

Straightforward gradient approximation for the exchange energy of s - p bonded solids

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In the present work we perform a straightforward gradient expansion of the exchange energy of a perturbed electron gas. Studied perturbations range from very weak to those that produce, e.g., a siliconlike band structure with a band gap. The expansions involve density gradients up to fourth degree and we include all terms originating in linear- and second-order response theory. The expansion reproduces our exactly calculated exchange energies with an accuracy of the order of a few mRy per electron for metallic systems. For systems with a bandgap the accuracy is reduced by an order of magnitude. When the coefficient of the fourth-degree gradient originating in second-order response theory is used as a variable parameter, we find a best fit to calculated exchange energies when the coefficient agrees with that obtained in previous work on second-order response theory. Thus, the present results corroborate our previous analytical work. We emphasize the possibility of obtaining very accurate exchange energies for s - p bonded solids and we discuss the possibility of also including correlation energies within the same simple scheme. [S0163-1829(96)01547-0]

I. INTRODUCTION

Numerous papers on density functional theory^{1,2} (DFT) start with the cliché that DFT has become the most widespread and accurate method for obtaining the ground-state properties of solids and large molecules. With the advent of the generalized gradient approximations³⁻⁵ (GGA's) the truth in this cliché is becoming even more obvious. Recently, a large community of researchers previously almost exclusively using so-called *ab initio* methods is gradually converting to DFT. The accuracy of the GGA's with regard to binding energies of molecules is approaching 1 kcal/mol and potential barriers are so well described that we might soon be able to use DFT to do realistic calculations on chemical reactions. There is, however, still a crucial distance in accuracy to traverse before this fantasy becomes reality.

Most existing GGA's involve only the first gradient of the density and many of them, but not all, are supported using arguments from linear response theory. In previous work^{6,7} we have argued that the electronic density of an atom is certainly not a linear perturbation of the homogeneous electron gas. We have also suggested that higher-degree gradients might be useful in attempts to model the true exchange-correlation or exchange functionals. Having said that, one is immediately facing the problem of how to obtain the proper coefficients of such gradient terms. In that paper,⁷ we made a not entirely conclusive effort to obtain the coefficient of the term $\int n^{-3} |\nabla n|^2 \nabla^2 n$ coming from the small momentum expansion of that response function which gives the third-order change in the exchange energy of the perturbed electron gas. The difficulties were associated with the singular nature of the integrals defining the above-mentioned response function. As a matter of fact, we still do not know whether or not the response function is analytic at zero momenta. Thus, a gradient expansion might not even exist in the strict mathematical sense of originating in a Taylor expansion of the response function around the origin in momentum space. This would, however, not mean that a gradient approximation is useless. Let us here digress for a moment and give the

reader the chance to appreciate this subtle and rarely discussed point. We first recall the normal procedure for obtaining gradient expansions using exchange energies as an illustrative example. The second-order change in the exchange energy of the electron gas is given by

$$\delta E_x = \frac{1}{2} \int K_x(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}) \delta n(\mathbf{r}') d^3 r d^3 r', \quad (1)$$

where δn is the deviation of the electron density from the homogeneous density n_0 . This equation actually defines the kernel K_x , which is a property of the homogeneous gas and therefore only depends on the distance between \mathbf{r} and \mathbf{r}' and the original density n_0 . Going to reciprocal space gives

$$\delta E_x = \frac{1}{2} \int K_x(\mathbf{q}) |\delta n(\mathbf{q})|^2 \frac{d^3 q}{(2\pi)^3}. \quad (2)$$

The next step is to assume that δn has appreciable Fourier components only for $q = |\mathbf{q}|$ less than $k_F = (3\pi^2 n_0)^{1/3}$. If this is the case, we will not lose much accuracy by replacing the kernel K_x by its Taylor expansion around the origin in momentum space. Thus,

$$K_x(\mathbf{q}) = 2A + 2Bq^2 + \dots \quad (3)$$

Then, returning to real space, we obtain

$$\delta E_x = \int A [\delta n(\mathbf{r})]^2 d^3 r + \int B |\nabla n(\mathbf{r})|^2 d^3 r. \quad (4)$$

In this way, we see how coefficients of gradient terms are related to derivatives of various response functions with respect to momenta at zero momentum. Thus, gradient terms are generated in the usual way¹ of simultaneously studying the slowly varying limit of Eq. (3) and the linear response regime of Eq. (1). Above, we have implicitly assumed that the largest part of the density lies close to the origin in momentum space. We also assumed that, in this region, the response function (K_x in our example above) is best approximated by its Taylor expansion around zero momentum. What

if the density has its largest Fourier components, say, around the local k_F ? An even more disturbing thought is that the response function might be singular and have no, or discontinuous, derivatives at zero momentum. The latter possibility might not be that far fetched. Consider for a moment a world with a Yukawa interparticle interaction ($e^{-\lambda r}/r$). Now clearly, in that world, physical properties like, e.g., exchange energies cannot be that different from those of the real world if the value of λ is very small. It is, by now, well known⁸⁻¹⁰ that K_x is analytic at zero momentum for all λ including $\lambda=0$ but that the λ -dependent coefficient B above is discontinuous at $\lambda=0$. This means that, at finite λ , the kernel K_x is well represented by its Taylor expansion around $q=0$, but only in a very small region of radius λ around the origin. Clearly, this region contains a very small part of the total density. Outside this region, K_x is instead well represented by a similar expression [Eq. (3)], but now with a quite different B corresponding to $\lambda=0$. Consequently, the gradient approximation of Eq. (4) will be very bad in the ‘‘Yukawa world’’ but might still give reasonable answers in the real world.

Our example above is admittedly a contrivance. One should keep in mind, however, that response functions do have singularities. It is, e.g., suggested by Langreth and Vosko¹¹ that the kernel K_{xc} is nonanalytic at $q=0$. (The kernel K_{xc} is defined similarly to K_x above but includes also correlation effects.)

The main message conveyed by the above example is, however, that a gradient correction will work provided that we find an accurate polynomial fit to the relevant response function over an extended region of momenta in which the particle density has appreciable Fourier components. Considering first the Fourier components of the density, nature has been kind to us. Most interesting molecules and solids have densities with Fourier components which are large at small momenta and then decay relatively rapidly at larger momenta. In fact, the criterion^{3,12} that ‘‘local’’ Fourier components of the density is smaller than twice the local Fermi momentum, k_F , is obeyed in most regions of solids and molecules where the density is large enough to give a non-negligible contribution to the energy. We can thus concentrate on finding polynomial fits to response functions in the momentum region from zero to $2k_F$. This turns out to be a feasible task which, as a premium, avoids possible nonanalyticities at zero momentum. This is the main idea behind the present work.

