Density Functional Theory and the Band Gap Problem

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Abstract

How can the fundamental band gap of an insulator be predicted? As a difference of ground-state energies, the fundamental gap seems to fall within the reach of density functional theory, yet the predicted gaps from band structure calculations within the local density approximation (LDA) are about 40% too small. It is argued here that even the exact Kohn-Sham potential $v_{eff}(\underline{r})$, which generates the exact density in a self-consistent-field calculation, generates a band structure which underestimates the gap. Within the context of the band gap problem, several recent developments in the density-functional theory of many-electron systems are reviewed: (1) The Langreth-Mehl approximation to the Kohn-Sham exchange-correlation energy and potential, based upon the Langreth-Perdew wavevector analysis of the density gradient expansion. This functional leads to more accurate ground-state energies and densities than those of the LDA with little change in the calculated band structures of solids. (2) The derivative discontinuity of the exchange-correlation energy, which is responsible for substantial underestimation of the fundamental gap by even the exact Kohn-Sham potential. (3) The self-interaction correction, which yields accurate gaps in insulators only by virtue of its *orbital-dependent* potential. (4) The density response function of the uniform electron gas, which suggests that the LDA gives a good estimate of the exact Kohn-Sham potential for a semiconductor with a weak periodic potential. In short, several very different (but admittedly approximate) numerical calculations suggest that most of the error in the LDA fundamental gap would persist in the gap of the exact Kohn-Sham band structure. This error would persist in any attempt to calculate the gap from LDA total energy differences for clusters of increasing size.

1. Introduction and Summary

The fundamental gap of an electronic system is the difference between the ionization energy I and electron affinity A. In any system, finite or infinite, the quantity of I-A plays the role of "chemical hardness" [1]. In a metallic crystal, I-A is zero. In an insulating crystal, I-A is the fundamental band gap or conductivity gap, the least excitation energy for a separated electron-hole pair.

The band theory of solids aims to calculate the ground-state density $n(\underline{r})$ and the single-particle spectrum, especially the fundamental gap. The density can be calculated as for a hypothetical system of noninteracting electrons moving in the effective potential $v_{eff}(\underline{r})$:

$$n(\underline{r}) = \sum_i f_i |\psi_i(\underline{r})|^2 , \tag{1}$$

where $f_i = \theta(\mu - \epsilon_i)$ is a fermion occupation number, and

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}(\underline{r})] \psi_i(\underline{r}) = \epsilon_i\psi_i(\underline{r}) . \tag{2}$$

That effective potential $v_{\text{eff}}(\underline{r})$ which generates the true density is known as the Kohn-Sham [2] potential. As discussed in Section 2, the Kohn-Sham potential is intimately related to the ground-state energy. Thus one might hope that the Kohn-Sham band structure would predict the true fundamental gap, which is a difference of ground-state energies. This paper discusses the failure of that expectation, the reason for this failure, and an alternative approach to the calculation of the fundamental gap. Instead of a full review of the band gap problem, this is the story of how several separate avenues of research have lined up to point in the same direction.

The organization of the paper is as follows:

Section 2 outlines the Hohenberg-Kohn-Sham density functional theory [2,3] and the local density approximation [2], the *de facto* basis for much of modern band theory. Within the local density approximation to the Kohn-Sham potential, the fundamental gaps of insulators and semiconductors are typically underestimated by 40%.

However, this observation leaves open the possibility that improved approximations to the Kohn-Sham potential might correct the gap. This possibility is explored in Section 3, which reviews the Langreth-Mehl [4] approximation based upon the Langreth-Perdew [5] wavevector analysis of the density gradient expansion. The Langreth-Mehl approximation corrects most of the error of the local density approximation in the total energy and electron density, but corrects little of the error in the fundamental gap.

This observation suggests that even the exact Kohn-Sham potential might not yield a band-structure with the correct fundamental gap. The reason for this failure of expectation, the derivative discontinuity of the exact exchange-correlation energy, is discussed in Section 4. This surprising nonanalyticity was discovered by Perdew, Parr, Levy and Balduz [6], and applied to the band gap problem in simultaneous papers by Perdew and Levy [7] and by Sham and Schlüter [8]. It is conjectured in Section 4 that the exact Kohn-Sham band structure normally provides a lower bound on the fundamental gap.

The spin-density generalization [9,10] of density functional theory is introduced in Section 5, and applied to an instructive model system: an expanded lattice of hydrogen atoms. The true energy cost to remove an electron from this system is the same, whether the electron is removed from a localized Wannier orbital or from a delocalized Bloch orbital. But the local spin density approximation is contaminated by a self-interaction error which is much worse in the Bloch picture than it is in the Wannier picture.

As an alternative to the Kohn-Sham method, the self-interaction corrected (SIC) method [11,12] offers an *orbital-dependent* potential which generates accurate electron densities and fundamental gaps in large-gap insulators. Section 6 reviews the self-interaction correction to the local spin density approximation, within the formalism of Perdew and Zunger [11]. Special attention is directed to the band-theory formulation of

SIC by Heaton, Harrison, and Lin [12], in which each Bloch orbital sees its own individual periodic potential. When this orbital-dependent is replaced by an orbital-independent Kohn-Sham potential, chosen by the method of Norman and Koelling [13] to optimize the SIC total energy, the good agreement between SIC-calculated and measured gaps is destroyed. This observation suggests that only an orbital-dependent potential $v^i_{eff}(r)$, or a nonlocal one $v_{eff}(r,r')$, can simultaneously generate the electron density and the fundamental gap.

A metal may be distinguished from an insulator either by its vanishing fundamental gap or by its perfect screening. In Section 7, the theory of static dielectric screening is reviewed, and a physical argument is presented for the equivalence of these two criteria for metallic behavior.

Recently, Antoniewicz and Kleinman [14] have suggested that the exact Kohn-Sham potential might, after all, yield the observed fundamental gap for semiconductors. Their suggestion is based upon the strong difference between the exact dielectric response for the uniform electron gas and that of the local density approximation, both within the *exchange-only* version of density functional theory. In Section 7, it is shown that recent estimates of the correlation effect upon the dielectric response function suppress this difference, making it unlikely that the exact Kohn-Sham potential (including correlation) could yield the observed gaps in semiconductors.

The failure of local potentials $v_{eff}(r)$ in band theory is not unanticipated. More than twenty years ago, Herman found a serious underestimation of the fundamental gap in relativistic local-potential calculations for germanium [15,44]. It has been known for some time that band theory requires in principle an energy-dependent, nonlocal self-energy [16,17] $\sigma(r,r';\epsilon)$. Recent progress [18–24] toward the evaluation of the self-energy will not be reviewed here.

Fourteen years ago, Kane [25] pointed out that any potential $v_{eff}(r)$ which fits the observed cyclotron masses (valence and conduction band shapes) in silicon yields a fundamental gap of 0.6 eV, which is closer to the local density gap [26] of 0.5 eV than to the true gap [25] of 1.1 eV. At the same time, Lipari and Kunz [27] reached similar conclusions for the alkali halides. Eleven years ago, Mott [28] made a prescient statement which could serve as the theme of this paper:

"But often it will not be sufficient, if we are to obtain even qualitatively the right separation between occupied and empty bands, to take the same potential $V(r)$ for the valence and conduction bands. Particularly in a tight-binding situation, as for a d-band, it would be a poor approximation to do so. An electron in the valence band of (say) solid argon sees the field of Ar^+, while an electron in the conduction band sees that of Ar. This should introduce a separation between the two bands of order I-A, where I is the ionization potential and A the electron affinity. This is a term depending on correlation, and if a one-electron formulation with the same function $V(r)$ for electrons in both bands gives good agreement with experiment for the energy gap, this must be something of an accident."

2. Overview of Density Functional Theory

Hohenberg and Kohn [3] have demonstrated the existence of a functional $E_v[n]$ which, when minimized over trial densities $n(r)$ integrating to N electrons, yields the

exact ground-state energy E and density for N electrons subject to an external potential $v(\underline{r})$. The Euler equation for this variational principle is

$$\delta\{E_v[n] - \mu\!\int d^3rn(\underline{r})\} = 0 , \tag{3}$$

or

$$\delta E_v/\delta n(\underline{r}) = \mu . \tag{4}$$

The Lagrange multiplier μ is evidently the chemical potential:

$$\mu = \partial E/\partial N . \tag{5}$$

Kohn and Sham [2] have shown how to implement this variational principle in practical calculations: Divide $E_v[n]$ into pieces,

$$E_v[n] = T_s[n] + \int d^3rv(\underline{r})n(\underline{r}) + U[n] + E_{xc}[n] , \tag{6}$$

where $T_s[n]$ is the ground-state kinetic energy for hypothetical noninteracting electrons of density $n(\underline{r})$, $U[n]$ is the classical repulsion

$$U[n] = \tfrac{1}{2}\int d^3r\!\int d^3r' \, n(\underline{r})n(\underline{r}')/|\underline{r}-\underline{r}'| , \tag{7}$$

and $E_{xc}[n]$ is the exchange-correlation energy. The true $n(\underline{r})$ is found from the self-consistent solution of the one-electron equations (1) and (2). The effective potential of the Kohn-Sham equation (2) is

$$v_{\text{eff}}([n];\underline{r}) = v(\underline{r}) + u([n];\underline{r}) + \delta E_{xc}/\delta n(\underline{r}) , \tag{8}$$

where

$$u([n];\underline{r}) = \delta U/\delta n(\underline{r}) = \int d^3r' \, n(\underline{r}')/|\underline{r}-\underline{r}'| . \tag{9}$$

Thus the many-electron problem has in principle been reduced to self-consistent-field form.

