

Bridging the gap between density functional theory and quantum materials

The focus on quantum materials has raised questions on the fitness of density functional theory for the description of the basic physics of such strongly correlated systems. Recent studies point to another possibility: the perceived limitations are often not a failure of the density functional theory per se, but rather a failure to break symmetry.

Alex Zunger

The demonstration of spectacular quantum effects in solids — such as special forms of superconductivity, topological network effects, Mott insulation or spin polarization without magnetism — have held physicists, and everyone else, in constant fascination. The distinction between the metallic and insulating behavior of solids and the ability to predict such behavior in different crystal phases of compounds has been a central challenge in condensed-matter science and its ensuing technologies. The explanation of such solid-state quantum effects has been historically conveyed in two different asymptotic views. On one hand, the approach of ‘electronic phases of matter’ has emphasized how the dance performed by the tiniest interacting objects — electrons, spins and phonons — has told the story. Indeed, the system where the quantum effect lives (meaning, the material) has often been regarded in such material-independent models of electronic phases as a featureless spectator entity, in which atoms rarely needed to be mentioned. On the other hand, a central focus in traditional solid-state physics, structural inorganic chemistry and metallurgy has been the observation of the connection between a property (P) and the identity of the material in which the property lives. Indeed, the fact that certain properties are manifested in specific materials and not in others has become the central magic that material-dependent theories aimed to demystify. A material can be succinctly defined by its ‘ACS descriptor’¹, consisting of the identity of its atoms (A), their composition (C) and structure (S). The latter represents spatial organizations of various crystallographic, magnetic or nanoscopic motifs that can be accessed at different laboratory conditions. Subtle changes in A, C or S can often come with vastly different material properties P(ACS). This is perhaps best illustrated by the widely different hardness, conductivity and color of the two forms of solid elemental carbon (that is,

graphite versus diamond), or by the fact that seemingly trivial changes in structure can transform an insulator into a metal.

The ping-pong between electronic states and structural motifs

Understandably, seeking a general-purpose, material-dependent theoretical and computational platform that could accept ACS as ‘input’ and provide some predicted properties P(ACS) as ‘output’ has been one of the central anticipated needs in the post-Landau era of condensed-matter theories of real materials. Electronic states are shaped not only by their interelectronic interactions but also by the nature of the microscopic degrees of freedom (m-DOF) in the lattice in which they live — such as atomic displacements. At the same time, the atomic displacements and other m-DOF are shaped by the electronic states which set up quantum mechanical forces acting on atoms possibly displacing them to more optimal (energy lowering) positions. Such a ‘ping-pong’ allows the electronic states and their specific lattice environment — including atomic displacements, and configurations, magnetic, and dipole degrees of freedom (columns of Fig. 1) to cross-influence each other. The result could be a configuration of local lattice motifs that is different from the one initially anticipated. One such general-purpose computational platform evolved from an existence theorem, articulated in the 1960s as the basis for the density functional theory (DFT).

Hohenberg and Kohn² showed in 1964 that the exact ground-state energy of interacting electrons can, in principle, be found from an effective one-electron Schrödinger equation, if the exact exchange-correlation (xc) energy, $E_{xc}[n, n_1]$ (where n refers to the spin-dependent electronic density), and its functional derivative with respect to the charge densities were known. A clever method that could generate the ground-state density from orbitals of non-interacting particles was proposed a year

later by Kohn and Sham³. It took some additional 20 years before DFT started to be used as a predictive tool for ground-state electronic, magnetic and phononic properties of solids. This incubation period was perhaps needed in part to find physical realizations of the Hohenberg–Kohn existence theorem² for the exchange-correlation functional, E_{xc} (ref. ⁴) and formulate the total energy and quantum forces expression in periodic solids in momentum space⁵, avoiding divergence of the individual terms. The availability of such first-principles evaluation of the total energy and forces on atoms became a crucial metric for enabling the ping-pong noted above.

