

A Tryst With Density

Walter Kohn and Density Functional Theory

Shobhana Narasimhan

Walter Kohn transformed theoretical chemistry and solid state physics with his development of density functional theory, for which he was awarded the Nobel Prize. This article tries to explain, in simple terms, why this was an important advance in the field, and to describe precisely what it was that he (together with his collaborators Pierre Hohenberg and Lu Jeu Sham) achieved.

Introduction

Walter Kohn was an Austrian-born Canadian and American scientist who made immense contributions to solid state physics. Though he worked on many important problems in the field, he is best known for developing the density functional theory (DFT). This is an extremely successful approach for handling many-body Schrödinger equations, whose popularity among chemists, physicists, materials scientists, and even biologists and geologists, continues to grow exponentially. Reflecting the transformative effect that DFT has had on entire fields of research, Kohn was awarded the Nobel Prize for chemistry in 1998¹.

The Quantum Many-Body Problem

What makes DFT remarkable is that it provides an approach for solving many-body problems in quantum mechanics that makes them unexpectedly easy to handle, yet usually gives very accurate results. To understand what a startling and noteworthy achievement this is, let us first consider two-body and three-body problems in classical mechanics or electrodynamics. When three objects interact with each other – for example, through gravity or



Shobhana Narasimhan is a Professor in the Theoretical Sciences Unit at the Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore. Her research focuses on making use of density functional theory in the rational design of novel nanomaterials for various applications. She is also interested in science writing, science education, and issues related to gender and science.

¹See K D Sen, The creative Kohn, *Resonance*, Vol.4, No.4, pp.56–63, 1999.

Keywords

Walter Kohn, density functional theory, many-electron problem, Hohenberg–Kohn theorems, Kohn–Sham equations.



electromagnetic fields, the resulting ‘three-body problem’ is notoriously difficult to solve, whereas the corresponding ‘two-body problem’ is relatively easy to handle. Thus, while one can write down a simple analytical equation for the elliptical orbit of the Earth around the Sun (a two-body problem, with the Earth and the Sun interacting with each other through the gravitational force), it is much harder to solve for the trajectories in the three-body problem of the Earth, the Moon and the Sun. Even if we were to assume that the Sun, being so much more massive than the Earth or the Moon, is stationary, one cannot write down a simple exact and analytical expression for the orbits of the Earth and the moon, since each of them experiences not just the gravitational pull of the Sun, but also of the other. Another three-body problem that has become famous in popular culture is that of the planet Tatooine. Fans of *Star Wars* will recognize that this is the planet that Luke Skywalker grows up on. Tatooine is unusual in that it orbits around not one, but two suns. Not even Yoda, Luke’s wise and all-knowing mentor, would be able to solve exactly the problem of Tatooine and its two suns, or perhaps even explain why Tatooine has a stable orbit!

Similarly, in quantum mechanics, one can obtain an exact analytical solution for the Schrödinger equation² of the hydrogen atom – a two-body problem consisting of an electron orbiting a proton – but not for the helium atom which can be viewed as a three-body problem, where two electrons interact with a nucleus consisting of an alpha particle. Such three-body problems can often be solved numerically (this becomes especially easy if one uses computers), utilizing approximations and techniques such as perturbation theory. However, as the number of interacting bodies becomes larger, the problem becomes increasingly harder to solve, with the computational requirements for CPU time and memory storage growing exponentially.

To obtain a theoretical understanding of the behaviour of atoms and molecules in chemistry, or solids in condensed matter physics, one needs to use quantum mechanics. Apart from the hydrogen atom, or a handful of examples that can be treated by mapping

²The central quantity of interest for a quantum mechanical system is usually its wavefunction ψ . Just as solving the Newton equation $\mathbf{F} = m\mathbf{a}$ enables one to understand the motion of a classical system, writing down and solving the Schrödinger equation provides the wavefunction of a (non-relativistic) quantum system. The physical interpretation of the wavefunction is that $|\psi|^2$ gives the probability density.



them onto other simple one-body problems like the quantum mechanical simple harmonic oscillator or a particle in a box, these are all many-body problems. Here, the number of interacting entities can be so huge that these problems present a seemingly unsurmountable challenge even to various approximate numerical techniques that have been developed over the years to deal with many-body problems. For example, in organic chemistry, one routinely deals with molecules that have hundreds or even thousands of electrons and nuclei interacting with one another, while in condensed matter physics, a solid of macroscopic dimensions has of the order of 10^{23} interacting electrons and nuclei.