The Kohn-Sham orbital energies ϵ_i have at least a formal meaning. Janak [29] (following arguments given by Slater [30]) proved that

$$\epsilon_i = \partial\tilde{E}/\partial f_i , \tag{10}$$

where

$$\tilde{E} = \sum_i f_i\langle\psi_i| -\tfrac{1}{2}\nabla^2|\psi_i\rangle + \int d^3r \, v(\underline{r}) \, n(\underline{r}) + U[n] + E_{xc}[n] . \tag{11}$$

Eq. (10) holds for any choice of the occupation numbers $\{f_i\}$; the orbitals $\{\psi_i\}$ are to be optimized or relaxed for each choice. The proof of Eq. (10) requires only self-

consistency, and so is valid for the exact $E_{xc}[n]$ or for any approximation to it. From Eq. (10), Janak [29] also derived an "aufbau" principle: If the occupation numbers f_i are permitted to take any value between 0 and 1, then $\tilde{E}$ is minimized when $f_i = 1$ for all $\epsilon_i < \mu$, and 0 for all $\epsilon_i > \mu$, where μ is the chemical potential. For fixed electron number N, $\tilde{E}$ at its minimum is just the ground-level energy $E(N)$. Fractional values of f_i and N arise in ensemble averages for open systems [6,29,31].

Let the orbital energies of the N-electron system be ordered as

$$\epsilon_1(N) \leq \epsilon_2(N) \leq \ldots \tag{12}$$

Then, for the J-electron system (J = any positive integer), the first ionization potential and electron affinity are respectively (from Eq. (10))

$$I(J) \equiv E(J-1) - E(J) = -\int_0^1 df\, \epsilon_J(J-1+f), \tag{13}$$

$$A(J) \equiv I(J+1) = E(J) - E(J+1) = -\int_0^1 df\, \epsilon_{J+1}(J+f). \tag{14}$$

According to Eqs. (13) and (14), the fundamental gap of the J-electron system is determined by the highest partly-occupied Kohn-Sham orbital energy of the N-electron ground-level, for $J-1 < N < J+1$. This is the only Kohn-Sham orbital energy which carries any exact physical meaning, since $\tilde{E}$ of Eqs. (10) and (11) has an exact physical significance only when the "aufbau" principle is obeyed. In a crystal ($J \to \infty$), the removal or addition of one electron can change the ground-state density $n(\underline{r})$ only infinitesimally. If this infinitesimal density change is associated with an infinitesimal change in the Kohn-Sham potential $v_{eff}([n]\underline{r})$, and hence in the Kohn-Sham orbital energies, then by Eqs. (13) and (14) the fundamental band gap will be predicted exactly by the Kohn-Sham band-structure of the neutral (J-electron) system:

$$I(J) - A(J) = \epsilon_{J+1}(J) - \epsilon_J(J). \tag{15}$$

This interesting argument, in essence, was presented by Williams and von Barth [32,33], and was foreshadowed in discussions by Slater and Wood [34] and by Worth and Trickey [35]. The argument is almost correct; what it overlooks is the possibility that the Kohn-Sham potential, and specifically $\delta E_{xc}/\delta n(\underline{r})$, might shift [6] by a constant C when N increases through the integer J. This possibility will be considered in Section 4.

The exchange-correlation energy $E_{xc}[n]$ can be interpreted as the electrostatic interaction between the electron density at each point $\underline{r}$ and the density $\rho_{xc}(\underline{r},\underline{r}')$ of the exchange-correlation hole around $\underline{r}$:

$$E_{xc}[n] = \tfrac{1}{2}\int d^3r \int d^3r'\, n(\underline{r})\, \rho_{xc}(\underline{r},\underline{r}')/|\underline{r}-\underline{r}'|, \tag{16}$$

where [36,37]

$$\rho_{xc}(\underline{r},\underline{r}') = \frac{1}{n(\underline{r})} \int_0^1 d\lambda\, \langle [\hat{n}(\underline{r}) - n(\underline{r})][\hat{n}(\underline{r}') - n(\underline{r}')] - n(\underline{r})\, \delta(\underline{r}-\underline{r}')\rangle_\lambda. \tag{17}$$

In Eq. (17), the density-density correlation function must be evaluated for all coupling strengths λ in the range $0 < \lambda < 1$. For each λ, there is a fictitious system of electrons with interparticle interaction $\lambda/|\underline{r} - \underline{r}'|$ in the presence of external potential $v_{\text{eff}}^{\lambda}(\underline{r})$, constructed to hold the ground-state density $n(\underline{r})$ at its true value. $\lambda = 1$ describes the real electronic system, while $\lambda = 0$ describes the Kohn-Sham noninteracting system. (The exchange energy $E_x[n]$ is defined by Eqs. (16) and (17) with $\langle \ldots \rangle_\lambda$ replaced by $\langle \ldots \rangle_0$, and the correlation energy $E_c[n]$ is defined as $E_{xc} - E_x$; these definitions differ slightly from the traditional ones of quantum chemistry.) For fixed integer electron number [37], or for fluctuating electron number in an infinite system [38,39], the hole obeys the sum rule

$$\int d^3r' \; \rho_{xc}(\underline{r},\underline{r}') = -1 \; . \tag{18}$$

Around a given electron, the average density is depleted by one electron.

In practice, the exchange-correlation functional $E_{xc}[n]$ must be approximated. A widely-used choice is the local density approximation [2] (LDA):

$$E_{xc}^{\text{LDA}}[n] = \int d^3r \; n(\underline{r}) \; \epsilon_{xc}(n(\underline{r})) \; , \tag{19}$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per particle of a uniform electron gas with density n. The LDA becomes exact only in the limit of slowly-varying density. Its formal validity condition is [4]

$$(q/k_F)^2 \ll 1 \; , \tag{20}$$

where q is the inhomogeneity wavevector

$$q = |\nabla k_F|/2k_F \; , \tag{21}$$

and k_F is the local Fermi wavevector

$$k_F = [3\pi^2 n(\underline{r})]^{1/3} \; . \tag{22}$$

The LDA exchange-correlation hole,

$$\rho_{xc}^{\text{LDA}}(\underline{r},\underline{r}') = \rho_{xc}^{u}(n(\underline{r}); |r - r'|) \; , \tag{23}$$

where $\rho_{xc}^{u}(n; |\underline{r} - \underline{r}'|)$ is the hole in a uniform electron gas of density n, obeys [37] the sum rule of Eq. (18).

Kohn-Sham theory in general, and the LDA in particular, are the *de facto* foundation for much of modern band theory. The LDA exchange-correlation potential,

$$\delta E_{xc}^{\text{LDA}}/\delta n(\underline{r}) = \mu_{xc}(n(\underline{r})) \; , \tag{24}$$

where $\mu_{xc}(n) = \partial(n\epsilon_{xc})/\partial n$, is easy to construct, and the LDA density is reasonably

TABLE I. Fundamental gaps of insulators, from the band structure within the local density approximation (LDA) and from experiment. The "LDA" value for antiferromagnetic NiO was actually obtained from the local *spin* density approximation. The second "LDA" values for Ge and GaAs include relativistic effects. The "experimental" value for BN may be an underestimate due to point defects in the crystal (eV).

Crystal	LDA	Exper.	Crystal	LDA	Exper.
Ne[a]	11.4	21.4	C[a]	4.1	5.5
Ar[a]	8.3	14.2	Si[a]	0.56	1.17
Kr[a]	7.0	11.6	Ge[d]	0.65	0.76
LiF[a]	9.9	14.2	Ge[e]	0.09	0.76
NaCl[a]	5.3	9.0	GaAs[f]	0.71	1.5
CsCl[a]	5.0	8.3	GaAs[e]	0.25	1.5
MgO[a]	4.5	7.7	$CuAlS_2^g$	2.1	3.5
CaS[a]	2.6	5.4	$CuAlSe_2^g$	1.7	2.7
BaS[a]	1.8	3.9	$CuGaS_2^g$	1.3	2.4
ZnS[b]	2.3	3.8	$CuGaSe_2^g$	0.5	1.7
ZnSe[b]	1.8	2.8	$CuInS_2^g$	0.0	1.5
GaP[b]	1.8	2.4	$CuInSe_2^g$	0.0	1.0
AlP[a]	1.6	2.5	CdS[h]	2.0	2.6
NiO[c]	0.3	4.3	BN[i]	8.7	6.4
			CuCl[j]	2.0	3.4

[a] Ref. 40.
[b] Ref. 41.
[c] Ref. 42.
[d] Ref. 43.
[e] Ref. 44.
[f] Ref. 45.
[g] Ref. 46.
[h] Ref. 47.
[i] Ref. 48.
[j] Ref. 49.

accurate. However, in LDA the fundamental band gaps of insulators and semiconductors are typically underestimated by 40% (Table I) [40–49].

