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1996 J. Phys.: Condens. Matter 8 6337

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# From the density-functional theory to ‘density-free’ approximation schemes; a one-particle-ensemble formalism

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Received 7 March 1996

**Abstract.** On the basis of some principles of the theory of density functionals, we obtain a fully specified ensemble of eigenstates of an effective (one-body) Hamiltonian whose average energy is identical to the ground-state *total energy* of the interacting system. It is shown that within the present framework accurate approximation schemes can be devised through which the ground-state total energy is obtained by the knowledge of two quantities only, the *average* density of the electrons, and the external potential.

## 1. Introduction

The density-functional theory (DFT) of Hohenberg and Kohn [1] allows rigorous determination of the ground-state properties of interacting systems. For instance, since [1] the ground-state energy is a functional of the electronic density  $n$ , denoted by  $E_v[n]$ , with  $E_v[n]$  achieving its lowest value at the exact ground-state charge density, minimization of  $E_v[n]$  not only provides the ground-state total energy, but also the exact ground-state electronic density. For systems of spin-compensated electrons the absolute minimum of  $E_v[n]$  is unique and thus  $n$  uniquely determines the ground-state wave function. In this way Hohenberg and Kohn [1] have shown that *all* ground-state properties are uniquely determined by  $n$ . In this paper we shall restrict our considerations to systems of spin-compensated electrons. Generalization of our formalism for dealing with other systems [2–6] is straightforward.

As an explicit exact form for  $E_v[n]$  is unknown, practical applications of the DFT are entirely based upon approximation schemes. Due to the sensitivity of the kinetic energy contribution  $T[n]$  to  $E_v[n]$ , straightforward approximations of  $E_v[n]$  have not proved satisfactory. A fruitful way of obtaining simple yet reliable approximations for  $E_v[n]$  in a fixed external potential has been provided by the formalism of Kohn and Sham [7]. In this,  $E_v[n]$  is decomposed as  $E_v[n] = T_s[n] + E_{ext}[n] + E_H[n] + E_{xc}[n]$  (we suppress here the inter-ionic interaction energy), in which  $T_s[n]$  stands for the kinetic energy of the set of fictitious particles in the ground state of the Kohn–Sham Hamiltonian,  $E_{ext}[n]$  for the explicitly expressible electrostatic energy of the electrons due to the external potential,  $E_H[n]$  for the electrostatic Hartree energy, and  $E_{xc}[n]$  for the so-called exchange–correlation energy; this latter contribution is in fact *defined* by the above expression for  $E_v[n]$ . In

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the scheme of Kohn and Sham,  $T_s[n]$ , which captures the essential aspects of  $T[n]$ , is evaluated exactly. Approximations of  $E_{xc}[n]$  have had less severe invalidating effects upon the calculated results than those of  $T_s[n]$ . For instance, whereas the local-density approximation (LDA) [1, 7] as applied to  $E_{xc}[n]$  yields relatively accurate results for many ground-state properties of real systems, its application to  $T_s[n]$  (the outcome being the Thomas–Fermi approximation [8] to  $T_s[n]$ ) is known to yield even fundamentally incorrect results in many instances (see, e.g., [9]).

The price to be paid for the advantages of the Kohn–Sham formalism is not low, as it involves a self-consistent solution of a non-linear partial differential equation, the Kohn–Sham equation. Roughly speaking, i.e. disregarding many technical advances made in recent years (for a review see [10]), the amount of computation time required for the self-consistent solution of the Kohn–Sham equation pertaining to a system of  $N_a$  atoms scales as  $N_a^3$ . This is substantial as compared with  $N_a$ , with which the computation time would scale were the explicit form of  $E_v[n]$  known. For this reason in the past, in particular in recent years, a considerable amount of effort has been put into obtaining accurate explicit expressions for  $T_s[n]$  (see [11–15]; see also chapter 5 in [16]). As an explicit expression for  $T_s[n]$  makes use of the Kohn–Sham formalism unnecessary [17], the methods dealing with these (approximate) expressions are collectively referred to as ‘orbital-free’ methods (‘orbital’ here refers to a Kohn–Sham orbital). The approach in this paper considers the problem at hand from an entirely different viewpoint. In short, we consider here  $E_v[n]$  in its entirety and *not* in terms of its constituent parts according to the decomposition scheme of Kohn and Sham. Based upon the formalism that results from this approach, a class of approximation schemes can be devised to which we refer as ‘density-free’ schemes, for in these schemes no explicit use is made of the ground-state charge density. What these schemes yield is the ground-state total energy corresponding to a given atomic configuration. Thus, in terms of the simplicity of calculations, our (approximate) quantum-mechanical schemes are comparable with those based upon the classical interatomic-force models. Further, the expression for  $E_v[n]$  that we present in this paper takes explicit account of one essential aspect of the exact  $E_v[n]$  that stands in the way of straightforward approximation of  $E_v[n]$ , when for this  $T_s[n] + E_{ext}[n] + E_H[n] + E_{xc}[n]$  is employed. This concerns a singularity in the dielectric response function of the uniform electron gas, as a function of a wavelength in the deviation of the exact charge density from a constant value, that renders a direct gradient expansion of  $E_v[n]$  (or of  $T_s[n]$ ) fundamentally invalid (see, e.g., [15]).

The formalism presented in this paper is also of some formal interest as it amounts to introduction of a completely specified ensemble of eigenstates of an effective Hamiltonian whose average energy is identical to the ground-state total energy of the interacting system. Like the Kohn–Sham theory [7], in the present formalism an effective Hamiltonian is shown to reproduce a property pertaining to the ground state of the fully interacting system. However, contrary to the Kohn–Sham case in which for the standard instance of a non-interacting  $v$ -representable charge density it is only the *ground state* of the effective Hamiltonian that determines the ground-state charge density of the interacting system, in our case *in principle* the entire set of eigenstates of the effective Hamiltonian contribute, in a ‘statistical’ sense, to the ground-state total energy of the interacting system. Another aspect in which the two formalisms differ is that whereas in the Kohn–Sham formalism with each interacting electron a fictitious particle is associated, each corresponding to one of the  $N_e$  eigenfunctions of the Kohn–Sham Hamiltonian with lowest eigenvalues, in the present formalism the number of fictitious ‘particles’ (associated with the eigenfunctions of our effective Hamiltonian, as forming the ensemble in question) is not equal to  $N_e$ , but to the dimension of the representation space of the effective Hamiltonian.

The general plan of this paper is as follows. In section 2 we present our theory, and in section 3 we give its underlying details. Based upon the proposed approach, in section 4 we present the relevant ingredients for application of our formal method within the framework of the perturbation theory, the perturbation here being the external potential multiplied by a constant in the range of 0 to 1. In subsections 4.1 and 4.2 we apply the zeroth- and first-order perturbation theories, and in subsection 4.3 we outline how in principle the perturbative incorporation of the effects of the external potential can be carried through to any arbitrary order. In section 5 we present and discuss some numerical results pertaining to a quasi-one-dimensional inhomogeneous system obtained through application of the schemes presented in this paper. Although in this paper we frequently make reference to the LDA scheme—we even explicitly make use of this scheme in section 5—our entire proposed strategy is independent of any approximation method. We end this paper with a summary and some concluding remarks in section 6.

