

Density Functional Theory of Electronic Structure

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Density functional theory (DFT) is a (in principle exact) theory of electronic structure, based on the electron density distribution $n(r)$, instead of the many-electron wave function $\Psi(r_1, r_2, r_3, \dots)$. Having been widely used for over 30 years by physicists working on the electronic structure of solids, surfaces, defects, etc., it has more recently also become popular with theoretical and computational chemists. The present article is directed at the chemical community. It aims to convey the basic concepts and breadth of applications: the current status and trends of approximation methods (local density and generalized gradient approximations, hybrid methods) and the new light which DFT has been shedding on important concepts like electronegativity, hardness, and chemical reactivity index.

1. Introduction and Basics

Density functional theory (DFT) is primarily a theory of electronic ground state structure, couched in terms of the electronic density distribution $n(r)$. Since its birth, about three decades ago, it has become increasingly useful for the understanding and calculation of the ground state density, $n(r)$, and energy, E , of molecules, clusters, and solids—any system consisting of nuclei and electrons—with or without applied static perturbations. It is an alternative, and complementary, approach to the traditional methods of quantum chemistry which are couched in terms of the many-electron wave function $\Psi(r_1, \dots, r_N)$. Both Thomas–Fermi and Hartree–Fock–Slater methods can be regarded as ancestors of modern DFT. But whereas those theories are intrinsically approximate, modern DFT is in principle exact.

Over the past 30 years, density functional theory has become the physicists' method of choice for electronic structures of solids. More recently chemists also use it extensively, by itself or joined to other methods. This article is aimed primarily at chemists. It is necessarily very incomplete, and we apologize for somewhat arbitrary choices, influenced by the authors' own interests.

Let us state right away the strengths and weaknesses of DFT, when compared with traditional methods. The latter are ordinarily preferable when dealing with few-atom systems, $N_{\text{at}} \lesssim 5-10$ and when high accuracy is required. DFT is preferable when $N_{\text{at}} \gtrsim 5-10$ and a more modest accuracy is acceptable. Apart from this quantitative complementarity, DFT and traditional methods are also conceptually complementary. The chief building blocks of traditional methods are single-electron orbitals, ψ_j , and many-electron wave functions, Ψ , constructed from them. The chief element of DFT is the electron density $n(r)$ and, in the Kohn–Sham version (below), the fictitious single-particle orbitals, φ_j^{KS} .

Finally, let us state an intrinsic limitation of “pure” DFT. In traditional methods, an arbitrary level of accuracy can in principle be obtained for any system, given a sufficiently powerful computer. DFT depends on the adequate knowledge of the exchange correlation energy functional $E_{\text{xc}}[n(r)]$ (below), and although more and more accurate forms are constantly being

developed, there is no known systematic way to achieve an arbitrarily high level of accuracy.

We shall now sketch the fundamentals of DFT. For details we refer to refs 1 and 2. We limit ourselves here to the simplest class of systems, N nonrelativistic, interacting electrons in a nonmagnetic state with Hamiltonian

$$H \equiv T + V + U \quad (1.1)$$

where (in atomic units)

$$T \equiv -\frac{1}{2} \sum_j \nabla_j^2, \quad V \equiv \sum_j v(r_j) \\ U = \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (1.2)$$

Notice that, for mathematical reasons, we are considering a broad class of Hamiltonians with electrons moving in an *arbitrary* external potential $v(r)$, not only the physically relevant Coulomb potentials due to point nuclei.

The starting point of DFT is the rigorous, simple lemma of Hohenberg and Kohn (HK):³ The specification of the ground state density, $n(r)$, determines the external potential $v(r)$ *uniquely* (to within an additive constant C),

$$n(r) \rightarrow v(r) \quad (\text{unique}) \quad (1.3)$$

Since $n(r)$ also determines N by integration, it determines the full Hamiltonian H and thence, implicitly, *all* properties determined by H . Examples are the full N -particle ground state wave function $\Psi(r_1, \dots, r_N)$, the electrical polarizability, the n th excitation energy, vibrational force constants, and potential energy surfaces for chemical reactions.

With the help of this lemma, a minimal principle for the energy as functional of $n(r)$ can be derived.³ For given $v(r)$ one defines the following energy functional of $n(r)$:

$$E_{v(r)}[n(r)] \equiv \int v(r) n(r) dr + F[n(r)] \quad (1.4)$$

where

$$F[n(r)] \equiv (\Psi[n(r)], (T+U)\Psi[n(r)]) \quad (1.5)$$

is a functional of $n(r)$, since Ψ is.⁴ The minimal principle is

$$E_{v(r)}[n(r)] \geq E_{v(r)}[n_0(r)] \equiv E \quad (1.6)$$

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where $n_0(r)$ and E are the density and energy of the ground state. The equality in (1.6) holds only if $n(r) = n_0(r)$.