In organic chemistry, one routinely deals with molecules that have hundreds or even thousands of electrons and nuclei interacting with one another, while in condensed matter physics, a solid of macroscopic dimensions has of the order of 10^{23} interacting electrons and nuclei.

When one wants to understand the quantum mechanical properties of a system, usually the first step one takes is to write down the Schrödinger equation (or, if relativistic effects are important, the Dirac equation) for the system. When one has to describe a quantum many-body system, it is important to realize that the hard part is not writing down the many-body Schrödinger equation, but solving it. This was stated, with typically elegant economy of words, a century ago by the physicist Paul Dirac: “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are . . . completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.”

When formulating the many-body Schrödinger equation for a molecule or a solid, in order to obtain the expression for the Hamiltonian, we need to first consider which interactions are important among the electrons and nuclei that the system is comprised of. It turns out that of the four fundamental forces in nature, we need to take into account only one of them – the electromagnetic force. In fact, we usually need to consider only the electrostatic Coulomb interaction, which has the simple form q_1q_2/r , where q_1 and q_2 are the charges of the two interacting particles, and r is the distance between them. Thus, we have pair-wise repulsive Coulomb interactions between the positively charged nuclei, pair-wise repulsive Coulomb interactions between the negatively charged electrons, and pair-wise attractive Coulomb interactions

When one has to describe a quantum many-body system, it is important to realize that the hard part is not writing down the many-body Schrödinger equation, but solving it.



between the nuclei and electrons. Unfortunately, being able to write down an equation does not necessarily mean that it is easy to solve!

There is one other complication. This is purely quantum-mechanical in origin. The solutions to the many-electron equation have to obey the Pauli exclusion principle, since the electrons, having spin $1/2$, are fermions³. This means that the many-electron wavefunction has to have the property that it changes sign when any two electrons are exchanged. This requirement can be thought of as being equivalent to having an additional interaction between pairs of electrons, which is known as the exchange interaction.

³The states of quantum mechanical particles are specified by a set of integers called the *quantum numbers*. Quantum particles with half-integral spin ($1/2, 3/2, \dots$) are called *fermions*, while those with integral spin ($0, 1, 2, \dots$) are called *bosons*. The *Pauli exclusion principle* states that no two identical fermions in a quantum system can have all their quantum numbers be the same. Though this may not seem immediately obvious, this also requires that the wavefunction of the system be antisymmetric with respect to exchange of two fermions.

Two Breakthrough Papers

Kohn's breakthrough in how to solve the many-electron problem – though only for the ground state – was presented in two landmark papers, written in a beguilingly low-key and accessible style, published in *Physical Review*. The first paper, written with Pierre Hohenberg in 1964, was titled 'Inhomogeneous electron gas' [1], while the second, co-authored with L J Sham and appearing a year later, was on 'Self-consistent equations including exchange and correlation effects' [2]. It is these two papers that gave birth to the field, and indeed the industry, of density functional theory. Each of these papers has now been cited tens of thousands of times in the literature, and undoubtedly the number of citations would be far higher, were it not for the fact that these papers are now considered much too well-known to need citing!

