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Some Fundamental Issues in Ground-State Density Functional Theory: A Guide for the Perplexed

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Abstract: Some fundamental issues in ground-state density functional theory are discussed without equations: (1) The standard Hohenberg–Kohn and Kohn–Sham theorems were proven for a Hamiltonian that is not quite exact for real atoms, molecules, and solids. (2) The density functional for the exchange–correlation energy, which must be approximated, arises from the tendency of electrons to avoid one another as they move through the electron density. (3) In the absence of a magnetic field, either spin densities or total electron density can be used, although the former choice is better for approximations. (4) “Spin contamination” of the determinant of Kohn–Sham orbitals for an open-shell system is not wrong but right. (5) Only to the extent that symmetries of the interacting wave function are reflected in the spin densities should those symmetries be respected by the Kohn–Sham noninteracting or determinantal wave function. Functionals below the highest level of approximations should however sometimes break even those symmetries, for good physical reasons. (6) Simple and commonly used semilocal (lower-level) approximations for the exchange–correlation energy as a functional of the density can be accurate for closed systems near equilibrium and yet fail for open systems of fluctuating electron number. (7) The exact Kohn–Sham noninteracting state need not be a single determinant, but common approximations can fail when it is not. (8) Over an open system of fluctuating electron number, connected to another such system by stretched bonds, semilocal approximations make the exchange–correlation energy and hole-density sum rule too negative. (9) The gap in the exact Kohn–Sham band structure of a crystal underestimates the real fundamental gap but may approximate the first exciton energy in the large-gap limit. (10) Density functional theory is not really a mean-field theory, although it looks like one. The exact functional includes strong correlation, and semilocal approximations often *overestimate* the strength of static correlation through their semilocal exchange contributions. (11) Only under rare conditions can excited states arise directly from a ground-state theory.

I. Introduction

The pleasure of doing density functional theory (DFT) arises from (1) the deep fundamental and intellectual challenge that it presents, (2) the great practical utility and importance of

the subject, which is now central to most electronic structure calculations in quantum chemistry and condensed matter physics, and (3) the opportunity to work or communicate with a good company of others who share this interest or passion.

This short article contains no equation, table, or new result. Instead it reviews some fundamental issues in DFT. Nearly all the answers it presents can be found in the literature (and

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even the given references are sketchy and incomplete), yet some of the answers are unknown to or forgotten by the users and even the developers of this theory. These answers, to the extent that they are not quite right or complete, will be corrected, refined, and extended in future work.

II. What Is the Hamiltonian?

The magic of Kohn–Sham density functional theory^{1–7} is that it transforms a computationally heavy many-electron problem into a computationally more tractable problem of noninteracting electrons moving in a self-consistent field, in a way that is exact in principle for the ground-state energy and density. This theory tells us much that we wish to know about what atoms, molecules, nanostructures, and solids can exist, with what geometries and other properties, and how much energy is needed to break bonds or remove electrons, etc.

The standard Hohenberg–Kohn (HK)¹ and Kohn–Sham (KS)² theorems that undergird DFT were proven for an electronic ground-state of a particular Hamiltonian of an N -electron system: the sum of the nonrelativistic kinetic energy of the electrons, the interaction of the electrons with a static scalar external potential which is a function of electron position (typically but not exclusively arising from Coulomb attraction to the nuclei), and the instantaneous Coulomb repulsion among pairs of electrons. For this Hamiltonian, the HK theorem asserts that the Hamiltonian itself (and in particular its ground-state wave function and energy) is determined in principle by the ground-state electron density; degeneracy is not a problem.³

The KS theorem asserts that the ground-state density can be found by solving exact self-consistent one-electron Schrödinger equations for Kohn–Sham orbitals with occupation numbers 1 or 0. The density is found by summing the squares of the occupied orbitals. The total energy is the sum of the kinetic energy of the occupied orbitals, the interaction of the density with the external potential, the Hartree electrostatic energy of the density interacting with itself, and the exchange-correlation energy. The multiplicative effective potential seen by a Kohn–Sham orbital arises from the external potential, the Hartree electrostatic potential due to the density, and a multiplicative position-dependent exchange-correlation potential which is the functional derivative of the exchange-correlation energy. The Kohn–Sham orbitals themselves are manifestly functionals of the density.