By making simple approximations for $F[n(r)]$, one can easily rederive the Thomas–Fermi approximation and its refinements. However, for most purposes a different approach has proved to be more useful.⁵ We extract from $F[n]$ its largest and elementary contributions, by writing

$$F[n(r)] = T_s[n(r)] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{xc}[n(r)] \quad (1.7)$$

where $T_s[n(r)]$ is the kinetic energy of a *noninteracting* system with density $n(r)$ (in the appropriate $\tilde{v}(r)$), and the next term is the classical expression for the interaction energy. The remaining E_{xc} , the so-called exchange correlation energy, is *defined* by eq 1.7.⁶

If E_{xc} is ignored, the physical content of the theory becomes identical to that of the Hartree approximation. It is then no surprise that the Euler–Lagrange equation associated with the stationarity of $E_v[n]$ can be transformed into a new set of self-consistent (so-called Kohn–Sham or KS) equations

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) - \epsilon_j \right) \phi_j(r) = 0 \quad (1.8a)$$

$$n(r) = \sum_{j=1}^N |\phi_j(r)|^2 \quad (1.8b)$$

$$v_{xc}(r) = \delta E_{xc}[n(r)] / \delta n(r) \quad (1.8c)$$

which differ from the Hartree equations only by the inclusion of the exchange correlation potential $v_{xc}(r)$. The *local* equations (1.8) must be solved self-consistently, like the Hartree equations, calculating v_{xc} in each cycle from eq 1.8c, with an appropriate approximation for $E_{xc}[n(r)]$ (see below). The extra computational work, compared to a Hartree calculation, is very minor. However, we point out that, in spite of the appearance of simple, single particle orbitals, the KS equations are in principle *exact* provided that the exact E_{xc} is used in (1.8c). In other words, the only error in the theory is due to approximations of E_{xc} . The ground state energy is given by

$$E = \sum_1^v \epsilon_j - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' - \int v_{xc}(r)n(r) dr + E_{xc}[n(r)] \quad (1.9)$$

where the ϵ_j and n are the self-consistent quantities.

The individual eigenfunctions and eigenvalues, ϕ_j and ϵ_j , of the KS equations (1.8) have no strict physical significance, with one exception: For isolated systems with $v(\infty) = 0$, the highest eigenvalue, ϵ_N , controls the asymptotic decay of $|\phi_N|^2$ and of the total physical density $n(r)$ and hence can be shown to be the negative of the exact, many-body, ionization potential.

At the same time, *all* ϵ_j and ϕ_j are of great semiquantitative value, much like Hartree–Fock energies and wave functions, often more so, because they reflect also correlation effects, and are consistent with the exact physical density, $n(r)$.

To put this theory to practical use, we need good approximations for $E_{xc}[n]$, of which the simplest, and at the same time surprisingly serviceable, is the local density approximation (LDA):⁵

$$E_{xc}^{\text{LDA}}[n(r)] \equiv \int \epsilon_{xc}(n(r)) n(r) dr \quad (1.10)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per particle of a uniform interacting electron gas of density n . This quantity is known to a very high accuracy ($\sim 0.1\%$). The LDA becomes exact when the length scale l over which $n(r)$ varies is large, in the sense

$$l \gg d, (da_0)^{1/2} \quad (1.11)$$

where d and a_0 are respectively the mean particle spacing ($\approx n^{-1/3}$) and the hydrogen radius. However, for fairly well-understood reasons, it also gives useful results for most physical and chemical applications, in which (1.11) generally is *not* satisfied. The KS orbitals in the LDA are usually very close to Hartree–Fock orbitals.

A next level of approximations are the so-called generalized gradient approximations

$$E_{xc}^{\text{GGA}} = \int f(n, |\nabla n|) dr \quad (1.12)$$

in which $f(n, |\nabla n|)$ is a suitably chosen function of its two variables. These and other approximations and illustrative applications are discussed section 2.

The computing time in DFT, for a system of many atoms with no geometric symmetries, grows roughly like N_{at}^2 or N_{at}^3 . This is much better than traditional methods, where computing time grows as $e^{\alpha N_{\text{at}}}$ ($\alpha \approx 1$). As previously remarked, this makes DFT attractive for many-atom systems; still, the present upper bound is $N_{\text{at}} \sim 100\text{--}200$, which excludes many interesting systems (macromolecules, solutions, many glasses, etc.). It is therefore significant that, in principle, DFT can be reformulated so that computing time grows only *linearly* in N_{at} (so-called $O(N)$ methods). The practicality of these methods is currently being explored.⁷

Although for simplicity we have limited our remarks to the simplest class of electronic systems, DFT has, since its inception, been applied to many other systems: spin-polarized ground states, magnetic and electric susceptibilities, relativistic corrections, finite temperature ensembles, excited states, superconductors, time-dependent phenomena, etc. However, so far its main usefulness has been in applications to spin-unpolarized or -polarized ground states. Much work remains to be done in the other areas.

We have discussed DFT as a *computational* tool for the study of electronic structure. However, it has also helped to illuminate important chemical *concepts*. This is the subject of section 3.

2. Density Functional Computational Chemistry

Real progress in the application of Kohn–Sham theory to chemistry was not realized until the early 1980s. There is considerable older literature on atomic systems, but initial molecular applications were clouded by numerical uncertainties. The first applications of DFT to chemistry (late 1960s) utilized scattered-wave or “muffin tin” numerical techniques adapted from the solid state repertoire.⁸ These proved inadequate to describe finite molecules. One-electron spectroscopic properties could be usefully estimated, but potential energy curves and accurate densities could not. Through the 1970s, various basis set methodologies were combined with numerical integration techniques to handle the nonanalytical exchange-correlation problem, and by 1980 reliable computational technologies for DFT chemistry were finally in place.⁹

With computational difficulties under control, assessments of the theory itself in chemical applications were possible. The old Xa model, a parametrized exchange-only DFT variant much popularized in the scattered-wave era, proved erratic in its

predictions of molecular properties. Bond energies, in particular, deviated from experiment by electronvolts in many cases and showed no obvious overbinding or underbinding trend. Early molecular tests of the local spin-density approximation (LSDA), the spin-dependent generalization of eq 1.8, also revealed large deviations from experiment.¹⁰ Later, a clear *overbinding tendency* emerged. The O₂ molecule, for example, is overbound in the LSDA by an enormous 55 kcal/mol, with average deviations of order 20–30 kcal/mol per bond. Nevertheless, other important properties such as bond lengths, bond angles, vibrational frequencies, charge moments, etc., tend to agree surprisingly well with experiment^{11,12} in “ordinary” chemical bonds (i.e., H bonds and van der Waals interactions excepted). The LSDA is therefore a remarkably useful structural, though not thermochemical, tool.