The LDA exchange potential, which dominates over correlation in Eq. (24), is $\mu_x(n) = -(3\alpha/2\pi)(3\pi^2 n)^{1/3}$, where α equals [2] 2/3. In Slater's $X\alpha$ method [30], the correlation term is dropped and the coefficient α is treated as an adjustable parameter. Khan and Callaway [50] found that self-consistent $X\alpha$ band-structure calculations for neon and argon could reproduce the observed fundamental gaps with an empirical coefficient $\alpha = 1.25$. Trickey, Ray and Worth [51] have observed that this exchange scaling seriously worsens the calculated band widths and cohesive properties. Almost surely, it worsens the calculated electron density as well.

Beside the Langreth-Mehl approximation of Section 3 and the self-interaction correction of Section 6, there have been several attempts to improve upon the LDA. One of them is the weighted density approximation [52–54]:

$$E_{xc}^{WDA}[n] = \frac{1}{2}\int d^3r \int d^3r' \; \frac{n(\underline{r})n(\underline{r}')}{|\underline{r}-\underline{r}'|} \; \frac{\rho_{xc}^u(\bar{n}(\underline{r}); |\underline{r}-\underline{r}'|)}{\bar{n}(\underline{r}')} \;, \tag{25}$$

TABLE II.   Fundamental gaps of insulators, from the band structure within the local density (LDA) and weighted density (WDA) approximations, and from experiment (eV).

Crystal	LDA	WDA	Exper.
Si[a]	0.56	0.71	1.17
Ge[a]	0.52	0.60	0.74
GaAs[b]	0.50	0.56	1.5

[a] Ref. 55 (uniform electron-gas input).
[b] Ref. 45.

where the weighted density $\bar{n}(\underline{r})$ is chosen to satisfy the sum rule of Eq. (18). Semiconductor fundamental gaps from WDA band structures are only slightly more realistic than those from LDA (Table II) [45,55].

A systematic correction to the LDA, in the slowly-varying limit, is provided by the gradient expansion approximation [3] (GEA):

$$E_{xc}^{GEA}[n] = E_{xc}^{LDA}[n] + \int d^3r \, C_{xc}(n)|\nabla n|^2/n^{4/3} \ . \tag{26}$$

The gradient coefficient $C_{xc}(n)$ is known [5,56]. Its exchange piece is $C_x = -1.667 \times 10^{-3}$, while its correlation piece is $C_c \approx +4.2 \times 10^{-3}$ at high and metallic densities. For realistic density variations, the GEA apparently gives no improvement in total energy over the LDA [57]. This misfortune is explained and corrected in Section 3.

In fact, it can be shown [4] that the gradient term in Eq. (26) gives the right correction to the LDA only when

$$6q/k_{FT} \ll 1 \ , \tag{27}$$

where k_{FT} is the local Fermi-Thomas screening wavevector

$$k_{FT} = 2(k_F/\pi)^{1/2} \ . \tag{28}$$

For physical electron densities, Eq. (20) is often satisfied reasonably well, while Eq. (27) is not.

3.   Langreth-Mehl Approximation to the Kohn-Sham Potential

In order to understand and correct the errors of the LDA and GEA, Langreth and Perdew [36] proposed the wavevector analysis

$$E_{xc} = \int\limits_0^\infty dk \, \frac{4\pi k^2}{(2\pi)^3} \, N \, [\bar{S}(k) - 1] \, \frac{1}{2} \, \frac{4\pi}{k^2} \ , \tag{29}$$

where $\bar{S}(k)$ is the structure factor of the inhomogeneous electronic system, averaged over the coupling strength λ and over the direction of the wavevector $\underline{k}$:

$$\bar{S}(k) = \int_0^1 d\lambda \int \frac{dk}{4\pi} \frac{1}{N} \int d^3r \int d^3r' \, e^{-i k \cdot (\underline{r} - \underline{r}')} \langle [\hat{n}(\underline{r}) - n(\underline{r})][\hat{n}(\underline{r}') - n(\underline{r}')] \rangle . \quad (30)$$

$\bar{S}(k)$ varies from 0 at $k = 0$ to 1 as $k \to \infty$. Eqs. (29) and (30) follow from Eqs. (16) and (17) upon Fourier analysis of the Coulomb interaction $1/|r - r'|$. In Eq. (29), the exchange-correlation energy is decomposed into contributions from dynamic density fluctuations of various sizes k^{-1}.

In the local density approximation,

$$N\bar{S}^{LDA}(k) = \int d^3r \, n(\underline{r}) \, \bar{S}_u(n(\underline{r});k) \quad (31)$$

where $\bar{S}_u(n;k)$ is the structure factor of a uniform electron gas of density n. The LDA is exact [36] for $k \gg 2k_F$, in agreement with the intuition that a localized density fluctuation sees only the local density. The LDA breaks down for $k \ll 2k_F$, but the breakdown is not too serious because of the small weight given to this region of phase space in three dimensions [36]. In fact $\bar{S}^{LDA}(k)$ is proportional to k^2 at small k, while the exact $\bar{S}(k)$ is also proportional to k^2 (with a different coefficient), except for surface energy contributions proportional to $|k|$ in semi-infinite systems [4,5,36].

The gradient expansion approximation of Eq. (26) provides a useful correction to the LDA at intermediate wavevectors [4,5,58]:

$$N\bar{S}^{GEA}(k) = N\bar{S}^{LDA}(k) + \int d^3r \, \frac{e^2 k_F^4}{4\pi^3} \, z_{xc}(k_F,0;k) \, \frac{q^2}{k_F^2} , \quad (32)$$

where $z_{xc} = z_x + z_c$. The exchange term is

$$z_x(k_F,0;k) = \frac{1}{2k_F} \left\{ -4y\theta(1-y) + \frac{11}{9} \delta(y-1) + \frac{1}{9} \delta'(y-1) \right\} \quad (33)$$

where $y = k/2k_F$. The wavevector analysis of the correlation term was performed by Rasolt and Geldart [58] and by Langreth and Perdew [5]. The result within the random phase approximation (RPA) [5] has been parametrized by Langreth and Mehl [4]:

$$z_c(k_F,0;k) \approx \frac{4\sqrt{3}}{k_{FT}} \exp(-2\sqrt{3} \, k/k_{FT}) . \quad (34)$$

Unlike the LDA, the gradient term in Eq. (32) is seriously wrong in the $k \to 0$ limit, tending to a large positive constant and not to zero.

The problem is that, for the GEA to be valid, q of Eq. (21) must be small compared to all relevant wavevectors, including k. As a simple remedy, Langreth and Mehl [4] replaced $z_c(k_F,0;k)$ of Eq. (34) by the cut-off form

$$z_c(k_F,q;k) = z_c(k_F,0;k) \, \theta(k - 6fq) \quad (35)$$

where $f \approx 0.15$. With this correction, they found, after integration over the wavevector k,

$$E_{xc}^{LM}[n] = E_{xc}^{LDA}[n] + a\int d^3r(2e^{-F} - 7/9)|\nabla n|^2/n^{4/3} \tag{36}$$

where

$$F = b|\nabla n|/n^{7/6} \tag{37}$$

and $a = 0.0021435$, $b = 1.745f$. Since the gradient term was derived within RPA, the LDA term is also to be evaluated within RPA. The Langreth-Mehl approximation to the exchange-correlation part of the Kohn-Sham potential is then

$$\delta E_{xc}^{LM}/\delta n(\underline{r}) = \mu_{xc}^{RPA}(n(\underline{r}))$$

$$+ 2an^{-1/3}\left\{\frac{7}{9}\left[\frac{\nabla\cdot\underline{\kappa}}{n} - \frac{2\kappa^2}{3n^2}\right] - 2e^{-F}\left[\frac{(1-F/2)\nabla\cdot\underline{\kappa}}{n}\right.\right.$$

$$\left.\left. - \left(\frac{2}{3} - \frac{11F}{6} + \frac{7F^2}{12}\right)\frac{\kappa^2}{n^2} + \frac{F(F-3)\underline{\kappa}\cdot\nabla|\underline{\kappa}|}{2n|\underline{\kappa}|}\right]\right\}, \tag{38}$$

where $\underline{\kappa} = \nabla n(\underline{r})$.

Truly impressive results have been achieved with the Langreth-Mehl (LM) approximation of Eqs. (36) and (38). It gives about the right negative correction to the LDA total energies of closed-shell atoms, and the right positive correction to the LDA surface energies of metallic crystals. The shell removal energies of atoms are also improved, as are the electron densities of the lighter atoms, where accurate densities are known from configuration-interaction studies. Unlike the LDA potential, the LM potential of Eq. (38) displays the cusp-like structures between atomic shells which are found in the exact exchange potential [59].

Figure 1 shows the deviations from LDA of the LM [60] and exact [61] electron densities in the neon atom, as well as the deviation [60] from LDA of the self-consistent LM effective potential $v_{eff}([n];\underline{r})$.