## 2. Theory

Consider a system of  $N_e$  interacting electrons moving in the field of the external potential  $v_{ext}(\mathbf{r})$ . The ground state of this system, according to Hohenberg and Kohn [1], is a functional of the electronic density  $n$ ;  $n(\mathbf{r}) = \langle \Psi_0 | \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}(\mathbf{r}) | \Psi_0 \rangle$ , in which  $|\Psi_0\rangle$  denotes the ground state and  $\hat{\Psi}^\dagger$ ,  $\hat{\Psi}$ , are creation and annihilation field operators. This functional, denoted by  $E_v[n]$ , through neglecting the inter-ionic interaction energy can be written as

$$E_v[n] = \int d^3r v_{ext}(\mathbf{r})n(\mathbf{r}) + F[n] \quad (1)$$

in which (we use Hartree atomic units throughout)

$$F[n] \equiv \langle \Psi_0 | \left\{ \int d^3r \hat{\Psi}^\dagger(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 \right] \hat{\Psi}(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}^\dagger(\mathbf{r}') v_c(\mathbf{r} - \mathbf{r}') \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \right\} | \Psi_0 \rangle \quad (2)$$

is explicitly independent of  $v_{ext}$  (i.e., it is universal [1]);  $v_c(\mathbf{r} - \mathbf{r}') \equiv 1/|\mathbf{r} - \mathbf{r}'|$  stands for the Coulomb interaction function. With  $|\Psi_0^{(\lambda)}\rangle$  the ground state pertaining to the system in the field of the external potential  $v_{ext}^{(\lambda)}(\mathbf{r}) \equiv \lambda v_{ext}(\mathbf{r})$ , and  $n^{(\lambda)}(\mathbf{r})$  the corresponding charge density ( $n$  is thus short for  $n^{(\lambda=1)}$ ), through application of the Hellmann–Feynman theorem one obtains [18, 19]

$$\frac{dE_v[n^{(\lambda)}]}{d\lambda} = \int d^3r v_{ext}(\mathbf{r})n^{(\lambda)}(\mathbf{r}). \quad (3)$$

Upon integration of both sides of equation (3) with respect to  $\lambda$  over  $[0, 1]$ , we obtain

$$E_v[n] = E_v[n^{(0)}] + \int d^3r v_{ext}(\mathbf{r})n_{eff}(\mathbf{r}) \quad (4)$$

in which  $E_v[n^{(0)}]$  is the ground-state energy of the uniform electron gas and

$$n_{eff}(\mathbf{r}) \equiv \int_0^1 d\lambda n^{(\lambda)}(\mathbf{r}). \quad (5)$$

With  $n^{(0)}$  independent of  $\mathbf{r}$  (thus for simplicity we exclude Wigner crystallization), we have  $E_v[n^{(0)}] = T_{TF}[n^{(0)}] + E_{xc}^{LDA}[n^{(0)}]$ , in which  $T_{TF}[n] \equiv \frac{3}{10}(3\pi^2)^{2/3} \int d^3r n^{5/3}(\mathbf{r})$  stands for the Thomas–Fermi kinetic energy functional [8] and

$$E_{xc}^{LDA}[n] \equiv \int d^3r \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r}) \quad (6)$$

for the LDA of the exchange–correlation energy functional—these do *not* imply approximation in our scheme, since  $n^{(0)}$  is assumed constant—with  $\epsilon_{xc}(n)$  the exchange and correlation energy per electron of the uniform electron gas at density  $n$ . Accurate interpolating expressions [20, 21] for this quantity based upon quantum Monte Carlo results [22] at different electronic densities are now available.

Suppose now that  $\lambda$  is varied to  $\lambda + d\lambda$ . As  $n^{(\lambda)}$  is a functional of  $v_{ext}^{(\lambda)}$ , to linear order in  $d\lambda$  for the change in  $n^{(\lambda)}(\mathbf{r})$  we have

$$\int d^3r' \chi^{(\lambda)}(\mathbf{r}, \mathbf{r}') [v_{ext}^{(\lambda+d\lambda)}(\mathbf{r}') - v_{ext}^{(\lambda)}(\mathbf{r}')] ]$$

which leads to

$$dn^{(\lambda)}(\mathbf{r})/d\lambda = \int d^3r' \chi^{(\lambda)}(\mathbf{r}, \mathbf{r}') v_{ext}(\mathbf{r}').$$

Here  $\chi^{(\lambda)}(\mathbf{r}, \mathbf{r}')$  stands for the density–density correlation function of the *interacting* system in the force field of the external potential  $v_{ext}^{(\lambda)}$ , defined as  $\chi^{(\lambda)}(\mathbf{r}, \mathbf{r}') \equiv \delta n^{(\lambda)}(\mathbf{r})/\delta v_{ext}^{(\lambda)}(\mathbf{r}')$ . Upon twice integrating the expression for  $dn^{(\lambda)}(\mathbf{r})/d\lambda$  with respect to  $\lambda$ , we obtain  $n_{eff}(\mathbf{r})$ . Thus using equations (4) and (5), while exchanging orders of the  $\mathbf{r}$ - and  $\lambda$ -integrations, we arrive at

$$E_v[n] = E'_v[n^{(0)}] + \int d^3r d^3r' v_{ext}(\mathbf{r}) \chi_{eff}(\mathbf{r}, \mathbf{r}') v_{ext}(\mathbf{r}') \quad (7)$$

in which

$$\chi_{eff}(\mathbf{r}, \mathbf{r}') \equiv \int_0^1 d\lambda (1 - \lambda) \chi^{(\lambda)}(\mathbf{r}, \mathbf{r}') \quad (8)$$

and

$$\begin{aligned} E'_v[n^{(0)}] &\equiv E_v[n^{(0)}] + n^{(0)} \int d^3r v_{ext}(\mathbf{r}) \\ &= \left\{ \frac{3}{10} \left( \frac{3\pi^2 N_e}{\Omega_c} \right)^{2/3} + \epsilon_{xc}(N_e/\Omega_c) + \tilde{v}_{ext}(\mathbf{G} = \mathbf{0}) \right\} N_e. \end{aligned} \quad (9)$$

Here  $\Omega_c$  stands for the volume of the system and  $\tilde{v}_{ext}(\mathbf{G})$  for a Fourier component of the external potential (for our conventions concerning the Fourier transforms, see [23]);  $\mathbf{G}$  denotes a reciprocal-lattice vector corresponding to the underlying Bravais lattice. On the basis of the fact that  $\chi^{(\lambda)}$  is negative semi-definite (in the space of non-constant functions it is negative definite) [24, 25], and that for  $\lambda \in [0, 1]$ ,  $(1 - \lambda)$  is non-negative, we conclude from equation (7) that  $E_v[n] \leq E'_v[n^{(0)}]$ ; strict inequality holds when  $v_{ext}(\mathbf{r})$  is not constant—as indicated, for constant  $v_{ext}$  the second term is vanishing. The expression presented in equation (7), in combination with that in equation (8), is the central result of this paper.

