

PERSPECTIVE

Insights into Current Limitations of Density Functional Theory

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Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, for many predicted properties, there are spectacular failures that can be traced to the delocalization error and static correlation error of commonly used approximations. These errors can be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Reducing these errors will open new frontiers for applications of density functional theory.

Interactions between electrons determine the structure and properties of matter from molecules to solids. To describe interacting electrons, the extremely simple three-dimensional electron density can be used as the basic variable within density functional theory (DFT) (1, 2), negating the need in many cases for the massive complex many-dimensional wave function.

Kohn noted in his Nobel lecture that DFT “has been most useful for systems of very many electrons where wave function methods encounter and are stopped by the exponential wall” (3). The beauty of DFT is that its formalism is exact yet efficient, with one determinant describing the electron density—all of the complexity is hidden in one term, the exchange-correlation functional. This term holds the key to the success or failure of DFT. Exchange arises from antisymmetry due to the Pauli exclusion principle, and correlation accounts for the remaining complicated many-body effects that need many determinants to be fully described. However, the form of exchange-correlation in terms of the density remains unknown and it is necessary to use approximations, so that in many cases DFT contains semi-empirical parameters. The great success of DFT is that simple approximations perform remarkably well for a wide range of problems in chemistry and physics (4–6), particularly for prediction of the structure and thermodynamic properties of molecules and solids.

Despite the widespread popularity and success of DFT, its application can still suffer from large pervasive errors that cause qualitative failures in predicted properties. These failures are not breakdowns of the theory itself but are only due to deficiencies of the currently used approximate exchange-correlation functionals. A systematic approach for constructing functionals that are universally applicable is a hard problem and has remained elusive.

A possible path forward is to have a deeper look at the errors embedded in currently used functionals to determine the origin of their pathologies at the most basic level. Recent work has traced many of the errors in calculations to violations of conditions of the exact functional (7, 8). These violations present themselves in extremely simple model atoms, which can be used for diagnosis, and more importantly, in many interesting and complex chemical and

physical systems. Identifying and understanding the basic errors offer a much needed path for the development of functionals, as well as a useful insight into potential pitfalls for practical applications.

What are some of the major failures in DFT calculations? First, they underestimate the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions, and charge transfer excitation energies. They also overestimate the binding energies of charge transfer complexes and the response to an electric field in molecules and materials. Surprisingly, all of these diverse issues share the same root—the delocalization error of approximate functionals, due to the dominating Coulomb term that pushes electrons apart. This error can be understood from a perspective that invokes fractional charges (7, 9). Furthermore, typical DFT calculations fail to describe degenerate or near-degenerate states, such as arise in transition metal systems, the breaking of chemical bonds, and strongly correlated materials. All of these problems are merely manifestations of another common error—the static correlation error of approximate functionals. This problem arises because of the difficulty in using the electron density to describe the interaction of degen-