The severe overbinding character of the LSDA is disappointing. A clear trend such as this, however, suggests that fundamental lessons and accompanying remedies are not far away. Extension of the LSDA to include local spin-density *gradients* is the next logical step. The lowest-order gradient correction of exchange type

$$\beta \frac{(\nabla n)^2}{n^{4/3}} \quad (2.1)$$

had been well-studied by the mid-1980s.¹³ It does not, unfortunately, offer improved chemistry, though evidence of this fact is sparse in the literature.¹⁴ As reported in 1986, however,¹⁵ a simple modification of eq 2.1 yields excellent DFT bond energies (rms error of only 0.3 eV or 7 kcal/mol) in first- and second-row homonuclear diatomic tests. This modification addressed the unacceptable asymptotic behavior of eq 2.1 far from a finite system: namely its divergent functional derivative, eq 1.8c. In the process, absolute atomic exchange energies themselves were significantly improved.¹⁵

This path to improved DFT chemistry attracted the interest of computational and theoretical researchers alike. Computational chemists found substantial applications in areas unreachable by traditional wave function methods (notably Ziegler in organometallic chemistry¹⁶), and theoreticians were encouraged by the promising practical dividends of exchange-correlation functional development. Several alternative gradient-corrected exchange and correlation functionals rapidly followed and are now known collectively as generalized gradient approximations (GGAs) as in eq 1.12.

The term GGA means, essentially, going beyond the lowest-order gradient correction of eq 2.1. Indeed, the *large* gradient limit,

$$\chi = \frac{|\nabla n|}{n^{4/3}} \rightarrow \infty \quad (2.2)$$

where χ is the appropriate *dimensionless* measure of local inhomogeneity, is nicely amenable to theoretical analysis in finite systems. Large χ corresponds in coordinate space to distances far from a finite system. There, the exchange energy takes the simple asymptotic form

$$E_x = -\frac{1}{2} \int_r^n dr, \quad r \rightarrow \infty \quad (2.3)$$

as the density itself becomes *exponential*. An exchange GGA has been found¹⁷ that exactly reproduces this asymptotic exchange energy behavior. We reproduce it below to display what a typical GGA looks like (σ is a spin-label):

$$E_x = E_x^{\text{LSDA}} - b \sum_{\sigma} \int n_{\sigma}^{4/3} \frac{\chi_{\sigma}^2}{(1 + 6b\chi_{\sigma} \sinh^{-1} \chi_{\sigma})} dr \quad (2.4a)$$

where

$$E_x^{\text{LSDA}} = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \sum_{\sigma} \int n_{\sigma}^{4/3} dr \quad (2.4b)$$

and

$$\chi_{\sigma} = |\nabla n_{\sigma}|/n_{\sigma}^{4/3} \quad (2.4c)$$

With one semiempirical fitted parameter, $b = 0.0042$ au, exchange energies of atomic systems are remarkably accurate. This functional is effectively an interpolation formula between the small- and large- χ limits of the exchange energy density. Also noteworthy is the 1986 exchange GGA of Perdew.¹⁸ Based on a parameter-free coordinate-space model of inhomogeneous systems, it gives chemical results very similar to those of eq 2.4.

Correlation GGAs (that is, for “dynamical”, electron-gas-like correlation) have also received considerable attention. The chemical consequences of gradient corrections for correlation are relatively small compared to their exchange counterparts,¹⁹ and we shall therefore limit our discussion of correlation GGAs accordingly. The most popular dynamical correlation functionals presently are those of Lee, Yang, and Parr²⁰ (based on the model of Colle and Salvetti²¹), Perdew 1986,²² and Perdew and Wang 1991.²³ The latter is a logical generalization of Perdew’s parameter-free coordinate-space model for exchange¹⁸ and is entirely free of empirical parameters as well. Of the many possible exchange-correlation combinations, several are currently in use. As long as both are of the same class (i.e., LSDA, GGA, or perhaps some future explicitly nonlocal variety), the specific choice of exchange and correlation functional is much less important than the differences between the LSDA and GGA themselves.

To summarize, the LSDA generally gives good molecular structures, vibrational frequencies, and charge densities^{11,12} in strongly bound systems (i.e., H bonds and van der Waals interactions excepted). It is not useful, however, for thermochemistry. GGAs, on the other hand, yield good thermochemistry, with average errors of order 6 kcal/mol in standard thermochemical tests.¹⁹ Their domain extends even to the energetics and structures of hydrogen-bonded systems.²⁴ It is at the level of the weakest chemical interactions, namely van der Waals interactions, that GGAs apparently fail.²⁵ Also, both the LSDA and the GGA leave much room for improvement in predicting reaction barrier heights.^{26,27}

We cannot end this overview of LDA and GGA chemistry without mentioning the dramatic impact of Kohn–Sham theory in the field of *ab initio* molecular dynamics. An elegant suggestion by Car and Parinello²⁸ in 1985, and related theoretical and computational developments,²⁹ have made large-scale simulations of molecules and materials a reality. Ongoing attempts to linearize the scaling of these methods promise even greater things. Let us mention as well that DFT treatment of excited states and multiplet structure has also progressed. The early model of Ziegler, Rauk, and Baerends³⁰ is now group theoretically automated,³¹ and recent formal advancements³² offer additional scope for further work. DFT predictions of electromagnetic properties are also under test,³³ and much awaits to be learned in this area.