Since  $\chi_{eff}$  is real and symmetric, it can be described by the following spectral representation:

$$\chi_{eff} = \sum_s \gamma_s |s\rangle \langle s| \quad (10)$$

in which  $|s\rangle$  is a normalized eigenvector of  $\chi_{eff}$  with  $\gamma_s$  the corresponding eigenvalue. Thus equation (7) can be written in the alternative form

$$E_v[n] = E'_v[n^{(0)}] + \sum_s \gamma_s |\xi_s|^2 \quad (11)$$

in which

$$\xi_s \equiv \langle v_{ext} | s \rangle. \quad (12)$$

Here  $v_{ext}(\mathbf{r}) = \langle \mathbf{r} | v_{ext} \rangle$ .

Now let us define the following effective Hamiltonian

$$\widehat{\mathcal{H}} \equiv \sum_s e_s |s\rangle \langle s| \quad (13)$$

in which

$$e_s \equiv \langle v_{ext} | v_{ext} \rangle \gamma_s. \quad (14)$$

Since  $\sum_s |\xi_s|^2 = \langle v_{ext} | v_{ext} \rangle$ , with

$$q_s \equiv \frac{|\xi_s|^2}{\langle v_{ext} | v_{ext} \rangle} \quad (15)$$

it is clear that

$$\widehat{\rho} \equiv \sum_s q_s |s\rangle \langle s| \quad (16)$$

is a density operator. Equation (11) can therefore alternatively be written as

$$E_v[n] = E'_v[n^{(0)}] + \text{Tr}(\widehat{\rho} \widehat{\mathcal{H}}). \quad (17)$$

Thus we have succeeded in obtaining an ensemble of eigenstates of an effective Hamiltonian (i.e.  $\widehat{\mathcal{H}}$ ) of which the energy is identical to the ground-state total energy of the many-body Hamiltonian. The wavefunction associated with each member of the present ensemble is  $\phi_s(\mathbf{r}) = \langle \mathbf{r} | s \rangle$ . Because  $\gamma_s \leq 0$  (in the space of non-vanishing functions with zero average,  $\gamma_s < 0$ ), it is clear that  $e_s \leq 0$  (or  $e_s < 0$ ). Note that as  $e_s$  is equal to a constant multiple of  $\gamma_s$ , for all  $s$ , the constant being  $c \equiv \langle v_{ext} | v_{ext} \rangle$ , we have  $\widehat{\mathcal{H}} = c \chi_{eff}$ .

Before ending this section, let us enumerate three features that we consider most appealing of the result in equation (7). First, because of  $(1 - \lambda)$  in equation (8), whose magnitude for  $\lambda \in [0, 1]$  decreases with increasing  $\lambda$ , the present formalism de-emphasizes the contributions of the most inhomogeneous states (corresponding to  $\lambda \sim 1$ ) to the ground-state total energy  $E_v[n]$ . Second,  $E_v[n]$  in equation (7) has an *explicit* quadratic dependence upon the external potential, implying that for reasonably weak external potentials it gives accurate energies even by taking for  $\chi_{eff}$  the one pertaining to the uniform electron gas. And finally, the failure of *ordinary* gradient expansions for  $E_v[n]$ , obtained through the gradient expansions for  $T_s[n]$  in  $T_s[n] + E_{ext}[n] + E_H[n] + E_{xc}[n]$ , has been ascribed to the logarithmic singularity in the density–density response function of the uniform electron gas, i.e. the Lindhard function, rendering a Taylor expansion in ‘powers’ of the gradient of the charge density formally inapplicable (see, e.g., [15]). Even when  $\chi_{eff}$  is replaced by the one pertaining to the uniform electron gas, the expression in equation (7) takes full account of this singularity (see in particular subsection 4.1 below).

### 3. Details

We devote this section to details concerning  $\chi^{(\lambda)}$  and  $\chi_{eff}$ . When no confusion arises, we suppress  $\lambda$  in  $\chi^{(\lambda)}$  and the related functions. We also assume that all calculations are being carried out within the framework of the DFT. In this way by ‘the non-interacting system’ we mean the system of the Kohn–Sham particles.

We present most results below in the momentum representation for crystals (see [23]). We shall indicate the momentum representation of the quantities by means of placing a tilde over their symbols in the abstract notation. Further, in the following we need to work not only with  $\chi$ , but also with its inverse  $\chi^{-1}$ . However, since  $\chi$  (as well as  $\chi_0$ , to be introduced below) has a vanishing eigenvalue corresponding to a constant eigenvector [25], it is required that the inverse be defined in the space of functions orthogonal to this eigenvector, i.e. the space of functions with zero average value. This will be assumed throughout.

The density–density correlation function for the fully interacting system,  $\chi$ , is obtained from that of the non-interacting system,  $\chi_0$ , as follows:

$$\chi = (I - \chi_0 C)^{-1} \chi_0 \quad (18)$$

in which

$$C \equiv v_c + K_{xc}. \quad (19)$$

In the coordinate representation we have  $K_{xc}(\mathbf{r}, \mathbf{r}'; [n]) \equiv \delta^2 E_{xc}[n]/(\delta n(\mathbf{r})\delta n(\mathbf{r}')) = \delta v_{xc}(\mathbf{r}; [n])/\delta n(\mathbf{r}')$ , in which  $v_{xc}(\mathbf{r}; [n])$  stands for the exchange–correlation potential. The latter is part of the effective potential  $v_{eff}(\mathbf{r}; [n]) \equiv v_{ext}(\mathbf{r}) + v_H(\mathbf{r}; [n]) + v_{xc}(\mathbf{r}; [n])$ , with  $v_H(\mathbf{r}; [n]) \equiv \int d^3 r' v_c(\mathbf{r} - \mathbf{r}')n(\mathbf{r}')$ , the Hartree potential, in the Kohn–Sham equation [7], i.e.

$$\left[ -\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}; [n]) \right] \Psi_i(\mathbf{r}) = \varepsilon_i \Psi_i(\mathbf{r}). \quad (20)$$

The exact functional form for  $K_{xc}[n]$  is not known. For uniform systems, however, an accurate expression for  $K_{xc}[n]$  based upon a combination of numerical and exact results has recently been proposed [25]. Using equation (6) we have

$$\begin{aligned} K_{xc}^{LDA}(\mathbf{r}, \mathbf{r}'; [n]) &= \kappa_{xc}(n(\mathbf{r})) \delta(\mathbf{r} - \mathbf{r}') \\ \kappa_{xc}(n(\mathbf{r})) &\equiv \frac{d\mu_{xc}(n(\mathbf{r}))}{dn(\mathbf{r})} \end{aligned} \quad (21)$$

in which  $\mu_{xc}(n) \equiv v_{xc}^{LDA}(n) = d(n\varepsilon_{xc}(n))/dn$  stands for the LDA exchange–correlation potential. In the momentum representation for a periodic system we have [23]

$$(\tilde{K}_{xc}^{LDA}[n])_{\mathbf{G}, \mathbf{G}'} = \tilde{\kappa}_{xc}(\mathbf{G} - \mathbf{G}'; [n]). \quad (22)$$