In band structure calculations for crystals, the LM approximation yields only small corrections to the LDA. In the transition metals Cu and V, the valence bands experience an s-d shift of only a tenth of an electron volt [62]. In the large-gap insulators Ne and Na Cl (Table III) [63], the fundamental gap $\epsilon_{J+1}(J) - \epsilon_J(J)$ in the Kohn-Sham band structure is increased, but only slightly—the discrepancy with the true fundamental gap I-A is barely reduced. In the semiconductor Si, the band gap discrepancy also persists [64].

These results suggest that even the exact Kohn-Sham band structure would fail to predict the fundamental gap. However, this conclusion is not firm because, as Langreth and Mehl [4] point out, the LM approximation breaks down in regions of very low density where $q \gtrsim 2k_F$. In a semiconductor or insulator, the unoccupied orbitals of interest may have nonnegligible components in these regions. In Sections 4, 6 and 7, stronger evidence will be presented to show that the exact Kohn-Sham band structure fails to predict the fundamental gap.
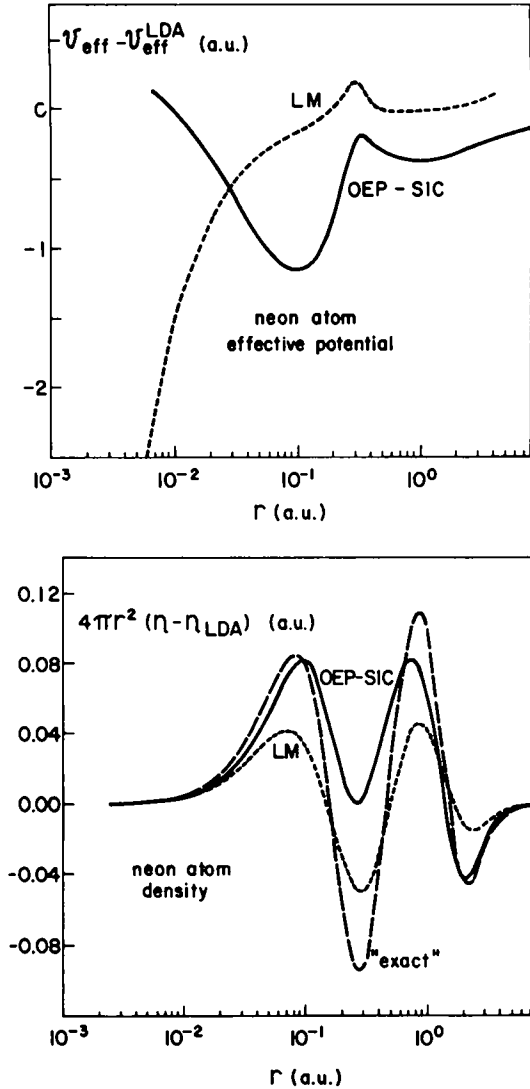
Figure 1.   (a) Deviation of the self-consistent Kohn-Sham potential $v_{eff}(r)$ in the neon atom from its form in the local density approximation (LDA). LM: Lengreth-Mehl approximation of Eq. (38). OEP-SIC: optimized effective potential for the self-interaction correction, from Eq. (69). The electron gas correlation-energy input is the Ceperley-Alder parametrization of Ref. 11 for the LDA and SIC calculations, and the random phase approximation for the LM calculation. To set the scale, $\langle r \rangle = 0.16$, 0.91 and 0.96 for the 1s, 2s, and 2p orbitals respectively. Note the inter-shell bumps in the potentials. (Figure from M. R. Norman, Ref. 60.) (b) Deviation of the self-consistent radial distribution $4\pi r^2 n(r)$ in the neon atom from its form in the LDA. The "exact" density is taken from the careful configuration-interaction study (150 configurations) of Ref. 61. The SIC and LM approximations to the density behave as might be expected: SIC is better at very large and very small r, while LM gives a better account of the depletion of the density in the inter-shell region.

TABLE III. Fundamental gaps of insulators, from the band structure within the local density (LDA) and Langreth-Mehl (LM) approximations, and from experiment (eV).

Crystal	LDA	LM	Exper.
Ne[a]	11.5	12.7	21.4
NaCl[a]	5.6	6.0	9.0

[a] Ref. 63.

4. Derivative Discontinuities of the Energy

The derivation of Eq. (15) from Eqs. (13) and (14) must be re-examined. The infinitesimal density change due to addition or removal of one electron in an infinite crystal can only be associated with a change in the Kohn-Sham potential $v_{\text{eff}}([n];\underline{r})$ which is an infinitesimal plus a possible finite constant C which may appear [6–8] as the electron number N increases through the integer J. Thus, if δ is a positive infinitesimal,

$$I(J) = -\epsilon_J(J-\delta) , \tag{39}$$

$$A(J) = -\epsilon_{J+1}(J+\delta) = -[\epsilon_{J+1}(J-\delta) + C] , \tag{40}$$

$$\begin{aligned} I(J) - A(J) &= \epsilon_{J+1}(J+\delta) - \epsilon_J(J-\delta) \\ &= \epsilon_{J+1}(J-\delta) - \epsilon_J(J-\delta) + C \\ &= \epsilon_{J+1}(J) - \epsilon_J(J) + C . \end{aligned} \tag{41}$$

The true fundamental gap equals the gap in the exact Kohn-Sham band-structure plus a possible finite constant C.

For example, consider a monatomic crystal in the separated-atom (infinite lattice constant) limit. The Kohn-Sham orbitals for the crystal are tight-binding linear combinations of the Kohn-Sham atomic orbitals. Suppose first that the underlying atom has an open subshell, so that $\epsilon_{J+1}(J) = \epsilon_J(J)$. Nevertheless, the crystal is a Mott insulator with a fundamental gap $I(J)-A(J)$ equal to that of the underlying atom; all of the fundamental gap comes from the positive constant C. Next suppose that the underlying atom is closed-shell, so that the atomic electron affinity is zero. Even though the neutral atom cannot bind an extra electron, it has an unoccupied Kohn-Sham bound orbital with energy $\epsilon_{Z+1}(Z-\delta)<0$ (because the atomic $v_{\text{eff}}([n];\underline{r})$ tends to $-1/r$ as $r \rightarrow \infty$). It follows from Eq. (40) that again $C>0$. The open-shell example is from Perdew, Parr, Levy and Balduz [6], while the closed-shell was presented by von Barth [33] as a possible objection to the Williams-von Barth [32,33] expression (15). Intimation of a correction to the exact Kohn-Sham gap in an insulator can also be found in Ref. 65.

Eqs. (13) and (14), which are valid in finite systems as well as infinite ones, refer to fractional electron number. The meaning of fractional N has been explained in Ref. 6. The ground level for N electrons, with N between the integers $J-1$ and J, is an

ensemble or statistical mixture of the $(J-1)$- and J-electron ground states, with probabilities $p = J - N$ and $1 - p = N - J + 1$ respectively. For $J - 1 \leqslant N \leqslant J$, the ground-level energy and density are

$$E(N) = (J - N) E(J - 1) + (N - J + 1) E(J) \qquad (42)$$

$$n(N;\underline{r}) = (J - N)n(J - 1;\underline{r}) + (N - J + 1)n(J;\underline{r}) . \qquad (43)$$

As a function of N, the energy $E(N)$ is a linkage of straight-line segments with possible slope discontinuities at integer values of N. The chemical potential μ according to Eqs. (5), (10) and (42) is

$$\mu = \begin{cases} \epsilon_J(N) = -I(J) & (J - 1 < N < J) \qquad (44) \\ \epsilon_{J+1}(N) = -A(J) & (J < N < J + 1) . \qquad (45) \end{cases}$$

As N increases through the integer J, the chemical potential $\mu = \delta E_v/\delta n(\underline{r})$ and the highest partly-occupied Kohn-Sham orbital energy jump discontinuously from one physical value (minus the ionization energy) to another (minus the electron affinity). The fundamental gap is thus the discontinuity [6–8] in the functional derivative:

$$I(J) - A(J) = \delta E_v/\delta n(\underline{r})|_{J+\delta} - \delta E_v/\delta n(\underline{r})|_{J-\delta} . \qquad (46)$$

With the energy functional $E_v[n]$ decomposed as in Eq. (6), it is clear that the discontinuity of Eq. (46) can arise only from the kinetic energy $T_s[n]$ and the exchange-correlation energy $E_{xc}[n]$. In the Kohn-Sham noninteracting system, with fixed effective potential $v_{eff}(\underline{r})|_J$, only the kinetic energy contributes [7,8]:

$$\epsilon_{J+1}(J) - \epsilon_J(J) = \delta T_s/\delta n(\underline{r})|_{J+\delta} - \delta T_s/\delta n(\underline{r})|_{J-\delta} . \qquad (47)$$

Therefore, the difference between the true fundamental gap and that from the Kohn-Sham orbital energies is [7,8]

$$C = \delta E_{xc}/\delta n(\underline{r})|_{J+\delta} - \delta E_{xc}/\delta n(\underline{r})|_{J-\delta} . \qquad (48)$$

Now the noninteracting kinetic energy $T_s[n]$ is a clever mathematical construct rather than a physical reality; a situation in which it displays a derivative discontinuity, while the exchange-correlation energy does not, can arise only by the purest accident. Therefore C, the discontinuity of $\delta E_{xc}/\delta n(\underline{r})$, is expected to be nonzero in all real finite systems [6,7] and real infinite insulators and semiconductors [7,8]. In a Mott insulator [28,66], where $\delta T_s/\delta n(\underline{r})$ and $\delta E_x/\delta n(\underline{r})$ are both continuous, all of the gap [6,39] arises from the discontinuity of the correlation potential $\delta E_c/\delta n(\underline{r})$.