Furthermore, this idea can be generalized in an obvious but, maybe to the purist, phenomenological way. From basic theory, we can determine the analytical forms of possible gradient terms involving, say, density gradients up to the fourth degree. The coefficients of these gradient terms can then be chosen in such a way that the resulting approximation for the exchange-correlation energy is very accurate for a set of particular systems of our choice. Provided the chosen set spans the most important varieties of exchange and/or correlation effects, one can hope to have found a generally valid and accurate GGA. As we shall see later on, for the systems we have studied, i.e., not too strongly perturbed electron gases, the chosen coefficients deviate little from what is obtained from *ab initio* theory.

In the present work, we have chosen to study exchange energies only. These are, in principle, exactly obtainable and serve as reference values to which we compare our different gradient approximations. We note in passing, that once we are able to calculate correlation energies to the same level of accuracy as exchange energies, the methods of the present work are easily extended to give accurate approximations to the full exchange-correlation functional of DFT. We also stress here that what is referred to as exchange energies in the present work are energies of the Talman-Shadwick scheme,¹³ which is also called the exchange-only approximation (EXOA). The difference between this scheme and the Hartree-Fock approximation is by now well known^{14,15} and we will not dwell further upon this point here.

The calculation of exchange energies would appear to be a relatively easy and straightforward task. Our particular way of obtaining gradient coefficients require, however, that we do not use too strong potentials and with weaker potentials the energy contributions from higher degree gradients become very small. Consequently, exchange energies must be calculated with a very high relative accuracy, $\sim 10^{-4}$. Because of the long-range nature of the Coulomb interaction, this turned out to be a difficult proposition, the efforts of which are described in Sec. II.

In the present work, we have basically used two major methods for obtaining gradient coefficients. One we refer to as the real-space method and it is described in Sec. III. The other method we call the reciprocal-space method and Sec. IV contains a full account of this method. Here we just mention the basic ideas behind the two methods. In the real-space method we chose a lattice potential represented by a set of Fourier components at some of the shortest vectors of the reciprocal lattice. The potential is considered to be the fully self-consistent effective potential of the EXOA. The resulting density is obtained to infinite order in the lattice potential by means of a plane-wave oriented band program and the orbitals are used to calculate the exact exchange energies. From the density in real space we then calculate the exchange energy in the local-density approximation (LDX) as well as all gradient terms resulting from linear and second-order response theory and containing at most fourth-degree gradients. A gradient approximation is then constructed by adding to the LDX result a linear combination of the gradient terms. For the low-degree gradient terms we use known, analytically obtained, coefficients while the coefficient of the highest gradient, $n^{-3}|\nabla n|^2\nabla^2 n$, from the second-order response theory is chosen so as to reproduce the exact exchange energy. This procedure is repeated for different potentials and, in the limit of small potentials, the resulting coefficient is found to approach our analytical result obtained previously from second-order response theory.⁷ Moreover, we find that the results improve for each higher-degree gradient that is added to the basic local-density approximation.

In the reciprocal-space method the procedure for obtaining densities and exchange energies is the same as in the real-space method. By multiplying the effective lattice potential by a scaling factor and calculating the exact exchange energies (E_x) for a range of scaling factors from zero and up, we can isolate that contribution to E_x which originates in second-order response (the third-order contribution). Assum-

ing that we know L_x , defined as the third-order derivative of the functional E_x with respect to density, the third-order contribution to E_x can be calculated exactly. Using potentials for which the resulting density only has appreciable components at the shorter vectors of the reciprocal lattice, it would be enough to know the kernel L_x at small momenta. One way to achieve this is to study high-density systems, i.e., those with many electrons per unit cell. We thus use a polynomial fit to the kernel L_x in momentum space. The constant and the q^2 coefficient are taken from analytical work⁶ and the q^4 coefficient is determined so as to reproduce our numerically calculated results. We again find a q^4 coefficient close to that obtained in our analytical work.⁷

In several aspects of the present work, perturbation theory is a key issue. For sufficiently weak potentials, perturbation theory is certainly appropriate in the mathematical sense. By this we mean that, when scaling the potential from zero and up, there is a radius of convergence pertaining to the scaling factor. Below this radius, we can obtain successively better results by going to a higher order in perturbation theory. Beyond that radius, we believe that, e.g., energies remain analytic functions of the scaling factor while we can no longer expect to be able to systematically improve our results by adding more terms in the perturbation expansion. The latter might, however, represent an asymptotic expansion in the sense that, for stronger potentials, accurate results are obtained in low-order perturbation theory while the results deteriorate by adding more terms in the perturbation expansion. These points are discussed in Sec. V. Finally, in Sec. VI we give our conclusions.

II. THE EXACT EXCHANGE ENERGY

The basic quantity needed in order to pursue the ideas presented in the introduction, is the exchange energy of perturbed electron gases. We will, in other words, expose the gas to some external potential and then calculate the resulting density and exchange energy within the EXOA. In order to avoid the implied self-consistency procedure, here we use the usual trick of directly specifying the effective Kohn-Sham potential V (within the EXOA). That is, we consider V to include the external potential as well as the Hartree potential from the electron distribution, and the exchange potential. For the purpose of solving the one-electron problem with relative ease, we have chosen to study periodic potentials. This means that we solve a one-particle Schrödinger equation of the form

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right] \varphi_{\mathbf{k},\nu}(\mathbf{r}) = E_{\mathbf{k},\nu} \varphi_{\mathbf{k},\nu}(\mathbf{r}), \quad (5)$$

in which the potential has the form

$$V(\mathbf{r}) = \sum_{\mathbf{g}} V(\mathbf{g}) e^{i\mathbf{g}\cdot\mathbf{r}}, \quad (6)$$

where \mathbf{g} is a vector of an fcc lattice. For the metallic systems, we have chosen nonvanishing components $V(\mathbf{g})$ of the total potential only at the two shortest “stars” of the reciprocal lattice. This means, at most, two numerical values for the potential amplitudes — one for the eight vectors of the form (1,1,1) and one for the six vectors of the form (2,0,0). For

the semiconductors, we have used potentials also with components at a few longer vectors of the reciprocal lattice.

Thus, the problem can be solved by using an ordinary band program based on plane waves. The zero of potential energy is chosen such that $V(\mathbf{g}=0)=0$. The exchange energy is given by

$$E_x = -\frac{1}{4} \int |n(\mathbf{r},\mathbf{r}')|^2 v(\mathbf{r}-\mathbf{r}') d^3r d^3r'. \quad (7)$$

here $v(\mathbf{r}-\mathbf{r}')$ is the bare Coulomb potential and $n(\mathbf{r},\mathbf{r}')$ is the density matrix, which for our spin-compensated system can be written as

$$n(\mathbf{r},\mathbf{r}') = 2 \sum_{\mathbf{k},\nu} \varphi_{\mathbf{k},\nu}(\mathbf{r}) \varphi_{\mathbf{k},\nu}^*(\mathbf{r}') n_F(\mathbf{k},\nu). \quad (8)$$

The Fermi-factor $n_F(\mathbf{k},\nu)$ restricts the sums in \mathbf{k} and ν to occupied states only. The electron density $n(\mathbf{r})$ of the system is obviously the diagonal of the density matrix, $n(\mathbf{r}) = n(\mathbf{r},\mathbf{r})$.