In the simplest version of spin-density functional theory,⁸ the interacting Hamiltonian also includes the interaction of the electron spins with a position-dependent external magnetic field pointing along a fixed z -axis. Then the exchange-correlation energy becomes a functional of the separate up- and down-spin densities, and the exchange-correlation potentials for the up- and down-spin electrons can differ. Even in the absence of an external magnetic field, this spin-density version is the one that is almost always used in electronic-structure calculations.

The underlying interacting Hamiltonian is realistic but not exact for the real atoms, molecules, nanostructures, and solids that need to be described. First there are relativistic

corrections,^{5,6,9} which can be treated rigorously in a covariant reformulation of the theory that also takes into account electron currents. When the relativistic effects are not too large, they can also be treated perturbatively for all the electrons or fully for core electrons and perturbatively for the valence electrons. Second, the nuclei are not really sources of a *static* external potential, because they move. The ground-state problem can be reformulated using a multicomponent DFT^{4,5,10} employing also the densities of the various kinds of nuclei, or, if the nuclei are sufficiently massive (i.e., classical), then the effect of their motions on the electrons can be accounted for using the standard Born–Oppenheimer adiabatic approximation.^{4,5}

III. What Is the Exchange-Correlation Energy?

Thanks to the work of Levy,³ the exact density functional for the exchange-correlation energy can be defined from a search over many-electron wave functions constrained to yield a given density. Thus many exact conditions (constraints which this functional must satisfy)⁷ can be derived, but actually implementing the search (directly or indirectly¹¹) would be harder than the already-very-hard traditional N -electron wave function approaches (which are impractical for the large- N case that is often of interest). So, simplifying approximations need to be made.

Fortunately the exchange-correlation energy is a relatively small part of the total energy of a typical system, although it is by far the largest part of “nature’s glue” that binds atoms together.¹² It arises because the electrons do not move randomly through the density but avoid one another, an effect that lowers the expectation value of the electron–electron Coulomb interaction (and more so when the electrons are closer together). The exchange-correlation energy consists of three contributions. The first is the potential energy of exchange (the Fock integral of the Kohn–Sham orbitals, including the self-exchange or self-interaction correction). The second is the potential energy of correlation (due to the effect of Coulomb repulsion on the interacting wave function). Both potential energies are negative because the expectation value of the repulsive electron–electron Coulomb interaction is thereby reduced. The third is a smaller positive kinetic energy of correlation (due to the extra swerving motion of the electrons as they avoid one another).

The motion of the electrons through the density (Figure 1) is like the motion of shoppers through a crowded mall.¹³ Each shopper is surrounded by his or her “personal space”, and each electron is surrounded by its exchange-correlation hole density. Just as a shopper never bumps into himself or herself, an electron never interacts with itself. Thus the exact exchange-correlation energy provides a self-interaction correction to the Hartree electrostatic energy.

IV. Spin Densities or Total Density?

When the external magnetic field tends to zero, the exact spin-density functional theory⁸ does not reduce to the exact total-density functional theory,² except in spin-unpolarized systems. While both theories should deliver the same ground-

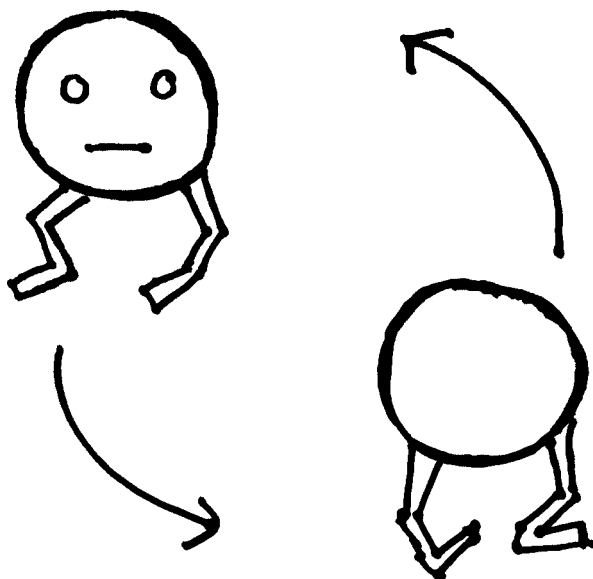


Figure 1. Electrons moving through the density swerve to avoid one another, like shoppers in a mall. The resulting reduction of the potential energy of mutual Coulomb repulsion is the main contribution to the negative exchange-correlation energy. The swerving motion also makes a small positive kinetic energy contribution to the correlation energy.

state energy and total density in this limit, only the former should deliver the separate exact densities of spin-up and spin-down electrons. When the exchange-correlation energy is approximated, even the energy and total density will typically differ (with better results¹⁴ from the spin-density functional calculation, since its inputs are richer and more detailed).