For uniform systems  $(\tilde{K}_{xc}^{LDA}[n])_{\mathbf{G}, \mathbf{G}'}$  is diagonal, with the diagonal elements equal to  $\tilde{\kappa}(0; [n])$ , for *all*  $\mathbf{G}$ . Contrary to this, within the framework of the exact DFT  $\tilde{K}_{xc}(q; [n])$  has a non-trivial dependence upon momentum  $q$ ; thus although for a uniform system  $(\tilde{K}_{xc}[n])_{\mathbf{G}, \mathbf{G}'}$  is also diagonal, the diagonal elements  $\tilde{K}_{xc}(q = |\mathbf{G}|; [n])$  are different for different  $|\mathbf{G}|$ . In this connection it should be noted that by definition

$$\tilde{K}_{xc}(q; [n]) \rightarrow \tilde{K}_{xc}^{LDA}[n] \quad \text{for } q \rightarrow 0.$$

From figure 9 in [25] it appears that replacing  $\tilde{K}_{xc}^{LDA}[n]$  by  $\tilde{K}_{xc}(q; [n])$ , as far as  $\tilde{\chi}(q; [n])$ —and thus  $\tilde{\chi}_{eff}(q)$ —is concerned, is most important for  $q$  in the vicinity of  $q = 2q_F$  (see

[26]). Observing that pseudopotentials are most dominant in this region [29], incorporation of  $\tilde{K}_{xc}(q; [n])$  in the calculations may lead to non-negligible improvements of the total-energy results in comparison with those according to the LDA (see [27]).

In terms of the time Fourier transform of the single-particle Green function pertaining to the Kohn–Sham (KS) system,  $G_{KS}(\mathbf{r}, \mathbf{r}'; \varepsilon)$ , we have

$$\chi_0(\mathbf{r}, \mathbf{r}'; [n]) = 2 \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi i} G_{KS}(\mathbf{r}, \mathbf{r}'; \varepsilon) G_{KS}(\mathbf{r}', \mathbf{r}; \varepsilon) \quad (23)$$

in which  $[n]$  in the argument of  $\chi_0$  indicates the charge density associated with the Kohn–Sham system. The factor 2 on the right-hand side accounts for the spin degeneracy of the Kohn–Sham one-particle states. It can be shown that like  $\chi$ ,  $\chi_0$  is negative semi-definite [24, 25]. In the space of non-vanishing functions with zero average value,  $\chi_0$  is negative definite.

#### 4. Approximation schemes

In the following two subsections two approximation schemes within the framework of the theory presented in section 2, which make use of the perturbation theory, will be introduced and discussed. In subsection 4.3 we sketch a generalization of these two schemes.

Before discussing these methods, it may be of interest to mention that as there are already a number of simplified but accurate expressions for  $\chi$  available (see [28]), one may consider employing these, rather than the perturbatively determined  $\chi$ s that will be presented below. However, these models may not be directly applicable, as all of the reliable models for  $\chi$  require an *a priori* knowledge of some exact properties of the system, such as the value for the average gap in the excitation spectrum and/or the ground-state charge-density profile. One of these models is due to Penn [30], which is specifically suited for dealing with semiconductors, as it takes account of the gap in the elementary excitations of these materials. A more recent model is due to Levine and Louie (see [31]), which has extensively been used in the calculations of the self-energy operator with the aim of evaluating the quasi-particle energies in semiconductors and insulators. For completeness, in [33] Car *et al* provide a quantitative analysis of the properties of a number of model response functions.

##### 4.1. A scheme based upon the zeroth-order perturbation theory

In the momentum representation, from equations (18) and (19) we obtain

$$\tilde{\chi}(q; [n]) = \frac{\tilde{\chi}_0(q; [n])}{1 - \{\tilde{v}_c(q) + \tilde{K}_{xc}(q; [n])\}\tilde{\chi}_0(q; [n])} \quad (24)$$

in which  $\tilde{v}_c(q) = 4\pi/q^2$ , and  $\tilde{\chi}_0(q; [n])$  is the well-known Lindhard function,

$$\tilde{\chi}_0(q; [n]) = -\frac{3n}{q_F^2} \left\{ \frac{1}{2} + \frac{q_F}{2q} \left( 1 - \frac{q^2}{4q_F^2} \right) \ln \left| \frac{q + 2q_F}{q - 2q_F} \right| \right\} \quad (25)$$

with  $q_F \equiv (3\pi^2 n)^{1/3}$  the Fermi wave number corresponding to the (constant) density  $n$ . Since  $\tilde{\chi}(q; [n])$  does not depend upon  $v_{ext}$ ,  $\tilde{\chi}_{eff}(q)$  is obtained immediately; with  $\int_0^1 d\lambda (1 - \lambda) = 1/2$  we have

$$\tilde{\chi}_{eff}(q) = \frac{1}{2} \tilde{\chi}(q; [n^{(0)}]). \quad (26)$$



We shall denote this function by  $\tilde{\chi}_{eff;u}(q)$ , with ‘u’ referring to the uniform electron gas. Thus, from equation (7) up to and including the second order in  $v_{ext}$  we have (see [23])

$$E_v[n] = E'_v[n^{(0)}] + \Omega_c \sum_{\mathbf{G}} \tilde{\chi}_{eff;u}(|\mathbf{G}|) |\tilde{v}_{ext}(\mathbf{G})|^2. \quad (27)$$

This expression is identical to that obtained earlier by Heine and Weaire [32].

It is obvious that calculation of the ground-state total energy according to equation (27) only requires knowledge of the total number of the electrons in the system,  $N_e$  (determining  $n^{(0)} = N_e/\Omega_c$ ), and the Fourier components of the external potential. This will remain so in the improved scheme to be presented in the following subsection. Finally, for the effective Hamiltonian  $\hat{\mathcal{H}}$  within the present approximate framework we have  $\hat{\mathcal{H}} = c\chi[n^{(0)}]/2$  (for  $c$  see the text following equation (17) above).

#### 4.2. A scheme based upon the first-order perturbation theory

In this subsection we shall present a formalism according to which  $\chi_0$  and  $C$  (see equation (18) above) are approximated to linear order in the external potential, but if desired these first-order corrections can *easily* be taken into account to infinite order in the calculation of  $\chi_{eff}$  (note the inversion involved in the expression for  $\chi$  in equation (18)). The external potential with which we shall be working in this subsection will be assumed to have zero average value [34].

