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Localization in the SCAN Meta-Generalized Gradient Approximation Functional Leading to Broken Symmetry Ground States for Graphene and Benzene

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Abstract:

Density functional theory calculations play a central role in understanding chemical and solid-state systems. Progress depends on density functionals that accurately reproduce both energies, for thermochemistry, and properly describe ground states and other properties that are of interest. The Cr dimer, benzene and graphene are particularly important benchmark systems for quantum chemistry and condensed matter physics. The Strongly Constrained and Appropriately Normed (SCAN) functional, which is an advanced meta-generalized gradient approximation functional that significantly improves molecular energies is shown to perform poorly for the Cr dimer. This is connected with its poor performance for itinerant solid-state magnets and is a consequence of over localization of electrons, thus illustrating an analogy between the Cr dimer and itinerant magnets. The Cr dimer is a notoriously difficult system for density functionals. However, we additionally find that SCAN predicts an incorrect symmetry broken ground state for 2D graphene and for the benzene molecule, which is surprising considering that ground states of these are known well described even by the simplest local density approximation. We show that SCAN overly favors localized spin polarized states, which is a serious deficiency of this approach. Thus, the challenge of finding density functionals that accurately treat both localized and delocalized electronic systems remains.

Keywords: Meta-GGA, self-interaction, magnetism

Density Functional Theory (DFT) based calculations are a widely used, useful and practically indispensable tool in chemistry, condensed matter physics, and materials science.[1-5] These calculations rely on approximate density functionals. Unlike variational wave function-based approaches, density functionals are not systematically improvable. Instead, one relies on empirical knowledge of the accuracy of the functionals on arrays of test cases as well as the extent to which given functionals reproduce known exact results. While DFT calculations are often used for calculating energies, for example in the context of thermochemistry, they are also very widely used in providing understanding of bonding and properties, including bonding, electronic structure and magnetism. Therefore, it is important that a functional reproduce not only total energies, but also other properties of interest, for example distinguishing between metallic and semiconducting states, describing ground state symmetries and producing spin densities and magnetic behaviors in accord with experiment.

A long-standing goal is the development of a tractable universal density functional, that is a functional that provides uniformly accurate results for all chemical and solid-state systems.[6-9] A particular challenge is the need to describe all types of electronic states in a universal functional. This includes both localized states, as in atoms and most small molecules, and delocalized states, as in aromatic molecules, such as benzene, and the states near the Fermi level in metals.[6, 10-14] This not only from the point of view of obtaining accurate total energies, but because of the importance in chemistry of frontier orbitals, and in condensed matter and materials of electronic states near band edges and at the Fermi level in metals. For example, while not particularly important for thermochemistry, the Dirac bands of graphene, as predicted by standard DFT, have been the focus of much interest in that material.[15-16]

There is a widely held expectation that as functionals incorporate more detailed information about the electron density they become more reliable. This is the concept of Jacob's ladder.[17-21] This concept starts with the local density approximation (LDA), with an energy functional built on the local density, as the first rung, followed by generalized gradient approximations (GGA), using the local density and its gradient as ingredients in the second rung, and meta-GGA functionals, that in the case we consider incorporate the local density, its gradient and the kinetic energy density, on the third rung. Going up this ladder adds more flexibility to the functionals. This flexibility can be used to satisfy known behaviors of the electron gas, and also for fitting if desired. One important constraint, especially for localized systems, is the fact that the energy has derivative discontinuities at integer electron numbers.[22-24] Building this fact into functionals favors integer occupations of orbitals and thus localization. This is essential for describing the behavior of atoms and localized systems such as Mott insulators.[12, 25-26] Therefore, this is an important constraint. It cannot be satisfied on the lowest two rungs of Jacob's ladder, but may be better satisfied on higher rungs, including semi-local functionals that incorporate kinetic energy densities.[26-27] The unanswered question is whether this can be accomplished without degrading the already very good description of delocalized systems from the lower rungs.

The recently developed Strongly Constrained and Appropriately Normed (SCAN) meta-GGA functional[28-29] is of particular note. This functional incorporates many exact constraints. Additionally, through these constraints and choices of norms (systems that the functional is constrained to describe exactly) it improves the dependence of the energy between integer occupations, thus better approximating the derivative discontinuities of the exact functional. It has been demonstrated to perform extremely well for the energetics and structures of sets of molecules and solids.[21, 28-32]

However, rather surprisingly, while describing energies and structures of many molecules extremely well, SCAN was found to perform poorly for bulk Fe metal, and some other metallic magnetic materials due to increased moments and magnetic energies.[33-39] These errors were attributed to errors in describing itinerant metallic electrons in these itinerant magnets, including excessive localization due to the emphasis in SCAN on reproducing the removal of self-interaction errors for atoms and small molecules.[34] It has also been noted that SCAN has inaccuracies for the weakly bonded alkali metals, where the interplay between localized semi-core states and itinerant metallic valence states was implicated.[40]

Correction of self-interaction errors is also important for many solid-state materials, including materials that are not strongly correlated, such as TiO_2.[41] In effect, the correction of self-interaction errors for molecules leads to errors in the treatment of extended, band like states in metallic Fe, Co and Ni. However, up to now, these problems have been isolated to extended solids. Here we show that these problems can manifest themselves also in small molecules, where electrons are necessarily localized spatially, and also in graphene, which is a prototypical two-dimensional material.