V. Is Spin Contamination Bad for Us?

The underlying interacting Hamiltonian of DFT, in a uniform or zero magnetic field, commutes with the square of the total electron spin and with its *z*-component. Then the real interacting ground-state wave function can be chosen as an eigenstate of both spin operators.

In open-shell systems, the wave function of the noninteracting Kohn–Sham system (typically and preferably a single Slater determinant of orbitals, as discussed in section VIII) is often *not* an eigenfunction of the square of total spin. This has been called “spin contamination”,¹⁵ and “restricted open-shell Kohn–Sham”¹⁶ methods have been developed to avoid it. But it is a contamination only to one who regards the Kohn–Sham wave function as an approximation to the true wave function. The more correct interpretation is that the Kohn–Sham determinant is an auxiliary quantity that generates the true ground-state spin densities. It comes from a spin-dependent Kohn–Sham potential and thus from a noninteracting Hamiltonian which does not commute with the square of the total spin. In some cases, this is the only way to generate the interacting ground-state spin densities in a noninteracting system.¹⁷ Kohn–Sham theory is only designed to yield the ground-state total energy and spin densities and not unrelated observables.

The exact exchange-correlation energy can be written^{18,19} as an average over the electron–electron coupling constant

that continuously connects the Kohn–Sham noninteracting system to the real interacting one, while holding the spin densities fixed. If the real interacting wave function is not a spin singlet ($S=0$), then the wave functions in this “adiabatic connection” may not be eigenfunctions of the square of the total spin, except at full or physical coupling strength.

VI. Can Symmetries Break?

As discussed in the preceding section, the Kohn–Sham noninteracting wave function need not display the symmetries of the interacting wave function. But of course it must produce the correct spin densities, which are influenced by symmetry. For example, the exact ground-state of the H_2 molecule is a spin singlet ($S=0$) at any bond length and thus is spin-unpolarized, with equal up- and down-spin densities. Semilocal approximations typically produce a spin-unpolarized density out to a critical bond length and then break symmetry by gradually localizing an up-spin electron on one nucleus and a down-spin electron on the other.¹⁹ While this leads to an incorrect spin-density, it still leads to the correct dissociation limit for the energy, with an intuitive picture of separate atoms at dissociation. The lower-level functionals can then be regarded²⁰ as faithful approximations to a theory in which the basic objects are not the up- and down-spin densities but the total density and on-top pair density. Probably functionals on the first four rungs of the ladder of approximations (as defined in section VII) require spin-symmetry breaking, while those on the fifth rung seem more properly to describe static correlation (sections IX and XI) without spin-symmetry breaking.²¹

VII. Are All Approximations Created Equal?

The exchange-correlation energy can be written as the integral over all space of a position-dependent exchange-correlation energy density (which is not unique, although its integral is). The approximation is said to be semilocal if this energy density depends only on the electron density and orbitals in an infinitesimal neighborhood of the given position, and otherwise it is said to be fully nonlocal. On the ladder²² of density functional approximations (Figure 2), the first rung or local spin-density approximation^{2,8} employs only the local spin densities, the second rung or generalized gradient approximation (GGA) [e.g., refs 23 and 24] adds the gradients of the local spin densities, and the third rung or meta-GGA adds the positive orbital kinetic energy density [e.g., refs 25–28] (or, almost equivalently,²⁹ the Laplacians of the spin densities). Such semilocal functionals often work because of proper accuracy for a slowly varying density or because of error cancelation between exchange and correlation over “normal” regions of space in which such a cancelation is expected.³⁰ When the semilocal exchange and correlation holes satisfy the same sum rules as the exact holes (section IX), error cancelation can occur because the exact exchange-correlation hole is usually more localized around its electron (and thus more semilocal) than the exact exchange hole. The “abnormal” regions in which no error cancelation is expected include one-electron, nonuniform high-density, and rapidly varying regions (in which exchange