It is known that for a *constant* external potential, and not too low charge densities (to exclude Wigner crystallization), the exchange and correlation potential is also constant (see, e.g., the appendix in [25]). By exposing this system to  $v_{ext}(\mathbf{r})$ , with  $\int d^3r v_{ext}(\mathbf{r}) = 0$ , to linear order in  $v_{ext}$  the change  $\delta n(\mathbf{r})$  in the charge density of the system with respect to  $n^{(0)}$  is obtained from

$$\delta n(\mathbf{r}) = \int d^3r' \chi_u(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}]) v_{ext}(\mathbf{r}'). \quad (28)$$

Again, to linear order in  $v_{ext}$  the *induced* potential (i.e., the potential besides  $v_{ext}$  itself) in the Kohn–Sham equation has the form

$$\int d^3r' [v_c(\mathbf{r} - \mathbf{r}') + K_{xc}(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}])] \int d^3r'' \chi_u(|\mathbf{r}' - \mathbf{r}''|; [n^{(0)}]) v_{ext}(\mathbf{r}'')$$

which is simply the *linear* variation of the Hartree potential  $v_H(\mathbf{r}; [n])$  in addition to that of the exchange–correlation potential. The term inside the square brackets is simply  $C(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}])$ , defined in equation (19). Thus for the *total* potential in the Kohn–Sham equation, correct to first order in  $v_{ext}$ , we have

$$v_{eff}(\mathbf{r}) = \int d^3r' \epsilon_{e,u}^{-1}(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}]) v_{ext}(\mathbf{r}')$$

(symbolically,  $v_{eff} = \epsilon_{e,u}^{-1} v_{ext}$ , or  $\tilde{v}_{eff}(q) = \tilde{\epsilon}_{e,u}^{-1}(q; [n^{(0)}]) \tilde{v}_{ext}(q)$ ), in which  $\epsilon_{e,u}^{-1} \equiv I + C\chi_u$  denotes the inverse of the so-called ‘electron’ dielectric function pertaining to the uniform electron gas with charge density  $n^{(0)}$ . This function is different from the inverse of the so-called ‘electron-test-charge’ dielectric function  $\epsilon_{TC;u}^{-1} \equiv I + v_c\chi_u$  (see [35]). It can easily be shown that  $\epsilon_e = I - C\chi_0$ . As we observe,  $v_{eff}$  is obtained through knowledge of  $n^{(0)} = N_e/\Omega_c$  and  $v_{ext}$ .

With the above-obtained  $v_{eff}$ , to linear order in  $v_{ext}$  (or  $v_{eff}$ ) for the single-particle Green function of the Kohn–Sham system we have  $G_{KS}(\mathbf{r}, \mathbf{r}'; \varepsilon) = G_0(|\mathbf{r} - \mathbf{r}'|; \varepsilon) + \int d^3r'' G_0(|\mathbf{r} - \mathbf{r}''|; \varepsilon) v_{eff}(\mathbf{r}'') G_0(|\mathbf{r}'' - \mathbf{r}'|; \varepsilon)$ , which follows from the first-order Born expansion of the

Dyson equation. In the momentum representation for a crystal this expression can be written as

$$G_{KS;G,G'}(\mathbf{q}; \varepsilon) = G_0(|\mathbf{q} + \mathbf{G}|; \varepsilon)\delta_{G,G'} + \tilde{v}_{eff}(\mathbf{G} - \mathbf{G}')G_0(|\mathbf{q} + \mathbf{G}|; \varepsilon)G_0(|\mathbf{q} + \mathbf{G}'|; \varepsilon) \quad (29)$$

in which  $G_0$  denotes the single-particle Green function of the uniform-electron-gas system. From this result, making use of equation (23), to linear order in  $v_{eff}$  we have

$$\chi_{0;G,G'}(\mathbf{q} = \mathbf{0}) = \tilde{\chi}_{0;u}(|\mathbf{G}|; [n^{(0)}])\delta_{G,G'} + 2\tilde{v}_{eff}(\mathbf{G} - \mathbf{G}') \int \frac{d^3k}{(2\pi)^3} I_{G,G'}(\mathbf{k}) \quad (30)$$

in which

$$I_{G,G'}(\mathbf{k}) \equiv J(|\mathbf{k} + \mathbf{G}|, |\mathbf{k} + \mathbf{G}'|, |\mathbf{k}|) + J(|\mathbf{k} - \mathbf{G}|, |\mathbf{k} - \mathbf{G}'|, |\mathbf{k}|) \quad (31)$$

with

$$J(q_1, q_2, q_3) \equiv \int \frac{d\varepsilon}{2\pi i} G_0(q_1; \varepsilon)G_0(q_2; \varepsilon)G_0(q_3; \varepsilon). \quad (32)$$

Making use of

$$G_0(q; \varepsilon) = \left\{ \frac{\Theta(q_F - q)}{\varepsilon - q^2/2 - i\eta} + \frac{\Theta(q - q_F)}{\varepsilon - q^2/2 + i\eta} \right\} \quad \eta \downarrow 0 \quad (33)$$

with  $q \equiv |\mathbf{q}|$ , and the residue theorem, we easily obtain

$$J(q_1, q_2, q_3) = 4 \left\{ \begin{aligned} & \frac{\Theta(q_F - q_1)\Theta(q_F - q_2)\Theta(q_3 - q_F)}{(q_2^2 - q_3^2)(q_3^2 - q_1^2)} \\ & - \frac{\Theta(q_1 - q_F)\Theta(q_2 - q_F)\Theta(q_F - q_3)}{(q_2^2 - q_3^2)(q_3^2 - q_1^2)} \\ & + \frac{\Theta(q_F - q_1)\Theta(q_2 - q_F)\Theta(q_F - q_3)}{(q_3^2 - q_2^2)(q_2^2 - q_1^2)} \\ & - \frac{\Theta(q_1 - q_F)\Theta(q_F - q_2)\Theta(q_3 - q_F)}{(q_3^2 - q_2^2)(q_2^2 - q_1^2)} \\ & + \frac{\Theta(q_F - q_1)\Theta(q_2 - q_F)\Theta(q_3 - q_F)}{(q_2^2 - q_1^2)(q_3^2 - q_1^2)} \\ & - \frac{\Theta(q_1 - q_F)\Theta(q_F - q_2)\Theta(q_F - q_3)}{(q_2^2 - q_1^2)(q_3^2 - q_1^2)} \end{aligned} \right\}. \quad (34)$$

Using this result, the 3-momentum integral in equation (30) can be evaluated fully analytically (the result will be presented elsewhere).

As for  $K_{xc}(\mathbf{r}, \mathbf{r}'; [n^{(0)} + \delta n])$ , to linear order in  $\delta n$  we have

$$K_{xc}(\mathbf{r}, \mathbf{r}'; [n^{(0)} + \delta n]) = K_{xc}(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}]) + \int d^3r'' \left. \frac{\delta K_{xc}(\mathbf{r}, \mathbf{r}'; [n])}{\delta n(\mathbf{r}'')} \right|_{n=n^{(0)}} \delta n(\mathbf{r}''). \quad (35)$$

Within the LDA, for the last term in this expression one has the following simple form

$$\int d^3r'' \left. \frac{\delta K_{xc}(\mathbf{r}, \mathbf{r}'; [n])}{\delta n(\mathbf{r}'')} \right|_{n=n^{(0)}} \delta n(\mathbf{r}'') = \kappa'_{xc}(n^{(0)}) \delta n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \quad (36)$$

$$\kappa'_{xc}(n) \equiv \frac{d^2\mu_{xc}(n)}{dn^2}$$

which will be the result to be employed in the absence of any better alternative (recall that  $K_{xc}(|\mathbf{r} - \mathbf{r}'|; [n^{(0)}])$  does not need to be replaced by, say, its LDA counterpart—see subsection 4.1). In the momentum representation we have the following hybrid [36] expression:

$$(\tilde{K}_{xc}[n^{(0)} + \delta n]_{G,G'}) = \tilde{K}_{xc}(|\mathbf{G}'|; [n^{(0)}])\delta_{G,G'} + \kappa'_{xc}(n^{(0)})\delta\tilde{n}(\mathbf{G} - \mathbf{G}'). \quad (37)$$

For  $\delta n(\mathbf{r})$  in equation (36) we employ the result given in equation (28), so that we have

$$\delta\tilde{n}(\mathbf{G} - \mathbf{G}') = \tilde{\chi}_u(|\mathbf{G} - \mathbf{G}'|; [n^{(0)}])\tilde{v}_{ext}(\mathbf{G} - \mathbf{G}') \quad (38)$$

in which  $\tilde{\chi}_u(q = |\mathbf{G} - \mathbf{G}'|; [n^{(0)}])$  is given in equation (24).

