

Investigation of density functionals to predict both ground-state properties and band structures

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By incorporating part of the correlation energy into a modified kinetic energy functional within a Kohn-Sham-like theory, it is possible to obtain significantly altered band structures, while preserving good agreement with experiment for ground state properties well described by the usual local density approximation (LDA). A particular such functional obtained by introducing a local density-dependent mass is investigated. By construction, it reproduces the valence-band narrowing of free-electron-like metals. Applied to semiconductors, a significant gap increase with respect to the LDA gap is observed in silicon and germanium; for diamond carbon, the correction is negligible. The proposed strategy is quite general and could facilitate the construction of density functionals which simultaneously predict ground state properties and band structures for a given class of materials. [S0163-1829(96)00236-6]

I. INTRODUCTION

Since its introduction, the Kohn-Sham version¹ of density functional theory (DFT) has been applied with enormous success to a vast variety of systems in condensed matter physics. For many materials, the theory predicts ground state properties such as lattice constants, bulk moduli, and phonon frequencies to within a few percent of their experimental values.²

The applications of DFT have long since moved beyond its original conception as a tool for the investigation of electronic ground states. In particular, DFT type calculations now routinely serve as the basis for theoretical investigations of excited states in solids, not only because it is relatively straightforward to calculate band structures using this formalism, but also because the DFT eigenvalues and orbital wave functions turn out to be surprisingly accurate,³ although DFT is not designed to describe these excited states.

There are, however, a number of discrepancies between DFT band structures and experiment. Perhaps best known is the fact that in most semiconductors and insulators, DFT calculations employing the local density approximation (LDA),⁴ and probably even the exact exchange-correlation functional,⁵⁻⁷ systematically underestimate the band gap. Another more subtle effect is related to the valence-band narrowing observed for free-electron-like metals,⁸ which none of the standard density functional theories can even hope to reproduce (see Sec. III).

These and related phenomena can be described within more refined many-body theories. For example, the so-called *GW* approximation⁹ has been shown over the past decade to resolve many of the discrepancies between the LDA band structures and experiment, in many cases predicting excitation energies to within 0.1 eV of their experimental value.¹⁰⁻¹² Similarly, quantum Monte Carlo calculations can be used to obtain reliable estimates of band gaps in insulators.¹³⁻¹⁵ Nonetheless, both of these techniques are

rather demanding on computational resources, and for many purposes, a simpler strategy would be desirable. Moreover, it would be of great interest to be able to monitor electronic excitation energies as a function of fully relaxed structural parameters, for example, during the course of a molecular dynamics simulation based on total energies. This requires a cheap and reasonably accurate simultaneous evaluation of excitation energies and total energies. Although it is possible, in principle, to calculate total energies within the *GW* scheme,¹⁶ it is by no means clear that the resulting energies would be accurate. Previous approximations to the *GW* self-energy operator, such as the quasiparticle local density approximation (QPLDA),¹⁷⁻²⁰ therefore sacrifice the calculation of reliable energy estimates for an improvement in the description of excited states.

In the present work, as a step towards a theory for *simultaneous* band structure and total energy calculations, we point out an inherent freedom in the choice of density functionals: the freedom of assigning part of the exchange-correlation energy to a modified kinetic energy or similar nonlocal functional. This freedom can be employed to devise theories whose accuracy for the prediction of ground state properties rivals that of the LDA, while at the same time they yield improved eigenvalue spectra. As an example, we propose a theory which, for the homogeneous electron gas, quantitatively reproduces the valence-band narrowing⁸ predicted by *GW* calculations, without affecting the long-wavelength density response (which is accurately described within the usual LDA). This is achieved by introducing a density-dependent effective mass into the kinetic energy functional. As an aside, we mention that in a different context, the introduction of a coordinate-dependent effective mass was recently also explored by Bulgac, Lewenkopf, and Mickrjukov²¹ as an approximation to the exchange energy within Hartree-Fock theories (see also Sec. V). Their work was motivated by similar approximations in nuclear physics.²²

The application of this density functional to the alkali metals Li and Na shows the expected narrowing of the valence-band width, without negatively affecting the calculated bulk moduli and lattice parameters. For semiconductors and insulators, the new functional also yields significantly increased band gaps compared to the LDA (see Sec. VI), although there remains discrepancy with experiment. It is hoped that the general strategy outlined here may in the future lead to other density functionals which simultaneously allow quantitative predictions of ground state properties and excitation spectra, at least for a given class of materials.

The paper is organized as follows. In Sec. II, after a brief outline of the standard Kohn-Sham partitioning of the density functional, a more general partitioning scheme is proposed. In Secs. III, IV, and V, we discuss as a specific example the implications of introducing a density-dependent mass into the kinetic energy functional, with particular emphasis on the valence-band narrowing and the density response in the homogeneous electron gas. In Sec. VI, we present results of plane-wave pseudopotential calculations for structural properties and band structures of silicon, germanium, and carbon in the diamond structure, as well as for metallic bcc lithium and sodium, using this density functional. We end with a summary and conclusions.

II. A MODIFIED KOHN-SHAM THEORY

DFT is based on a theorem by Hohenberg and Kohn²³ which states that the ground state energy $E[\rho]$ of an assembly of electrons with density ρ can be written as the sum of a universal functional $F[\rho]$ of the density of the system and the electrostatic energy of the electrons in the external potential V_{ext} :

$$E[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}). \quad (1)$$

In the usual Kohn-Sham version¹ of DFT, the density ρ is expressed in terms of a fictitious set of occupied one-particle orbitals ψ_i as

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2. \quad (2)$$

The unknown functional $F[\rho]$ is then partitioned as

$$F[\rho] \equiv T_s[\rho] + E_H[\rho] + E_{\text{xc}}[\rho], \quad (3)$$

where the kinetic energy in atomic units²⁴ is expressed in terms of the one-particle wave functions,

$$T_s[\rho] \equiv \frac{1}{2} \sum_i^{\text{occ}} \int |\nabla \psi_i(\mathbf{r})|^2, \quad (4)$$

and the Hartree energy is given as

$$E_H[\rho] \equiv \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (5)$$

Within the LDA, the unknown exchange-correlation functional $E_{\text{xc}}[\rho]$ is approximated in terms of the exchange-correlation energy per particle $\epsilon_{\text{xc}}(\rho)$ of a homogeneous electron gas of density ρ ,

$$E_{\text{xc}}[\rho] \approx \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})). \quad (6)$$

Other, more sophisticated approximations to E_{xc} have been proposed,² such as generalized gradient approximations,²⁵ but they usually retain an explicit density dependence and leave the basic partitioning in Eq. (3) unchanged.