At first it seems very peculiar that the Kohn-Sham exchange-correlation potential $\delta E_{xc}/\delta n(\underline{r})$ can jump by a constant C. Shouldn't $\delta E_{xc}/\delta n(\underline{r})$ tend to zero far outside an electronic system? Yes it should, but sometimes one must go far outside to reach this limit. Consider for example a large but finite insulating crystal. For the neutral system, with $N = J - \delta$ electrons ($\delta \to 0^+$), the exchange-correlation potential $\delta E_{xc}/\delta n(\underline{r})$

effectively goes to zero at some microscopic distance outside the surface. But, when an extra electron is added to the conduction band, $\delta E_{xc}/\delta n(\underline{r})$ does not go to zero until $\underline{r}$ is so far outside the surface that the density $n(J+1;\underline{r})$ is dominated by the density of the one extra electron, and not by that of the J original electrons. For a full discussion of this and related questions, see Ref. 39.

A discontinuity in $\delta F/\delta n(\underline{r})$ (where F is any functional) must not be confused with a discontinuity in $\partial F/\partial N$. The latter can arise without the former, as a consequence of the discontinuity in $\partial n(\underline{r})/\partial N$. Note however that the discontinuity in $\partial n(\underline{r})/\partial N$ is caused by that of $\delta E_v/\delta n(\underline{r})$.

Derivative discontinuities of the energy manifest themselves not only in open electronic systems but also in closed ones with fixed integer electron number. In the latter situation, certain "unconventional" number-conserving density variations [67] $\delta n(\underline{r})$ about the ground-state density lead to energy variations δE_v of order $|\delta n|$, and not of order $(\delta n)^2$ as might have been expected.

A formal expression for the gap correction C of Eq. (41) may be developed. The quantities $-I(J)$ and $-A(J)$ are eigenvalues of a one-electron Schrödinger equation like Eqs. (2) and (8), but with a nonlocal, energy-dependent self-energy [16,17] $\Sigma_{xc}(\underline{r},\underline{r}';\epsilon)$ in place of $\delta E_{xc}/\delta n(\underline{r})$. If the difference $\Sigma_{xc} - \delta E_{xc}/\delta n$ is regarded as a perturbation on the Kohn-Sham equation (2), the correction C to the gap in the Kohn-Sham eigenvalues may be found by perturbation theory. To first order in this difference [39],

$$
\begin{aligned}
C &= [I(J) - A(J)] - [\epsilon_{J+1}(J-\delta) - \epsilon_J(J-\delta)] \\
&= \langle \psi_{J+1} | \{\Sigma_{xc} - \delta E_{xc}/\delta n|_{J-\delta}\} | \psi_{J+1}\rangle - \langle \psi_J | \{\Sigma_{xc} - \delta E_{xc}/\delta n|_{J-\delta}\} | \psi_J\rangle .
\end{aligned}
\tag{49}
$$

The second expectation value vanishes, so

$$
C = \langle \psi_{J+1} | \{\Sigma_{xc} - \delta E_{xc}/\delta n|_{J-\delta}\} | \psi_{J+1}\rangle ,
\tag{50}
$$

where ψ_{J+1} is the lowest unoccupied Kohn-Sham orbital. Eq. (50) is not quite exact, because there are terms of higher order in $\Sigma_{xc} - \delta E_{xc}/\delta n$, which have been formally summed by Sham and Schlüter [8]. These higher-order terms could be very small. To leading order in e^2, they corresponded to the difference between the Hartree-Fock orbitals and the exact Kohn-Sham exchange-only orbitals, a difference which is almost negligible in atomic calculations [59]. (Unlike the derivation in Ref. 8, the present derivation of Eq. (50) applies even to finite systems.)

Return to Eq. (49). In a normal insulator, there is a finite difference between $\psi_J(\underline{r})$ and $\psi_{J+1}(\underline{r})$. In a Mott insulator [28,66] this difference is infinitesimal, and C arises entirely from a discontinuous change in Σ_{xc} across the Fermi level. As discussed previously, the latter discontinuity is a pure correlation effect.

The local density and Langreth-Mehl approximations display no discontinuity of $\delta E_{xc}/\delta n(\underline{r})$. Instead they average over it, yielding for an open-shell J-electron system reasonable estimates [7,39] of the averaged exchange-correlation potential

$$
\frac{1}{2}\{\delta E_{xc}/\delta n(\underline{r})|_{J+\delta} + \delta E_{xc}/\delta n(\underline{r})|_{J-\delta}\} = \delta E_{xc}/\delta n(\underline{r})|_{J-\delta} = C/2 ,
\tag{51}
$$

except in very low-density regions of space (where the exact $\delta E_{xc}/\delta n(\underline{r})|_{J-\delta}$ tends [7,68] asymptotically to zero).

It is conjectured here that, for static external potential $v(\underline{r})$, normally $C \geq 0$. In the Kohn-Sham system of noninteracting electrons, the total energy is certainly a semiconvex function of the electron number N (i.e., the ionization energy is never smaller than the electron affinity). It seems intuitively right that the total energy of interacting (repelling) electrons should be no less convex than that of noninteracting electrons of the same density. (Possible exceptions, with "negative electronic U," are certain transition-metal impurities in semiconductors [69].)

If this conjecture is true, then every crystal with a static external potential and a nonvanishing fundamental gap in its exact Kohn-Sham band structure is an insulator. The exact Kohn-Sham band structure then predicts an *upper bound* (or possibly an exact value) for the volume per unit cell at which metallization occurs under pressure. Band structure calculations within the local spin density approximation have been performed for highly-compressed monatomic hydrogen [70], xenon [71], neon [72], Ba S, Ba Se and Ba Te [73]. The calculated metallization volumes for Ba Se and Ba Te exceed the observed ones by 2 to 16%.

5. Spin-Density Functional Theory and the Expanded Lattice of Hydrogen Atoms

In spin-density functional theory [9,10], the density $n(\underline{r})$ is replaced as basic variable by the separate "up" and "down" spin densities $n_{\uparrow}(\underline{r})$, $n_{\downarrow}(\underline{r})$:

$$E_v[n_{\uparrow},n_{\downarrow}] = T_s[n_{\uparrow},n_{\downarrow}] + V[n] + U[n] + E_{xc}[n_{\uparrow},n_{\downarrow}] , \qquad (52)$$

where $V[n] = \int d^3 r\, v(\underline{r}) n(\underline{r})$. The Kohn-Sham equation (2) then involves a spin-dependent effective potential

$$v_{eff}^{\sigma}(\underline{r}) = v(\underline{r}) + u([n];\underline{r}) + \delta E_{xc}/\delta n_{\sigma}(\underline{r}) . \qquad (53)$$

The density-functional expressions of Sections 1 and 2 have straightforward spin-density analogs. In particular, there is a local spin density (LSD) approximation:

$$E_{xc}^{LSD}[n_{\uparrow},n_{\downarrow}] = \int d^3 r\, n(\underline{r})\, \epsilon_{xc}(n_{\uparrow}(\underline{r}),n_{\downarrow}(\underline{r})) \qquad (54)$$

$$\delta E_{xc}^{LSD}/\delta n_{\sigma}(\underline{r}) = \mu_{xc}^{\sigma}(n_{\downarrow}(\underline{r}),n_{\downarrow}(\underline{r})) , \qquad (55)$$

where $\epsilon_{xc}(n_{\uparrow},n_{\downarrow})$ is the exchange-correlation energy per particle of a uniform electron gas with up- and down-spin densities $n_{\uparrow}$, $n_{\downarrow}$, and $\mu_{xc}^{\sigma}(n_{\uparrow},n_{\downarrow}) = \partial(n\epsilon_{xc})/\partial n_{\sigma}$. An accurate parametrization of $\epsilon_{xc}(n_{\uparrow},n_{\downarrow})$ may be found in Ref. 11. In a spin-unpolarized system, LSD reduces to LDA.

While the Kohn-Sham band structures of the Mott insulators [28,66] all look "metallic" within density functional theory, they sometimes look "insulating" within spin-density functional theory. Thus the LSD band structures [74] of the antiferromagnetic Mott insulators MnO and NiO display small nonzero fundamental gaps, while

those of FeO and CoO do not. This situation probably persists within the exact Kohn-Sham spin-density functional theory, provided that the functionals are defined from constrained searches over pure states rather than ensembles [75].

The simplest example of a Mott insulator, a lattrice of hydrogen atoms in the limit of infinite lattice constant, provides an instructive case study of the ionization problem from a *total-energy* viewpoint. In the separated-atom limit, the properties of the crystal may be deduced from free-atom properties. When the atoms are hydrogen atoms, the many-body problem also reduces to the one-body problem. To keep the following discussion as simple as possible, replace the Coulomb interaction $1/r$ everywhere by $\exp(-r/\lambda)/r$, and let the range λ tend to infinity only after the lattice constant tends to infinity.