Having obtained both  $\chi_0$  and  $C$  to first order in  $v_{ext}$  (equations (30), (19) and (35)), we now proceed with determining  $\chi$ . To this end we first write  $\chi_0^{(\lambda)} = \chi_0^{(0)} + \lambda\delta\chi_0 + \mathcal{O}(\lambda^2)$  and  $C^{(\lambda)} = C^{(0)} + \lambda\delta C + \mathcal{O}(\lambda^2)$ . From the Dyson-type equation  $\chi = \chi_0 + \chi_0 C \chi$  (see equation (18)) we obtain  $\chi^{-1} = \chi_0^{-1} - C$  and consequently  $\chi = (\chi_0^{-1} - C)^{-1}$ . Thus with  $\chi_0^{(\lambda)} = \chi_0^{(0)} + \lambda\delta\chi_0 = \chi_0^{(0)}(I + \lambda\chi_0^{(0)-1}\delta\chi_0)$  we have  $\chi_0^{(\lambda)-1} = (I + \lambda\chi_0^{(0)-1}\delta\chi_0)^{-1}\chi_0^{(0)-1} = \chi_0^{(0)-1} - \lambda\chi_0^{(0)-1}\delta\chi_0\chi_0^{(0)-1} + \mathcal{O}(\lambda^2)$ , so  $\chi_0^{(\lambda)-1} - C^{(\lambda)} = [\chi_0^{(0)-1} - C^{(0)}] - \lambda[\delta C + \chi_0^{(0)-1}\delta\chi_0\chi_0^{(0)-1}] + \mathcal{O}(\lambda^2)$ . In this way we arrive at the following symmetric expression:

$$\chi^{(\lambda)} = -(-[\chi_0^{(0)-1} - C^{(0)}] + \lambda[\delta C + \chi_0^{(0)-1}\delta\chi_0\chi_0^{(0)-1}])^{-1} + \mathcal{O}(\lambda^2). \quad (39)$$

The first term inside the parentheses is  $-\chi^{(0)-1}$ , and is thus symmetric and positive (semi-)definite. In fact since  $-\chi^{(0)-1}$  pertains to the uniform electron gas ( $\lambda = 0$ ), it is diagonal in the momentum representation. We write

$$-[\chi_0^{(0)-1} - C^{(0)}] = D^{1/2}D^{1/2} \quad (40)$$

which defines the (diagonal) matrix  $D$  (see [37]). Thus  $\chi^{(\lambda)}$  to first order in  $\lambda$  can be written as

$$\chi^{(\lambda)} = -D^{-1/2}(I + \lambda\mathcal{F})^{-1}D^{-1/2} \quad (41)$$

in which

$$\mathcal{F} \equiv D^{-1/2}(\delta C + \chi_0^{(0)-1}\delta\chi_0\chi_0^{(0)-1})D^{-1/2}. \quad (42)$$

Since both  $\chi_0^{(0)}$  and  $D^{1/2}$  are diagonal in the momentum representation, their inverses are readily obtained. The desired  $\chi^{(\lambda)}$ , correct to first order in  $v_{ext}$ , is thus

$$\chi^{(\lambda)} = \chi^{(0)} + \lambda D^{-1/2}\mathcal{F}D^{-1/2} \quad (43)$$

from which we obtain the first-order result

$$\chi_{eff} = \frac{1}{2}\chi^{(0)} + \frac{1}{6}D^{-1/2}\mathcal{F}D^{-1/2}. \quad (44)$$

Note the three-times-smaller pre-factor of the second term on the right-hand side of this expression, as compared with that of the first term; the pre-factor of the  $m$ th-order contribution amounts to  $1/(m^2 + 3m + 2)$ , the quadratic decrease with respect to increasing  $m$ , rather than a linear one, being a direct consequence of  $(1 - \lambda)$  in the defining expression for  $\chi_{eff}$  (see equation (8) above).

The operator  $\mathcal{F}$  is symmetric. Let therefore  $\{|\ell\rangle\}$  denote the complete set of eigenfunctions of  $\mathcal{F}$  with  $\{v_\ell\}$  the corresponding eigenvalues. By completeness (i.e.  $\sum_\ell |\ell\rangle\langle\ell| = I$ ) we can write

$$I + \lambda\mathcal{F} = \sum_\ell (1 + \lambda v_\ell)|\ell\rangle\langle\ell|. \quad (45)$$

Consequently, we have

$$(I + \lambda\mathcal{F})^{-1} = \sum_{\ell} \frac{1}{1 + \lambda v_{\ell}} |\ell\rangle\langle\ell|. \quad (46)$$

Thus from equation (41) it follows that

$$\chi^{(\lambda)} = \sum_{\ell} \frac{-1}{1 + \lambda v_{\ell}} |\ell\rangle\langle\ell| \quad (47)$$

in which

$$|\ell\rangle \equiv D^{-1/2} |\ell\rangle. \quad (48)$$

Since  $\chi^{(\lambda)}$  must be negative (semi-) definite, from equation (47) we deduce that the validity of a first-order expansion is, strictly speaking, limited to cases in which  $v_{\ell} > -1$ , for all  $\ell$ .