We did DFT calculations using the VASP code.[42-43] The Cr_2 molecule was modeled in an 8.0 x 8.1 x 15 Å periodic box with the molecule oriented in the z-direction. The energy of an isolated Cr atom was calculated using an 8.0 x 8.1 x 8.2 Å box. For graphene, the vacuum is 10 Å along the z-direction, and with a Brillouin zone sampling 21 x 21 x 2 **k**-mesh. Benzene was modeled in a 12 x 12 x 6 Å periodic box with the molecule lying within plane. High energy cutoffs of 600 eV were used in these calculations. Importantly, the calculations were done with broken spin symmetry. In addition, as tests, we did calculations for the three systems using the all-electron FHI-aims code, using the tightest basis set provided by the code.[44] This method avoids pseudopotential approximations, which could be important for meta-GGA functionals,[45] and has an efficient but more restricted basis set than the planewaves used in VASP. For benzene, which is a particularly delicate case, we also did calculations with VASP using even higher cutoff parameters, specifically a planewave cutoff of 800 eV with an augmentation cutoff of 1000 eV. In addition, we did calculations with different real space grids. For benzene, we also tested two different pseudopotentials, specifically the default PBE pseudopotentials and hard PBE pseudopotentials. The key results, specifically, that SCAN behaves similar to functions that over-localize orbitals in Cr_2, and that the ground states of graphene and benzene are incorrectly described as magnetic and symmetry broken are independent of these choices.

We begin with the neutral Cr_2 dimer. This is a notoriously challenging case for wave-function-based approaches, and has often been used as a benchmark.[46-54] It is also an interesting test case for density functionals due to its multiple bonding involving six orbitals per atom, although the actual bonding is thought to involve a balance between spin-polarization (in broken spin symmetry calculations) and bonding.[55] The binding curve shows a relatively short bond length, with weak binding and a shoulder structure, reflective of competing electronic states.[56-57] We performed calculations for the LDA (here we use the standard LDA based on parameterization of Monte Carlo data for the uniform electron gas[58] and the random phase approximation spin dependence,[59] as implemented in the VASP code),[60] the PBE GGA,[61] the SCAN,[28] TPSS,[20] and revTPSS (RTPSS)[62] meta GGAs, the M06L alternate local density functional,[63] and the HSE06,[64] and B3LYP[65] hybrid functionals. Our calculated binding energies curves are shown in Figure 1a.

The LDA shows accord with experiment as far as the binding energy and bond length is concerned, as has been noted previously.[66-67] PBE also shows a reasonable accord with experiment in terms of the bond length, but it has an under-binding in terms of energy, also as noted previously. Both PBE and LDA show weaker decreases in binding energy and longer distances than might be expected based on other systems. There is also a secondary minimum at longer bond length in the experimental curve. This characteristic has been associated with competition between spin polarization and binding. Other functionals, including hybrid functionals that are typically regarded as more accurate for the description of molecules, including B3LYP, very significantly underbind Cr_2, by favoring a more strongly spin symmetry broken, longer bond length solution. Hybrid functionals that poorly describe Cr_2 by producing strong spin polarization, also show poor behavior for itinerant ferromagnetic metals.[8, 34, 68-69] No functional very closely reproduces the shape of the experimental binding energy curve. However, the LDA, PBE GGA, and the generally similar TPSS and revTPSS functionals are apparently closest.

Interestingly, SCAN behaves similarly to the hybrid functionals. This is associated with the tendency of the exchange interaction to favor more strongly spin-polarized antiferromagnetic solutions, along with reducing self-interaction. SCAN, differently from hybrid functionals, does not involve mixing of exact exchange and is strictly semi-local, but does attempt to have less self-interaction error through the choice of norms. SCAN yields higher spin polarization at all bond lengths, as seen in Figure 1b. These solutions correspond to the higher bond-length shoulder in the binding energy curve. In any case, it is clear that none of the density functionals provides a truly adequate description Cr_2, and that functionals that are designed to reduce self-interaction errors degrade agreement with experiment for this system. This is understood to be a consequence of over localization of orbitals in these functionals for itinerant systems, and also in the Cr_2 molecule.