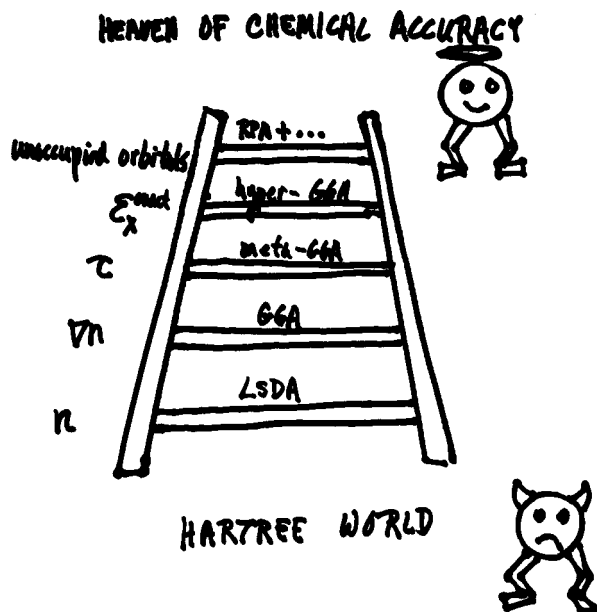


Figure 2. The Jacob's ladder of density functional approximations to the exchange-correlation energy adds local ingredients successively, leading up in five steps from the Hartree world ($E_{xc} = 0$) of weak or no chemical bonding to the heaven of chemical accuracy (with errors in energy differences of order 1 kcal/mol=0.0434 eV).

dominates correlation). A second class of abnormal systems includes the open systems of fluctuating electron number discussed in sections IX and XI (over which the semilocal holes do not satisfy the exact sum rules).

There are also two fully nonlocal rungs: the fourth rung or hyper-GGA [e.g., ref 30], which adds the exact exchange energy density, and the fifth rung or generalized random phase approximation [e.g., ref 31], which adds the unoccupied orbitals. Climbing up the ladder, the approximations become more complicated, more sophisticated, and typically more accurate. Computation times increase modestly from the first to the third rungs and much more steeply after that. The added ingredients on each higher rung of the ladder can be used to satisfy more exact constraints (nonempirical approach³²), or to better fit data (semiempirical approach), or both. The first three rungs and the fifth require no fitting, but empiricism seems unavoidable³⁰ on the fourth rung. The ladder classification is not an exclusive one. Although it finally brings in van der Waals interaction on the fifth rung, there are simpler ways to do that, some involving an approximation for the exchange-correlation energy as a double integral of a function of the densities and their gradients at two points in space.³³

Mel Levy has stressed that, when an investigator reports a "failure of density functional theory", he or she is typically reporting the failure of a given density functional approximation and should say that. Users should also report results on several different rungs, where possible, both as a check on consistency and as guidance for functional developers.

It appears that the densities and energies (if not the Kohn–Sham potentials) of most atoms, and of most molecules and solids close to equilibrium, can be evaluated with increasingly satisfactory accuracy by climbing the first three

or semilocal rungs of the ladder.^{26–28} But, wherever stretched bonds connect open subsystems of fluctuating electron number,^{34–38} full nonlocality may be unavoidably needed, as discussed in sections IX and XI.

Readers who still ask "Which functional should I choose?" could consult ref 39.

VIII. Is One Slater Determinant Enough?

Starting from the Levy constrained search,³ many different formally exact Kohn–Sham theories can be constructed.⁴⁰ In all of them, a search is made over a class of simple objects (of given electron number N) that all yield a given ground-state density (or spin densities), to find the one that minimizes the expectation value of the kinetic energy. The various components of the total energy are then defined for this density, and the total energy is minimized over all N -electron densities. The class might be all single Slater determinants, all fermion wave functions, or most generally all ensembles. The minimizing object then represents the state of the Kohn–Sham noninteracting system of that density; it is either a single determinant, or a linear combination of a few determinants, or an ensemble of such wave functions. The more this class is restricted, the greater the chance that it may be an empty set for the interacting ground-state density of interest. In other words, the desired interacting ground-state density may not be "noninteracting v -representable"⁴¹ over a restricted class, in which case even the "exact" Kohn–Sham theory will fail. Even if a minimizing Slater determinant exists for a given density, it might be an excited state (not a ground state) of the Kohn–Sham noninteracting system.