Let each hydrogen atom be centered in its own unit cell of a Bravais lattice $\{R_\upsilon\}$, with N unit cells ($N \to \infty$). Let each electron have spin "up" due to a weak external magnetic field. The Kohn-Sham orbitals can be chosen as site-localized Wannier functions $w_{\upsilon\sigma}(r) = w\sigma(|r - R_\upsilon|)$, or equivalently as delocalized Bloch functions $b_{k\sigma}(r) = \Sigma_\upsilon e^{ik \cdot R_\upsilon} w_{\upsilon\sigma}(r)/\sqrt{N}$. All occupied orbitals have the same exact Kohn-Sham orbital energy $\epsilon = -13.6$ eV. The orbital densities are related in the following way:

$$|w_{\upsilon\sigma}(r)|^2 = \begin{cases} N|b_{k\sigma}(r)|^2 \text{ for } r \text{ in the } \upsilon\text{-th cell} \\ 0 \text{ otherwise .} \end{cases} \tag{56}$$

The exact energy needed to remove an electron from either a Wannier or a Bloch orbital is

$$\Delta E^w = \Delta E^b = -\epsilon = \Delta T_s + \Delta V , \tag{57}$$

or 13.6 eV. When an electron is removed from the crystal, the hole so created remains on one site for a long (macroscopic) time before it tunnels to a neighboring site. However, the hole is still delocalized over the entire crystal on the infinite-time average.

Consider the detailed calculaton of ΔE^w and ΔE^b, according to Eq. (52):

$$\Delta E^w = E_\upsilon[n - |w_{\upsilon_\uparrow}|^2] - E_\upsilon[n] = \Delta T_s^w + \Delta V^w + \Delta U^w + \Delta E_{xc}^w , \tag{58}$$

$$\Delta E^b = E_\upsilon[n - |b_{k_\uparrow}|^2] - E_\upsilon[n] = \Delta T_s^b + \Delta V^b + \Delta U^b + \Delta E_{xc}^b . \tag{59}$$

It is not hard to see, from the definitions of $T_s[n]$ and $V[n]$, that $\Delta T_s^w = \Delta T_s^b$ and $\Delta V^w = \Delta V^b$. The quantity

$$\Delta U^w + \Delta E_{xc}^w = -\{U[|w_{\upsilon_\uparrow}|^2] + E_{xc}[|w_{\upsilon_\uparrow}|^2, 0]\} , \tag{60}$$

is zero because an electron does not interact with itself. The quantity

$$\Delta U^b + \Delta E_{xc}^b = -\int d^3r |w_{\upsilon_\uparrow}(r)|^2 \{u([n];r) + \delta E_{xc}/\delta n(r)|_{N-\delta}\} , \tag{61}$$

obtained via Eq. (56) from the Taylor expansion of Eq. (59), is zero for the same reason.

Now consider what is found in the LSD approximation. The right-hand side of Eq. (60) becomes a small nonzero number (-0.6 eV), while the right-hand side of Eq. (61) becomes a somewhat bigger number (-6.3 eV): The self-interaction error of the LSD total energy is magnified in the LSD potential. Thus in LSD the energy $\Delta E^{w,\text{LSD}}$ needed to create a localized hole is 13.0 eV, not far from the exact value of 13.6 eV. However, the energy needed to create a delocalized hole is

$$\Delta E^{b,\text{LSD}} = -\epsilon^{\text{LSD}}, \tag{62}$$

or 7.3 eV, far less than 13.6 eV. The LSD total energy of the crystal with one hole is minimized by delocalizing the hole, although the only realistic LSD estimate of the ionization energy is obtained by localizing the hole.

These results persist qualitatively in real crystals (or at least in large-gap insulators), and account for the LSD band-theory underestimation of the fundamental gap. In particular, it is easy to see from Eq. (10) that Eq. (62) still relates the LSD eigenvalue at the top of the valence band to the LSD total-energy cost to create a delocalized hole, and that both quantities contain a serious self-interaction error. In fact, Zunger and Freeman [76] found that the fundamental gap in Li F could be estimated accurately within LDA, not from the LDA bandstructure but from the LDA total energy in a self-consistent calculation with a localized hole. This kind of self-consistent solution may be a local extremum of the LDA total energy. The global minimum, however, delocalizes the hole over the volume of the crystal (or over its surface, if more than one hole is present).

Carlsson [40] has presented a very interesting total-energy analysis of the LDA band gap problem, and an approximate remedy based upon a modification of the long-range behavior of the LDA expression for $\rho_{xc}(\underline{r},\underline{r}')$ of Eq. (17). Harrison [77] has discussed a screened intraatomic Coulomb repulsion as a correction to the LDA band gap.

Finally, it is instructive to compare the local density and Hartree-Fock approximations. In each, a realistic estimate of the ionization energy of an insulating crystal may be found from the total-energy cost to create a localized hole self-consistently, including the dielectric polarization of the medium around the hole (i.e., to create an "electronic polaron" [78]). Again in each, the orbital energy at the top of the valence band, relative to the vacuum level, gives the corresponding total-energy cost to create a delocalized hole. In LDA, the energy of the crystal with one delocalized hole does not lie high enough above the energy of the neutral crystal, leading to band-structure underestimation of the fundamental gap. In the Hartree-Fock approximation, the energy of the crystal with one delocalized hole lies too high above the energy of the neutral crystal, leading in part to band-structure overestimation of the fundamental gap. (For example, the Hartree-Fock band gap of silicon [79] is 9.4 eV—eight times bigger than the true gap.) As Kunz et al [80] have pointed out, the equivalence of Slater determinants constructed in the Wannier and Bloch pictures holds only for a filled band; in the presence of a hole, the Slater determinant in the Wannier picture can have the lower Hartree-Fock energy.

6. Self-Interaction Correction to the Local Spin Density Approximation

The LSD self-interaction error discussed in Section 5 may be excised by the method of self-interaction correction (SIC) of Perdew and Zunger [11]:

$$E_{xc}^{SIC} = E_{xc}^{LSD} [n_\uparrow, n_\downarrow] - \sum_i \{U[n_i] + E_{xc}^{LSD} [n_i, 0]\} , \qquad (63)$$

where $n_i(\underline{r}) = f_i |\psi_i(\underline{r})|^2$ is the i-th orbital density. Minimization of the SIC energy

$$\tilde{E}^{SIC} = \sum_i f_i \langle \psi_i | - \tfrac{1}{2} \nabla^2 |\psi_i\rangle + V[n] + U[n] + E_{xc}^{SIC} , \qquad (64)$$

with respect to the orbitals $\psi_i(\underline{r})$, subject to the constraint of orbital normalization, implies the Euler equation

$$\frac{\delta}{\delta \psi_i^*(\underline{r})} \{\tilde{E}^{SIC} - \sum_j \epsilon_j^{SIC} f_j \int d^3r |\psi_j(\underline{r})|^2\} = 0 . \qquad (65)$$

This is a single-particle problem like Eqs. (2) and (8), but with $\delta E_{xc}/\delta n(\underline{r})$ replaced by its LSD approximation $\mu_{xc}^{\sigma,LSD}(n_\uparrow(\underline{r}), n_\downarrow(\underline{r}))$ plus an orbital-dependent correction

$$\Delta v_{xc}^{i,SIC}(\underline{r}) = - u([n_i]; \underline{r}) - \mu_{xc}^\downarrow(n_i(\underline{r}), 0) . \qquad (66)$$

Like LSD, SIC is exact for the uniform electron gas—an old conjecture [11] which Norman [81] has recently proved.

In self-consistent calculations for atoms [11], SIC yields improvements over LSD in the total energy, the separate exchange and correlation energies, the binding energies of negative ions (which find no self-consistent solution within LSD), and the long-range behavior of the density and effective potential.

The SIC exchange-correlation hole obeys the sum rule [11]

$$\int d^3r \, \rho_{xc}^{SIC}(\underline{r}, \underline{r}') = - \sum_i f_i n_i(\underline{r})/n(\underline{r}) . \qquad (67)$$

The right-hand side of Eq. (67) equals -1 in a finite system with fixed integer electron number (all f_i's 0 or 1), or in the ground-state of an infinite system with fluctuating electron number. In a finite system with fluctuating (i.e., fractional) electron number, the right-hand side of Eq. (67) is between 0 and -1, as is the sum rule for the exact exchange-correlation hole [38,39]. Thus SIC gives a significantly better account of fractional electron number than LSD does. For a detailed review of SIC, see Ref. 82.

The SIC orbital energies ϵ_i^{SIC} equal $\partial \tilde{E}^{SIC}/\partial f_i$, so SIC theory obeys the "aufbau principle." Moreover, in an atom $\tilde{E}^{SIC}$ is often approximately linear in f_i, so that $-\epsilon_i^{SIC}$ is a good approximation to $\Delta \tilde{E}_i^{SIC}|_{rel}$, the relaxed SIC removal energy from orbital i:

$$-\epsilon_i^{SIC} \approx \Delta \tilde{E}_i^{SIC}|_{rel} . \qquad (68)$$

Thus SIC provides an analog of Koopmans' theorem which includes intraatomic relaxation.