The Hohenberg–Kohn Theorems: *D* for Density

The mathematician G H Hardy described the method of proving a theorem by the method of *reductio ad absurdum*⁴ as “one of the mathematician's finest weapons”. In their paper, Hohenberg and Kohn showed that physicists too can use this method to brilliant effect. By first assuming the contrary, and showing that this resulted in a contradiction, they proved that in order to determine the ground-state properties of a many-electron system, it

⁴The method of *reductio ad absurdum* is also known as 'proof by contradiction'. One starts by assuming the opposite of what it is that one wants to prove, and shows that this assumption leads to a contradiction, or an absurd result.



suffices to know the ground-state density. This is a startling result, because while one pretty much takes it for granted that these properties can be determined from knowledge of the ground-state wavefunction, which is a function of $3N$ variables (where N is the number of electrons, which can be a very large number), it is not at all intuitive that the same can be determined from the density, which is a function of just the 3 spatial coordinates of the system⁵.

I was once present when a world-famous mathematical physicist first encountered this statement of the Hohenberg–Kohn theorem, and he greeted it with howls of outrage: “This CANNOT be true! I REFUSE to accept it!” However, when confronted with Hohenberg and Kohn’s simple four-line proof of this theorem (which can easily be understood by any undergraduate physics student), he had to reluctantly concede defeat, and spent the rest of the seminar frowning unhappily as he tried to come to terms with the theorem and its implications. Physicists accept that the wavefunction contains all the requisite information needed to compute the properties of a system. Of course, if one knows the wavefunction, then the density is easily obtained by computing the squared modulus of the wavefunction⁶. One tends to feel that essential information is being lost in the process of going from the wavefunction to the density, and therefore one might think that knowledge of the density alone should not suffice, even if one is restricting oneself to ground-state properties – hence the discomfort expressed by the renowned mathematical physicist!

In his Nobel lecture [3], Kohn contrasts DFT, with its emphasis on the electron density, with wavefunction-based methods such as the Hartree–Fock method⁷ and its successors, which are beloved of quantum chemists. Because of the large number of variables, the computational cost of carrying out a wavefunction-based calculation rises sharply as N , the number of electrons, increases, becoming prohibitively expensive at quite a small value of N (in 1998, he estimated the upper limit as about $N = 10$, though today it is somewhat larger). However, Kohn also emphasizes the fact that, unlike the wavefunction, the density is a physically

⁵The many-electron wavefunction has the form $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, where \mathbf{r}_i denotes the three spatial coordinates specifying the position of the i th electron. Thus, it depends on $3N$ variables, not counting the electron spin indices. In contrast, the density has the form $n(\mathbf{r}) = n(x, y, z)$, *i.e.*, it depends on just the three spatial coordinates (x, y, z) .

⁶The many-electron wavefunction ψ and the electron density $n(\mathbf{r})$ are related by the equation $n(\mathbf{r}) = N \int d^3 r_2 \dots d^3 r_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$.

⁷Hartree–Fock is an approximate wavefunction-based method for solving the many-electron Schrödinger equation. The many-electron wavefunction ψ is approximated by a linear combination of products of one-electron terms, combined in a way which guarantees that the Pauli exclusion principle is satisfied.



measurable quantity. Thus, by giving the density a central role, DFT achieved two things: it not only made calculations more computationally feasible, it also stressed the importance of quantities that could, at least in principle, be measured in experiments.

The Hohenberg–Kohn Theorems: F for Functional

So now that we’ve dealt with the ‘D’ for density, let’s focus next on the ‘F’ in ‘DFT’. The electron density is an example of a quantity that is a ‘function’ in that it depends on a variable or variables – in this case, on the three variables specifying a position in three-dimensional space. A ‘functional’, in contrast, is something that is a function of a function, *e.g.*, it can be a function of the density. Hohenberg and Kohn went on to show that there is a universal functional of the density that becomes a minimum at the true ground-state density of the many-electron system. This minimum value is then equal to the true ground-state energy of the system.

The Hohenberg-Kohn formulation means that, in principle, one could consider solving the many-electron problem using the calculus of variations⁸. However, there remains a big problem. Hohenberg and Kohn could only prove that such a universal function exists, they did not tell us what form it takes! However, one should not underestimate the importance of an existence proof – it supplies a moral justification for one’s subsequent endeavours along those lines. It plays the crucial role of assuring those searching for the final solution that the pot of gold really does exist at the end of the rainbow, and is not a mirage. ‘Do not despair!’ is its important message.