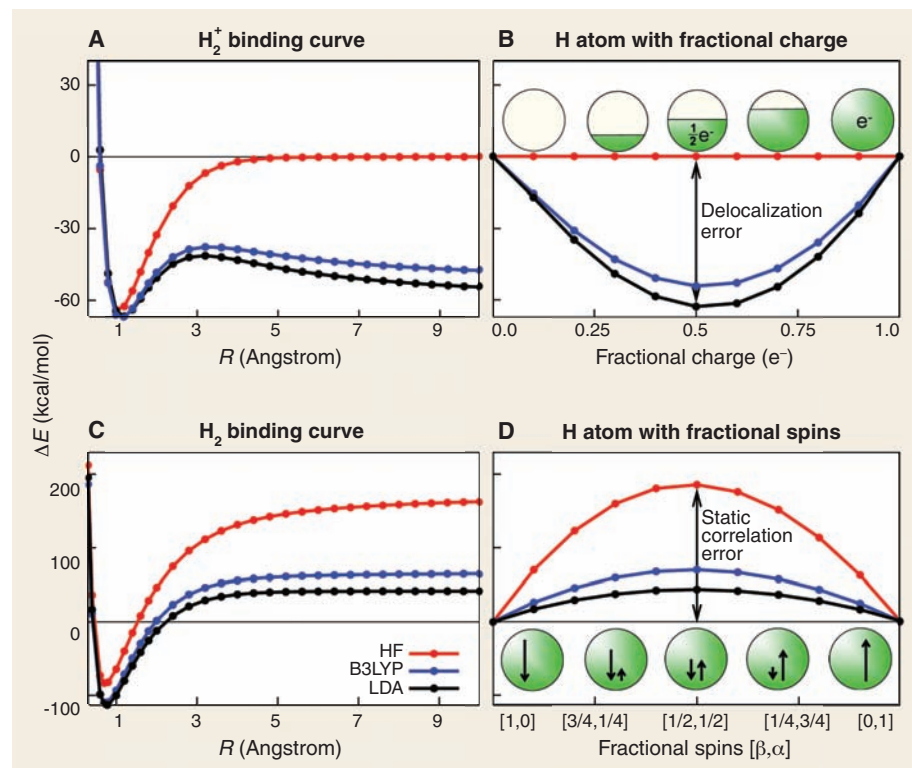


Fig. 1. DFT approximations fail. The dissociation of H_2^+ molecule (A) and H_2 molecule (C) are shown for calculations with approximate functionals: Hartree-Fock (HF), local density approximation (LDA), and B3LYP. Although DFT gives good bonding structures, errors increase with the bond length. The huge errors at dissociation of H_2^+ exactly match the error of atoms with fractional charges (B), and for H_2 they exactly match the error of atoms with fractional spins (D). The understanding of these failures leads to the characterization of the delocalization error and static correlation error that are pervasive throughout chemistry and physics, explaining a host of problems with currently used exchange-correlation functionals.

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erate states and can be understood in another perspective, that of fractional spins (8).

Delocalization Error and Fractional Charges

To understand the delocalization error inherent in approximate functionals and its effects, we can consider the simplest possible molecule, H_2^+ . Functionals describe the chemical bond well, but fail dramatically as the molecule is stretched (Fig. 1A). At the dissociation limit, the result is two H atoms with half an electron each, and an energy that is much too low. The H atom with half an electron is a curious object; what do we know, in general, about atoms with fractional numbers of electrons? The exact energy of the atom as a function of the charge is a straight-line interpolation between the integers (10), because of the discrete nature of electrons. However, approximate functionals are incorrectly convex between the integers (Fig. 2A), with large errors, and they predict an energy that is much too low for fractional charges (Fig. 1B).

Stretched H_2^+ clearly shows that the energy is too low if the electron is delocalized over the two centers. This reflects the delocalization error, which refers to the tendency of approximate functionals to spread out the electron density artificially. This phenomenon is related to a familiar term in the literature, the “self-interaction error” (11, 12), well defined only for one-electron systems, with analogy made for many-electron systems (13, 14). However, the erroneous convex behavior of the energy as a function of the fractional charge is best characterized as the delocalization error, as it captures the physical nature of the problem (7).

What are the consequences of the delocalization error? In chemical reactions, approximate functionals predict transition state energies and hence reaction barriers that are much too low (15), because the transition state resembles that of stretched H_2^+ and has electrons delocalized over more than one center (12). In an applied electric field, approximate functionals give the system an energy that is too low and a polarizability that is too high because fractional charges appear at the edges of the molecule (16). Approximate DFT can also predict unphysical charge transfer between the molecule and the metal leads in molecular electronic devices, and cause an overestimation of electronic conductance (17, 18). When adding or removing an electron from a system, approximate functionals produce an overly disperse dis-

tribution for the added electron or hole (Fig. 2B). This effect can be magnified in large systems because the delocalization error increases with system size. Thus, the delocalization error may be a particular concern for cluster calculations that attempt to approach the bulk limit.

For the exact functional, its straight-line behavior (Fig. 2A) means that the derivatives of the

tribution within DFT. Nonetheless, recent studies offer insight and promise (8).

To analyze the error, consider one half of the closed-shell H_2 molecule at the dissociation limit: an H atom with half a spin-up electron and half a spin-down electron, which is an exotic system with fractional spins. The exact energy of this system should be the same as that of the normal H atom in an integer-spin state. More generally, the constancy condition for the exact functional (8) requires that systems with fractional spins have an energy equal to that of the normal-spin states. However, approximate functionals do not accurately describe the interaction between the degenerate spin-up and spin-down states and have a massive error for these fractional-spin states. In the case of the H atom, the overestimation of this energy exactly matches the error of stretched H_2 (Fig. 1D). The violation of the constancy condition for fractional spins gives rise to the static correlation error and explains the difficulty in using the electron density to describe degenerate states.