Nonlocality. Both the LSDA and the GGA are based on *localized* model exchange-correlation holes. Only local density information (or local density gradient information) is utilized at each reference point. The fact that LSDA and GGA model holes satisfy the same normalization constraints as “real” holes accounts for much of their success. Their intrinsic locality further implies that real exchange-correlation holes in molecular systems are also relatively localized. This conclusion, though largely true, is certainly not absolute. Special situations, such as H_2^+ at large separation, simply cannot be modeled by localized holes. Even in ordinary chemical bonds, exchange-correlation holes undoubtedly have a small nonlocal component.

Very recently, proposals to incorporate nonlocality into DFT chemistry³⁴ have spawned a new class of hybrid Hartree–Fock/GGA theories with precision surpassing that of pure GGAs. They are motivated by the following centrally important formula, the *adiabatic connection* or *coupling strength integration* formula³⁵ for the exchange-correlation hole in Kohn–Sham DFT:

$$h_{xc}(r,r') = \int_0^1 h_{xc}^\lambda(r,r') d\lambda \quad (2.5)$$

where the hole generates E_{xc} through the following double integration:

$$E_{xc} = \frac{1}{2} \int \int \frac{n(r)}{r_{12}} h_{xc}(r,r') dr dr' \quad (2.6)$$

Spin decomposition of these formulas is possible, but will not concern us here.³⁶ Equation 2.5 literally “connects” the Kohn–Sham independent-particle reference system ($\lambda = 0$) with the real, fully interacting system ($\lambda = 1$) through a coupling strength parameter λ . The parameter λ smoothly turns on interelectronic Coulomb repulsion while an appropriate one-body potential (also λ dependent) holds the total electronic density fixed. Notice, however, that $h_{xc}^\lambda(r,r')$ has *nonlocalized* character at $\lambda = 0$, because the hole in this independent particle limit is the pure and exact exchange hole of the Kohn–Sham Slater determinant (i.e., no correlation whatsoever). This hole is *poorly represented* by localized LSDA or GGA models in *molecular bonds*, and hence the small- λ region of the coupling strength integration is problematic.^{34,36}

A simple but effective cure for the $\lambda = 0$ problem is replacement of the *model* GGA hole at $\lambda = 0$ with the exact hole, resulting in the following exchange-correlation expression:^{34,36}

$$E_{xc} = E_{xc}^{\text{DFT}} + a_0(E_x^{\text{Exact}} - E_x^{\text{DFT}}) \quad (2.7)$$

The parameter a_0 reflects the importance of nonlocality in the real exchange-correlation hole. In current practice, it is fit to experimental thermochemical data, taking values of 20% or higher depending on the choice of correlation GGA. This kind of exact-exchange mixing reduces average bond energy errors from about 6 kcal/mol for pure GGAs to roughly 2 kcal/mol. Improvements are particularly striking in nonhydride and multiple bonds, where pure GGAs suffer overbinding errors as high as 20 kcal/mol. Reaction barrier heights are also improved by exact-exchange mixing,²⁷ though a thorough study of this important area remains to be undertaken.

In the past few years, modifications of well-established and powerful Hartree–Fock programs to include density functional computations^{12,37} have stimulated an explosion of interest in DFT. All the features of Hartree–Fock technology, including energy second derivatives, are now available for DFT applica-

tions in convenient and widely distributed software packages. Critical assessment of popular functionals on a scale heretofore unseen is thus under way in all areas of computational chemistry. It is an exciting time for density functional theory. Furthermore, these recent technical advances have beautifully facilitated the testing and application of the exact-exchange mixing scheme described above. A true marriage of density functional and Hartree–Fock ideas and technologies has emerged, and a potentially very beneficial cross-fertilization between DFT and traditional wave function methods has begun.

3. Chemical Concepts

A great strength of the density functional language is its appropriateness for defining and elucidating important universal concepts of molecular structure and molecular reactivity. In traditional quantum chemistry this has, of course, also been a major goal, but it is tortuous to try to conceptualize how many-body wave functions are related to structure and behavior. In DFT not only is the electron density itself very easy to visualize, but there is the big advantage that the electron number N has a central place in the theory. After all, much of chemistry is about the transfer of electrons from one place to another.

Consider an electronic ground state for a system of N electrons moving in an external potential $v(r)$, usually just the potential due to the nuclei. Solution of the minimization problem of eq 1.6 will give the electron density and energy. The minimization in the first instance is constrained to be at fixed N . However, we can enlarge the domain of the minimization principle to include all N if we append the constraint condition with a Lagrange multiplier, the value of which is to be determined. So we have, as an important extension of eq 1.6,

$$\delta\{E[n(r)] - \mu[N[n(r)]]\} = 0 \quad (3.1)$$

where μ is the *chemical potential* of the system, a function of N and a functional of $v(r)$, $N[n] = \int n(r) dr$, and the subscript v on E has been suppressed. One must imagine solving (3.1) for every μ and then selecting the μ value which gives the correct number of electrons for the system of interest.