We next define the square of the density matrix

$$m(\mathbf{r},\mathbf{r}') = |n(\mathbf{r},\mathbf{r}')|^2. \quad (9)$$

Since the density matrix $n(\mathbf{r},\mathbf{r}')$ is periodic with respect to simultaneous lattice translations in \mathbf{r} and \mathbf{r}' , $m(\mathbf{r},\mathbf{r}')$ has the same symmetry and can be expanded in a Fourier series,

$$m(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{g}\mathbf{g}'\mathbf{q}} m_{\mathbf{g}\mathbf{g}'\mathbf{q}} e^{i(\mathbf{g}+\mathbf{q})\mathbf{r}} e^{-i(\mathbf{g}'+\mathbf{q})\mathbf{r}'}, \quad (10)$$

where \mathbf{q} only runs over the first Brillouin zone (BZ). Inserting Eq. (10) into Eq. (7) and Fourier transforming, we obtain

$$E_x = -\frac{\Omega}{4} \sum_{\mathbf{g}\mathbf{q}} m_{\mathbf{g}\mathbf{g}}(\mathbf{q}) v(\mathbf{g}+\mathbf{q}), \quad (11)$$

where $v(\mathbf{g}+\mathbf{q}) = 4\pi/|\mathbf{g}+\mathbf{q}|^2$ is the Fourier transform of the Coulomb potential, and Ω is the volume of the full system. Due to the small- q singularity of the Coulomb potential, we add and subtract a term $m_{00}(0)$ giving

$$E_x = -\frac{\Omega}{4} \sum_{\mathbf{g}\mathbf{q}} [m_{\mathbf{g}\mathbf{g}}(\mathbf{q}) - m_{00}(0)] v(\mathbf{g}+\mathbf{q}) - \frac{\Omega}{4} m_{00}(0) \sum_{\mathbf{g}\mathbf{q}} v(\mathbf{g}+\mathbf{q}). \quad (12)$$

The first term in the equation above is finite for $\mathbf{g}=0$ and $\mathbf{q}\rightarrow 0$. The second term contains no matrix elements and can be evaluated exactly. In practice, we add and subtract $m_{00}(0)$ only within the first BZ, that is for $\mathbf{g}=\mathbf{0}$. In order to avoid explicit evaluation of the second derivative of $m_{\mathbf{g}\mathbf{g}'}(\mathbf{q})$ with respect to q at $\mathbf{q}=0$, we use a mesh within the first BZ which excludes the point $\Gamma(\mathbf{q}=0)$.

The diagonal elements $m_{\mathbf{g}\mathbf{g}}(\mathbf{q})$ are given by a sum over the first BZ and contains all the Fermi-surface dependence through the two Fermi factors.

$$m_{\text{gg}}(\mathbf{q}) = \frac{4}{\Omega^2} \sum_{\mathbf{k}, \nu, \nu'} n_F(\mathbf{k}, \nu) n_F(\mathbf{k} - \mathbf{q}, \nu') \times |\langle \mathbf{k}, \nu | e^{i(\mathbf{q} + \mathbf{g})\mathbf{r}} | \mathbf{k} - \mathbf{q}, \nu' \rangle|^2. \quad (13)$$

Accurate evaluation of Eq. (13) is of crucial importance for the success of the present work. As will be discussed later, the errors in the exchange energies must be smaller than contributions from high-degree gradient terms which are typically in the range $10^{-3} - 10^{-4}$ Ry for the systems studied.

For the case of a metal, evaluation of Eq. (13) turns out to be rather difficult. A straightforward integration using, e.g., the tetrahedron method with Blöchl's¹⁶ corrections is prohibited by the coupling between the Fermi factors $n_F(\mathbf{k}, \nu)$ and $n_F(\mathbf{k} - \mathbf{q}, \nu')$. We have instead adopted two simpler methods, namely, broadening of the Fermi factors with some finite temperature and so-called simple sampling.

The temperature dependence (T) of the exchange energy of an electron gas displays an unphysical $T^2 \ln T$ (Ref. 17) divergence. Moreover, for a real system the coefficients of the $T^2 \ln T$ and T^2 terms are not known. However, one can still use a Fermi broadening and subsequently determine the zero temperature limit by fitting the result to the following form:

$$E_x(T) = C_0 + C_1 T^2 \ln T + C_2 T^2, \quad (14)$$

where C_0 obviously represents the desired limit $E_x(T=0)$. For the even more robust sampling method we simply adjust the weight of the last \mathbf{k} point lying at the Fermi energy in such a way so as to obtain the correct number of particles.

We have tested these two methods versus known results for the homogeneous electron gas. Somewhat surprisingly, the simple sampling method turns out to work better than a method based on a broadening of the Fermi surface. In addition, the sampling method does not require any fine tuning of the broadening parameter. Therefore, the calculations on metallic systems reported here are done using the simple sampling method. The price we pay is a nonuniform convergence. Using a \mathbf{k} mesh with up to 18 points in each direction an accuracy of better than 0.1% in the total exchange energy per electron is obtained.

III. THE REAL-SPACE METHOD

Having obtained accurate exchange energies from the method described in Sec. II, we are now in a position to proceed with our program described in the introduction. By a simultaneous study of the slowly-varying limit and the limit of low-order response, both the forms and the coefficients in front of different gradient corrections can be determined.⁶ We will now investigate the possibility of modeling the exact exchange functional by retaining these forms, while using the coefficients as adjustable parameters.

Defining the following separate gradient contributions,

$$\epsilon_x^{\text{LDX}}[n] = A_x \int n(\mathbf{r})^{4/3} \frac{d^3 r}{N},$$

$$\epsilon_x^{\text{GE1}}[n] = B_x^{(2)} \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}} \frac{d^3 r}{N} + B_x^{(4)} \int \frac{|\nabla^2 n(\mathbf{r})|^2}{n(\mathbf{r})^2} \frac{d^3 r}{N},$$

$$\epsilon_x^{\text{GE2}}[n] = C_x^{(4)} \int \frac{|\nabla n(\mathbf{r})|^2 \nabla^2 n(\mathbf{r})}{n(\mathbf{r})^3} \frac{d^3 r}{N}, \quad (15)$$

the total exchange energy per electron, $\epsilon_x[n]$, can be written as

$$\epsilon_x[n] = \epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}} + \epsilon_x^{\text{GE2}} + \dots, \quad (16)$$

where N is the total number of electrons in the system. The coefficients in Eq. (15) are given by^{6,8,10}

$$A_x = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3},$$

$$B_x^{(2)} = -\frac{5}{216\pi(3\pi^2)^{1/3}},$$

$$B_x^{(4)} = -\frac{73}{64800\pi^3},$$

$$C_x^{(4)} = \frac{1}{54\pi^3} (L_4 - L'_4) = \frac{73}{64800\pi^3} - \frac{1}{54\pi^3} L'_4. \quad (17)$$

In this work all quantities are in atomic units, except energies, which are in Rydbergs (Ry).