From equations (8) and (47) we obtain

$$\chi_{eff} = \sum_{\ell} \alpha_{\ell} |\ell\rangle\langle\ell| \quad (49)$$

in which

$$\alpha_{\ell} \equiv \int_0^1 d\lambda \frac{(\lambda - 1)}{1 + \lambda v_{\ell}} = \frac{1}{v_{\ell}} - \left( \frac{1}{v_{\ell}} + \frac{1}{v_{\ell}^2} \right) \ln |1 + v_{\ell}|. \quad (50)$$

The non-perturbative nature of the above result for  $\chi_{eff}$  is apparent. Even if the eigenvalues  $\{v_{\ell}\}$  in equation (50) are determined perturbatively, rather than by exact diagonalization of  $\mathcal{F}$ , this result retains its non-perturbative nature and therefore, on general grounds, is more accurate than that obtained by *direct* perturbative determination of  $\chi_{eff}$  (equation (44)). The numerical results, to be presented in section 5, clearly confirm the validity of this statement. The first-order result given in equation (44) follows from the more general expression given in equation (49) simply through employing the first-order expansion of  $1/(1 + \lambda v_{\ell})$ , i.e.  $1 - \lambda v_{\ell}$ , in equation (46), from which it follows that  $\alpha_{\ell} = -\frac{1}{2} + \frac{1}{6} v_{\ell}$ . By comparison of the expression in equation (49) and that in equation (10), we observe that within the present approximation scheme  $\alpha_{\ell} \Leftrightarrow \gamma_s$  and that  $|s\rangle \Leftrightarrow |\ell\rangle$ . With  $\phi_{\ell}(\mathbf{r}) \equiv \langle \mathbf{r} | \ell \rangle$ , and  $\tilde{\phi}_{\ell}(\mathbf{G})$  a corresponding Fourier component, we have  $\xi_{\ell} = \Omega_c^{1/2} \sum_{\mathbf{G}} \tilde{\phi}_{\ell}(\mathbf{G}) \tilde{v}_{ext}(\mathbf{G})$  (see [23]). From this, making use of equation (11),  $E_v[n]$  is readily obtained.

The amount by which  $v_{\ell}$  deviates from zero is a direct measure for the importance of the inhomogeneity in the system. As a result, the amount by which  $\alpha_{\ell}$ , or indeed  $\gamma_s$ , deviates from  $-\frac{1}{2}$  (see equation (50)) reflects the effects of  $v_{ext}$  upon the behaviour of the system. Further, like  $\gamma_s$ ,  $\alpha_{\ell}$  should be negative. A positive  $\alpha_{\ell}$  signals failure of the first-order perturbation theory as employed in this subsection.

Finally, the use of the perturbation theory does not need to be limited to taking the state corresponding to  $\lambda = 0$  (the uniform electron gas) as the unperturbed state. Indeed, any other state, corresponding to  $\lambda = \lambda_0 \neq 0$ , also qualifies for being chosen as 'unperturbed' (perturbation then amounts to  $v_{ext}^{(\lambda)} - v_{ext}^{(\lambda_0)}$ ). Such a choice may be advantageous, since for reasons related to the symmetry of the ground state use of the state corresponding to  $\lambda_0 \rightarrow 0$  may yield more accurate value for  $E_v[n]$  than that corresponding to  $\lambda_0 = 0$  (in section 5 this is shown to be indeed the case). In such cases, exact, as opposed to perturbative, evaluation of  $\chi^{(\lambda_0)}$  within, e.g., the LDA is practicable even for very complex systems: for  $\lambda_0 \rightarrow 0$ , the number of plane waves for representing the Kohn–Sham Hamiltonian and wavefunctions ( $\{\psi_i(\mathbf{r})\}$ )—see equation (20) above) can be very limited (see [38]).

### 4.3. A scheme based upon an arbitrary-order perturbation theory

The application of the method of obtaining a closed expression for  $\chi^{(\lambda)}$ , without the need for an explicit inversion of  $I + \lambda\mathcal{F}$ , is not restricted to the case in which  $C$  and  $\chi_0$  are expanded to first order in  $v_{ext}$ , as indeed a straightforward generalization of the method employed above is possible. In the following we shall assume that the  $\chi^{(\lambda)-1}$ s, as obtained by lower-order perturbation expansions (i.e., lower than the desired order), are all like the exact  $\chi^{(\lambda)-1}$  negative definite; a non-negative definite  $\chi^{(\lambda)-1}$  for some order of the perturbation theory and a range of values of  $\lambda$  signals failure of the perturbation theory in that order for the mentioned range of values of  $\lambda$ . Within the present general scheme, the effective Hamiltonian  $\widehat{\mathcal{H}}$  presented in equation (13) is also directly obtained. We restrict our analysis here to the case in which  $\chi^{(\lambda)-1}$  has been evaluated to second order in  $v_{ext}$ ; generalization to other orders is trivial.

Suppose  $\chi^{(\lambda)} = (A_0 + \lambda A_1 + \lambda^2 A_2)^{-1} + \mathcal{O}(\lambda^3)$ , in which for clarity of presentation we have introduced the symmetric operators  $A_0$ ,  $A_1$  and  $A_2$  ( $A_0$  and  $A_1$  can be deduced from equation (39)). As stated, we assume  $A_0 + \lambda A_1$  to be negative definite for all  $\lambda$ ,  $\lambda \in [0, 1]$ . It is easily verified that  $\chi^{(\lambda)} = (-[A_0 + \lambda A_1])^{-1/2}(I + \lambda^2(-[A_0 + \lambda A_1])^{-1/2}A_2(-[A_0 + \lambda A_1])^{-1/2})^{-1}(-[A_0 + \lambda A_1])^{-1/2} + \mathcal{O}(\lambda^3)$ . Since as far as  $\chi^{(\lambda)-1}$  is concerned we are interested in the result correct to second order in  $v_{ext}$ , we can equally write

$$\chi^{(\lambda)} = (-[A_0 + \lambda A_1])^{-1/2}(I + \lambda^2(-A_0)^{-1/2}A_2(-A_0)^{-1/2})^{-1}(-[A_0 + \lambda A_1])^{-1/2} + \mathcal{O}(\lambda^3).$$

Thus from the spectral representation for  $\mathcal{F}' \equiv (-A_0)^{-1/2}A_2(-A_0)^{-1/2}$ , and that of  $A_0 + \lambda A_1$ , which is assumed to have already been calculated, the explicit  $\lambda$ -dependence of  $\chi^{(\lambda)}$  is obtained. In this way the  $\lambda$ -integral in the expression for  $\chi_{eff}$  can be evaluated analytically. For non-negative definite  $A_0 + \lambda A_1$ ,  $[-(A_0 + \lambda A_1)]^{-1/2}$ , if not singular, is essentially complex valued. Finally, the matrices  $A_0$ ,  $A_1$ , etc, do not need to be evaluated through application of the perturbation theory; these can be identified as the appropriate coefficients of a polynomial interpolation of  $\chi^{(\lambda)-1}$ , with  $\chi^{(\lambda)-1}$  being evaluated exactly at a number of small values for  $\lambda$ . As stated earlier, direct evaluation of  $\chi^{(\lambda)-1}$  for small values of  $\lambda$  is computationally not demanding.