Approximations to $E_{\text{xc}}[\rho]$ with such an explicit density dependence are unable to reproduce the nonanalyticities which this functional is known to have. For example, E_{xc} contains nonanalytic contributions due to the difference $T[\rho] - T_s[\rho]$ between the kinetic energy of the interacting and noninteracting systems, and the exchange-correlation potential $V_{\text{xc}} \equiv \delta E_{\text{xc}} / \delta \rho$ in semiconductors can exhibit a discontinuity upon addition of a single electron.⁵⁻⁷

To remedy this situation, it seems natural and perfectly legitimate to express some part of the exchange-correlation energy in the form of a nonlocal functional, whose density dependence is not explicit, but implicit through its dependence on the wave functions ψ_i , in the hope that this will incorporate some of the nonanalyticities. In fact, the usual kinetic energy functional $T_s[\rho]$ in Eq. (4) has just this form, and its nonanalytic dependence on the density is the reason why within the LDA, there can be a band gap at all. Hence, we write more generally

$$F[\rho] \equiv T_s[\rho] + E_H[\rho] + E_{\text{xc}}[\rho] + E_{\text{nl}}[\rho] + E_l[\rho], \quad (7)$$

where

$$E_{\text{nl}}[\rho] \equiv \sum_i^{\text{occ}} \int \int d\mathbf{r} d\mathbf{r}' \psi_i^*(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}'; [\rho]) \psi_i(\mathbf{r}'). \quad (8)$$

Σ is some symmetric nonlocal operator which may depend upon the density, to be discussed in more detail later.

If $E_{\text{xc}}[\rho]$ were the exact exchange-correlation potential, Eqs. (3) and (7) would obviously imply $E_{\text{nl}}[\rho] + E_l[\rho] \equiv 0$. However, if E_{xc} is approximated, for example by the LDA, Eq. (3) yields the correct energy only for homogeneous densities ρ^h , and we, therefore, choose the local functional $E_l[\rho]$ such as to ensure that $E_{\text{nl}}[\rho^h] + E_l[\rho^h] \equiv 0$ for such densities. In the spirit of the LDA, a natural choice is to write

$$E_l[\rho] \equiv - \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_l(\rho(\mathbf{r})), \quad (9)$$

where $\epsilon_l(\rho)$ is just the energy per particle associated with the operator Σ in the homogeneous electron gas:

$$\epsilon_l[\rho^h] = \frac{2}{\rho^h} \frac{1}{8\pi^3} \int_{|\mathbf{k}| < k_F} d\mathbf{k} \Sigma(\mathbf{k}; [\rho^h]). \quad (10)$$

The factor 2 accounts for spin degeneracy, and the integral is over all wave vectors \mathbf{k} smaller than the Fermi wave vector $k_F = (3\pi^2 \rho^h)^{1/3}$.

In principle, the density dependence of Σ can itself be implicit through a dependence on the orbitals ψ_i . For example, if Σ is chosen as the Fock exchange operator, we obtain a hybrid Hartree-Fock energy functional in which the exchange is described by the nonlocal Fock operator and the correlation energy is added in a local density fashion. An example of an operator Σ with explicit density dependence will be given in the next section. In general, the density

dependence of the operator Σ renders the variation of the energy functional in Eq. (7) with respect to the orbitals ψ_i somewhat more complicated than in the usual Kohn-Sham scheme. This is certainly the case for the Hartree-Fock formalism. In many cases, though, especially when the density dependence of Σ is explicit, the additional computational demand will not be significant. Finally, we remark that the strategy outlined above is easily generalized to spin-density-dependent functionals replacing the usual local spin density approximation (LSDA).

III. A LOCAL MASS APPROXIMATION

As a specific application of the scheme proposed in Sec. II, we now consider a density functional which reproduces the valence-band narrowing in simple metals. We introduce this functional in a rather empirical, *ad hoc* manner, although its general form can be justified in a more rigorous way (see Sec. V).

It has been suggested from *GW* calculations on the homogeneous electron gas⁸ that the experimentally observed²⁶ reduction in the width of the valence band in some free-electron-like metals with respect to its free-electron value is at least partly caused by many-body correlation effects. Of course, the presence of the lattice must also be taken into account to obtain quantitative agreement with experiments.

In the standard Kohn-Sham partitioning of the density functional, whatever the precise form of the exchange-correlation functional $E_{xc}[\rho]$, its variation with respect to the density always results in a constant exchange-correlation potential V_{xc} for a homogeneous density. As a consequence, the spectrum is always that of a free-electron gas, and the valence band width is given by the Fermi-energy $\epsilon_F = \frac{1}{2}k_F^2$. The change in the valence-band width cannot be reproduced within such a scheme. Hartree-Fock theory, on the other hand, predicts a widening of the valence band by a factor of 1.5–2 for typical metallic densities, contrary to experiment.

However, it is possible to introduce a nonlocal operator Σ as in Eq. (8) which does reproduce the correct valence-band narrowing. Mahan and Sernelius⁸ have determined the change in the width of the valence band in the homogeneous electron gas for a range of electron densities. Using their data calculated within a *GW* approximation neglecting vertex corrections in the calculation of the dielectric function and self-energy operator (labeled RPA in their paper), we find (Fig. 1) an almost perfect linear dependence²⁷ of the relative change in the width of the valence band $\Delta\epsilon/\epsilon_F$ on the density parameter $r_s \equiv (4\pi\rho/3)^{-1/3}$:

$$\frac{\Delta\epsilon}{\epsilon_F} = \alpha + \beta r_s \equiv f(\rho), \quad (11)$$

where $\alpha = 0.079\,431$ and $\beta = -0.047\,964$. Of course, this expression cannot be valid for very low densities (large r_s), where it becomes less than -1 , and to avoid divergencies in atoms and on surfaces, f may need to be modified at such low densities.

Using this information, we construct the desired density functional with the nonlocal operator

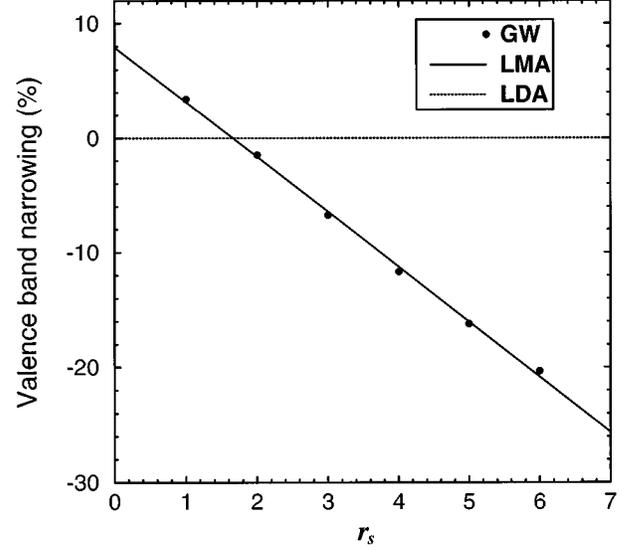


FIG. 1. Relative valence-band narrowing $\Delta\epsilon/\epsilon_F$ using the *GW* results without vertex corrections by Mahan and Sernelius (Ref. 8) and the fit according to Eq. (11) (solid line).

$$\hat{\Sigma}[\rho] \equiv -\frac{1}{2}\nabla f(\rho(\mathbf{r}))\nabla. \quad (12)$$

The new density functional, which we call local mass approximation (LMA), is then given by

$$F^{\text{LMA}}[\rho] = \frac{1}{2}\sum_i^{\text{occ}} \int [1 + f(\rho(\mathbf{r}))] |\nabla\psi_i(\mathbf{r})|^2 d\mathbf{r} + E_H[\rho] + E_{xc}[\rho] - \int d\mathbf{r} f(\rho(\mathbf{r}))\rho(\mathbf{r})t_s(\rho(\mathbf{r})), \quad (13)$$

where the last term corresponds to $E_l[\rho]$ in Eqs. (7) and (9) and involves, for our particular choice of $\hat{\Sigma}$, the average kinetic energy per electron of a homogeneous gas of density ρ , $t_s = 3k_F^2/10$.