The Kohn–Sham Equations

So now we know why the method introduced by Hohenberg and Kohn is called the ‘density functional’ theory. However, almost no one actually solves the many-electron problem by directly applying a variational procedure to the energy functional with respect to the density. This is because the next year, Kohn and Sham went on to suggest an alternative procedure that is not only much easier to apply, but also lends itself more easily to physical

⁸The ‘calculus of variations’ is a mathematical approach where one solves a problem by varying a functional until it achieves either a maximum or minimum value. Examples of applications in physics are calculating the path of a ray of light in optics using Fermat’s principle of least time, and the Rayleigh–Ritz variational principle in quantum mechanics.



interpretation. While the Hohenberg–Kohn paper of 1964 gave the name to the technique and the field it spawned, and provided the underlying foundation for the work that followed, “that alone doesn’t win you a Nobel Prize”, says the physicist Richard Martin, who is widely acknowledged as a foremost authority in the field, and has written the standard reference book [3] on the subject. “It was the Kohn–Sham paper of 1965 that really was the game-changer.”

In this paper, Kohn and Sham showed that for the ground state, the many-electron problem can be mapped (in principle, exactly) onto a system of one-electron equations, known as the Kohn–Sham equations⁹. But we know how to solve one-electron equations! So, does this then mean that we now have gained, seemingly magically, the ability to solve many-electron equations? Doesn’t this seem too good to be true? Alas, it is indeed. The price we pay is that the Kohn–Sham equations (unlike the original many-body Schrödinger equation) now contain a term whose form is unknown. The equations no longer have just simple Coulombic pair-wise interactions in the Hamiltonian, all the ugly many-body stuff (such as the effects of the Pauli exclusion principle or the unknown form of the universal Hohenberg–Kohn energy functional) gets dumped into an additional term, called the ‘exchange-correlation potential’ in the Hamiltonian of the Kohn–Sham equations. The Italian physicist Stefano Baroni likes to call the exchange-correlation term ‘the stupidity term’, since it represents our stupidity – it contains all the stuff that we are (at least as yet) too stupid to know how to write down an expression for.

The Kohn–Sham equations are eigenvalue equations that look very much like one-electron Schrödinger equations. It is therefore very tempting to interpret the eigenvalues of the Kohn–Sham equations as electronic energies, and the eigenvectors as electronic wavefunctions, though there is no formal justification for doing so. Strictly speaking, the only quantities that have physical meaning are the ground-state energy and the ground-state density constructed from the eigenvalues and eigenvectors. These are guaranteed (if we knew the true exchange-correlation func-

⁹It is important to note that the Kohn–Sham Hamiltonian contains no free parameters or empirical input. To write down and solve the Kohn–Sham equations for a system, the only input required is the atomic numbers of the elements. For this reason, DFT calculations are also often called ‘first principles’ or ‘ab initio’ calculations.

Kohn and Sham showed that for the ground state, the many-electron problem can be mapped (in principle, exactly) onto a system of one-electron equations.



tional, which is a big ‘if’) to be exactly equal to the ground-state energy and density of the many-electron system whose properties we want to determine. However, in practice, scientists often tend to make use of the eigenvalues and eigenvectors of the Kohn–Sham equations by interpreting them as one-electron energies and wavefunctions. Much of the time, such a procedure leads to a physically reasonable outcome, *i.e.*, the theoretical results agree at least qualitatively with experiments (such as photoemission spectroscopy) that measure such quantities and help us interpret them. Still, one should not forget that this procedure has a shaky foundation built on sand – we can shrug our shoulders and argue that it is fine to use it because it generally seems to work. However, maybe every once in a while we will carelessly venture onto an earthquake-prone zone, then all hell will break loose, and our towers will come crashing down!