Stretched H_2 and similar problems are dealt with in traditional approaches using multi-determinant wave functions. For larger systems with many degeneracies, the number of determinants quickly becomes unmanageable. In contrast, DFT is based on a single determinant, and the above solution may not apply. However, the concept of fractional spins formulates the very same problem in a different light that illuminates the error of approximate functionals and, moreover, indicates that all that is needed in DFT to address the problem is to impose the constancy condition on an approximate functional.

Static correlation is pervasive. Breaking any chemical bond leads to failures similar to those seen in H_2 , with a static correlation error that is proportional to the number of electron pairs involved. For transition metal dimers, which have multiple bonds and hence multiple degeneracies, the static correlation error dominates. As such, DFT calculations cannot accurately describe the chemical bonding in metal dimers. Another simple example is the calculation of the open-shell boron atom, which has a threefold spatial degeneracy among the p orbitals. DFT calculations of the spherical density give an excessively high energy because of multiple fractional-spin occupations.

Magnetic properties, such as the magnetic coupling constants of cuprates, rely on the accurate calculation of both singlet and triplet states.

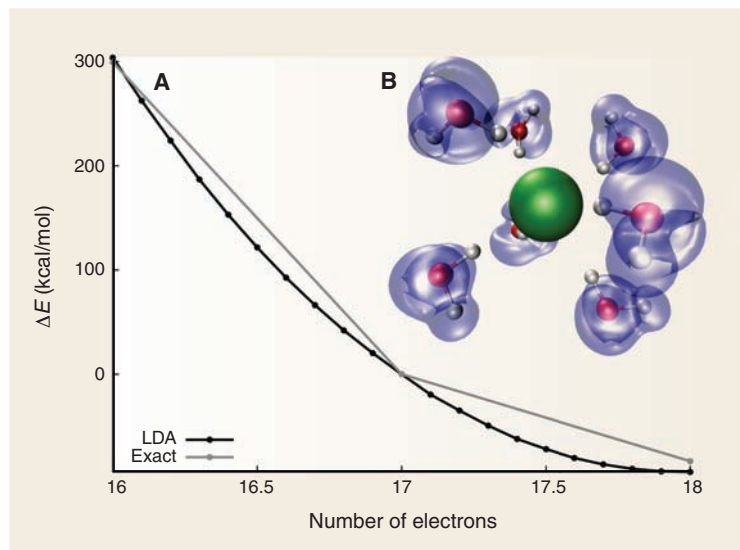


Fig. 2. Seeing the delocalization error. The incorrect convex behavior of the LDA energy is seen for the Cl atom with fractional numbers of electrons (A). Despite good agreement with the exact values at the integer points, the convex behavior means that a lower energy can be achieved with fractional charges. This leads to an unphysical delocalization of the electrons in a simulation of the solvated anion, as shown (in blue) by the difference of the LDA density between the solvated Cl and solvated Cl^- (B).

energy with respect to fractional charge give the ionization energy and the electron affinity (9). Functionals with delocalization error get these derivatives wrong because of incorrect convex behavior. This explains the well-known underestimation of the band gap. Functionals with incorrect concave behavior, like the Hartree-Fock approximation (which is an orbital functional within DFT), have the opposite characteristic and suffer from a localization error that saturates with system size (7). Hybrid functionals contain both convex and concave components and may benefit from error cancellation in some cases, thus reproducing good band gaps for solids with midsize gaps; however, they do not provide general solutions.