The dimensionless number L_4 is known exactly from a simple density derivative relation between the first- and second-order exchange response kernels K_x and L_x .⁶ On the other hand, the number L'_4 has been approximately obtained from a study of the second-order response kernel L_x .⁷ We obtained the value $L'_4 \approx -1.5L_4$, with a numerical uncertainty of some 30%.

Note that, due to the appearance of the spatially dependent density $n(\mathbf{r})$ in the denominators of Eq. (16), we are not exclusively confined to the study of densities which deviate little from a constant density n_0 .⁷ The fact that our forms are based on density gradients does, however, mean that the systems studied should not be too far from the slowly varying limit.

In a first attempt to reproduce exchange energies by means of Eq. (16), we soon realized that adding terms from Eq. (16) with the known coefficients from Eq. (17) led to successively more accurate results. This can be seen in the Tables I and II where the contribution ϵ_x^{GE2} has been calculated using our previously obtained result for $L'_4 (= -1.5L_4)$. We notice that, with this value of L'_4 , the addition of ϵ_x^{GE2} reduces the error by one order of magnitude, i.e., to a few tenths of a percent. With the purpose of further reducing this error, we decided to fix the coefficients A_x , $B_x^{(2)}$, and $B_x^{(4)}$ at their theoretical values, and to treat only the less certain coefficient $C_x^{(4)}$ as adjustable.

As typical examples of metallic s - p bonded systems, we have chosen two sets of lattice potentials. One set is characterized by $V_{111} = V_{200} = \lambda \epsilon_F$ at the eight nearest neighbors and the six next nearest neighbors of the reciprocal of the fcc lattice. Here λ is a dimensionless strength parameter. All other Fourier components of the potential are zero. For the other set of potentials we choose $V_{111} = 1.5V_{200} = \lambda \epsilon_F$ as the only nonvanishing 14 components. For each set of potentials

TABLE I. Calculated exchange energies per electron for different values of the effective potential V . All exchange energies are in Rydbergs. The rightmost columns are results from the GGA's due to Becke (B) and Perdew *et al.* (P), respectively. $V_{111}(=V_{200})$ is in units of $\epsilon_F=0.4765$ Ry.

| V_{111} | Exact | ϵ_x^{LDX} | $\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}}$ | $\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}} + \epsilon_x^{\text{GE2}}$ | $\epsilon_x^{\text{GGA}} (B)$ | $\epsilon_x^{\text{GGA}} (P)$ |
|-----------|---------|---------------------------|---|---|-------------------------------|-------------------------------|
| 0.038854 | -0.3327 | -0.3318 | -0.3327 | -0.3327 | -0.3333 | -0.3332 |
| 0.077709 | -0.3425 | -0.3388 | -0.3424 | -0.3425 | -0.3445 | -0.3445 |
| 0.116563 | -0.3580 | -0.3508 | -0.3585 | -0.3582 | -0.3623 | -0.3622 |
| 0.155417 | -0.3778 | -0.3668 | -0.3797 | -0.3781 | -0.3847 | -0.3846 |
| 0.165131 | -0.3831 | -0.3712 | -0.3855 | -0.3834 | -0.3907 | -0.3906 |
| 0.174844 | -0.3884 | -0.3757 | -0.3914 | -0.3887 | -0.3968 | -0.3967 |
| 0.184558 | -0.3939 | -0.3803 | -0.3975 | -0.3941 | -0.4029 | -0.4028 |
| 0.194271 | -0.3993 | -0.3849 | -0.4036 | -0.3996 | -0.4091 | -0.4089 |
| 0.203985 | -0.4047 | -0.3896 | -0.4098 | -0.4050 | -0.4153 | -0.4151 |

we compute the exchange energies and the electron densities. We can thus define two functions of the parameter λ as follows:

$$\Delta(\lambda) = \epsilon_x(\lambda) - \epsilon_x^{\text{LDX}}(\lambda) - \epsilon_x^{\text{GE1}}(\lambda), \quad (18)$$

and

$$\Gamma(\lambda) = \int \frac{|\nabla n_\lambda(\mathbf{r})|^2 \nabla^2 n_\lambda(\mathbf{r}) d^3r}{n_\lambda(\mathbf{r})^3} \frac{d^3r}{N}. \quad (19)$$

Due to the previously described difficulties (Sec. II) associated with obtaining very accurate exchange energies, there is an inherent uncertainty in $\Delta(\lambda)$ of the order of a few tenths of a mRy ($\sim 10^{-4}$ Ry). Thus, the need for numerically significant values of Δ requires λ to be sufficiently large. For our fitting procedure, yet to be described, we have chosen λ values in the range 0.02–0.9 for the two sets of potentials the results of which are displayed in Tables I and II. With these values, the quantity Δ is of the order of 0.5 mRy. Note, however, that we would not like to make λ very large. At small λ , i.e., within the regime of linear response, the electron density will have Fourier components only at the same reciprocal lattice vectors as the potential. The number of electrons per unit cell (3 in the calculations reported in Tables I and II) is such that $q/(2k_F)$ is smaller than 1 [$q/(2k_F)$ is 0.77 and 0.89 for the vectors (1,1,1) and (2,0,0), respectively], and the criterion for a slowly varying

density¹⁴ is thus obeyed. When λ is made larger, a higher-order response will cause the density to acquire Fourier amplitudes at longer reciprocal lattice vectors. In such a case, a straightforward gradient expansion will become less appropriate, and might require the introduction of some cutoff procedure at large $q:s$.

Assuming some systematic constant error, Δ_0 , in calculated exchange energies, we fit our calculated $\Delta:s$ to the form

$$\Delta(\lambda) = \Delta_0 + C\Gamma(\lambda), \quad (20)$$

where C obviously represents the best possible choice of $C_x^{(4)}$. For the first set of potentials ($V_{111}=V_{200}$, Table I), we obtain $\Delta_0=0.3$ mRy, and a value of C corresponding to $L'_4 = -1.45L_4$. The largest error in this fit is indeed small (0.04 mRy), thus giving us confidence in the procedure. For the second set of potentials (Table II), we obtain a value of C corresponding to $L'_4 = -1.75L_4$. The corresponding predicted systematic error (0.8 mRy) in the calculated exchange energies is somewhat larger than we had expected from other estimates. The maximum error in this fit is also larger than before (0.16 mRy)—perhaps indicating that, in this case, we are leaving the slowly varying limit at the higher $\lambda:s$.