Traditionally bonded compounds first

Applications of DFT focused initially on examining traditional compounds with uncomplicated bonding patterns (for instance, diamond, silicon, ionic solids and transition metals), and eventually extended into complex architectures (for instance, surfaces, nanostructures, superlattices, disordered alloys, defects and impurities) of similarly traditional building-block compounds. These developments brought into the ivory tower of solid-state theory some welcome strangers interested in the application of such platforms to technological questions of the day, such as semiconductor electronics, renewable energy, lithium ion batteries, structural metal alloys and more. In combination with computational search approaches (such as genetic algorithms) and artificial intelligence, DFT progressed from looking at one material at the time, towards searching groups of systems, including (inverse) design of materials with target properties, which eventually led to the birth of the DFT-based ‘materials genome’.

The challenge of ‘strongly correlated’ compounds

The looming concern, however, has been that this approach may not work for the

important groups of materials characterized as electronically open-shell, that is, those with an odd number of localized electronic orbits. Such solids would be initially expected to have band degeneracy between occupied and empty states (metals), a situation referred to as 'strongly correlated' (other cases would be normally correlated). How would theory be able to predict when such a solid would remain degenerate (a metal, such as SrVO_3), or become an insulator (such as LaTiO_3 or SrMnO_3)? A mean-field-like approach (in which a single, averaged potential is seen by all particles) such as traditional band theory could not possibly lift the degeneracy of the bands and would universally predict all such compounds to be metals.

The 1937 spectroscopic measurement of de Boer and Verwey on *d*-electron metal oxides⁶ led Mott⁷ to the conclusion that band theory would invariably predict an erroneous metallic state rather than the observed insulating phase for solids with partially filled *d* bands, later known as 'Mott insulators'. In the alternative approach of Mott and Hubbard^{7,8}, the insulating behavior of such compounds having 'open-shell atoms' emerged from the interelectronic repulsion that localizes these electrons on certain doubly occupied atomic sites, separated by an insulating energy gap from the empty orbitals on other sites. The subsequent emergence of the rich and distinguished field of theory of strongly correlated electrons led to a fundamental understanding of different exotic phenomena as driven by what interacting electrons can do⁹. Yet, lattice DOFs — such as atomic displacements, or the establishment of certain symmetry-breaking configurations of magnetic moments or dipole moments — took a back seat in such model Hamiltonian approaches. Indeed, modification in lattice DOFs were largely viewed as consequences of the primary electron localization, and therefore, as afterthoughts that could be dealt with later as separate problems and not a possible cause of the creation of the insulating bandgap.

This conclusion marked a historical shift and rift in the field, reborn with vengeance at the discovery of high-temperature cuprate oxide superconductors, where some band theory calculations incorrectly predicted a 'false metallic' behavior in the undoped compound. When rare-earth nickelates were discussed¹⁰, it was concluded that "standard DFT ... methods fail to describe the phase diagram, with DFT predicting that all compounds remain metallic and un-disproportionated. These results establish that strong electronic correlations are crucial to structural phase stability and

methods beyond DFT and DFT+U are required to properly describe them." This impression was echoed again last year¹¹ by E. Pavarini pointing out that LaMnO_3 was found to be a metal in the Kohn–Sham version³ of DFT band theory, but it is an insulator in reality, adding, "there are entire classes of materials for which this practice fails qualitatively due to strong local electron–electron repulsion effects." Similarly, E. Gull and collaborators indicated very recently¹² regarding SrVO_3 and SrMnO_3 that "standard electronic structure methods such as DFT and GW are not able to reproduce it due to the missing correlations in their partially filled transition metal shells. The quasiparticle bandwidth in SrVO_3 is too wide, and SrMnO_3 is metallic, rather than insulating." Scores of other papers have demonstrated over the years that the DFT band structure of strongly correlated compounds miss the fundamental nature of metal versus insulator character and related properties. Strong correlation has become the default term for everything that DFT does not get right, and since DFT was thought to fail often, strong correlation was sighted everywhere.