The Local Density Approximation

Wait a minute, you might say, what use is all this anyway, if the form of the exchange-correlation potential (‘the stupidity term’) is not known? Another really important thing that Kohn–Sham paper of 1965 did was to give us a simple but rather surprisingly successful approximation for this term.

The title of the Hohenberg–Kohn paper emphasizes that the inhomogeneous electron gas is more interesting and relevant for applications in physics and chemistry, though the homogeneous electron gas is easier (though not easy!) to study¹⁰. We have rather good analytical expressions as well as very precise numerical results for how the exchange-correlation potential for a homogeneous electron gas depends on its density.

Kohn and Sham suggested making the simplest possible approximation for the inhomogeneous electron gas. At every point in space, the exchange-correlation potential is locally approximated by that for a homogeneous electron gas of that local density. This is known as the local density approximation (LDA).

The LDA seems like a rather crude approximation. However, it

¹⁰A homogeneous electron gas is one that has the same density everywhere in space. In an inhomogeneous electron gas, the electron density varies from point to point in space.



turns out that it works very well (almost too well!) – so much so that it continues to be widely used today, even when more sophisticated alternatives are available. One reason for the success of the LDA is that it happens to satisfy certain sum rules¹¹ that should be obeyed by any valid exchange-correlation functional.

The area of developing better functionals continues to be an active and important area of research (where, one is tempted to comment, angels rush in but fools fear to tread). Many of the major advances have come from the group of John Perdew, who describes the step-wise progress towards the ‘heaven’ of the exact exchange-correlation functional in terms of a ‘Jacob’s ladder’. This term is derived from an incident in the Bible where the Hebrew patriarch Jacob dreams about angels ascending and descending a ladder connecting earth to heaven. Successive levels of approximation in the form of the exchange-correlation functional represent ever higher rungs in the ladder climbing up. The LDA corresponds to the lowest rung of the ladder. The surprise is that there are quite a few systems for which this lowest rung works rather better than rungs that lie higher up the ladder! At present, we think that much of the time, this is just a coincidence, though it might also sometimes hint at something deeper.

¹¹A sum rule is an equation that has to be satisfied by the integral of a function or functional. Any reasonable approximation to the exchange-correlation functional has to obey a sum rule that ensures that in the immediate neighborhood of a given electron, there is a reduced probability of finding another electron.

So What’s the Big Deal? An Anthropomorphic Analogy....

To try to understand why DFT and the Kohn–Sham equations represent such a huge advance in physics and chemistry, consider the cartoon analogy shown in *Figure 1*. Several people (with two genders, which we can consider to correspond to electrons and nuclei) are present in a room, with complicated interpersonal interactions among them (see *Figure 1(a)*). The challenge posed to us is to move the people around so that we achieve the highest level of global happiness. This is obviously a daunting problem, whose difficulty increases as the number of ‘bodies’ increase. We could simplify it by making what is known as the Born–Oppenheimer approximation: if the ‘males’ move slowly and sluggishly compared to the light-on-their-feet ‘females’, we do not have to si-