We note here, that we have no obvious reason to expect that the phenomenological path followed in the present section would lead to gradient coefficients equal to those obtained from first principles. In this section, we wanted the

TABLE II. Same as in Table I, but $V_{111}=1.5V_{200}$.

| V_{111} | Exact | ϵ_x^{LDX} | $\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}}$ | $\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}} + \epsilon_x^{\text{GE2}}$ | $\epsilon_x^{\text{GGA}} (B)$ | $\epsilon_x^{\text{GGA}} (P)$ |
|-----------|---------|---------------------------|---|---|-------------------------------|-------------------------------|
| 0.023313 | -0.3303 | -0.3302 | -0.3304 | -0.3304 | -0.3306 | -0.3305 |
| 0.069938 | -0.3376 | -0.3354 | -0.3376 | -0.3377 | -0.3390 | -0.3390 |
| 0.116563 | -0.3515 | -0.3460 | -0.3518 | -0.3517 | -0.3550 | -0.3550 |
| 0.163188 | -0.3704 | -0.3613 | -0.3720 | -0.3711 | -0.3770 | -0.3768 |
| 0.186500 | -0.3809 | -0.3702 | -0.3836 | -0.3820 | -0.3892 | -0.3891 |
| 0.209813 | -0.3919 | -0.3796 | -0.3959 | -0.3931 | -0.4019 | -0.4017 |
| 0.233126 | -0.4030 | -0.3893 | -0.4086 | -0.4043 | -0.4147 | -0.4145 |
| 0.256438 | -0.4140 | -0.3991 | -0.4215 | -0.4155 | -0.4275 | -0.4273 |
| 0.279751 | -0.4248 | -0.4089 | -0.4346 | -0.4264 | -0.4402 | -0.4399 |

gradient corrections to absorb the deviation from a constant density and at the same time the effects of higher-order responses.

Let us, however, consider the underlying theory in more detail. Suppose that our densities are within the slowly varying regime, but that the potentials are relatively strong. We should still be able to obtain our densities from perturbation theory although of some very high order. These are precisely the criteria for the applicability of expansions like that of Eqs. (15), (16). Assuming that gradients of higher degree than 4 can be neglected for our densities, no other terms can appear as gradient corrections but those of Eq. (15) plus a term of the form $\int n^{-4} |\nabla n|^4 d^3r$ from third-order response theory (not considered here). Response theory of fourth or higher order produce gradient terms containing gradients of the density of at least the sixth degree. They also produce terms of lower powers of the density gradients but these are already included by using the full spatially dependent densities (not just the original homogeneous density of the gas) in the denominators of Eq. (15).⁷ Moreover, the coefficient of a certain contribution must be that which is predicted by the corresponding response function. We will return to this point in Sec. V.

Strictly speaking, we should have included the third-order gradient term mentioned above. This term is, however, of higher order in perturbation theory than those considered. Contributions from such terms are expected to be so small that the numerical accuracy of our calculated exchange energies would not allow for a determination of one additional gradient coefficient.

It is comforting that the gradient coefficients obtained here are close to those obtained from the study of response functions. The fact that the corresponding gradient corrections lead to systematic improvements is indeed gratifying and the very small errors ($\sim 10^{-4}$ Ry) obtained in realistic model systems suggests a more universal applicability. We finally observe that the results obtained here are more than an order of magnitude more accurate than those of the two most commonly used GGA schemes due to Becke¹⁸ and Perdew *et al.*¹⁹ (see Tables I and II). Incidentally, we also see that these schemes give very similar results.

IV. RECIPROCAL-SPACE METHOD

Encouraged by the success of the previous section, we will now investigate whether or not our calculated exchange energies are accurate enough to allow for a more first-principles determination of gradient coefficients. Note, however, that we will still avoid the cumbersome task of taking derivatives at zero momentum of various response functions. To this end we will, as usual, simultaneously study the limits of small deviations from a constant density and slowly varying densities. As a model system we consider one of the sets of potentials described in Sec. III, namely, the one with $V_{111} = V_{200} = \lambda \epsilon_F$. The applicability of linear response is assured by choosing very small values of λ . The second criterion, i.e., slowly varying densities, is guaranteed by a larger number of electrons per unit cell (3, 5, and 7, respectively). Being interested in the second-order response function L_x giving a third-order contribution to the exchange energy, we will have to isolate that part of the exact exchange energy

which is strictly to *third* order in the effective potential V .

Let us first formally define a number of necessary response functions the detailed definition of which can be found in Refs. 6 and 20.

$$\frac{\delta^2 T_0[n]}{\delta n \delta n'} = -\chi_0^{-1}, \quad (21)$$

$$\frac{\delta^3 T_0[n]}{\delta n \delta n' \delta n''} = \chi_0^{-1} \chi_0^{-1} \chi_0^{-1} \phi_0, \quad (22)$$

$$\frac{\delta^2 E_x[n]}{\delta n \delta n'} = K_x, \quad (23)$$

and

$$\frac{\delta^3 E_x[n]}{\delta n \delta n' \delta n''} = L_x, \quad (24)$$

Let us then, based on corresponding limits at small momenta, introduce dimensionless scaled quantities as follows:

$$\mathbf{g} = k_F \mathbf{G}, \quad n(\mathbf{g}) = n_0 \tilde{n}(\mathbf{G}), \quad V(\mathbf{g}) = \epsilon_F \tilde{V}(\mathbf{G}). \quad (25)$$

and

$$\chi_0(\mathbf{q}; n_0) = -\frac{k_F}{\pi^2} \tilde{\chi}_0(\mathbf{Q}),$$

$$\phi_0(\mathbf{q}, \mathbf{q}'; n_0) = \frac{1}{\pi^2 k_F} \tilde{\phi}_0(\mathbf{Q}, \mathbf{Q}'), \quad (26)$$

$$K_x(\mathbf{g}; n_0) = -\frac{\pi}{k_F^2} \tilde{K}_x(\mathbf{G}),$$

$$L_x(\mathbf{g}, \mathbf{g}'; n_0) = \frac{2\pi^3}{k_F^5} \tilde{L}_x(\mathbf{G}, \mathbf{G}'). \quad (27)$$

Here, \mathbf{g} is a reciprocal lattice vector of the fcc lattice, n_0 is the original homogeneous density of the gas, k_F is the Fermi momentum, and $\epsilon_F = k_F^2/2$ is the Fermi energy. Up to the third order in $\tilde{n}(\mathbf{G})$, the exchange energy, $\epsilon_x[n]$, can then be written as⁷

$$\begin{aligned} \epsilon_x[n] = \epsilon_x[n_0] & \left[1 + \frac{2}{9} \sum_{\mathbf{G}} \tilde{K}_x(\mathbf{G}) |\tilde{n}(\mathbf{G})|^2 \right. \\ & \left. - \frac{4}{81} \sum_{\mathbf{G}\mathbf{G}'} \tilde{L}_x(\mathbf{G}, \mathbf{G}') \tilde{n}(\mathbf{G}) \tilde{n}(-\mathbf{G}') \tilde{n}(\mathbf{G}' - \mathbf{G}) + \dots \right], \end{aligned} \quad (28)$$

where $\epsilon_x[n_0] = -3k_F/4\pi$. A third-order expression for the exchange energy requires the density response to the second order in V .

$$\begin{aligned} \tilde{n}(\mathbf{G}) &= -\frac{3}{2}\tilde{\chi}_0(\mathbf{G})\tilde{V}(\mathbf{G}) \\ &+ \frac{3}{8}\sum_{\mathbf{G}'}\tilde{\phi}_0(\mathbf{G},\mathbf{G}')\tilde{V}(-\mathbf{G}')\tilde{V}(\mathbf{G}'-\mathbf{G}), \end{aligned} \quad (29)$$

Note that $\mathbf{G}=0$ is excluded from all sums over reciprocal lattice vectors. Incidentally, we see from Eq. (29) that $|\tilde{V}(\mathbf{G})| \ll 1$ or $|V(\mathbf{G})| \ll \epsilon_F$ is roughly equivalent to $n(\mathbf{G}) \ll n_0$ as a ‘‘linear response regime’’ requirement.