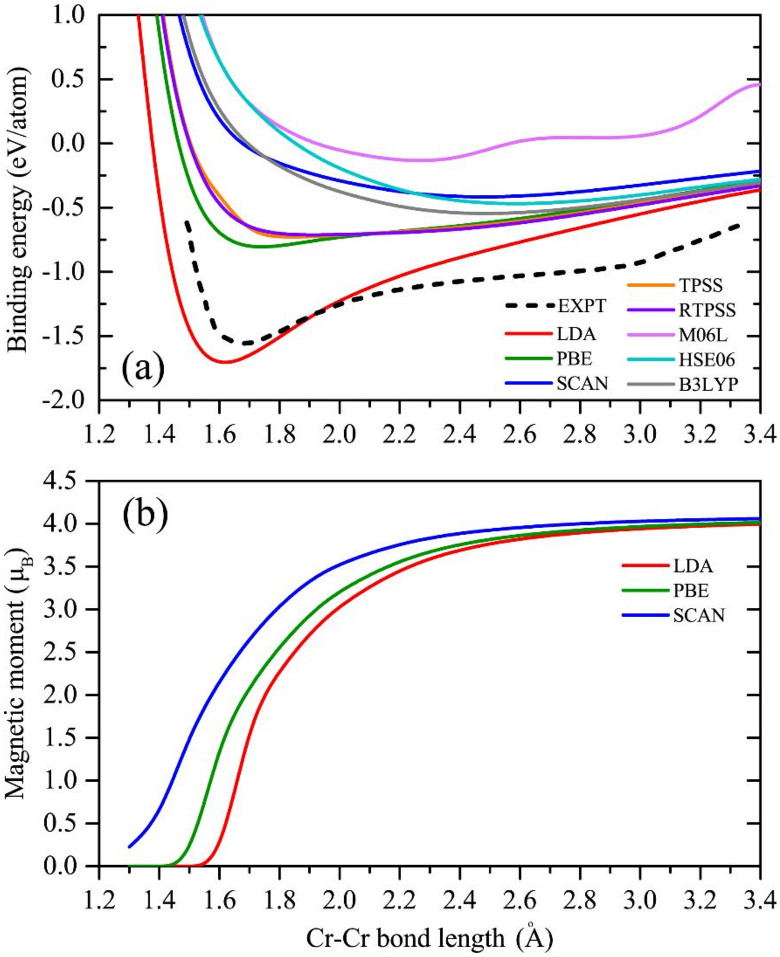

Figure 1. (a) Binding energy curves for the neutral Cr dimer using different density functionals. The experimental curve is from Casey and Leopold.[56] (b) Cr spin moment as a function of bond length..

We now turn to graphene, which is a prototypical 2D material of importance in chemistry and condensed matter physics.[15, 70-71] The honeycomb lattice symmetry leads to a semi-metallic electronic structure featuring Dirac cone bands at the K and K' points of the 2D Brillouin zone. This high symmetry and ensuing Dirac bands are among the most important and widely discussed features of graphene. Breaking of the honeycomb lattice symmetry, by either chemical ordering (e.g. replacing C by alternating B and N) or by magnetism (e.g. an antiferromagnetic field) leads to gap opening. In addition, graphene is a classic example of resonant bonding in an extended structure.

Experimentally, graphene does not have magnetic moments, and instead shows orbital diamagnetism, similar to graphite.[72] Standard density functionals, including the LDA and PBE GGA well reproduce the electronic structure of graphene as well as the fact that it is a non-magnetic material. The SCAN result for the band structure (Figure 2) is similar to LDA and PBE, when symmetry breaking due to magnetism is not allowed. However, when magnetism is allowed the SCAN functional incorrectly predicts antiferromagnetic moments on the two sublattices, with a resulting gap opening, which amounts to more than 1 eV. This is a very sizable error. The calculated spin moment on the C atoms is 0.10 μB as obtained by integration of the spin density in a sphere of radius 0.863 Å. The moment can alternatively be determined by integration of the absolute value of the difference between the up-spin density and the down-spin density over space. This yields a larger moment of 0.15 μ_B/C. Therefore, SCAN predicts a qualitatively incorrect, symmetry broken ground state for graphene. The energy gain from spin polarization is relatively small, consistent with the small moments, 9.1 meV/atom. Thus, while the ground state is incorrect, the thermochemistry is relatively unaffected by this fact. This illustrates the importance of looking at the properties of a material and not only the energy when assessing approximate density functionals.