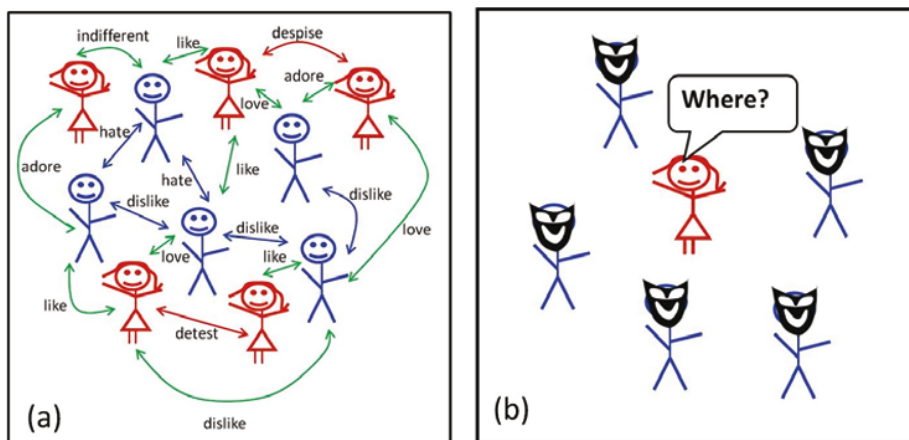


Figure 1. Anthropomorphic analogies to (a) the many-body problem, and (b) the auxiliary Kohn–Sham one-body problem. The blue and red people are supposed to correspond to nuclei and electrons, respectively. The masks in panel (b) are intended to be schematic representations of the exchange–correlation potential.

multaneously optimize the positions of everybody. We can keep the males stationary, and for each fixed position of the males, we have to optimize the positions of only the females. However, since there are many females, and they are interacting with one another, this is still a hard-to-solve many-body problem.

Now along comes Hohenberg, Kohn and Sham, and they tell us that instead of breaking our heads trying to deal with the mess depicted in *Figure 1(a)*, we can instead address the situation depicted in *Figure 1(b)*. We have a bunch of ‘males’ (nuclei) and we have to decide where to place just one ‘female’ (electron), again so as to achieve global happiness. And the beauty of it is that Kohn and Sham tell us that the solution of 1(b) will be exactly the same as the solution to 1(a)! Of course, there are some many-body effects, so now the males look a little different, as indicated by the masks they wear¹². The challenge that remains unsolved to this day is how to design the ‘masks’ (the exchange–correlation potential) so that indeed the solutions to 1(a) and 1(b) are exactly identical in all situations. As of now, we have some rather good mask designs, which work quite well in many cases, but we do not (yet) know the design of THE mask, that will give us the EXACT solution in ALL cases. Is it indeed possible to design such a mask? Could one write down an analytical (or even numerical) expression for the exact exchange–correlation functional? These are open questions, and anyone who answers them satisfactorily

¹²One should however remember that the exchange–correlation interaction arises from interactions between pairs of electrons (females) and not between nuclei and electrons (males and females).

is pretty much assured of fame and glory, and probably a Nobel Prize as well.

“The really clever thing that Hohenberg and Kohn and Sham did,” says Richard Martin, “is that they did not try to solve the full many-electron problem, because that is just hopeless. They realized that they could break it up into bits, and they could solve just the ground-state bit, and that’s what they did, and that is just a terrific achievement.”

Solving the Equations of DFT

Unlike some one-electron Schrödinger equations like those for the hydrogen atom, the particle in a box, or the simple harmonic oscillator, for which one can obtain analytical solutions using pen-and-paper, the Kohn–Sham equations have to be solved numerically using a computer. Moreover, as indicated in the title of the Kohn–Sham paper of 1965, these equations have to be solved in a self-consistent loop. This is because the various terms in the Hamiltonian are functionals of the density, *i.e.*, in order to evaluate the terms in the Hamiltonian, one needs to first know the density. However, when one begins the calculation, one does not know the density, since finding out the density is the final goal of the calculation! So one makes an initial guess for the density, and checks if the output density obtained on solving the Kohn–Sham equations corresponding to the Hamiltonian obtained using this test density is consistent with this guess, repeatedly iterating the procedure until self-consistency is achieved.

A good part of the recent explosive success of DFT has to be attributed to the massive improvements made in computer hardware over the last 50 years, as well as the development of faster algorithms. In the early years of the field, DFT codes used to be run on mainframe computers that occupied a large room, and took days if not months to yield results. Today, for simple systems like crystalline silicon or aluminium, a DFT calculation can be performed in a few seconds on a laptop, or even a mobile phone (see the video posted on the web by Nicola Marzari) [4]!

A good part of the recent explosive success of DFT has to be attributed to the massive improvements made in computer hardware over the last 50 years, as well as the development of faster algorithms.