Equation (29) inserted into Eq. (28) gives an expansion of the exchange energy which we give below to third order in \tilde{V} .

$$\begin{aligned} \epsilon_x[n] &= \epsilon_x[n_0] \left[1 + \frac{1}{2}\sum_{\mathbf{G}}\tilde{K}_x(\mathbf{G})|\tilde{\chi}_0(\mathbf{G})|^2|\tilde{V}(\mathbf{G})|^2 \right. \\ &- \frac{1}{4}\sum_{\mathbf{G}\mathbf{G}'}\tilde{K}_x(\mathbf{G})\tilde{\chi}_0(\mathbf{G})\tilde{\phi}_0(\mathbf{G},\mathbf{G}')\tilde{V}(\mathbf{G})\tilde{V}(-\mathbf{G}')\tilde{V}(\mathbf{G}'-\mathbf{G}) \\ &\left. + \frac{1}{6}\sum_{\mathbf{G}\mathbf{G}'}\tilde{\chi}_0(\mathbf{G})\tilde{\chi}_0(\mathbf{G}')\tilde{\chi}_0(\mathbf{G}'-\mathbf{G})\tilde{L}_x(\mathbf{G},\mathbf{G}')\tilde{V}(\mathbf{G})\tilde{V}(-\mathbf{G}')\tilde{V}(\mathbf{G}'-\mathbf{G}) + \dots \right]. \end{aligned} \quad (30)$$

$$\quad (31)$$

Since $\tilde{V}(\mathbf{G}) = \lambda$ for all the 14 shortest reciprocal lattice vectors, Eq. (31) can be rewritten as

$$\epsilon_x[n(\lambda)] = \epsilon_x[n_0][1 + \alpha_2\lambda^2 + \alpha_3\lambda^3 + \dots], \quad (32)$$

where the first coefficients α_n are given by

$$\alpha_2 = \frac{1}{2}\sum_{\mathbf{G}}\tilde{K}_x(\mathbf{G})|\tilde{\chi}_0(\mathbf{G})|^2, \quad (33)$$

$$\alpha_3^{(2)} = -\frac{1}{4}\sum_{\mathbf{G}\mathbf{G}'}\tilde{K}_x(\mathbf{G})\tilde{\chi}_0(\mathbf{G})\tilde{\phi}_0(\mathbf{G},\mathbf{G}'), \quad (34)$$

$$\alpha_3^{(3)} = \frac{1}{6}\sum_{\mathbf{G}\mathbf{G}'}\tilde{\chi}_0(\mathbf{G})\tilde{\chi}_0(\mathbf{G}')\tilde{\chi}_0(\mathbf{G}'-\mathbf{G})\tilde{L}_x(\mathbf{G},\mathbf{G}'), \quad (35)$$

and it is understood that not only the vectors \mathbf{G}, \mathbf{G}' but also $\mathbf{G}'-\mathbf{G}$ must belong to the 14 shortest \mathbf{G} vectors. We have here split $\alpha_3 = \alpha_3^{(2)} + \alpha_3^{(3)}$ into a part, $\alpha_3^{(2)}$, which is completely known,^{8,10,21,22} and a part, $\alpha_3^{(3)}$, containing the unknown \tilde{L}_x .

In order to enhance the accuracy of our calculations, we next take the difference $\Delta\epsilon_x[n(\lambda)] = \epsilon_x[n(\lambda)] - \epsilon_x[n(-\lambda)]$ between calculations with the same potential strengths but opposite sign of λ . From Eq. (32) we see that the coefficient α_3 is now given to the leading order by

$$\frac{\Delta\epsilon_x[n(\lambda)]}{2\epsilon_x[n_0]\lambda^3} = \alpha_3 + \alpha_5\lambda^2 \dots \quad (36)$$

From this we obtain $\alpha_3^{(3)}$ as $\alpha_3^{(3)} = \alpha_3 - \alpha_3^{(2)}$. Being in the slowly varying regime allows us to use the following polynomial expansion for \tilde{L}_x^6 in Eq. (35) above:

$$\begin{aligned} \tilde{L}_x(\mathbf{G},\mathbf{G}') &= 1 + L_2(G^2 + G'^2 - \mathbf{G} \cdot \mathbf{G}') \\ &+ L_4(G^2 + G'^2 - \mathbf{G} \cdot \mathbf{G}')^2 \\ &+ L_4'[G^2G'^2 - (\mathbf{G} \cdot \mathbf{G}')^2]. \end{aligned} \quad (37)$$

Having done this we finally solve Eq. (35) with respect to L_4' :

$$L_4' = \frac{6(\alpha_3 - \alpha_3^{(2)}) - F_1}{F_2}, \quad (38)$$

where

TABLE III. Results from Eq. (34), (36), (39), and (40).

| N_c | λ | $\Delta\epsilon_x/(2\epsilon_x\lambda^3)$ | $\alpha_3^{(2)}$ | F_1 | F_2 |
|-------|-----------|---|------------------|-------|--------|
| 3 | 0.009714 | -24.33 | -39.65 | 86.90 | 141.87 |
| | 0.019427 | -28.78 | | | |
| | 0.029141 | -27.97 | | | |
| | 0.038854 | -26.58 | | | |
| | 0.048568 | -25.50 | | | |
| | 0.058281 | -23.65 | | | |
| 5 | 0.020730 | -13.16 | -28.15 | 91.08 | 101.30 |
| | 0.027640 | -14.61 | | | |
| | 0.034550 | -13.67 | | | |
| | 0.041460 | -13.56 | | | |
| | 0.048370 | -11.13 | | | |
| 7 | | | -25.08 | 89.42 | 74.34 |
| | 0.017669 | -11.05 | | | |
| | 0.026503 | -11.12 | | | |
| | 0.035338 | -11.07 | | | |
| | 0.044172 | -11.37 | | | |
| | 0.053007 | -11.77 | | | |

TABLE IV. Exchange energies for Si and Si-related models. The symbol Δ indicates that the corresponding quantity is given as a difference to the exact result.