It seems likely that, for most but perhaps not all real ground-state systems of interest, one can find a Kohn–Sham noninteracting system that is in its ground-state and described by a single Slater determinant. The commonly used density functional approximations are only expected to be reliably accurate when a single Slater determinant can be found. These approximations, whether nonempirical or semiempirical, are all based on general properties of or fits to systems in which the Kohn–Sham wave function is a single Slater determinant (and thus the orbital occupation numbers are integers). In particular, semilocal functionals are accurate in part because they model an on-top hole density that is exact for exchange⁴² and often accurate for correlation.⁴³ If one Slater determinant is not enough, then these approximations cannot be reliably accurate. In other words, if energy-minimized self-consistent calculations with an approximate functional and broken symmetry do not lead to integer occupation numbers for all the orbitals, be careful.

IX. Are Open Systems Different from Closed Ones?

A closed system is one with a fixed number of electrons. It can be composed of several open subsystems among which the electron numbers fluctuate (Figure 3). Since correlation suppresses fluctuation,⁴⁴ the fluctuation between subsystems at the noninteracting or Kohn–Sham level is expected to be greater than or equal to that in the real interacting system.

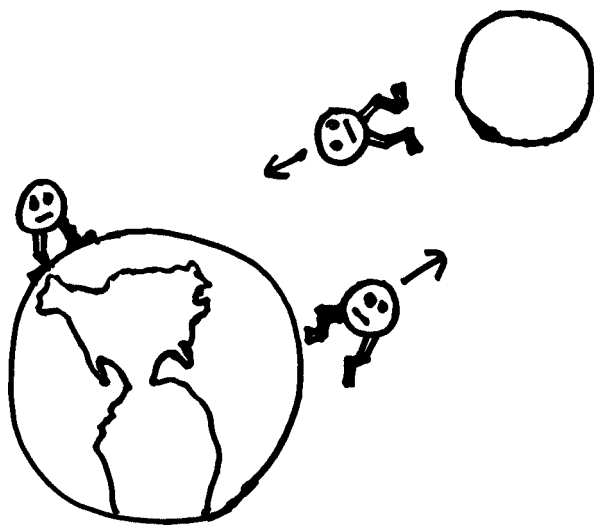


Figure 3. Weakly correlated electrons can fluctuate between the moon (an isolated open system of fluctuating electron number) and the earth (a reservoir). But strongly correlated electrons can localize and thus not fluctuate. The Hartree–Fock approximation neglects correlation, while semilocal approximations often overestimate it.

When fluctuation occurs, some occupied Kohn–Sham orbitals share an electron between the two open subsystems, equivalent to a noninteger occupation number (section VIII) in each. If these open systems are sufficiently separated (connected by *stretched* bonds), then semilocal functionals can make serious errors not only in their separate exchange and correlation energies but also in the sum of the two,^{34–38} whose magnitude can be greatly overestimated. These errors can be related directly to the sum rules on the exact exchange³⁸ and exchange–correlation³⁵ hole densities around an electron, which integrate to -1 over a closed system but to a value between 0 and -1 over an open system of fluctuating electron number.

It is known^{34,35} that the exact energy of an isolated open system varies linearly as a function of its average electron number between adjacent integer numbers. This result follows from both the exact ensemble approach to the open subsystem³⁴ and the exact wave function approach to the combined closed system.³⁵ The semilocal functionals make the energy variation concave upward^{34,35,38} over this range. (In contrast, the exact-exchange-only or Hartree–Fock approximation makes it concave downward³⁸ and thus requires a strong negative static correlation correction at noninteger average electron number in order to recover the correct straight-line behavior.)

The resulting “many-electron self-interaction error”^{37,45} (or “delocalization error”⁴⁶) of semilocal functionals produces some striking failures thereof: (a) Many asymmetric molecules AB dissociate not to neutral atoms A and B but improperly to fractionally charged fragments $A^{+q}...B^{-q}$.^{36–38} (b) Radical symmetric molecules A_2^{+1} at infinite bond length have the correct charge state $A^{+0.5}...A^{+0.5}$ but thereby energies far below the proper energy of $A...A^{+1}$ [e.g., ref 37]. (c) Long-range charge transfers are overestimated.⁴⁷ (d) Because the transition states of chemical reactions have long stretched

bonds, the energy barriers that control the reaction rates are underestimated or even absent [e.g., ref 30].

The exact energy of an isolated open system has a derivative discontinuity at integer average electron number, where one straight line meets another.³⁴ As a result, the exact Kohn–Sham potential (and specifically the functional derivative of the exchange–correlation energy) jumps discontinuously by an additive constant at each integer.^{34,35,48–50} This is counterintuitive to one who regards the Kohn–Sham potential as a physical object, but not to one who recalls that it is a mathematical object that acts on a nonphysical system of noninteracting electrons.