Post-Kohnian DFT

After the initial work by Hohenberg, Kohn and Sham, there have been several extensions of the basic theory. For example, the theory has been extended to apply for spin-polarized systems, *i.e.*, magnetic systems where the densities of up-spin and down-spin electrons differ, and for excited states and time-dependent situations. For a long time, one big drawback was that the available functionals could not adequately describe weak van der Waals (dispersion) interactions, which become especially important in many organic and biomolecular systems. However, in the past decade, significant progress has been made in this area, so that this no longer remains a major challenge.

Perhaps the biggest failure of DFT in its present avatar is for what are called ‘strongly correlated’ systems. These are (almost by definition) systems where the present approximations for the exchange-correlation functional fail pretty miserably, and therefore DFT gives quite incorrect results. Several important classes of materials, such as the high- T_c cuprate superconductors and heavy fermion systems, are known to be strongly correlated. In order to understand the underlying physics and chemistry in such systems, DFT calculations are only of partial utility, and have to be combined with other techniques from many-body physics, such as those that make use of model Hamiltonians¹³.

As the field has grown in size and stature, the nature of the work done has changed too. At first, DFT calculations were used to either confirm experimental results or, better still, to explain them by yielding insight into underlying mechanisms. Nowadays, with methodological improvements and the speed-up in computational hardware, the density functional theorist can afford to further flex her muscles and be even more ambitious! It is now often cheaper and quicker to do a DFT calculation than to conduct the corresponding experiment. Of course, this in and of itself wouldn’t be of much use, unless one could be reasonably confident that performing the calculation would indeed be equivalent to (*i.e.*, give one the same results as) carrying out the experiment. Most of the

¹³In a model Hamiltonian method, some or all of the parameter-free terms in the many-body Schrödinger equation are replaced by simple analytical expressions which somehow capture the essential physics of interest. Each such term is prefaced by a coefficient whose value is typically obtained by fitting to experiment or, sometimes, to DFT calculations. While some model Hamiltonians have exact analytical solutions, others have to be solved numerically.



time, one can indeed say that yes, this is so!

Moreover, DFT can now be used to design novel materials with desired properties. One usually first uses DFT to gain some understanding of why materials have the properties they do. One can then go on to use DFT to predict which hypothetical material might possess a certain property to an optimal extent, check whether this material is stable, and confirm, by performing the appropriate DFT calculation, that it indeed has the desired property. Since even a theorist has to concede that the proof of the pudding is in the eating, one should then carry out an experiment to confirm that the predictions of DFT are indeed borne out in reality. Barring a few unexpected surprises (since nature, on occasion, yields her secrets reluctantly), such endeavours have, on the whole, been extremely successful. Thus, for example, DFT has been used to predict the existence of a material¹⁴ harder than diamond [5], to design cheaper and/or better catalysts than those currently used for various industrially important reactions [6], and to suggest a simple way of altering the morphology of nanoparticles [7,8]. These are only a few out of a multitude of examples existing in the literature. DFT is also a useful tool if one would like to make use of a computer to simulate conditions that are difficult or impossible to achieve in a lab, *e.g.*, those prevailing in the interior of the planet Jupiter.

Two astonishing numbers bear witness to the growing dominance of DFT in not just condensed matter physics, but in an increasing number of areas: in the last year alone, over 40,000 papers have been published that make use of or mention DFT; and the sixteen most cited papers ever in the *Physical Review* group of journals are all related to one or another aspect of DFT.

Pre-DFT Kohn

Another important contribution of Walter Kohn to solid state physics was his theory of the Kohn anomaly¹⁵ in 1959. In this case, the particular anomaly is that when one plots the graph of the frequency of phonons versus their wave-vector, instead of ob-

¹⁴Diamonds are not just valued as jewellery. Of all the materials existing in nature, they are the hardest, and are therefore used in various industrial applications such as drilling. In 1989, Amy Liu and Marvin Cohen showed, by DFT calculations, that it should be possible to make a material called beta carbon nitride that they predicted would be harder than diamond. This material was subsequently synthesized in the group of Charles Lieber. However, up to now, experimentalists have succeeded in making only very tiny samples.