| Model | Exact | $\Delta \epsilon_x^{\text{LDX}}$ | $\Delta(\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}})$ | $\Delta(\epsilon_x^{\text{LDX}} + \epsilon_x^{\text{GE1}} + \epsilon_x^{\text{GE2}})$ | $\Delta \epsilon_x^{\text{GGA}} (B)$ | $\Delta \epsilon_x^{\text{GGA}} (P)$ |
|-----------|---------|----------------------------------|---|---|--------------------------------------|--------------------------------------|
| Si | -0.5321 | 0.0280 | 0.0072 | 0.0148 | 0.0058 | 0.0060 |
| SiX | -0.5539 | 0.0353 | -0.0006 | 0.0219 | 0.0071 | 0.0074 |
| <i>M1</i> | -0.5340 | 0.0233 | 0.0090 | 0.0125 | 0.0049 | 0.0050 |
| <i>M2</i> | -0.5550 | 0.0283 | 0.0079 | 0.0157 | 0.0055 | 0.0057 |

$$\begin{aligned}
F_1 = & \sum_{\mathbf{G}\mathbf{G}'} \tilde{\chi}_0(\mathbf{G})\tilde{\chi}_0(\mathbf{G}')\tilde{\chi}_0(\mathbf{G}'-\mathbf{G}) \\
& \times [1 + L_2(G^2 + G'^2 - \mathbf{G} \cdot \mathbf{G}') \\
& + L_4(G^2 + G'^2 - \mathbf{G} \cdot \mathbf{G}')^2], \quad (39)
\end{aligned}$$

and

$$F_2 = \sum_{\mathbf{G}\mathbf{G}'} \tilde{\chi}_0(\mathbf{G})\tilde{\chi}_0(\mathbf{G}')\tilde{\chi}_0(\mathbf{G}'-\mathbf{G})[G^2 G'^2 - (\mathbf{G} \cdot \mathbf{G}')^2]. \quad (40)$$

The results of these calculations are given in Table III. Here we used very small potentials and would thus expect results for $\Delta \epsilon_x[n(\lambda)]/(2\epsilon_x[n_0]\lambda^3)$ to be almost constant plus a small term quadratic in the potential. We see, however, from Table III that values scatter around such a behavior indicating numerical difficulties. The reason is, of course, that small potentials lead to very small differences in exchange energies thus putting our numerical procedure for obtaining such energies to a very stringent test. When the three series of data in Table III are fitted to a constant plus a quadratic term, we obtain $L'_4/L_4 = -1.6, -1.8, -1.0$ for 3, 5, and 7 electrons in the unit cell, respectively. Any attempt to include higher powers of the potential in the fit will just cause the fit to try to follow numerical ripple.

As mentioned in the beginning of this section, we are trying to simultaneously reach the slowly varying limit and the limit of small density deviations. Our numerical accuracy will, of course, determine how closely we can approach the latter limit, and it appears as if we are just on the verge of getting accurate results. With regard to the slowly varying limit, we obviously need to be able to neglect terms of order G^6 and higher in Eq. (37). The importance of these terms will decrease with the number, N_c , of electrons per unit cell (actually as N_c^{-2} because $k_F \sim N_c^{1/3}$). With three electrons per unit cell the length of our longest G vector—(2,0,0)—is 1.77, i.e., rather close to the boundary of the slowly varying regime, which is $G=2$. In order not to have to worry about higher powers of G , we have increased N_c up to 7. Unfortunately, the calculation of L'_4 from Eq. (38) involves the cancellation of large numbers such that a relative error in an extrapolated α_3 becomes a ten times larger error in L'_4 . Taking an average of our obtained values of L'_4 the results of the present section suggest that $L'_4/L_4 = -1.4 \pm 0.5$. Consequently, we conclude that our present numerical accuracy does not allow for the reciprocal-space method to improve on our previous knowledge of L'_4 . Still, this section demonstrates how one, in principle, could obtain a very accurate

value of L'_4 , and we stress that the result here is entirely consistent with previous results (Sec. III and Ref. 7).

V. APPLICATION TO SEMICONDUCTORS

In Sec. IV, we successfully applied the GEA to cases with slowly varying and small density variations. In Sec. III we increased the strength of the potential but still tried to stay within the slowly varying regime. Again the GEA gave an accurate description of exchange energies. In this section we will further increase the strengths of the potentials until band gaps occur, and also include potentials with Fourier components at longer lattice vectors. We will thus also leave the slowly varying regime. As our first example, we choose a pseudopotential for Si (Ref. 23) which gives a reasonable Si band structure. ($V_{111} = -0.21$ Ry, $V_{220} = 0.04$ Ry, $V_{311} = 0.04$ Ry.) The fact that Si has two atoms (and eight valence electrons) in the primitive cell of the fcc lattice causes the disappearance of V_{200} . In this case the “slowly varying criterion” is obeyed for density components at the vectors (1,1,1) and (2,0,0) but *not* at (3,1,1) or for density components generated beyond the linear response.

In our next example we simply increased the previous Si potential by 20%, thus making the band gaps larger. In the third example we consider a hypothetical material with an fcc structure, one atom per unit cell and eight valence electrons. The potential was characterized by $V_{111} = -0.30$ Ry, $V_{200} = -0.15$ Ry, $V_{220} = 0.03$ Ry, $V_{311} = 0.05$ Ry, and the resulting band structure has a band gap. The small potential components V_{220} and V_{311} were mainly added to cancel the small density components at these reciprocal lattice vectors — components generated by V_{111} and V_{200} through response of higher than linear order. Density components at other vectors than (1,1,1) and (2,0,0) are thus very small. Finally, our fourth example is a slight modification of our third, and is obtained by changing V_{111} from -0.30 Ry to -0.38 Ry. Again several small potential components at longer reciprocal lattice vectors were added in order to nearly eliminate the density components at long vectors. The results are displayed in Table IV where Si and SiX label our first two examples corresponding to normal silicon and silicon with a larger band gap (SiX). The last two examples are labeled *M1* and *M2* and correspond to systems which are in the slowly varying regime.

Though there are significant differences between the two sets of results, they have certain features in common. Within the LDX approximation all systems display an underestimate of the (absolute value) of the exchange energies of the order of 5–6%. This error is strongly reduced by adding gradient corrections from linear response and including gradients to