X. Is the Kohn–Sham Band Gap Wrong?

The jump of the Kohn–Sham potential (discussed in the last paragraph of section IX) also explains^{51–54,46} how the fundamental band gap of an insulator (ionization energy minus electron affinity) can be larger than the gap in the exact Kohn–Sham band structure. (Note that accurate fundamental gaps for semiconductors are predicted not by the band structure of the Kohn–Sham potential but by that of a hybrid of the multiplicative Kohn–Sham and nonmultiplicative Hartree–Fock potentials.⁵⁵) Since in an atom the first excitation energy is often approximated by the difference between the lowest unoccupied and highest occupied exact Kohn–Sham orbital energies,⁵⁶ it follows that in a large-gap insulator the gap in the exact Kohn–Sham band structure approximates the first exciton energy (the least energy to create an electron–hole pair localized on one atom), which is smaller than the fundamental gap. The fundamental gap (if it is direct or optical one) is however the limit of a Rydberg series of exciton energies.

XI. Can DFT Describe Strong Correlations?

Some practitioners of “strong correlation” define it as “anything not described by DFT” but probably mean by that “some things not described correctly by the common semilocal density functional approximations”. “Strong correlation” has two different meanings: (1) It can refer for example to the correlations present in a superconductor or a Luttinger liquid, which may have a small effect on bonding energies but are qualitatively different from the correlations given by low-order perturbation theory or by the random phase approximation. (2) It can refer to static correlations⁵⁷ that arise from near- or exact degeneracies at the Kohn–Sham level and are especially important when there are stretched bonds between open systems of fluctuating electron number^{34–38} (section IX). (In the limit of infinite stretch, there is degeneracy between the bonding and unoccupied antibonding molecular orbitals that are shared between two open subsystems, each of fluctuating electron number.) These static correlations can be large and important on the scale of bonding energies. Even in equilibrium, they can perhaps arise from subsystems composed of localized d-electrons (as in some transition-metal oxides) or f-electrons (as in some lanthanides and actinides).³⁸ Static correlation, also known as electron localization or the suppression of electron fluctuation, can occur in both molecules and solids.

It is often said that DFT (at least in semilocal approximations) is a “mean field approximation” (like Hartree–Fock theory) which “does not include strong correlation”. Neither of these statements is really correct. DFT solves mean-field-like equations but includes in principle all correlations via the exact exchange–correlation functional. Semilocal approximations account for static correlation not in the correlation term but in the exchange term.⁵⁷ In the case of stretched bonds between open systems of fluctuating electron number (section VIII), they typically *overestimate* the magnitude of the sum of exact exchange and exact correlation (including static correlation).³⁸ This error is often reduced in hybrid functionals that mix a fraction $a \approx 0.25$ ⁵⁸ of exact exchange with a fraction $1-a$ of semilocal exchange plus full semilocal correlation. But in other cases (e.g., stretched spin-restricted singlet H₂) they somewhat *underestimate* the magnitude of the static correlation, and in these cases the hybrid functionals can be worse than the semilocal ones. Accurate description of these strong correlations seems to require fully nonlocal (fourth- or even fifth-rung) functionals.

Strong correlations of type (2) above are often treated with a “DFT+U” approach, where the positive empirical parameter U can be understood^{59,38} as an energy penalty for fractional occupation that corrects the semilocal DFT error described in sections IX and XI.

XII. Do Excited States Arise Directly from a Ground-State Theory?

In principle, the ground-state density in the absence of a magnetic field determines the Hamiltonian and thus all excited states and their energies. But solutions of the exact Kohn–Sham equations do not predict exact excited-state energies and densities, except under special circumstances.^{60,61} If the ground-state density functional for the energy has extrema lying above the minimum, those extrema predict the energies and densities of excited states. In particular, self-consistent solutions of the exact Kohn–Sham equations in which all spin–orbitals have occupations 1 below (or at) and 0 above a Fermi level represent either ground or excited states.

In principle and in practice, excited-state energies can be found from time-dependent DFT or from excited-state DFT.^{4–6}

Note Added after ASAP Publication. This article was released ASAP on March 2, 2009. On March 3, 2009 additional information was added to ref 24. Additional information was added to ref 63 on March 17, 2009. The correct version was posted on March 18, 2009.

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