The variation of this energy functional with respect to the wave functions ψ_i yields a modified Schrödinger equation

$$\hat{H}_{\text{eff}}[\rho]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad (14)$$

with

$$\hat{H}_{\text{eff}}[\rho] \equiv -\frac{1}{2}\nabla[1 + f(\rho(\mathbf{r}))]\nabla + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + f'(\rho(\mathbf{r}))V_{\text{lma}}(\mathbf{r}) + V_l(\mathbf{r}), \quad (15)$$

where $f' \equiv df/d\rho$, V_H and V_{xc} are the usual Hartree and exchange-correlation potentials, $V_l \equiv \delta E_l/\delta\rho$, and

$$V_{\text{lma}}(\mathbf{r}) \equiv \frac{1}{2}\sum_i^{\text{occ}} |\nabla\psi_i(\mathbf{r})|^2. \quad (16)$$

Like in the usual Kohn-Sham scheme, Eqs. (14)–(16) together with Eq. (2) have to be solved self-consistently.

For a homogeneous gas, the potentials V in Eq. (15) are all constant, and therefore the eigenvalue spectrum is given by

$$\epsilon_k^h = \frac{k^2}{2} [1+f] + V_{xc} + f' V_{lma} + V_l, \quad (17)$$

thereby resulting in the desired density-dependent change of the bandwidth. $m^*/m \equiv 1/[1+f]$ can obviously be interpreted as a density-dependent effective mass, hence the term local mass approximation. Moreover, it is easy to verify that the highest occupied eigenvalue, as in the LDA, agrees with the exact value $\epsilon_{k_F}^h = \epsilon_F + V_{xc}$.

IV. LINEAR RESPONSE WITHIN THE LMA

The question now is whether this LMA functional still accurately describes the total energy in the presence of an external potential. For near-homogeneous systems, the answer can be found analytically, by calculating the density response function $\chi(|\mathbf{r}-\mathbf{r}'|) \equiv \delta\rho(\mathbf{r})/\delta V_{\text{ext}}(\mathbf{r}')$ and comparing it to the corresponding quantity within the LDA and to a quasixact quantum Monte Carlo calculation.

The Fourier transform of χ is often written in the form

$$\chi(q; r_s) = \frac{\chi_0(q; r_s)}{1 - v(q)[1 - G(q; r_s)]\chi_0(q; r_s)}, \quad (18)$$

where $v(q) \equiv 4\pi/q^2$ is the Fourier transform of the Coulomb interaction $v(r) = 1/r$ and χ_0 is the Lindhard response function of a noninteracting electron gas,

$$\chi_0(q; r_s) = -\frac{k_F}{\pi^2} \left[\frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \right], \quad (19)$$

where $x = q/(2k_F)$. The local field factor $G(q; r_s)$ screens the bare Coulomb interaction and accounts, crudely speaking, for the effect of vertex corrections in the perturbation expansion of χ in terms of the Coulomb interaction v .

It is well established that for $q \lesssim 2k_F$, the q dependence of the exact $G(q; r_s)$ is reproduced extremely well by the LDA, which predicts

$$G^{\text{LDA}}(q; r_s) = \gamma(r_s)(q/k_F)^2, \quad (20)$$

with

$$\frac{4\pi}{k_F^2} \gamma(r_s) = - \left. \frac{dV_{xc}}{d\rho} \right|_{\rho=3/(4\pi r_s^3)}. \quad (21)$$

In fact, it turns out that Eq. (20) also holds for the exact $G(q; r_s)$ in the limit $q \rightarrow 0$. G and G^{LDA} differ significantly only for $q \gtrsim 2k_F$.

It is straightforward to see that the local field correction G^{LMA} resulting from the new density functional in Eq. (13) also satisfies Eq. (20) in the limit $q \rightarrow 0$. In fact, the only requirement for a density functional to satisfy this equation is that it must give the correct energy of the homogeneous gas at all densities, and hence the general functionals considered in Sec. II will always satisfy this equation in the limit $q \rightarrow 0$ by construction.

The calculation of $G^{\text{LMA}}(q; r_s)$ for arbitrary q is more involved and has been included in the Appendix. As it turns out [see Fig. 2(a)], $G^{\text{LMA}}(q; r_s)$ is almost identical to $G^{\text{LDA}}(q; r_s)$ for $q \lesssim k_F$. For $q > k_F$, $G^{\text{LMA}}(q; r_s)$ contains terms which grow as q^4 and which are absent in the

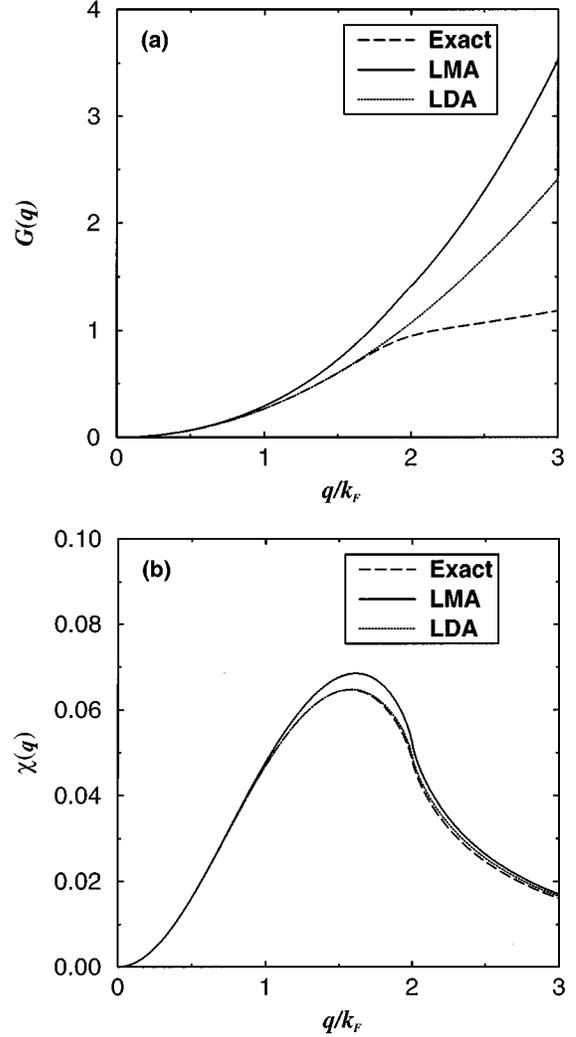


FIG. 2. (a) Comparison of local field corrections $G^{\text{LDA}}(q)$ and $G^{\text{LMA}}(q)$ to the parametrization of the exact $G(q)$ given in Ref. 28 for $r_s=2$. (b) Density response functions $\chi(q)$ following from Eq. (18) for the local field corrections shown in (a).