Consequential questions

The question of what controls whether a system is intrinsically a metal or an insulator, matters. So does the fundamental understanding of related effects, including orbital order, charge disproportionation and mass enhancement. Whereas these effects were all considered at one time or another to reflect strong correlation effects, they turned out later to be also predicted by much simpler symmetry broken DFT. Indeed, such understanding would define the 'design principles' for an educated search of materials with target functionalities. The question of what the minimal theoretical approach required is to treat the class of quantum materials behaving unexpectedly, sometimes as insulators and sometimes as metals, turned out to be of great significance in quantum computing, catalysis, batteries, transparent conductors and other technologies critical to society.

Quantum materials

This debate is also relevant to the more recent re-labeling of strongly correlated materials as 'quantum materials'¹³. This quantum materials label was now wisely extended to materials that are not claimed to be strongly correlated, but are interesting nonetheless, including topological insulators and spin–orbit coupling materials (harboring the Dresselhaus and Rashba splitting of energy bands), which are generally based on traditional *sp*-bonded

compounds without agents of strongly correlated electron effects such as localized open-shell atoms. Indeed, the 'quantum materials' label is used more often to describe systems where traditional text-book teachings on what derives their properties are not exactly right.

Which DFT failed

It turns out that the impressions regarding systemic failures of DFT band theory (for example, refs. ^{10–12} and scores of other papers) were based on the use of the highest-possible symmetry described by the smallest-possible, periodically repeated unit cells (illustrated in the top row of Fig. 1). In this view, the presence of a vanishing global $\mu_{\text{global}} = 0$ (such as null magnetization in a paramagnet) has been interpreted to result from the assumption that each and every corresponding local motif is individually also zero ($\mu_{\text{local}} = 0$). This perspective resulted in describing para-phases as virtual average configurations that have vanishing local and global atomic displacements (3a in Fig. 1, that is, 'non-displacive'), vanishing magnetic moments (3b in Fig. 1, that is, non-magnetic) and vanishing dipole moments (3c in Fig. 1, that is, non-electric). Such a symmetry-unbroken 'monomorphous' picture with a minimal unit cell cannot lift level degeneracy in any band-structure electronic structure description, resulting therefore in 'false metals'. While omitting such symmetry-breaking motifs has been considered a reasonable practice in dynamic theories of electron phases of matter approaches (where they are not taking the role of being a possible cause of the opening of the insulating gap), this was no longer the case in a band theoretic approach. Did DFT fail in describing Mott and related quantum systems because of fundamental deficiencies in describing interelectronic interactions, or because of the absence of a suitable representation of the local lattice motifs? The first option would imply abandoning DFT, replacing it by strongly correlated methods; the second one would imply that leapfrogging from DFT to the other methods is premature. Examining the ability of DFT mean-field-like band theory to describe this phenomenology is required, however, considering a broad range of compounds, phases and effects, to establish if the right trends exist. This includes compounds that are intrinsically metals (SrVO_3), or temperature-induced (YNiO_3) or pressure-induced (LaTiO_3) metals but otherwise insulators. Similarly, one would need to examine long-range ordered phases as well as phases lacking LRO (that is, para-phases), including the metal–insulator transition,


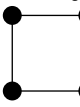

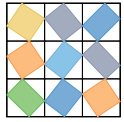
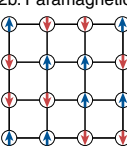
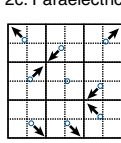

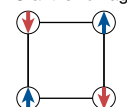

Local motifs Configurations	a. μ = atomic displacements	b. μ = magnetic moments	c. μ = dipole moments
3. Symmetry-unbroken monomorphous $\mu_{\text{global}} = 0$ $\mu_{\text{local}} = 0$	3a. Non-displacive 	3b. Non-magnetic 	3c. Non-electric 
2. Symmetry-broken polymorphous $\mu_{\text{global}} = 0$ $\mu_{\text{local}} \neq 0$	2a. Paraelastic 	2b. Paramagnetic 	2c. Paraelectric 
1. Symmetry-broken LRO $\mu_{\text{global}} \neq 0$ $\mu_{\text{local}} \neq 0$	1a. LRO ferroelastic 	1b. LRO antiferromagnetic 	1c. LRO ferroelectric 

Fig. 1 | Three types of possible local motif μ_{local} characterizing the microscopic structure of phases.