From the fundamental theory of Lagrange multipliers, μ measures how sensitive the extremum E is to a change in N ,

$$\mu = (\partial E / \partial N)_v \quad (3.2)$$

Here E is assumed to be a smooth function of N , an assumption to which we return at the end of this section.³⁸ This result contains considerable chemistry $\mu = \mu[N, v]$ characterizes the escaping tendency of electrons from the equilibrium system.³⁹ Systems (e.g., atoms or molecules) coming together must attain at equilibrium a common chemical potential. This chemical potential is none other than the negative of the electronegativity concept of classical structural chemistry. For, the finite-difference approximation to μ for a system with ionization potential I and electron affinity A is

$$\mu = -\frac{I + A}{2} \quad (3.3)$$

and one half of $I + A$ is just the original Mulliken formula for electronegativity. The idea that electronegativity is a chemical potential originates with Gyftopoulos and Hatsopoulos.⁴⁰

The chemical potential μ of the DFT variational principle of eq 3.1 is a small one-electron energy much less than the total electronic energy E which enters the variational principle of traditional quantum chemistry. DFT thus promises relief from

the old curse of needing to difference large numbers in making chemical predictions.

Long ago, Sanderson postulated that there was a principle in chemistry that electronegativity tends to equalize. Electronegativity being synonymous with chemical potential, the correctness of Sanderson's principle immediately follows from the fact that the chemical potential of DFT is a property of an equilibrium state. The chemical potential (electronegativity) is expected to be sensitive to the external potential and may not be necessarily easy to calculate, but it is a concept securely rooted in DFT. Semiempirical electronegativity equalization methods now are widely used.⁴¹

E versus N plots are not straight lines but are generally convex upward. Their curvatures define another property of substantial importance, the *hardness*.⁴²

$$\eta = (\partial^2 E / \partial N^2)_v = (\partial \mu / \partial N)_v \quad (3.4)$$

The finite-difference approximation for this is

$$\eta = I - A \geq 0 \quad (3.5)$$

The inverse of hardness is *softness*.⁴³

$$S = (\partial N / \partial \mu)_v \quad (3.6)$$

Accordingly, one may write, if only N changes,

$$E = E^0 + \mu(N - N^0) + \frac{1}{2}\eta(N - N^0)^2 + \dots \quad (3.7)$$

and one can verify that to second order the number of electrons transferred between A and B induced by a difference in chemical potentials between A and B is given by

$$\Delta N = \frac{|\mu_B^0 - \mu_A^0|}{\eta_B^0 + \eta_A^0} \quad (3.8)$$

where $\mu_A^0 = \mu_A(N_A^0)$, etc. The hardness can be thought of as a resistance to charge transfer. The softness measures ease of transfer; softness is associated with high polarizability.⁴⁴

The hardness and softness defined in eqs 3.4 and 3.6 are the "hardness" and "softness" that enter two well-known principles in chemistry: the HSAB principle and the maximum hardness principle. The hard and soft acids and bases principle states that hard acids "prefer" hard bases and soft acids prefer soft bases, thermodynamically and kinetically.⁴⁵ The maximum hardness principle asserts that molecular systems usually tend to states of high hardness.⁴⁶ Though it is not easy to deduce these principles rigorously or completely, they are consequences of eq 1.6 and/or its generalization to states at finite temperature.⁴⁷ From (1.6) energy decreases in going from nonequilibrium to equilibrium. From its finite-temperature extension, the grand potential decreases. The problem with cleanly deriving the HSAB principle is to simply but properly model the system of approaching entities.⁴⁸ The problem with proving the maximum hardness principle is to find the right constraints to guarantee its validity.⁴⁹ One strategy for proving the HSAB principle is to first establish the maximum hardness principle. The constant chemical potential constraint often is pertinent for chemical problems.⁵⁰ For the latest on these various subtle matters, one may consult the contemporary literature.^{51,52}

It can be seen that the finite-difference expression for hardness, eq 3.5, is no more no less than the *band gap* that plays such an important role in solid state physics and solid state chemistry—the difference between the HOMO and LUMO orbital energies in a simple orbital theory. When the gap is

large (other things being equal), one expects high stability and low reactivity. When it is small, one expects low stability and high reactivity. These predictions are well borne out in the good correlation that exists between HOMO–LUMO gap and the organic chemists' concept of *aromaticity*.

Now let us turn to changes in N and v . The most general differential energy change will be given by

$$dE = \mu dN + \int n(r) dv(r) dr \quad (3.9)$$

where the second term follows from conventional first-order perturbation theory. Note how apt this equation is for chemistry, where the main action so often is addition or subtraction of electrons. There is no reason to restrict eq 3.9 to an isolated system. It can be applied to atoms or weakly coupled functional groups in a molecule, which are open systems⁵³ to which a generalized density functional theory will apply. (Compare the great Gibbs extension of closed-system thermodynamics to open-system thermodynamics.)