“exact”,²⁸ $G(q; r_s)$. Overall, we find that $G^{\text{LMA}}(q; r_s)$ is somewhat too large for $q > k_F$, and we therefore expect the LMA to slightly overestimate the strength of density variations with large wave vectors [see, also, Fig. 2(b)].

For $q > 2k_F$, G^{LDA} and G^{LMA} are both very different from the exact form. For many materials, this does not matter: as evidenced by the success of the LDA, this q region of $G(q; r_s)$ is rarely explored by the relatively smooth density variations of the valence electrons. We, therefore, expect that for systems within the linear response regime of the homogeneous gas, total energy calculations with the new density functional will give energies very close to the LDA energies. In Sec. VI, we will confirm this expectation for real calculations on alkali metals. We will also show that even for semiconductors, the new functional is at least as successful in predicting lattice constants and bulk moduli as the LDA, while simultaneously changing the band structure significantly.

V. RELATIONSHIP TO SELF-ENERGY APPROXIMATIONS

We have introduced the LMA in a semiempirical fashion as a means of reproducing the valence-band narrowing in simple metals. Here, we would like to discuss possible generalizations and justify the general form of the effective Hamiltonian \hat{H}_{eff} in Eq. (15) as the sum of a kinetic term with a coordinate-dependent mass and a local potential more rigorously.

We first show, by generalizing an argument in Ref. 21, that a coordinate-dependent mass arises naturally as a second-order approximation to any short-ranged symmetric nonlocal operator Σ as in Eq. (8). Our derivation also corrects the neglect of off-diagonal elements of the mass tensor in Eq. (16) of Ref. 21.

Introducing center-of-mass coordinates $\mathbf{x} \equiv (\mathbf{r} + \mathbf{r}')/2$ and $\mathbf{s} \equiv \mathbf{r}' - \mathbf{r}$, we can rewrite Eq. (8) as

$$E_{\text{nl}} = \sum_I^{\text{occ}} \int \int d\mathbf{r} d\mathbf{s} \psi_I^*(\mathbf{r}) \tilde{\Sigma} \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{s} \right) \psi_I(\mathbf{r} + \mathbf{s}), \quad (22)$$

where $\tilde{\Sigma}(\mathbf{x}, \mathbf{s}) \equiv \Sigma(\mathbf{r}, \mathbf{r}'; [\rho])$. Expanding $\psi_I(\mathbf{r} + \mathbf{s})$ and $\tilde{\Sigma}(\mathbf{r} + \mathbf{s}/2, \mathbf{s})$ into a second-order Taylor series around $\psi_I(\mathbf{r})$ and $\tilde{\Sigma}(\mathbf{r}, \mathbf{s})$, respectively, we find that the first-order terms vanish because $\tilde{\Sigma}(\mathbf{r}, \mathbf{s}) = \tilde{\Sigma}(\mathbf{r}, -\mathbf{s})$, and we obtain

$$E_{\text{nl}} \approx \frac{1}{2} \int d\mathbf{r} \sum_I^{\text{occ}} \sum_{i,j=1}^d \frac{\partial \psi_I^*}{\partial r_i} \tilde{\mu}_{i,j}^{-1}(\mathbf{r}) \frac{\partial \psi_I}{\partial r_j} + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{nl}}(\mathbf{r}). \quad (23)$$

Here

$$\tilde{\mu}_{i,j}^{-1}(\mathbf{r}) \equiv - \int d\mathbf{s} \tilde{\Sigma}(\mathbf{r}, \mathbf{s}) s_i s_j, \quad (24a)$$

$$V_{\text{nl}}(\mathbf{r}) \equiv \int d\mathbf{s} \left\{ \tilde{\Sigma}(\mathbf{r}, \mathbf{s}) + \frac{1}{8} \sum_{i,j=1}^d \frac{\partial^2 \tilde{\Sigma}(\mathbf{r}, \mathbf{s})}{\partial r_i \partial r_j} s_i s_j \right\}, \quad (24b)$$

and d is the dimensionality of the system.

Although the expansion leading to Eq. (23) is strictly valid only if $\psi_I(\mathbf{r})$ and $\tilde{\Sigma}(\mathbf{r}, \mathbf{s})$ vary slowly as a function of \mathbf{r} compared to the range of nonlocality of Σ , a suitably chosen effective mass operator can mimic the operation of the true nonlocal operator Σ onto a given subset of wave functions closely even when this condition is not fully satisfied. For a collection of spherically symmetric atoms, we can alternatively incorporate the off-diagonal elements of the effective mass tensor by treating Σ as a superposition of nonlocal pseudopotentials centered on the atomic sites \mathbf{R}_I . If we then replace the action of that pseudopotential on the wave functions by that of a pseudo-Hamiltonian,²⁹ we can write

$$\sum_{i,j=1}^d \frac{\partial}{\partial r_i} \tilde{\mu}_{i,j}^{-1}(\mathbf{r}) \frac{\partial}{\partial r_j} \approx - \frac{1}{2} \nabla a(\mathbf{r}) \nabla + \sum_I \frac{b(|\mathbf{r} - \mathbf{R}_I|) \hat{L}_I^2}{|\mathbf{r} - \mathbf{R}_I|}, \quad (25)$$

where \hat{L}_I is the usual angular momentum operator with respect to atom I , and a and b are suitably chosen functions. Possible generalizations of the LMA via such an angular momentum dependent term are left for future investigations;

at present, it is not clear how to choose the density dependence of the function b . However, we note in passing that an operator as in Eq. (25) could also be useful in finding one-electron Hamiltonians which minimize the exchange energy, generalizing the one-electron Hamiltonians used in the optimized effective potential methods.^{21,30,31}

It is apparent that in the homogeneous electron gas, a scalar effective mass can be used instead of a tensor mass. In the homogeneous gas, the choice of $\tilde{\Sigma}$ in Eq. (12), which leads to the quasiparticle dispersion in Eq. (17), can be viewed as a quadratic approximation to the GW self-energy $\Sigma_{GW}^h(k, E^h(k))$. The latter results in the quasiparticle dispersion,

$$E^h(k) = \frac{k^2}{2} + \Sigma_{GW}^h(k, E^h(k)), \quad (26)$$

shown in, for example, Fig. 35 of Ref. 2. Such a quadratic approximation is reasonably accurate for $k \leq 2k_F$; for $k \geq 2k_F$, it breaks down, and therefore the LMA should not be expected to be accurate for states with energies much larger than the Fermi energy. The LMA also neglects a small term linear in k at small k present in $\Sigma_{GW}^h(k, E^h(k))$, and it does not incorporate the change in the quasiparticle weight resulting from the energy dependence of the true self-energy operator.