These include μ_{local} representing atomic displacements, magnetic moments or dipole moments (shown as the titles in columns a, b and c, respectively). Rows 1, 2 and 3, illustrate three types of lattice configuration made by packing such local motif: LRO phases (row 1), symmetry-broken para-phases represented by an extended supercell with internal distribution of local motifs (row 2) and symmetry-unbroken phases represented by minimal, symmetrized unit cells lacking local motifs (row 3).

extending static DFT to its molecular dynamics finite temperature limit.

It turned out that the imposed symmetry constraints constituted a self-fulfilling prophecy, being a key reason for the incorrect predictions. This limitation was not part of the DFT method itself, representing instead a naive application of the DFT method. Removing the artificially imposed high symmetry resulted in lowering the total energy (meaning, stabilization), simultaneously converting false metals into real Mott insulators even without strong correlation.

The simplest case of long-range-ordered quantum phases at $T < T_{(\text{LRO})}$

Row 1 in Fig. 1 illustrates long-range-ordered (LRO) periodic organization of local lattice motifs that typically occur below the ordering temperatures, $T < T_{(\text{LRO})}$. Such local motifs include patterns of atomic displacements (1a in Fig. 1), magnetic moments (1b in Fig. 1) or dipole moments (1c in Fig. 1), and are commonly observed experimentally as crystallographic, magnetic or ferroelectric long-range order. Using such observed organization of local lattice motifs as input to DFT (or optimizing them via total energy minimization) generally produces a good description of the metal versus insulator phenomena at $T < T_{(\text{LRO})}$. Examples of predictions of such true insulators replacing the false metals found from naive DFT include cuprate superconductors¹⁴.

The mechanism for gapping depends on the dominant symmetry-breaking modes, be that atomic distortion in LaMnO_3 (1a in Fig. 1), magnetic moment ordering in antiferromagnets LaTiO_3 and SrMnO_3 (1b in Fig. 1), or ferroelectric dipoles (1c in Fig. 1). If, however, the magnitude symmetry breaking is too weak and insufficient to open the gap, the result of DFT is a failed Mott insulator, or simply a ‘true metal’ (for example, SrVO_3). Thus, symmetry-broken DFT generally works well unless one artificially imposes a highly symmetric periodic cell where symmetry breaking is geometrically excluded, even if it were to lower the total energy. This would then result in a false metal instead of a real insulator, irrespective of the DFT exchange correlation used.

Para-phases above the $T > T_{(\text{LRO})}$

Unlike the LRO ground-state structures of row 1 in Fig. 1, para-phases (rows 2 or 3 in Fig. 1) appearing at higher temperatures lack long-range order (but they can have correlated disorder and short-range order). They can appear as paraelastic (2a in Fig. 1), paramagnetic (2b in Fig. 1) or paraelectric (2c in Fig. 1). Much like a chemically disordered A_xB_{1-x} alloy that also lacks long-range order, in all of these cases the cell size and cell-internal motifs needed for their description in band theory are generally unknown. Such para-phases were simplistically imagined to be made of single motifs (‘monomorphous’ in row 3 in Fig. 1),

as gleaned also from characterization techniques that delivered the global averaged structure. Band-structure calculations for such monomorphous high-symmetry structures generally predicted a (false) metallic state for systems with an odd number of electrons per cell^{10,11,14}. In retrospect, this practice of using the average configuration, washing out all local motifs, as input to electronic structure calculations misdirected the field.

