the mid 1980s LDA calculations often reproduced chemical trends, but they consistently and embarrassingly predicted molecular binding energies 1–2 eV greater than those seen in experiment. That problem motivated quantum chemist Axel Becke to adopt a spirit of practicality and empiricism: He fit a parameterized GGA to Hartree–Fock exchange-energy data for atoms, added the LDA correlation energy, and used the resulting potential to solve the Kohn–Sham equations for a series of diatomic molecules. His calculation reduced the error in bond energies by 75% compared with a standard LDA calculation. Subsequent research improved matters even more and dovetailed with the GGAs that physicists proposed on nonempirical grounds.

In 1991 Becke spoke at an international congress of quantum chemistry. The closing address was given by John Pople, a computational chemist whose widely used Gaussian computer program made it possible for nontheorists to perform high-quality wavefunction calculations. Pople remarked that he found Becke's results "stimulating and intriguing," and barely a year later, his group published a systematic comparison of the best quantum chemical calculations with DFT calculations for 32 molecules.[15] Pople and his collaborators concluded that the best density functionals outperformed the best wavefunction methods and that the wavefunction methods were computationally more expensive. DFT was promptly incorporated into the Gaussian program, and with that endorsement, many chemists joined their physics colleagues in recognizing the value of DFT as the fastest way to calculate electronic properties with an accuracy sufficient to address many of their scientific questions. (Figure 4 shows one example.) In 1998 Pople shared the Nobel Prize in Chemistry with Kohn "for his development of computational methods in quantum chemistry."

The legacy of DFT

The long-term legacy of DFT depends largely on the continued value of the DFT computer programs that practitioners use daily. One could argue that the algorithms implemented in those programs reflect a long sequence of approximations and extensions made by many individuals to the original Hartree–Fock method to solve the *N*-electron Schrödinger equation. The sequence begins with Slater's density-dependent approximation for the exchange potential. It proceeds to density-dependent correlation effects originally derived by many-body theorists for other purposes. Next come density-gradient corrections, which were also first used for other purposes and later added to Slater's exchange potential. The sequence ends with the adoption of empirical and semiempirical potential functions that deliver the present level of agreement between calculations and experiment.

Although accurate in detail, those operational steps give the wrong impression about the evolution of charge-density-based electronic-structure calculations after 1965 precisely because they do not mention the Hohenberg–Kohn theorem or the Kohn–Sham formalism. The numerical results, however good, would always be suspect as having been derived from ad hoc, albeit physically motivated, considerations unanchored to an underlying fundamental theory. Ultimately, DFT provides both the scientific justification and the basis for understanding the meaning behind the algorithms used in the computer codes. That would be true even if no aspects of DFT had been known to the practitioners.

If DFT had not been invented in the mid 1960s, the superior results obtained from today's codes would eventually force suspicions that an exact many-body theory based entirely on charge density must exist. It is to the great credit of Hohenberg, Kohn, and Sham that they had such a suspicion and acted on it, even in the face of scant supporting evidence. Indeed, their key idea was not "in the air," and the zeitgeist of many-body theory was moving steadily in other directions for both physicists and chemists. That is why the deep insight demonstrated by Walter Kohn and his young collaborators must be counted as much a part of DFT's legacy as the quality of the numerical results obtained by its current manifestations.

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