Even in an inhomogeneous system, a scalar effective mass arises if we replace $\tilde{\Sigma}(\mathbf{r}, \mathbf{s})$ in Eq. (24a) by the GW self-energy Σ_{GW}^h of a homogeneous electron gas:

$$\tilde{\Sigma}(\mathbf{r}, \mathbf{s}) = \Sigma_{GW}^h\{|\mathbf{s}|, E(k) - \mu + \mu^h[\rho(\mathbf{r})]; \rho(\mathbf{r})\}, \quad (27)$$

where μ and μ^h are chemical potentials of inhomogeneous and homogeneous systems, respectively, and where $E(k)$ are the quasiparticle energies of the inhomogeneous system, which themselves implicitly depend on Σ . This is precisely the replacement made in the QPLDA.¹⁷⁻²⁰ With this choice of $\tilde{\Sigma}$, the off-diagonal elements of the effective mass tensor $\tilde{\mu}_{i,j}^{-1}$ given by Eq. (24a) vanish, and the diagonal elements become identical. We have therefore demonstrated that the kinetic term in the LMA can be viewed as a local second-order expansion of the self-energy used in the QPLDA. We note, however that the energy argument $E(k) - \mu + \mu^h[\rho(\mathbf{r})]$ in the QPLDA depends implicitly on the quasiparticle energies $E(k)$ of the inhomogeneous system, whereas the nonlocal operator in the LMA, as explained above, approximates a self-energy similar to Eq. (27) with $E(k)$ replaced by the quasiparticle energies $E^h(k)$ of the homogeneous system. This seemingly innocuous replacement has unfortunate consequences for the accuracy of the description of Fermi surfaces within the LMA, which will be discussed in Sec. VI.

For strongly inhomogeneous systems, such as semiconductors and insulators, Wang and Pickett^{19,20} have shown that the dependence of $\Sigma_{GW}^h(|\mathbf{s}|, E)$ on the energy E should actually be modified to correspond to a homogeneous electron gas with an artificial gap. In this version of the QPLDA, $\Sigma_{GW}^h(k, E(k))$ can no longer be approximated by a quadratic function in k , and an energy-dependent effective mass seems to be required. It is not clear how this could be incorporated into a total energy functional. On the other hand, even for an

energy-independent mass, the formulation of the LMA via a total energy functional results in additional local potentials V_{lma} and V_l [see Eq. (15)] which are absent in the QPLDA and which have a significant effect on the band structure. Ultimately, the success and limitations of the LMA for strongly inhomogeneous systems must therefore be decided empirically.

VI. COMPARISON OF LDA AND LMA STRUCTURAL AND ELECTRONIC PROPERTIES

We have performed plane-wave pseudopotential calculations for the alkali metals Li and Na in the bcc structure and for the semiconductors Si, Ge, and C in the diamond structure in order to compare the LMA to the usual LDA. The numerical techniques employed are standard,³² except for obvious modifications necessary for the calculation of the nonstandard kinetic energy operator and the potentials V_{lma} and V_l in Eq. (15).

The pseudopotentials were generated using an algorithm due to Kerker.³³ We remark that the atomic calculations used for the generation of the pseudopotentials were performed within the usual LDA and not within the LMA. We justify this inconsistency by noting that it is common to apply self-energy corrections only to the valence electrons within a pseudopotential scheme¹² (see, however, Ref. 34). In fact, within the QPLDA, it has been suggested (e.g., in Ref. 35) that the core electrons should not be included in the electron density arguments entering Eq. (27).

We also did not include nonlinear core exchange-correlation corrections,³⁶ which were found to improve³⁶⁻³⁸ the transferability of pseudopotentials in materials with strong spatial core-valence overlap such as the alkali metals. A consistent way of implementing these corrections within the LMA would require them to also be applied to the density argument of $f(\rho)$ in the LMA kinetic energy functional. This would be sensible only if the pseudopotential were also generated within the LMA. We did not want to cloud the direct comparison of LMA and LDA with such numerical complexities, the effects of which are secondary for our discussion. Instead, we chose to generate the pseudopotentials for the alkali metals within a neutral valence configuration, which we believe to be fairly close to the solid environment, since the structural properties calculated with these pseudopotentials are in fairly good agreement with all-electron calculations.

The valence configurations and cutoff radii employed in the construction of the pseudopotentials are shown in Table I, together with the plane-wave cutoffs and the number of Monkhorst-Pack³⁹ special points employed in the calculations on the solids. We verified that all the calculations were well converged with respect to the size of the basis set and the number of \mathbf{k} points used for Brillouin zone integrations.

Although the valence electrons in the alkali metals feel only a very weak pseudopotential and are very free-electron like, the LDA generally yields surprisingly poor results for their structural properties compared to experiment. For example, the lattice constant of Na is underestimated by about 5% within pseudopotential LDA schemes,³⁶ and the situation is not much improved in all-electron calculations.^{40,41} Moreover, different parametrizations of the exchange-correlation

TABLE I. Numerical parameters used in the plane-wave pseudopotential calculations. The first two columns describe the valence configuration and cutoff radii r_c used in the Kerker (Ref. 33) construction of the pseudopotentials. Also given are the plane-wave cutoffs E_{PW} and number N_k of irreducible \mathbf{k} points used for Brillouin zone integrations in the calculations on the solids.

	Config.	r_c	E_{PW} (Ry)	N_k
Li	$2s^{0.8}2p^{0.1}3d^{0.1}$	2.30 1.90 3.50	25	68
Na	$3s^{0.8}3p^{0.1}3d^{0.1}$	2.50 3.00 3.00	20	68
C	$2s^2 2p^{0.8} 3d^{0.2}$	1.11 1.01 1.36	100	10
Si	$3s^2 3p^{0.8} 3d^{0.2}$	1.58 1.93 1.93	15	10
Ge	$4s^2 4p^{0.8} 4d^{0.2}$	1.54 1.98 2.42	25	10

energy of the homogeneous electron gas can result in sizeable differences in the structural properties and even change the predicted ground state structures (bcc or fcc).^{36,37,42} For all the calculations in the present study, we employed the Ceperley-Alder form of the exchange-correlation energy.⁴³

We have no reason to believe that the structural properties should be more accurately described by the LMA than by the LDA; what we wish to demonstrate is that LMA and LDA predictions for structural properties agree closely, while the description of excitation energies is improved within the LMA. Table II shows that this is indeed the case: for the metals and semiconductors considered, the LDA and LMA lattice constants agree to within 1% and the bulk moduli to within 5%. For semiconductors, the LMA lattice constants are larger and closer to experiment than the LDA values; for Li and Na, they are smaller.

The calculations of excitation energies were performed at the experimental lattice constants shown in Table II. Within the LDA, the valence bandwidth for Na is virtually unchanged by the presence of the lattice compared to its free-electron value. We find a slight increase of 0.25% from 3.235 eV to 3.243 eV, which compares well with all-electron results.^{31,41} In lithium, the presence of the lattice reduces the valence-band width by 27% compared to the free-electron value (4.75 eV) (other authors find 25.6% (Ref. 41) and 26.6% (Ref. 31)).

The LMA then leads to a reduction of 12.82% for Li and 11.05% for Na with respect to these LDA values (Fig. 3),

TABLE II. Lattice constants a and bulk moduli B calculated within the local mass approximation described in Sec. III as compared to the LDA predictions and experiment for metallic bcc lithium and sodium and diamond carbon, silicon, and germanium.

	a (Å)			B (Mbar)		
	LDA	LMA	Expt.	LDA	LMA	Expt.
Li	3.308	3.275	3.480 ^a	0.138	0.146	0.127 ^a
Na	4.025	3.989	4.220 ^b	0.081	0.085	0.073 ^b
C	3.533	3.565	3.567 ^c	4.51	4.38	4.43 ^c
Si	5.384	5.406	5.429 ^c	0.96	0.92	0.99 ^c
Ge	5.545	5.579	5.652 ^d	0.80	0.71	0.77 ^d

^aReference 49.