Second-order energy changes will be covered by integration of eq 3.9 provided that we can master the N and v dependencies of the quantities μ and $v(r)$. The first needed differential coefficient is the hardness η of eq 3.4, already discussed. The second is a quantity long familiar and much discussed in chemical physics, the *linear response function* (polarizability kernel)

$$[\delta n(r) / \delta v(r')]_N = [\delta n(r') / \delta v(r)]_N \quad (3.10)$$

Finally, we have the Fukui function⁵⁴

$$f(r) = [\partial n(r) / \partial N]_v = [\delta \mu / \delta v(r)]_N \quad (3.11)$$

This quantity integrates to unity. Note the use here of Maxwell reciprocal relations. Combining these results gives the fundamental equation

$$d\mu = \eta dN + \int f(r) dv(r) dr \quad (3.12)$$

in which all quantities have the greatest chemical and physical interest.

The name Fukui function is appropriate for $f(r)$ because it clearly is a chemical reactivity index in the sense of "frontier orbital" theories of reactivity. The HOMO and LUMO orbital densities are known to be decisive for determining chemical reactivity: high or low frontier density at a molecular site often confers high chemical reactivity to that site. This, in essence, is what the Fukui function is measuring. For the finite-difference formula for $f(r)$, when electrons are added to a species S , will be $n(S^-) - n(S) = n_{\text{LUMO}}$, when electrons are subtracted $n(S) - n(S^+) = n_{\text{HOMO}}$. So, clearly, $f(r)$ is a proper chemical reactivity measure. A difference between "right derivative" and "left derivative" is predicted in DFT.⁵⁵ A variational principle for direct determination of $f(r)$ and band gap is known.⁵⁶

Local softness is an important quantity which combines the site reactivity index $f(r)$ with the global softness measure S :

$$s(r) = [\partial n(r) / \partial \mu]_N = f(r)S \quad (3.13)$$

There is an interesting fluctuation formula for this quantity in finite-temperature DFT, where the averages are over all members of a grand ensemble at temperature T .⁴³ This formula and other similar DFT fluctuation formulas^{57,58} may provide a basis for fluctuation theories of catalysis. $s(r)$ is measurable using scanning tunnel microscopy. For an infinite system, $s(r)$ is approximately the local density of states at the Fermi level and S the total density of states at the Fermi level.^{43,60}

There is no unique simple inverse of $s(r)$. However, there can be usefully defined two-variable hardness and softness kernels, from which can be generated local softness, global softness, Fukui function, a local hardness, and global hardness.⁶¹ Defining $u(r) = v(r) - \mu$, we have the softness kernel

$$s(rr') \equiv -\delta n(r)/\delta u(r') \quad (3.14)$$

and the hardness kernel

$$\eta(r,r') = -\delta u(r)/\delta n(r') - \delta^2 F/\delta n(r) \delta n(r') \quad (3.15)$$

These satisfy

$$\int s(r,r') \eta(r',r'') dr' = \delta(r-r'') \quad (3.16)$$

Then we find

$$s(r) = \int s(r,r') dr' \quad (3.17)$$

and if we define⁶²

$$\eta(r) = \int f(r) s(r,r') dr' \quad (3.18)$$

we obtain

$$\int s(r) \eta(r) dr = 1 \quad (3.19)$$

and

$$S = \int s(r) dr \quad (3.20)$$

and

$$\eta = \iint f(r) \eta(r,r') f(r') dr dr' \quad (3.21)$$

We also find

$$\eta(r) = \eta \quad (3.22)$$

which would be very good if it were not for the fact that it appears to eliminate $\eta(r)$ as a candidate for a physically meaningful local hardness. An alternative definition has recently been suggested.⁵⁸

We have here put emphasis on the effects of N change and v change on the *electron* density. There also are shifts in the *nuclear* positions, of course, which ultimately must be incorporated in a complete theory. Very recently, there has been a vigorous start in this direction.^{60,63} Modeling of the hardness kernel of eq 3.15 has been an active field for some time.⁶⁴

The Problem of Discontinuities in N . Historically, DFT had its antecedent in the so-called “statistical” theory of Thomas, Fermi, Dirac, and Slater. Also, the first good approximate functionals in DFT, the family of LDA functionals, came out of the “uniform gas” model, and modern improved functionals largely arose from modifications of LDA (as described in section 2). It might seem that large N would be the condition for DFT to work well. This is not correct, however; DFT works just fine—at least in principle—even from systems with as few as one or two electrons. The reason is that DFT is a proper transcription of the Schrodinger equation for *any* number of electrons.

The total number of electrons in any particular system we are interested in is an integer—the variable N possesses only integral values. Does this cause a problem? Certainly not when we are calculating on an actual problem of interest. We need only have good enough functionals for a given N to calculate at that N . For moving from one N to another (which, as we have emphasized, is highly relevant for chemical processes), no error is introduced if we arrange to connect all the correct integral N functionals by applying suitable interpolation methods, to give functionals that are continuous in N . The

interpolations can, but need not, use finite-difference methods, producing finite-difference formulas for properties of interest for systems of integral N .⁶⁵ In this way, we can imagine finite-difference formulas for all derivatives and functional derivatives that enter the formal theory in which N is treated as a continuous variable. The literature on the band gap (HOMO–LUMO gap) well illustrates the subtleties in these matters.^{66,67}

There is a quite different situation in which N enters as a continuous, nonintegral variable. Chemists perform must be much concerned with atoms or functional groups in molecules, that is, with what are *subsystems* of a system with an integral number of electrons. Consider, for example, the hydrogen atom in the series HH, HF, HCl, HI, HBr. It varies, essentially continuously, from one molecule to the next, and it bears exactly one electron only in the first. If one accepts Bader’s definition of the atom,⁵³ its charge distribution is precisely calculable, for example by DFT, and it constitutes a subsystem which in general has a nonintegral number of electrons. The same is true for an early DFT definition of an atom in a molecule.³⁹ For such subsystems there are no discontinuities in N , and the conceptual ideas we have described in this section ought to apply. Neighboring atoms in a molecule are strongly interacting, however, and a correct detailed theory of their interaction is very difficult to achieve.^{68,69}