¹⁵An 'anomaly' is something that is unusual, abnormal or unexpected.



¹⁶Phonons are quantized vibrations of an atomic lattice.

taining the usual smooth curve, sometimes one finds that this graph displays an unexpected kink at a certain value of the wave-vector¹⁶. This kink results from an unusually strong electron-phonon coupling at that wave-vector, as a result of which the frequency of the phonon is lowered; in extreme cases the phonon frequency can become zero or imaginary, indicating an instability of the lattice to a distortion with that particular wave-vector. He is also known for the Korringa–Kohn–Rostoker (KKR) method, which makes use of multiple scattering theory for solving the Schrödinger equation in periodic solids.

Conclusion

I end by (mis)quoting Jawaharlal Nehru’s famous speech of 15 August 1947, and issuing a challenge to future generations of scientists: “Long years ago, Walter Kohn made a tryst with density, and now that time comes, when we are redeeming his pledge, not wholly or in full part, but very substantially . . . The achievement we celebrate . . . is but a step, an opening of opportunity, to the greater triumphs and achievements that await us. Are we brave enough and wise enough to grasp this opportunity and accept the challenge of the future?”

Acknowledgements

It is a pleasure to thank Richard Martin for informative discussions, and Srikanth Sastry, M S Narasimhan and Rajdeep Banerjee for helpful comments on the manuscript.

Suggested Reading

- [1] P Hohenberg and W Kohn, Inhomogeneous Electron Gas, *Phys. Rev.*, Vol.136, p.B864, 1964.
- [2] W Kohn and L J Sham, Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.*, Vol.140, p.A1133, 1965.
- [3] W Kohn, Nobel Lecture, 1998; *Rev. Mod. Phys.*, Vol.71, p.1253, 1999.
- [4] R Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press, 2004.



- [5] N Marzari, <http://mml.materials.ox.ac.uk/Main/QEN900>.
- [6] A Y Liu and M L Cohen, Prediction of New Low Compressibility Solids, *Science*, Vol.245, p.841, 1989.
- [7] B Hammer and J K Nørskov, Theoretical Surface Science: Calculations and Concepts, *Adv. in Catalysis*, Vol.45, p.71, 2000.
- [8] N Mammen, S Narasimhan and S de Gironcoli, Tuning the Morphology of Gold Clusters by Substrate Doping, *J. Am. Chem. Soc.*, Vol.133, p.2801, 2011.
- [9] X Shao, S Prada, L Giordano, G Pacchioni, N Nilius and H -J Freund, Tailoring the Shape of Metal Ad-Particles by Doping the Oxide Support, *Angew. Chem. Int. Ed.*, Vol.50, p.11525, 2011.
- [10] M Schlüter and L J Sham, Density Functional Theory, *Physics Today*, 35, 2, 36, 1982.
- [11] A Zangwill, A Half Century of Density Functional Theory, *Physics Today*, 68, 34, 2015.

Address for Correspondence

Shobhana Narasimhan
Theoretical Sciences Unit
JNCASR Jakkur
Bangalore 560 064, India

Email:
shobhana@jncasr.ac.in



ANNUS MIRABILIS

DFT began
In nineteen sixty four
(A wonder year for sure)
When Hohenberg and Kohn and Sham
Did work we all adore.

Up to then there'd only been
Just Thomas and Fermi,
Or better still Hartree,
And if you'd like to go for a spin,
Then Hartree-Fock maybe.

All were groping in the dark
Of many-body hell,
Till Walter found the spell
That swept away the gloomy murk
Just astonishingly well.

Then all at once the fog dispersed:
Stop playing blind man's buff!
No longer was the problem tough
(It came as quite a shock at first):
The density's enough!

So I remain just such a fan
Of nineteen sixty four
(A wonder year for sure)
When Hohenberg and Kohn and Sham
Did work we all adore.

(Shobhana Narasimhan; after Philip Larkin)