Unlike the effective potential $v_{eff}(\underline{r})$ in Kohn-Sham theory, the SIC effective potential $v_{eff}^i(\underline{r})$ is *orbital-dependent*. Because it is both orbital-dependent and self-interaction-free, the SIC potential can to some extent mimic the nonlocal, energy-dependent self-energy [16,17] $\Sigma(\underline{r}, \underline{r}'; \epsilon)$. Thus in SIC calculations for atoms, Eq. (68) is close to an

TABLE IV. Energy eigenvalues for the $1s\uparrow$ and $1s\downarrow$ orbitals, and gap in the orbitals energies, for the hydrogen atom (eV).

Approximation	$\epsilon_1(1-\delta)$ ($1s\uparrow$)	$\epsilon_2(1+\delta)$ ($1s\downarrow$)	$\epsilon_2(1+\delta)-\epsilon_1(1-\delta)$ (gap)
LDA	-6.4	-6.4	0.0
LSD	-7.3	-2.3	5.1
SIC	-13.6	-2.0	11.6
exact Kohn-Sham	-13.6	-0.8	12.8

equality for all the occupied orbitals [11]. Within exact Kohn-Sham theory, by contrast, $-\epsilon_i = \Delta\tilde{E}_i|_{\text{rel}}$ is an exact equality [6,33] for the highest-occupied orbital i, but the orbital energy is not very close to the removal energy for the deeper orbitals [83,84].

Can the SIC orbital energies predict the fundamental gap? Table IV, for the hydrogen atom, suggests that they might. While the gap in the orbital energies is zero in LDA, and too small in LSD, it is about right in SIC. Table V, for the neon atom, tells a similar tale: The LSD and Langreth-Mehl orbital energies underestimate the gap, while the SIC orbital energies predict the gap with good accuracy.

The ability of the SIC orbital energies to predict the gap is mostly a consequence of the orbital-dependence of Eq. (66). Norman and Koelling [13] have constructed an optimized effective potential (OEP) for SIC. That orbital-independent potential whose orbitals ψ_i minimize the SIC energy is obtained from the solution of

$$\sum_i f_i \int d^3r' \, \psi_i^*(\underline{r}') \Delta v_{xc}^{\text{OEP}}(\underline{r}') G_i(\underline{r}',\underline{r}) \psi_i(\underline{r})$$

$$= \sum_i f_i \int d^3r' \, \psi_i^*(\underline{r}') \Delta v_{xc}^{i,\text{SIC}}(\underline{r}') G_i(\underline{r}',\underline{r}) \psi_i(\underline{r}) , \tag{69}$$

where

$$G_i(\underline{r}',\underline{r}) = \sum_{j\neq i} \psi_j(\underline{r}') \psi_j^*(\underline{r})/(\epsilon_j - \epsilon_i) . \tag{70}$$

The OEP-SIC effective potential may be the best approximation we have to the exact

TABLE V. Fundamental gap for the neon atom, from the orbital energy eigenvalues in various approximation and from experiment (with $A = 0$). LSD: local spin density approximation. LM: Langreth-Mehl approximation. SIC: self-interaction correction. OEP-SIC: Norman and Koelling's optimized effective potential version of SIC (eV).

LSD[a]	LM[b]	OEP-SIC[a]	SIC[a]	Exper.[a]
13.5	15.7	17.5	22.9	21.6

[a] Ref. 13.
[b] Ref. 60.

TABLE VI.   Fundamental gaps of insulators, from the band structure within the local spin density (LSD) and self-interaction corrected (SIC) approximations, and from experiment. The SIC numbers are based on *atomic* estimates of the self-interaction correction (eV).

Crystal	LSD	SIC	Exper.
Ne[a]	11.2	21.1	21.4
Ar[a]	8.3	14.1	14.2
Kr[a]	6.8	11.7	11.6

[a] Ref. 11.

Kohn-Sham potential in the neon atom (Fig. 1). Table V shows that the OEP-SIC orbital energies seriously underestimate the fundamental gap.

In atomiclike insulators, such as the rare-gas solids, the self-interaction correction to the fundamental gap for an atom may be added to the LSD band gap of the solid, yielding an estimate of the true solid state gap [11] (Table VI). (Improved gaps from a different brand of self-interaction correction were found by Kunz et al. [80].)

For these atomiclike insulators, SIC has an immediate intuitive appeal. It asserts that an electron in the valence band of argon, like a valence electron in the neutral Ar atom, sees an Ar^+-like potential in each unit cell, while an "excess" electron in the conduction band sees an Ar°-like potential in each cell, as demanded by Mott [28]. LSD, on the other hand, forces an Ar°-like potential for both bands [11].

However, it is not so clear how SIC should be applied in more general classes of solids. In fact a straightforward application of Eqs. (63) and (66) to the Bloch orbitals yields no correction to LSD in the infinite-volume limit.

Perdew and Norman [83] addressed this problem by constructing an energy-dependent effective potential which simulates the self-interaction correction in atoms:

$$\Delta v_{xc}^{SSIC}(\underline{r},\epsilon) = -0.104\,\hat{u}\cdot\frac{\nabla\rho(\underline{r},\epsilon)}{\rho(\underline{r},\epsilon)}\,,\tag{71}$$

where $\hat{u} = \nabla n/|\nabla n|$ is a unit vector, and

$$\rho(\underline{r},\epsilon) = \sum_i f_i|\psi_i(\underline{r})|^2\delta(\epsilon-\epsilon_i)\,,\tag{72}$$

is the local density of occupied one-electron states. The SSIC potential for a given band in a solid is actually constructed from Eq. (71), with $\rho(\underline{r},\epsilon)$ replaced by its integral over energies in the band. With Bloch functions $\psi_i(\underline{r})$, this scheme involves a band-dependent periodic correction to the LSD periodic potential. Fundamental gaps from self-consistent SSIC band structures [63,72] of Ne and Na Cl are shown in Table VII.

The simulated self-interaction correction (SSIC) has also been applied [85] to the semiconductor Si, where it increases the fundamental gap from its LDA value of 0.6 eV to 2.0 eV—an overshoot of the true gap (1.2 eV). It's hard to say whether this is a failure of SIC itself, or merely of its simulation in SSIC. At any rate, there is evidently a need for a better-founded implementation of SIC in solids.

TABLE VII. Fundamental gaps of insulators, from the band structure within the local spin density (LSD) and self-interaction corrected (SIC) approximations, and from experiment. The self-consistent SIC band structure calculations follow the methods of Ref. 63 and Ref. 12 (eV).

Crystal	LSD	SIC	Exper.
Ne[a]	11.5	20.2	21.4
NaCl[a]	5.6	9.2	9.0
Ar[b]	7.9	13.5	14.2
LiCl[b]	6.0	10.6	9.9

[a] Ref. 63.
[b] Ref. 12.

This need is met, at least for large-gap insulators, by the SIC band-structure scheme of Heaton, Harrison and Lin [12]. They first introduce off-diagonal Lagrangian multipliers to insure orthogonality of the SIC orbitals, and then interpret the solutions of the resulting single-particle equations,

$$\{-\tfrac{1}{2}\nabla^2 + v(\underset{\sim}{r}) + u([n];\underset{\sim}{r}) + \mu_{xc}^{\sigma_i}(n_\uparrow(\underset{\sim}{r}),n_\downarrow(\underset{\sim}{r})) + \Delta v_{xc}^{i,SIC}(\underset{\sim}{r})\} w_i(\underset{\sim}{r}) = \sum_j \epsilon_{ji}^{SIC} w_j(\underset{\sim}{r}),$$
(73)

as site-localized Wannier orbitals $w_{n\upsilon}(\underset{\sim}{r}) = w_n(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon)$. It is these Wannier orbitals which are employed to evaluate the SIC exchange-correlation energy (63). The corresponding delocalized Bloch orbitals,

$$b_{n\underset{\sim}{k}}(\underset{\sim}{r}) = N^{-1/2} \sum_\upsilon e^{i k \cdot R_\upsilon} w_n(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon),$$
(74)

obey a single-particle equation like (73), but with the band- and wavevector-dependent periodic correction to the LSD periodic potential

$$\Delta v_{xc}^{n\underset{\sim}{k},SIC}(\underset{\sim}{r}) = \sum_\upsilon \theta_{n\underset{\sim}{k}}(\underset{\sim}{r} = \underset{\sim}{R}_\upsilon) \Delta v_{xc}^{n,SIC}(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon),$$
(75)

where

$$\theta_{n\underset{\sim}{k}}(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon) = N^{-1/2} e^{i k \cdot R_\upsilon} w_n(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon)/b_{n\underset{\sim}{k}}(\underset{\sim}{r})$$
(76)

is a weighting factor which sums over sites υ to unity.

Heaton, Harrison and Lin [12] have used these equations to generate self-consistent SIC band structures $\epsilon_{n\underset{\sim}{k},n\underset{\sim}{k}}^{SIC}$ for Ar and Li Cl. The resulting fundamental gaps, displayed in Table VII, show about the same degree of improvement over LSD as do those of SSIC [63]. However, Lin's method is preferable to SSIC because it is variationally based and its SIC bands reduce exactly to the original SIC orbital energies in the separated atom limit.