4. Concluding Remarks

In addition to the two reference texts which have been mentioned,^{1,2} there have been published many reviews and edited volumes on DFT. We note in particular the book by Norman March⁷⁰ and a volume in the NATO ASI series.⁷¹

Thousands of papers have appeared in this subject area, and interest in it is accelerating. Furthermore, not only is the methodology for calculation steadily improving, but the content of the theory is still evolving. Mathematical problems remain, and the precise directions in which the subject will be moving are not clear. One should remember that conventional quantum-chemical methods have taken 70 years to develop. The present account is thus neither definitive nor complete.

The calculational promise of DFT is, to a certain degree, already achieved. As described in section 2, current methods of calculation are of an accuracy that is approaching what quantum chemists call “chemical accuracy”: a few percent of a chemical binding energy.

On the more purely theoretical side of the subject, we briefly note two important contemporary lines of investigation. First, much can be learned from examining the scaling properties of the various functionals.⁷² Second, one now knows how to efficiently determine very accurate exchange-correlation *potentials*, $v_{xc}(r)$, when an accurate electron density is known, and this furnishes data and discipline to the search for better approximate exchange-correlation potentials and energies.^{73,74}

Continued research is needed on the problem of finding the various unknown exchange-correlation functionals. Much of the progress to date is rooted in the original LDA paper,⁵ where one builds on what is known about the uniform electron gas. But a different route is possible: to take advantage of the considerable knowledge of the density-matrix transcription of wave function theory. Here one starts from a proper description of the electron–electron repulsion when electrons are close together and the empirical fact that the Hartree–Fock or Kohn–Sham electron density is nearly correct. Hopefully, work on improving functionals will eventually lead to a procedure to improve DFT calculations systematically, from one approximation to the next.

Finally, in our opinion the vocabulary of DFT ought to, indeed will, more and more permeate the description of electronic structure of atoms, molecules, clusters, surfaces, and solids. DFT is a convenient and universal language for electronic structure theory, which substantially helps unify organic chemistry, inorganic chemistry, surface chemistry, and materials science. It helps unify chemistry and physics.