^bReference 50.

^cCited in Ref. 51.

^dCited in Ref. 52.

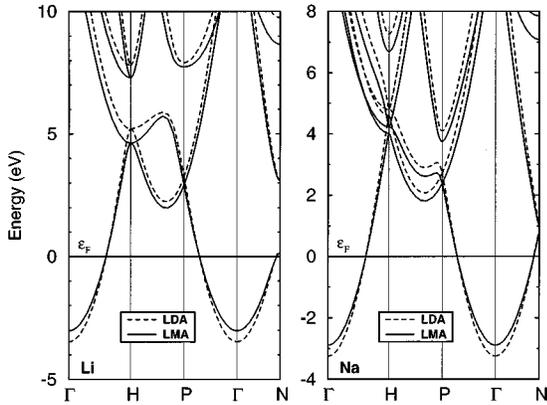


FIG. 3. Comparison of LDA and LMA pseudopotential band structures for bcc Li and Na.

which should be compared to the prediction of Eq. (11) for $r_s = 3.25$ (7.63%) and $r_s = 3.93$ (10.93%), respectively. Although Li has a higher electron density than Na, the relative bandwidth reduction is larger in Li than in Na, contrary to what might be expected from Eq. (11). This is easily understood if we assume that the absolute distortion of the valence bandwidth due to the lattice is the same within the LDA and LMA, i.e., the valence band in both cases is about 1.30 eV narrower than in a homogeneous gas of the same average density. Since the LMA bandwidth of a homogeneous system with $r_s = 3.25$ is about 4.38 eV, we can then estimate the LMA bandwidth in the presence of the lattice potential to be about 3.08 eV, which is close to the value 3.02 eV of the full calculation.

While the LMA clearly improves some aspects of the band structures in simple metals, disappointingly it does not improve the unsatisfactory description of the shape of the Fermi surface within the LDA. It is known that the LDA overestimates the amount by which the Fermi surface differs from a perfect sphere by about a factor of two in the alkali

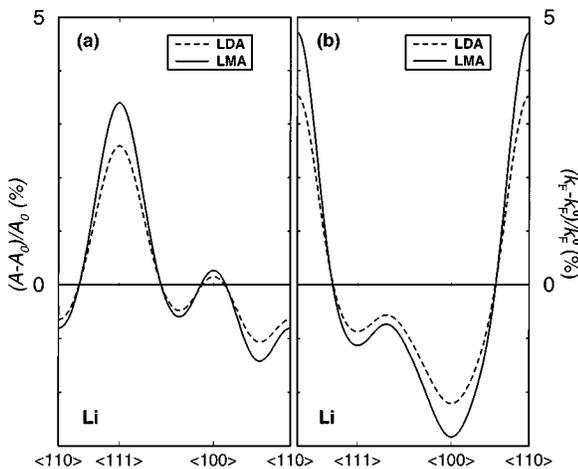


FIG. 4. Relative distortions with respect to their free-electron values of (a) Fermi surface extremal areas $A(\hat{\Omega})$ (for a definition, see, e.g., Ref. 18), and (b) Fermi wave vectors $k_F(\hat{\Omega})$, calculated within LDA and LMA along different directions $\hat{\Omega}$ on the unit sphere, for Li.

metals. MacDonald¹⁸ has shown that this discrepancy with de Haas–van Alphen measurements⁴⁴ is largely corrected for by the QPLDA. Since the LMA can be viewed as an approximation to the QPLDA (see Sec. V), one might naively expect a similar improvement. We, therefore, performed accurate Fermi surface fits within LDA and LMA, using the same cubic harmonic expansion and Gaussian integration techniques⁴⁵ as MacDonald. The resulting deviations of the Fermi wave vector k_F and Fermi surface extremal areas A (defined as in Ref. 18) in Li are shown in Fig. 4. While our LDA pseudopotential results agree closely with MacDonald's all-electron LDA results, it is apparent that the LMA does not reduce the Fermi surface distortions; on the contrary, it slightly increases them.

This deficiency can be traced back to the energy argument entering the approximation to Σ in Eq. (27). As shown in Ref. 18, the change in the Fermi surface distortions resulting from the use of a nonlocal (NL) self-energy can be estimated as

$$\frac{k_F^{\text{NL}}(\hat{\Omega}) - k_F^0}{k_F^{\text{LDA}}(\hat{\Omega}) - k_F^0} \approx \left(1 + m_b(\hat{\Omega}) \frac{1}{2k_F^0} \frac{\partial \Sigma_{\text{NL}}}{\partial k} \Big|_{k_F^0} \right)^{-1}, \quad (28)$$

where $m_b(\hat{\Omega})$ is the band mass in the direction $\hat{\Omega}$. As discussed in Sec. V, Σ_{NL} within the LMA is approximately given by the right hand side (RHS) of Eq. (27) if the quasi-particle energies $E(k)$ of the inhomogeneous system are replaced by the energies $E^h(k)$ of the homogeneous electron gas. Then the derivative on the RHS of Eq. (28) is slightly negative, resulting in a small increase of the Fermi surface distortions instead of the desired decrease. On the other hand, within the QPLDA, Σ_{NL} on the Fermi surface is obtained from Eq. (27) if we replace $E(k)$ by the constant chemical potential μ ; then the derivative on the RHS of Eq. (28) is positive, resulting in a fairly large reduction of the distortions as observed by MacDonald.

Turning our attention to semiconductors, we find that in Si and Ge, the LMA results in a substantial increase of the indirect band gap, from 0.5 eV to 1.0 eV in Si (Table III) and from 0 to 0.5 eV in Ge (Table IV). In both cases, the increase in the direct band gap is somewhat less dramatic. Note that the effect of spin-orbit splitting was not included in our germanium calculation. The valence-band width in Si and Ge decreases slightly with respect to the LDA, but remains in reasonable agreement with experiment.

In diamond carbon (Table V), the band structures predicted by the LDA and LMA are almost identical. Clearly, this indicates that the LMA is not a sufficiently accurate approximation for self-energy effects in strongly inhomogeneous insulators such as carbon. This is not surprising, since the LMA was constructed with simple metals in mind. It is nonetheless encouraging that the LMA accurately predicts structural properties even for semiconductors and insulators and moves the excitation spectra of Si and Ge in closer agreement with experiments. It is likely that the implementation of the general scheme of Sec. II will have no drastic effects on structural properties also for different choices of the nonlocal operator Σ .

A comparison of cohesive energies would be desirable in order to further substantiate our claim that the LMA yields

TABLE III. Comparison of selected LDA and LMA eigenvalue differences (in eV) for silicon. Also shown are the results of the *GW* calculation in Ref. 12 and experimental results quoted therein.