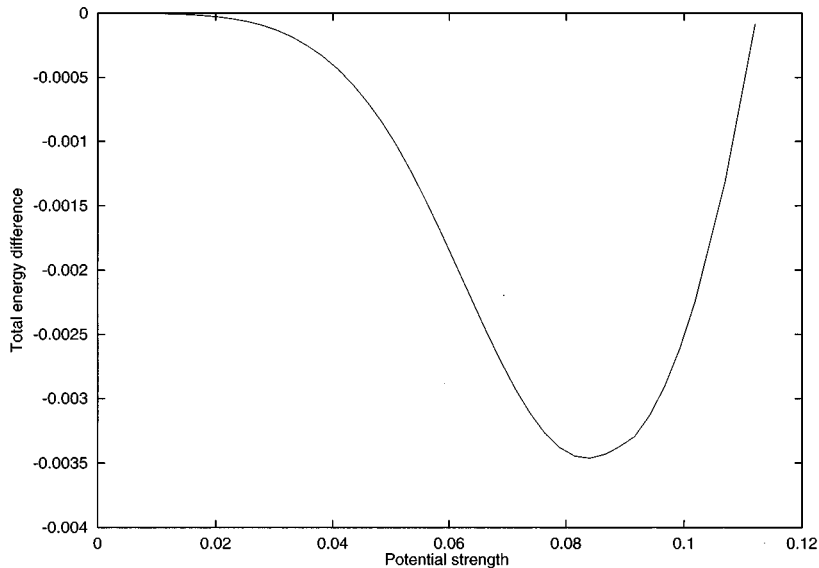


FIG. 1. Total energy difference $\Delta E = E - E_0 - E_1 - E_2 - E_3$ for the noninteracting solid versus strength of the effective potential. Here E is the total energy and E_n the n th-order contribution from perturbation theory (arb. units).

the fourth degree. Here the term containing the fourth-degree gradient correction carries a substantial amount of the total linear contribution, more for systems with faster density variations. Notice that, in this section, we have made no attempt to adjust coefficients. They are fixed at the values obtained from first- and second-order response theory.

At the level of linear response, the errors are of the order of 1–2% and very similar to those of the GGA's used for comparison^{18,19}. Unfortunately, the next correction from second-order response theory and again including gradients up to the fourth degree makes things worse. Errors increase up to some 4%. Consequently, the total gradient correction cuts the LDX error in half, i.e., not a very impressive result. The sign of the second-order correction is positive which probably is physically correct, but the negative contribution from the linear response is too small to allow for a correction of opposite sign from second-order response.

We can only speculate upon the reasons for this partial failure. For the siliconlike examples, it is clear that some Fourier components are beyond the convergence criterion for gradient corrections [$|\nabla n|/(2k_F n) < 1$]. The corrections should perhaps have been cutoff whenever the gradient of the density exceeds this limit. In this way, the results for Si and SiX would have improved, but not by much, and not in the cases of $M1$ and $M2$. The reason is thus more profound.

We have argued that the real-space method does not require us to stay with potentials that can be treated within low-order response theory. Nevertheless, one should emphasize that the whole gradient procedure relies on the existence of a convergent perturbation series. Accurate results are thus obtainable from finite-order perturbation theory, albeit of a very high order. It should thus be possible to expand physical properties around the origin of a parameter λ describing the strength of the potential. Most likely, this is not a valid assumption. This does not mean that physical properties are not analytic functions of the strength parameter λ . It means that the radius of convergence of a Taylor series around zero potential is smaller than the value where, e.g., a band gap occurs. Physical properties might still be, and probably are, analytic functions of λ . As an example of a similar situation, we remind the reader of the well-known theorem by Kohn

and Majumdar²⁴ stating that the charge density induced by an impurity in a metallic system remains analytic as a function of the strength of the impurity even beyond the point where a bound state is pulled down from the continuum. Again the density can, however, not be described as a Taylor series around the origin of the strength of the impurity. The point is illustrated in Fig. 1 showing the total energy per unit cell of a solid of noninteracting electrons as a function of the strength of the lattice potential. From the total energy, E , which in this noninteracting case is just the sum of the one-electron eigenvalues, has been subtracted the contributions from zero-, E_0 , first-, E_1 , second-, E_2 , and third-order, E_3 , perturbation theory. Displayed in the curve is the difference $\Delta E = E - E_0 - E_1 - E_2 - E_3$. We would thus expect ΔE to start out as V^4 which really is the case up to $V \sim 0.05$. Beyond this point perturbation theory appears to break down. Of course, one could not exclude the possibility that higher-order perturbation theory would make the curve turn around. Knowing, however, that a band gap opens up at $V \sim 0.05$ it is much more tempting to blame the apparent breakdown of perturbation theory on this fact. The failure of perturbation theory in connection with band gaps should, in principle, also affect the accuracy of our results for metals—especially in the cases with many electrons per unit cell. This problem is, however, expected to be less severe in metals, as discussed by Harrison²⁵, and is indeed so in the case of our calculations (Sec. III). We conclude this section with the remark that the appearance of band gaps must somehow be accounted for in the response functions in order to deal with the problems discussed in this section.

VI. SUMMARY AND CONCLUSIONS

The aim of the present work has been to construct gradient corrections to the local-density approximation for exchange energies of itinerant electrons in solids. For this purpose we have exposed the electron gas to weak and slowly varying periodic potentials, and we have calculated the resulting exact exchange energies. By varying the strength of the potentials, gradient terms originating in different orders of perturbation theory can be discerned. A further decompo-

sition of the exchange energy into contributions from density components at different wavelengths leads to the possibility of identifying individual gradient terms and to determine their coefficients. In this way we have obtained the coefficient of the gradient correction $\int n^{-3} |\nabla n|^2 \nabla^2 n$. Our coefficient is consistent with the result previously obtained by us⁷ in a study of second-order response functions. Unfortunately, the proposed method relies on having access to extremely accurate exchange energies (errors of $< 10^{-5}$). In this work, the accuracy has not been quite high enough to allow for a more accurate determination of coefficients in comparison with previous work.

While staying within the slowly varying regime, we also increased the strengths of potentials and applied a more phenomenological approach. A sum of gradient terms have been fitted to reproduce exact exchange energies. Not surprisingly, coefficients obtained in the fitting procedure closely agree with those of more *ab initio* methods like the one above or in Ref. 7. We have given an explanation for why this is to be expected. Again, our accuracy is just good enough to corroborate previous results, but not to improve upon them. An important conclusion of the present work is, in our opinion, that a straightforward gradient expansion gives us the possibility of calculating exchange-energies of metallic *s-p* bonded systems with an extraordinary accuracy, a few mRy per electron. This accuracy is an order of magnitude better than that of presently available generalized gradient approxi-

mations. Our investigation shows, however, that the accuracy is reduced by an order of magnitude when the same technique is applied to semiconducting systems. It is then found to be better to include only gradients originating in linear response theory. In that case, the accuracy becomes comparable to that of existing GGA's. We have hinted at the cause of the problem, and suggested ways to remedy the situation.

Another important aspect of this work is the possibility of including correlation energies within the same framework. Assuming that we are able to calculate accurate exchange-correlation energies of perturbed electron gases, we could apply the same fitting schemes as used here, in order to obtain accurate gradient approximations for exchange and correlation energies. What we have in mind is either using Monte Carlo techniques or many-body perturbation theory for calculating correlation energies. We stress, however, that the problem of correlations is inherently more difficult than the problem associated with exchange energies. With correlations included there is an additional length scale in the system given by the screening length, i.e., the inverse of the Thomas-Fermi wave vector, k_{TF} . As a consequence, gradient corrections should be cutoff at smaller values of the local-density gradient. Another consequence is that the coefficients of gradient terms no longer are dimensionless constants, but weakly density dependent functions. We will return to these problems in a future publication.

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