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References and Notes

- Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- Dreizler, R. M.; Gross, E. K. V. *Density Functional Theory*; Springer: Berlin, 1990.
- Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. We give here the derivations for systems with nondegenerate ground states. For degenerate ground states, see refs 4, 1, and 2.
- An alternative, broader definition of $F[n(r)]$ is $F[n(r)] \equiv \min(\Psi_{n(r)}, (T+V)\Psi_{n(r)})$ where the minimum is from among all antisymmetric wave functions $\Psi_{n(r)}$ with density $n(r)$. Levy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6062; *Phys. Rev. A* **1982**, *26*, 1200. Lieb, E. H. In *Physics as Natural Philosophy*; Shimony, A., Feshbach, H., Eds.; MIT Press: Cambridge, MA, p 111.
- Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
- Except for a uniform electron gas, this is *not* the same as the exchange-correlation energy of traditional methods.
- For a recent bibliography, see: Parr, R. G.; Yang, W. *Annu. Rev. Phys. Chem.* **1995**, *46*, 701.
- Reviewed in: Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1. Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.
- Baerends, E. J.; Ros, P. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *12*, 169. Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396, 4993. Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949. These STO, GTO, and numerical LCAO-based programs, respectively, have seen considerable evolution and propagation. For later developments, see: Boerrigter, P. M.; Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87. St-Amant, A.; Salahub, D. R. *Chem. Phys. Lett.* **1990**, *169*, 387. Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280. Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.
- Becke, A. D. *Phys. Rev. A* **1986**, *33*, 2786.
- Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991. Delley, B. *J. Chem. Phys.* **1991**, *94*, 7245. Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.
- Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.
- Sham, L. J. In *Computational Methods in Band Theory*; Marcus, P. M., Janak, J. F., Williams, A. R., Eds.; Plenum: New York, 1971. Kleinman, L. *Phys. Rev. B* **1984**, *30*, 2223 and references therein. Herman, F.; Van Dyke, J. P.; Ortenburger, I. B. *Phys. Rev. Lett.* **1969**, *22*, 807; *Int. J. Quantum Chem., Quantum Chem. Symp.* **1970**, *3*, 827.
- Becke, A. D. *Int. J. Quantum Chem.* **1985**, *27*, 585.
- Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
- For references to early work, see: Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. For references to later work, see: Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.
- Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- Perdew, J. P. *Phys. Rev. Lett.* **1985**, *55*, 1665. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1986**, *33*, 8800.
- Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155; **1992**, *97*, 9173.
- Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- Colle, R.; Salvetti, O. *J. Chem. Phys.* **1983**, *79*, 1404 and references therein.
- Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822; **1986**, *34*, 7406.
- Perdew, J. P.; Wang, Y. Unpublished. Perdew, J. P. In *Electronic Structure of Solids*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhals, C. *Phys. Rev. B* **1992**, *46*, 6671.
- Sim, F.; St-Amant, A.; Papai, I.; Salahub, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 4391.
- Kristyan, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175. Perez-Jorda, J. M.; Becke, A. D. *Chem. Phys. Lett.* **1995**, *233*, 134.
- Fan, L.; Ziegler, T. *J. Am. Chem. Soc.* **1992**, *114*, 10890. Sosa, C.; Lee, C. *J. Chem. Phys.* **1993**, *98*, 8004. Deng, L.; Ziegler, T.; Fan, L. *J. Chem. Phys.* **1993**, *99*, 3823. Stanton, R. V.; Merz, Jr., K. M. *J. Chem. Phys.* **1994**, *100*, 434. Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100.
- Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys.* **1995**, *102*, 2063.
- Baker, J.; Andzelm, J.; Muir, M.; Taylor, P. R. *Chem. Phys. Lett.* **1995**, *237*, 53. Baker, J.; Muir, M.; Andzelm, J.; Scheiner, A. *ACS Symp. Ser.*, to be published.
- Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
- Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045. Remler, D. K.; Madden, P. A. *Mol. Phys.* **1990**, *70*, 921. Pastore, G.; Smargliassi, E.; Buda, F. *Phys. Rev. A* **1991**, *44*, 6334. Galli, G.; Parrinello, M. In *Proceedings of the NATO ASI*; Meyer, M., Pontikis, V., Eds.; Kluwer Academic: Dordrecht, 1991.
- Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261.
- Daul, C. *Int. J. Quantum Chem.* **1994**, *52*, 867.
- Gross, E. K. U.; Oliveira, L. N.; Kohn, W. *Phys. Rev. A* **1988**, *37*, 2805, 2809. Oliveira, L. N.; Gross, E. K. U.; Kohn, W. *Phys. Rev. A* **1988**, *37*, 2821.
- Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. Colwell, S. M.; Handy, N. C. *Chem. Phys. Lett.* **1994**, *217*, 271.
- Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; **1996**, *104*, 1040.
- Harris, J.; Jones, R. O. *J. Phys. F* **1974**, *4*, 1170. Gunnarsson, O.; Lundqvist, B. I. *Phys. Rev. B* **1976**, *13*, 4274. Langreth, D. C.; Perdew, J. P. *Phys. Rev. B* **1977**, *15*, 2884.
- A detailed analysis may be found in: Becke, A. D. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.
- Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett.* **1993**, *209*, 506. Murray, C. W.; Handy, N. C.; Laming, G. J. *Mol. Phys.* **1993**, *78*, 997. Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.
- Parr, R. G.; Bartolotti, L. J. *J. Phys. Chem.* **1983**, *87*, 2810.
- Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
- Gyftopoulos, E. P.; Hatsopoulos, G. N. *Proc. Natl. Acad. Sci. U.S.A.* **1965**, *60*, 786.
- Mortier, W.; Ghosh, S. K.; Shankar, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 4315.
- Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
- Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723.
- Politzer, P. J. *J. Chem. Phys.* **1987**, *86*, 1072.
- Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
- Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.
- Mermin, N. D. *Phys. Rev.* **1965**, *137*, A1441.
- Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855.
- Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854.
- Parr, R. G.; Gazquez, J. L. *J. Phys. Chem.* **1993**, *97*, 3939.
- Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett.* **1995**, *237*, 171.
- Parr, R. G.; Yang, W. *Annu. Rev. Phys. Chem.* **1995**, *46*, 701.
- Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.
- Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
- Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, Jr., J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691.
- Chattaraj, P. K.; Cedillo, A.; Parr, R. G. *J. Chem. Phys.* **1995**, *103*, 7645.
- Harbola, M. K.; Chattaraj, P. K.; Parr, R. G. *Isr. J. Chem.* **1991**, *31*, 395.
- Baekelandt, B. G.; Cedillo, A.; Parr, R. G. *J. Chem. Phys.* **1995**, *103*, 8548.
- Galvan, M.; Dal Pino, Jr., A.; Wang, J. *J. Phys. Chem.* **1993**, *97*, 783.
- Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrovsky, J. J. *Chem. Phys.* **1994**, *101*, 8988.
- Berkowitz, M.; Parr, R. G. *J. Chem. Phys.* **1988**, *88*, 2554.
- Ghosh, S. K. *Chem. Phys. Lett.* **1990**, *172*, 77.
- Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrovsky, J. J. *Chem. Phys.* **1995**, *103*, 3543.
- Nalewajski, R. F. Z. *Naturforsch.* **1988**, *43A*, 65.
- Tachibana, A. *Int. J. Quantum Chem.* **1996**, *57*, 423.
- Perdew, J. P.; Levy, M. *Phys. Rev. Lett.* **1983**, *51*, 1884.
- Sham, L. J.; Schlüter, M. *Phys. Rev. Lett.* **1983**, *51*, 1888.
- Tachibana, A.; Parr, R. G. *Int. J. Quantum Chem.* **1992**, *41*, 527.
- Cioslowski, J.; Stefanov, B. B. *J. Chem. Phys.* **1993**, *99*, 5151.
- March, N. H. *Electron Density Theory of Many-Electron Systems*; Academic Press: New York, 1991.
- Gross, E. K. U.; Dreizler, R. *Functional Theory*; Plenum Press: New York, 1993.
- Gorling, A.; Levy, M. *Phys. Rev. B* **1993**, *47*, 105.
- Zhao, Q.; Morrison, R. C.; Parr, R. G. *Phys. Rev. A* **1994**, *50*, 2138.
- Gritsenko, O. V.; Leeuwen, R. v.; Baerends, E. J. *Phys. Rev. A* **1995**, *52*, 1870.