Silicon	LDA	LMA	GW ^a	Expt. ^b
E_g	0.5	1.0	1.29	1.17
$\Gamma_{1v} \rightarrow \Gamma'_{25v}$	11.9	11.6	12.0	12.5 ± 0.6
$\Gamma'_{25v} \rightarrow \Gamma'_{15c}$	2.6	2.7	3.4	3.4
$\Gamma'_{25v} \rightarrow \Gamma'_{2c}$	3.2	3.5	4.1	4.2
$X_{4v} \rightarrow \Gamma'_{25v}$	2.9	2.7	3.0	2.9–3.3
$\Gamma'_{25v} \rightarrow X_{1c}$	0.7	1.1	1.4	1.3
$L'_{2v} \rightarrow \Gamma'_{25v}$	9.6	9.4	9.8	9.3 ± 0.4
$L_{1v} \rightarrow \Gamma'_{25v}$	7.0	6.7	7.2	6.7 ± 0.2
$L'_{3v} \rightarrow \Gamma'_{25v}$	1.2	1.2	1.3	1.2–1.5
$\Gamma'_{25v} \rightarrow L_{1c}$	1.5	1.8	2.3	2.1–2.5
$\Gamma'_{25v} \rightarrow L_{3c}$	3.3	3.5	4.2	4.15 ± 0.1
$L'_{3v} \rightarrow L_{1c}$	2.7	3.0	3.5	3.45
$L'_{3v} \rightarrow L_{3c}$	4.5	4.7	5.5	5.50

^aReference 12.

^bCited in Ref. 12.

total energies with a similar degree of accuracy as the LDA. To avoid ambiguities in the cohesive energies related to the use of LDA pseudopotentials and to the neglect of nonlinear core corrections (see above), we have recently implemented the LMA within an all-electron Gaussian molecular orbital code. Preliminary results⁵⁵ for Si₂₀ clusters indicate that for geometries optimized within the LDA, the LMA cohesive energies in silicon are about 20% smaller in magnitude than the LDA cohesive energies, thereby correcting the well-known overbinding observed in LDA calculations. This may be fortuitous, and further investigations are under way to see if the improvement is systematic also for other materials.

TABLE IV. Comparison of selected LDA and LMA eigenvalue differences (in eV) for germanium. Our LDA and LMA results for Ge do not include relativistic effects, in contrast to the *GW* results.

Germanium	LDA	LMA	GW ^a	Expt. ^b
$\Gamma_{8v} \rightarrow L_{4,5c}^1$	0	0.5	0.75	0.744
$\Gamma_{6v} \rightarrow \Gamma_{8v}$	12.7	12.7	12.9	12.6–13.1
$\Gamma_{8v} \rightarrow \Gamma_{7c}$	0.1	0.3	0.7	0.89
$\Gamma_{8v} \rightarrow \Gamma_{6c}$	2.6	2.7	3.0	3.006
$X_{5v}^1 \rightarrow \Gamma_{8v}$	8.9	8.9	9.1	9.3 ± 0.2
$X_{5v}^2 \rightarrow \Gamma_{8v}$	3.0	3.2	3.2	3.0–3.7
$\Gamma_{8v} \rightarrow X_{5c}$	0.7	1.2	1.2	1.3 ± 0.2
$L_{6v}^1 \rightarrow \Gamma_{8v}$	10.7	10.4	10.9	10.6 ± 0.5
$L_{6v}^2 \rightarrow \Gamma_{8v}$	7.6	7.3	7.8	7.7 ± 0.2
$L_{4,5v} \rightarrow \Gamma_{8v}$	1.4	1.3	1.4	1.4 ± 0.3
$\Gamma_{8v} \rightarrow L_{4,5c}^2$	3.6	3.9	4.3	4.2 ± 0.1
$\Gamma_{8v} \rightarrow L_{6c}$	7.1	7.5	7.6	7.6 ± 0.1

^aReference 12.

^bCited in Ref. 12.

TABLE V. Comparison of selected LDA and LMA eigenvalue differences (in eV) for diamond carbon.

Diamond	LDA	LMA	GW ^a	Expt. ^b
E_g	4.1	4.1	5.6	5.48
$\Gamma_{1v} \rightarrow \Gamma'_{25v}$	21.3	22.9	23.0	20–25
$\Gamma'_{25v} \rightarrow \Gamma'_{15c}$	5.6	5.8	7.5	7.3
$\Gamma'_{25v} \rightarrow \Gamma'_{2c}$	13.6	13.1	14.8	15.3 ± 0.5
$L'_{2v} \rightarrow \Gamma'_{25v}$	15.5	16.5	17.3	15.2 ± 0.3
$L_{1v} \rightarrow \Gamma'_{25v}$	13.3	13.7	14.4	12.8 ± 0.3
$\Gamma'_{25v} \rightarrow L'_{2c}$	15.4	16.3	17.9	20.0 ± 1.5

^aReference 12.

^bCited in Ref. 12.

VII. CONCLUSIONS

The main purpose of the present work was to demonstrate that the search for density functionals beyond the LDA should include not only functionals with explicit density dependence, but should be extended to nonlocal functionals whose dependence on the density is implicit through the Kohn-Sham orbitals. In contrast to other orbital-dependent functionals in the literature, such as self-interaction corrected (SIC) density functional theories,^{46–48} the functionals considered here lead to a single orbital-independent Schrödinger equation for all orbitals.

We have conjectured that the additional freedom gained by the introduction of a nonlocal orbital-dependent term can be used to absorb some of the nonanalyticities of the usual $E_{xc}[\rho]$ as a function of ρ . In this manner, it should be possible to construct density functionals where the (unknown) discontinuity of the exchange-correlation potential upon addition of a single electron in semiconductors and insulators is much smaller than for the standard Kohn-Sham partitioning of the density functional.

As a specific example, we have proposed a density functional with a modified, density-dependent effective mass. This LMA functional, like the LDA, is exact in the homogeneous electron gas, and the long-wavelength density response is given accurately. However, in contrast to the LDA, the LMA also reproduces the valence-band narrowing in simple metals due to self-energy effects, because it is constructed in such a way that the resulting modified Schrödinger equation contains terms approximating the self-energy operator in near-homogeneous systems. The functional, moreover, yields improved eigenvalue spectra even in semiconductors. Despite these successes, we have also pointed out difficulties, such as the failure of the LMA to improve the poor LDA predictions of Fermi surface shapes in the alkali metals and the remaining discrepancies between LMA band gaps and experiment in semiconductors. Possible modifications to remedy these problems are currently under investigation.

An obvious generalization of the approach described here would be to combine the LMA with improved density functionals such as generalized gradient approximations. Furthermore, we have indicated that the introduction of a scalar density-dependent mass is only the crudest approximation for self-energy effects and that, in general, the nonlocal op-

erator Σ should also contain angular momentum-dependent terms. This should also be kept in mind in constructing optimized effective potentials for Hartree-Fock-like theories.

We have verified through calculations on several metallic and semiconducting systems that structural properties are described equally well by the LMA as by the LDA, a property which should also hold for many other functionals constructed according to the general prescription given in Sec. II. On the other hand, the LMA eigenvalue spectrum differs significantly from the LDA spectrum and generally agrees closer with experimental observations.