Static Correlation Error and Fractional Spins

Next, we consider the apparently simple problem of stretching H_2 . Approximate functionals describe the covalent bond well, but the energy is severely overestimated upon dissociation (Fig. 1C). This well-known problem is attributed to static correlation that arises in situations with degeneracy or near-degeneracy (19–21), as in transition metal chemistry and strongly correlated systems. These are very complicated problems with no clear so-

At present, the accurate calculation of closed-shell singlets is not always possible in DFT because of static correlation error, which has led to the routine use of broken-symmetry open-shell singlets. The use of broken-symmetry solutions in all of the above cases can be understood as only attempting to circumvent the static correlation error of the functional by using a different state that avoids fractional spins. Static correlation error is particularly important in strongly correlated systems, as exemplified by Mott insulators, including transition metal oxides, where DFT is unable to predict the correct insulating state. Related problems exist in high-temperature superconductors. Functionals that include Hartree-Fock, such as hybrid functionals, have a larger error than normal functionals (Fig. 1D) and are expected to perform even worse on static correlation problems.

DFT can suffer from large errors that manifest themselves in a wide range of applications. However, they also appear in the simplest systems, even atoms, which can be used to understand and diagnose problems. In this manner, perspectives based on the behavior of the energy for fractional charges and fractional spins give insight into the errors of functionals and illuminate a path for fur-

ther development. Indeed, new functionals have been constructed to minimize the delocalization error, and these are found to improve many related predictions (22), but there is still much work to do. It is important to describe errors of functionals in terms of violations of requirements of the exact functional; for example, the delocalization error originates from the violation of linearity of the energy as a function of fractional charges, and the static correlation error emerges from the violation of constancy of the energy as a function of fractional spins. A clear understanding of the errors from the most basic principles will enable the development of functionals to open new frontiers for applications of DFT.

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Frontiers in Surface Scattering Simulations

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Theorists have recently made substantial progress in simulating reactive molecule-metal surface scattering but still face major challenges. The grand challenge is to develop an approach that enables accurate predictive calculations of reactions involving electronically excited states with potential curve crossings. This challenge is all the more daunting because collisions involving molecules heavier than H₂ may be accompanied by substantial energy exchange with the surface vibrations (phonons), and because an electronic structure approach that allows molecule-surface interaction energies to be computed with chemical accuracy (1 kilocalorie per mole) is not yet available even for the electronic ground state of molecule-metal surface systems.

The goal of molecule-surface reaction dynamicists is to determine in detail how molecules react on surfaces. On surfaces, a wealth of physical and chemical processes are possible (Fig. 1): Examples include diffractive scattering of light atoms and molecules (1), in which the projectile's translational momentum parallel to the surface is altered in a quantized way; vibrationally inelastic scattering (2, 3), in which the molecule either accumulates or dis-

sipates springlike internal vibrational energy from the collision; and dissociative chemisorption (4, 4-6), in which a bond in the incident molecule breaks and the fragments bond chemically to the surface. Theorists study these processes to understand how the molecule-surface interaction affects the elementary reactions that together constitute heterogeneously catalyzed processes. Such reactions are important; the production of most synthetic chemical compounds involves heterogeneous catalysis. One of the achievements recognized by the 2007 Nobel Prize in Chemistry, awarded to G. Ertl, was the unraveling of the fundamental mechanism of the Haber-

Bosch process, by which vast quantities of ammonia, a raw material for fertilizer, are produced.

Selecting a model for a surface reaction requires decisions about how to treat the electronic and nuclear degrees of freedom. In the Born-Oppenheimer (BO) approximation, the assumption is made that the electrons adapt instantaneously to the motion of the nuclei, so that the molecule-surface interaction can be represented using just one potential energy surface (PES). This assumption does not hold true for non-adiabatic processes involving, for instance, spin changes (6) or electron transfer (7). The modeling of such processes requires computing a diabatic PES (a diabatic state is characterized by a physical feature other than electronic energy—for instance, the molecular spin state) or multiple PESs with couplings connecting them. Low-energy electron-hole pair excitations, which form another example of a nonadiabatic process, can occur in scattering from a metal in which the highest occupied electronic band is only partially filled; these can be treated by replacing them with effective frictions [molecular dynamics with electronic friction (MDEF)] (8). The equations of motion of the nuclei can be solved using the time-independent or time-dependent Schrödinger equation to treat all molecular degrees of freedom [often the approach taken for dissociative chemisorption of a light molecule such as H₂ (9)] or to treat only the most important molecular degrees of freedom [often applied to reactions of heavy diatomic (7) or polyatomic (10) molecules]. Surface vibrations, or phonons, can be incorporated

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