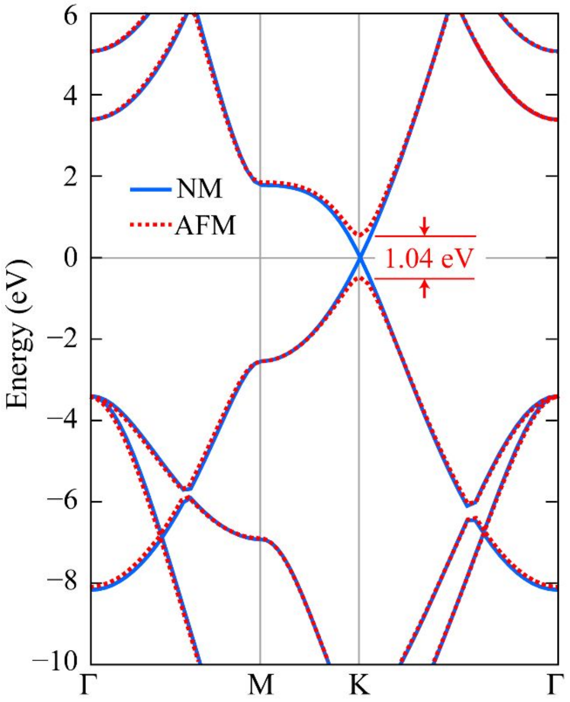

Figure 2. Band structure of graphene as obtained with SCAN, from non-spin-polarized calculations (NM) and allowing collinear antiferromagnetism with opposite spins on the two sublattices.

We find that the same problem occurs in benzene. In particular, similar to graphene, the SCAN functional predicts a spin-symmetry broken state for benzene, with alternating spin moments on the C atoms. In the case of benzene, the calculated energy lowering due to this symmetry breaking is small 0.86 meV/C, but nonetheless non-zero. We carefully checked that this result is robust. Use of a harder pseudopotential with a higher planewave cutoff of 800 eV, leads to the same result, with a slightly smaller magnetic energy of 0.79 meV/C. It has been noted that the choice of grid is potentially important in meta-GGA calculations, particularly for SCAN.[45] We therefore additionally checked the convergence with respect to the real space grid, which can be important for meta-GGA functionals. Doubling the grid density in each direction (eight times the number of grid points) led to a negligible change in the magnetic energy consisting of an increase of 0.01 meV/C. We note that symmetry breaking, including this type of spin polarization symmetry breaking, is a common feature of strongly correlated electron systems. For example, in cuprates, such as the parent phases of the high temperature superconductors, simple density functionals such as the PBE functional and the LDA incorrectly predict non-spin-polarized metallic ground states,[73] while hybrid functionals predict local moment antiferromagnetic ground states in accord with experiment. Interestingly, even though simple density functionals predict the wrong ground state for the cuprate parent compounds, they perform well for energetics of these materials, for example yielding accurate phonon frequencies.[74-75] However, the analogy between the behavior for graphene and cuprates is not perfect. We did HSE03 calculations for graphene as well. For graphene we do not find a broken symmetry spin polarized ground state with HSE03 (note HSE03 is similar to HSE06 but with a larger screening parameter).[76-77] We note that hybrid functionals are different from the SCAN meta-GGA functional in that SCAN is semi-local and designed to be one electron self-interaction free, while hybrid functionals retain non-local exchange by mixing a certain fraction of exact Coulomb or screened exchange to reduce self-interaction error.

As mentioned, development of a universal functional is a long-standing goal in density functional theory. Standard generalized gradient approximations, such as PBE, yield near chemical accuracy for many molecules, and accurate properties for many solid-state systems. However, they fail qualitatively in describing Mott insulators, such as the parent compounds of the high temperature cuprate superconductors.[73, 78-79] These failures are understood as a consequence of a tendency to delocalization related to self-interaction errors and the resulting inadequate tendency towards integer orbital occupations.[80] Thus, it is very exciting that the

SCAN functional, which is based on satisfaction of many exact constraints for the electron gas, was shown to yield both improvements over standard GGA functionals in the thermochemistry of sets of molecules and an improved description of many solids, including especially promising results for correlated materials.[81]

The present results show, however, that in addition to quantitative inaccuracies for itinerant transition metal ferromagnets, such as Ni and Fe, the SCAN functional shows large errors for the Cr dimer, as well as qualitatively incorrect symmetry broken descriptions of benzene and graphene. While Cr_2 is known to be a particularly challenging case for theory, where no density functional yields very close agreement with experiment, the qualitative failures of SCAN in the descriptions of graphene and benzene are remarkable. Therefore, the challenge of simultaneously treating localized and delocalized electronic systems remains. In particular, SCAN does not provide a universal density functional, and the quest for such a functional and strategies for finding one is open.

Conflicts of Interest:

There are no conflicts of interest to declare.

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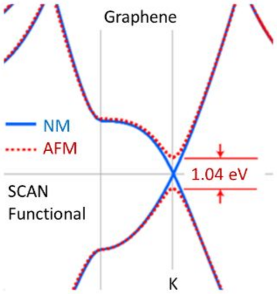
TOC Graphic:



SCAN over localizes orbitals leading to spin symmetry broken ground states in graphene and benzene