Recently, generalizations of the Kohn-Sham scheme similar to those proposed in Sec. II were independently put forward in a paper by Seidl *et al.*⁵³ The screened exchange functional⁵⁴ investigated by these authors is very different and more costly than the LMA, since it requires the numerical effort of a self-consistent Hartree-Fock calculation.

ACKNOWLEDGMENTS

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APPENDIX: LINEAR RESPONSE FOR THE LOCAL MASS APPROXIMATION

In this appendix, we present some details of the calculation of the density response function $\chi^{\text{LMA}}(q; r_s)$ and the local field correction $G^{\text{LMA}}(q; r_s)$ resulting from the local mass approximation introduced in Sec. III. For simplicity, we will suppress the superscript LMA and the argument r_s in G and χ in the derivation.

Starting from the effective one-particle Hamiltonian \hat{H}_{eff} in Eq. (15), the change in this Hamiltonian due to an applied external potential $\delta V_{\text{ext}} \cos(\mathbf{q} \cdot \mathbf{r})$ is given by

$$\frac{\delta \hat{H}_{\text{eff}}}{\delta V_{\text{ext}}} = [1 + f' \tilde{\chi}(q) + C(q) \chi(q)] \cos(\mathbf{q} \cdot \mathbf{r}) - f' \chi(q) \frac{1}{2} \nabla \cos(\mathbf{q} \cdot \mathbf{r}) \nabla, \quad (\text{A1})$$

where

$$\tilde{\chi}(|\mathbf{r} - \mathbf{r}'|) \equiv \frac{\delta V_{\text{lma}}(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')}, \quad (\text{A2})$$

and

$$C(q) \equiv v(q) + \frac{dV_{\text{xc}}}{d\rho} + \frac{dV_l}{d\rho} + f'' V_{\text{lma}} = v(q) + \frac{dV_{\text{xc}}}{d\rho} - f \frac{\pi^2}{k_F} - f' k_F^2. \quad (\text{A3})$$

Using perturbation theory, it follows that the first-order change in the charge density resulting from this first-order change in the effective Hamiltonian is given as

$$\delta \rho(\mathbf{r}) = \frac{4}{\Omega} \sum_{|\mathbf{k}| < k_F < |\mathbf{k}'|} \frac{\cos[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]}{\epsilon_k - \epsilon_{k'}} \langle \mathbf{k}' | \delta \hat{H}_{\text{eff}} | \mathbf{k} \rangle, \quad (\text{A4})$$

where Ω is a normalization volume. Similarly, the first-order change in the LMA potential V_{lma} is given as

$$\delta V_{\text{lma}}(\mathbf{r}) = \frac{4}{\Omega} \sum_{|\mathbf{k}| < k_F < |\mathbf{k}'|} \frac{\mathbf{k} \cdot \mathbf{k}'}{2} \frac{\cos[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]}{\epsilon_k - \epsilon_{k'}} \times \langle \mathbf{k}' | \delta \hat{H}_{\text{eff}} | \mathbf{k} \rangle. \quad (\text{A5})$$

Note that the ϵ_k in Eqs. (A4) and (A5) are given by Eq. (17). Substituting Eq. (A1) into Eq. (A4) and evaluating the matrix elements, we then find for $\delta \rho / \delta V_{\text{ext}}$ (suppressing the argument q):

$$\chi = \tilde{\chi}_0 + \tilde{\chi}_0 C \chi + f' (\chi_1 \chi + \tilde{\chi} \tilde{\chi}_0). \quad (\text{A6})$$

Similarly, $\delta V_{\text{lma}} / \delta V_{\text{ext}}$ is given by

$$\tilde{\chi} = \chi_1 + \chi_1 C \chi + f' (\chi_1 \tilde{\chi} + \chi_2 \chi). \quad (\text{A7})$$

In Eq. (A6),

$$\tilde{\chi}_0(q) = \frac{1}{4\pi^3} \int d\mathbf{k} \frac{n_F(\epsilon_{\mathbf{k}}) - n_F(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} = \frac{\chi_0(q)}{1 + f(\rho)}, \quad (\text{A8})$$

where n_F is the Fermi function. $\tilde{\chi}_0$ is a mass-corrected Lindhard function describing the response of the charge density to a change in the total potential; it is obtained from Eq. (A4) for the matrix elements $\langle \mathbf{k}' | \cos(\mathbf{q} \cdot \mathbf{r}) | \mathbf{k} \rangle$. χ_1 in Eq. (A6) describes the response of the charge density to a change in the kinetic part of the Hamiltonian, which follows by evaluating Eq. (A4) with the matrix elements $\langle \mathbf{k}' | -\frac{1}{2} \nabla \cos(\mathbf{q} \cdot \mathbf{r}) \nabla | \mathbf{k} \rangle$:

$$\chi_1(q) = \frac{1}{8\pi^3} \int d\mathbf{k} \frac{n_F(\epsilon_{\mathbf{k}}) - n_F(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}). \quad (\text{A9})$$

It is easy to see that the same expression results if we calculate the change in V_{lma} with respect to changes in the total potential, i.e., using $\langle \mathbf{k}' | \cos(\mathbf{q} \cdot \mathbf{r}) | \mathbf{k} \rangle$ in Eq. (A5), which explains the occurrence of the same χ_1 in Eq. (A7). χ_2 in Eq. (A7) describes the response of V_{lma} to changes in the kinetic part of the Hamiltonian:

$$\chi_2(q) = \frac{1}{4\pi^3} \int d\mathbf{k} \frac{n_F(\epsilon_{\mathbf{k}}) - n_F(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} [\mathbf{k} \cdot (\mathbf{k} + \mathbf{q})]^2. \quad (\text{A10})$$

The integrals defining χ_1 and χ_2 can be evaluated and the result can be expressed in terms of χ_0 as follows [$x = q/(2k_F)$]:

$$(1 + f) \chi_1 = -\frac{k_F^2}{4} \left[\frac{k_F}{\pi^2} + (3x^2 - 1) \chi_0 \right], \quad (\text{A11})$$

and

$$(1 + f) \chi_2 = \frac{k_F^5}{36\pi^2} (7x^2 - 6) + \frac{k_F^4}{12} (7x^4 - 5x^2 + 1) \chi_0. \quad (\text{A12})$$

Finally, Eqs. (A6) and (A7) can be solved for χ :

$$\chi = \frac{\chi_0}{1+f-C\chi_0-2(1+f)f'\chi_1+f'^2(1+f)(\chi_1^2-\chi_2\tilde{\chi}_0)}. \quad (\text{A13})$$

We find that the error introduced by disregarding the term of order f'^2 in the denominator of this expression is negligibly small. Then G^{LMA} is given explicitly as

$$G^{\text{LMA}}(q;r_s) = G^{\text{LDA}}(q;r_s) + \frac{3}{32\pi} q^4 f'(\rho) + \frac{1}{v(q)} \left(\frac{1}{\chi_0(q;r_s)} + \frac{\pi^2}{k_F} \right) \times \left(f(\rho) + \frac{3}{2} \rho f'(\rho) \right). \quad (\text{A14})$$

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