It turned out that such an imposed symmetry constraint was the key factor for the false-metal predictions in para-phases of Mott insulators. Significantly, the calculated total energy of such high-symmetry ‘virtual crystal’, symmetry-unbroken para-phases^{15–18} were predicted to be 1–2 eV higher than the symmetry-broken magnetic cases, pointing to the fact that such symmetry-unbroken models (including refs. ^{11,12}) are irrelevant competing phases.

Recent developments

Research in the DFT community pointed out that there are avenues for removing the constraints on such naive DFT^{15–19} rather than disposing of DFT altogether. Considering larger-than-minimal unit cells instead revealed a significant lowering of the total energy by breaking the symmetry of the assumed ideal configurations, simultaneously converting paramagnets (LaTiO_3 , LaMnO_3 , SrMnO_3 and NiO) from false metals into real insulators even without strong correlation. The rise of the insulating gap relative to its approximate false metal reference is often a result of different forms of symmetry breaking. The fall of the insulating gap in forming a metallic phase (insulator to metal transition) is often the result of the weakening or elimination of symmetry breaking by temperature or pressure.

On the experimental side, increasing use of local probes that do not average over large volumes has meant that it is possible to ‘see’ the local positional, magnetic and dipolar configurations. Recent observations^{20,21} have reported that the nominally cubic paraelectric oxide phases of BaTiO_3 and KNbO_3 are piezoelectric, suggesting that it is cubic only as a global average, but not locally.

It has also been recently noted that in several materials that were traditionally believed to be controlled primarily by strong interelectronic physics manifesting ‘electronic phase of matter’, including Mott insulators and paramagnetic nickelates, “the lattice in fact plays a crucial role”²².

So where has all the strong correlation gone?

The apparent explanations of similar physical effects by (1) symmetry-broken,

mean-field-like DFT and by (2) explicitly highly correlated symmetry-preserving methods beg the obvious question: what happened to the strong correlation when symmetry was broken in a larger cell? Indeed, correlation is representation dependent rather than being an absolute statement on the intrinsic physical nature of a compound or a phase, as we have been conditioned to think. What is strong correlation in symmetry-unbroken representation may transform to weak correlation in symmetry-broken representation²³. Perhaps *d*-electron oxides are not necessarily strongly correlated, just complicated?

Open questions

It now appears that many of the traditional fears that DFT band theory fails intrinsically to predict Mott insulation and its many accompanying effects are not a failure of the DFT per se, but rather a failure of naive applications. The strongly correlated methodologies applied to such open shell compounds (exemplified by refs. ^{9–12}) are surely sophisticated and fundamental. The question is when are they needed. It is thus important to figure out specifically when a highly correlated description is unescapable. For example, it will be important to determine which systems and phases would maintain strongly correlated behavior even if they cannot lower their energy by symmetry

breaking (just as perhaps in multiplet theory for atoms). No longer can one cry out that ‘strong correlation is everywhere’. Indeed, identifying compounds and properties where DFT fails fair-and-square will provide legitimate opportunities for explicitly correlated theories to shine.

Recent progress in developing experimental probes that can resolve local positional, magnetic or dipolar motifs in materials should join with the theoretical efforts now able to predict the emergence of (static or dynamic) symmetry-breaking, energy-lowering local motifs. The experimental and theoretical communities working on complex phenomena discussed here must join forces with open minds to solve the essential remaining difficult problems in this field. We all want to know which minimal, enabling physics concepts are needed to understand the trend in properties *P* across the Periodic Table of materials ACS¹. Once progress is made in this direction of connecting quantum properties with the body in which such properties live, discovery and design can be successfully extended from traditional to quantum materials. □

Alex Zunger[✉]

Renewable and Sustainable Energy Institute and Materials Science and Engineering, University of Colorado, Boulder, CO, USA.

[✉]e-mail: Alex.Zunger@Colorado.edu

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Competing interests

The author declares no competing interests.