An essential step in the evaluation of Eq. (75) is the construction of the wannier orbitals from the Bloch orbitals:

$$w_n(\underset{\sim}{r} - \underset{\sim}{R}_\upsilon) = N^{-1/2} \sum_{\underset{\sim}{k}} e^{-i k \cdot R_\upsilon} b_{n\underset{\sim}{k}}(\underset{\sim}{r}).$$
(77)

The summation over the Brillouin zone is tedious, and can be replaced by a simpler sum [12] in atomiclike insulators. In semiconductors, where this replacement is not justified, no SIC calculation has yet been performed. However, the SIC method has been generalized and applied successfully to molecules [86].

In fact, application of SIC to semiconductor band structure would be fully justified only after certain fundamental questions were answered: (1) Should there be some correction to the bottom of the LSD conduction band, [12,40] in addition to that for the top of the LSD valence band? (2) While the Wannier orbital densities can be used in the SIC exchange-correlation energy of Eq. (63) when all bands are either full or empty, what orbital densities should be used for partly-filled bands? This question is important not only for metals, but also for insulators with extra electrons or holes. (3) Does the SIC total energy of Eq. (64) properly account for the extra-atomic relaxation effects that occur when an electron is added to or removed from a semiconductor? (4) Away from the separated-atom limit, how do the orbital energies $\epsilon_{n\mathbf{k},n\mathbf{k}}^{SIC}$ from Eq. (75) relate to SIC total-energy differences?

7.   Dielectric Screening

So far in this paper, the criterion for metallic behavior has been a vanishing fundamental gap. An alternative criterion for metallicity is perfect screening: When an infinitesimal external charge δN_+ (of either sign) is introduced into a metal, which is in equilibrium at zero temperature with an electron reservoir, the metal draws δN_+ electrons from the reservoir to neutralize the external charge. By energy arguments, these two criteria are equivalent.

The response of the electron density to an infinitesimal external perturbation $\delta v(\mathbf{r})$ is

$$\delta n(\mathbf{r}) = \int d^3r' \, \chi(\mathbf{r},\mathbf{r}')\delta v(\mathbf{r}') \, . \tag{78}$$

The inverse of the density response function is [87] the second functional derivative of the Hohenberg-Kohn energy of Eq. (3):

$$\chi^{-1}(\mathbf{r},\mathbf{r}') = -\, \delta^2 E_v/\delta n(\mathbf{r})\delta n(\mathbf{r}') \, . \tag{79}$$

By Eq. (6),

$$\chi^{-1}(\mathbf{r},\mathbf{r}') = \chi_s^{-1}(\mathbf{r},\mathbf{r}') - 1/|\mathbf{r}-\mathbf{r}'| - K_{xc}(\mathbf{r},\mathbf{r}') \, , \tag{80}$$

where χ_s is the density response function of the Kohn-Sham noninteracting system and

$$K_{xc}(\mathbf{r},\mathbf{r}') = \delta^2 E_{xc}/\delta n(\mathbf{r})\delta n(\mathbf{r}') \, . \tag{81}$$

The change in the exchange-correlation potential $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta n(\mathbf{r})$ due to a change in density is evidently

$$\delta v_{xc}(\mathbf{r}) = \int d^3r' \, K_{xc}(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}') \, . \tag{82}$$

Eq. (78) can also be cast in the more familiar form [36]

$$\chi(\underline{r},\underline{r}') = \chi_s(\underline{r},\underline{r}')$$

$$+ \int d^3r'' \int d^3r''' \chi_s(\underline{r},\underline{r}'') \left[|\underline{r}'' - \underline{r}'''|^{-1} + K_{xx}(\underline{r}'',\underline{r}''')\right] \chi(\underline{r}''',\underline{t}) . \tag{83}$$

An insulator is distinguished from a metal by the condition $\int d^3r \delta n(\underline{r}) = 0$, or

$$\int d^3r \, \chi(\underline{r},\underline{r}') = 0 . \tag{84}$$

Eq. (84) should follow mathematically from Eq. (79) and from the nonzero derivative discontinuity, Eq. (46), for an insulator. From Eq. (82), it follows that for an insulator

$$\lim_{Q \to 0} \chi(Q) = 0 , \tag{85}$$

where

$$\chi(Q) = \Omega^{-1} \int d^3r \int d^3r' \, \chi(\underline{r},\underline{r}') e^{iQ \cdot (\underline{r} - \underline{r}')} , \tag{86}$$

and Ω is the volume of the crystal.

For the uniform electron gas, Eq. (83) Fourier transforms into [2]

$$\chi(Q) = \chi_s(Q) + \chi_s(Q) \{4\pi/Q^2 + K_{xc}(Q)\} \chi(Q) , \tag{87}$$

where $\chi_s(Q)$ is the Lindhard function, and Eq. (82) becomes

$$\delta v_{xc}(Q) = K_{xc}(Q) \, \delta n(Q) . \tag{88}$$

Expansion of $K_{xc}(Q)$ in powers of Q,

$$K_{xc}(Q) = K_{xc}(0) + \tfrac{1}{2} K_{xc}''(0) Q^2 + \dots , \tag{89}$$

amounts to a density-gradient expansion of the exchange-correlation potential. The leading term in (89), $K_{xc}(0)$, is the LDA term.

Recently Antoniewicz and Kleinman [14] have calculated $K_x(Q)$ exactly within the exchange-only version of density-functional theory. They find that $K_x(Q)/K_x(0)$ increases smoothly from 1 to ~ 2 in the range $0 \leqslant Q \leqslant 2k_F$. Thus, in a uniform electron gas perturbed by a weak external potential $\delta v(Q)$, the exact Kohn-Sham exchange potential $\delta v_x(Q)$ can be 50–100% stronger than it is in LDA.

Antoniewicz and Kleinman [14] then propose a model for a semiconductor: a uniform electron gas perturbed by a weak periodic external pseudopotential. The important reciprocal lattice vectors for the diamond and zincblende semiconductors fall in the range $0 < Q \leqslant 2k_F$. The exact exchange potential is enhanced by about 50% over the LDA exchange potential in this range. This enhancement, corresponding roughly to
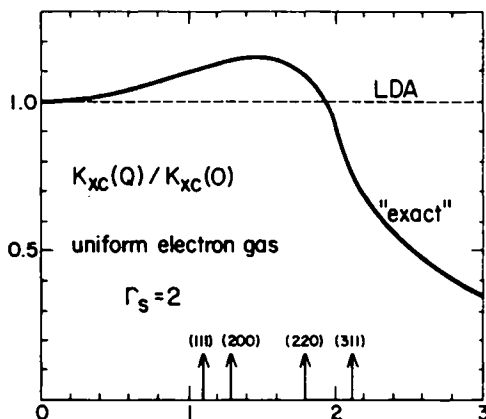
Figure 2.   Exchange-correlation response function $K_{xc}(Q)$ of Eq. (88) for the uniform electron gas with $r_s = 2$, according to the estimate of Ref. 89. The Q-independent behavior of the local density approximation (LDA) is indicated by the dashed line. Vertical arrows indicate the (111), (200), (220) and (311) reciprocal lattice vectors of the zincblende structure, according to Ref. 14.

$\alpha = 1$ in place of $\alpha = 2/3$ in an $X\alpha$ band-structure calculation, is large enough to bring the calculated band gaps into agreement with experiment. Antoniewicz and Kleinman therefore suggest that the exact Kohn-Sham potential can yield the observed fundamental gap in a semiconductor, despite the LDA underestimate of the gap.

The exact $K_{xc}(Q)$ for the uniform electron gas, including correlation as well as exchange, is not known. However, Taylor [88] has observed that the Geldart-Taylor estimate of $K_{xc}(Q)/K_{xc}(0)$ does not deviate much from unity over the range $0 < Q \lesssim 2k_F$. This behavior is also found in more recent estimates of $K_{xc}(Q)$. For example, Utsumi and Ichimaru [89] have estimated the "local field correction" $G(Q)$ in the uniform electron gas with a high degree of internal consistency, and presented an analytic parametrization of it from which

$$K_{xc}(Q) = (-4\pi/Q^2)G(Q) , \tag{90}$$

has been constructed in Figure 2. Thus, when correlation is included, the Antoniewicz-Kleinman model of a semiconductor actually suggests that the exact Kohn-Sham potential underestimates the true gap by about as much as the LDA does.

8.   Conclusions

(1) The fundamental gap in the exact Kohn-Sham bandstructure of an insulator is not equal to the true gap I-A. (2) The difference arises because the exchange-correlation potential $\delta E_{xc}/\delta n(\underline{r})$ changes discontinuously, by a finite constant, as the conduction band begins to fill. (3) Several very different (but admittedly approximate) numerical calculations suggest that most of the error in the gap of the local density approximation would persist in the gap of the exact Kohn-Sham bandstructure.

Acknowledgments

Note. Some of the questions raised at the end of Section 6 have been addressed recently by M. R. Pederson, R. A. Heaton and C. C. Lin (unpublished), and by R. A. Heaton and C. C. Lin, Bull. Am. Phys. Soc. **30**, 225, (1985).

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