## 5. Some numerical results

We have applied the formalism presented in this paper to a quasi-one-dimensional model of an inhomogeneous electronic system. This is a generalization of a model originally introduced by Sham, Schlüter and Lannoo [39], and is employed subsequently by several authors. For details concerning the self-consistent LDA calculations for this model we refer the reader to [19]. The Kohn–Sham equation dealt with in this section has the form  $[-\frac{1}{2}d^2/dx^2 + v_{eff;\alpha}(x; [\bar{n}])]\Psi_i(x) = \varepsilon_i\Psi_i(x)$ , in which  $v_{eff;\alpha}(x; [\bar{n}]) \equiv \int d^2r_{\perp} \Phi_{\alpha}^2(\mathbf{r}_{\perp})v_{eff}(\mathbf{r}; [n])$ , with  $\Phi_{\alpha}^2(\mathbf{r}_{\perp}) \equiv (\alpha^2/\pi)\exp(-\alpha^2r_{\perp}^2)$ ; here  $r_{\perp}^2 \equiv y^2 + z^2$ , with  $y$  and  $z$  the remaining Cartesian coordinates of  $\mathbf{r}$ . For the calculations of this section we have chosen  $\alpha = 2.513$ . In what follows we shall suppress the bar on  $n$ , i.e. henceforth  $n$  will denote  $n(x)$  rather than  $n(\mathbf{r})$ . For the external potential in our calculations we have chosen  $v_{ext}(x) = A\cos(2\pi x/a_c)$  (notice that  $\tilde{v}_{ext}(G = 0) = 0$ ), which defines  $a_c$  as the length of the unit cell of the periodic system under consideration; the results to be presented below pertain to  $a_c = 5$  au. For  $A$  we have chosen the following five values:  $A = 0.05, 0.1, 0.15, 0.3, 0.5$  (Hartree). We have assumed that there are two electrons per unit cell of our system, implying one filled band in the ground state of the Kohn–Sham

system. Taking into account that the width of the valence band in the present calculations varies in the range 0.15–0.2 Hartree, it is clear that the values for  $A$  considered here represent a very wide range of inhomogeneities. All of the LDA quantities employed here have been obtained from exact expressions [19], except  $K_{xc}^{LDA}[n]$  which we have obtained through use of a finite-difference method; the relative change in the amplitude of  $n$  that we have used amounts to  $10^{-9/2}$ . As a check for the accuracy of our results, we have carried out an explicit calculation of  $E_v[n]$  according to equation (7)—with the  $\lambda$ -integration involved in the calculation of  $\chi_{eff}$  (see equation (8)) evaluated by means of a 10-point Gauss–Chebyshev quadrature method. For the case corresponding to  $A = 0.15$  we have obtained  $-0.519\,299$  hartrees per electron, to be compared with  $-0.519\,305$  which has been obtained through the standard Kohn–Sham approach. For the Thomas–Fermi kinetic energy functional, as required for the evaluation of  $E'_v[n^{(0)}]$  (see the text following equation (5)), in the present model we have [19]  $T_{TF}[n] \equiv (\pi^2/24) \int_{-L_c/2}^{L_c/2} dx n^3(x) \rightarrow (\pi^2/24)(N_e/L_c)^2 N_e$  for the constant density  $n = n^{(0)} = N_e/L_c$ , in which  $L_c$  stands for the length of the system (the equivalent of  $\Omega_c$ ).

The calculations that we have carried out have been based upon both the zeroth-order perturbation theory as considered in subsection 4.1, and the first-order perturbation theories discussed in subsection 4.2; we have considered both the case in which  $(I + \lambda\mathcal{F})^{-1}$  is replaced by  $I - \lambda\mathcal{F}$  (method I), and the case in which  $(I + \lambda\mathcal{F})^{-1}$  is fully incorporated through use of the spectral representation as given in equation (46) (method II). As mentioned in subsection 4.2, method I amounts to approximating  $\alpha_\ell$  as given in equation (50) by  $-\frac{1}{2} + \frac{1}{6}\nu_\ell$ . Clearly, the zeroth-order results follow from further approximating  $\alpha_\ell$  by  $-\frac{1}{2}$ . For the purpose of the present zeroth-order calculations we have employed for  $\tilde{\chi}_0$  and  $\tilde{K}_{xc}$  (see equation (24)) those calculated at a finite but small value of  $\lambda$ ; for this, denoted by  $\lambda_0$ , we have chosen two different values,  $\lambda_0 = 0.0302$ , and  $0.01$  [40]. For the first-order calculations, we have determined  $\delta C$  and  $\delta\chi_0$  through the finite-difference expression  $\delta Y = [Y^{(\lambda_1)} - Y^{(\lambda_0)}]/(\lambda_1 - \lambda_0)$ , in which  $Y^{(\lambda)}$  stands for either  $C^{(\lambda)}$  or  $\chi_0^{(\lambda)}$ . For  $\lambda_0, \lambda_1$  we have chosen two sets of values,  $\lambda_0 = 0.0302, \lambda_1 = 1.001\lambda_0$ , and  $\lambda_0 = 0.01, \lambda_1 = 1.01\lambda_0$ . For each value of  $A$  we have also carried out self-consistent calculations with the Kohn–Sham equation and obtained in this way the total energies which we refer to as ‘Exact’. We have carried out all of the calculations by making use of two sets of plane-wave basis functions, one consisting of 5 plane waves and the other of 11 plane waves (see [41]). The results of the two calculations agree with each other to at least 1 part in  $10^5$ .

In table 1 we present the zeroth-order results for the total energies and  $\Delta E_v[n] \equiv E_v[n] - E'_v[n^{(0)}]$ —see equation (7). For comparison, for each value of  $A$  we present also the ‘Exact’ results. It is  $\Delta E_v[n]$  that gives the contribution of the external potential to the total energy. Consequently, in order to observe more clearly the relevance of  $\Delta E_v[n]$  as calculated perturbatively, we also present the *relative deviations* of  $\Delta E_v[n]$  with respect to the Exact values, i.e.  $\delta E_v[n] \equiv (\Delta E_{v;\text{Exact}}[n] - \Delta E_v[n])/\Delta E_{v;\text{Exact}}[n]$ . It appears that in all of the cases considered, the perturbatively determined total energies are *lower* than the Exact values; this trend is opposite to that corresponding to the results obtained within the framework of the first-order perturbation theory to be discussed below. From the data in table 1 it is easily deduced that for the cases corresponding to  $\lambda_0 = 0.0302$ , the relative deviations in the perturbative values for the *total* energies vary between  $-2.25$  and  $-0.01\%$  of the Exact results; for the cases corresponding to  $\lambda_0 = 0.01$ , for this range we have  $-2.86$  to  $-0.02\%$ . These results are clearly very encouraging.

In table 2 we compare the results for the total energies and  $\Delta E_v[n]$ s as obtained by methods I and II. Here we also present the *relative deviations*  $\delta E_v[n]$  of the  $\Delta E_v[n]$ s, as

**Table 1.** Ground-state total energies (in units of hartrees per electron) obtained through use of the zeroth-order perturbation theory along with the contributions due to the inhomogeneity of the external potential (i.e.,  $\Delta E_v[n] \equiv E_v[n] - E'_v[n]$ ). The relative deviations,  $\delta E_v[n]$ , of  $\Delta E_v[n]$  with respect to the exact results (indicated by ‘Exact’) are also presented; these ‘Exact’ results are obtained through application of the standard Kohn–Sham formalism. The  $K_{xc}$  and  $\chi_0$  employed (see equation (24)) are  $K_{xc}^{(\lambda)}$  and  $\chi_0^{(\lambda)}$ , evaluated at  $\lambda = \lambda_0$ ; the un-enclosed entries correspond to  $\lambda_0 = 0.0302$ , and those enclosed inside parentheses to  $\lambda_0 = 0.01$ . The calculations have been carried out within a basis of five plane waves.

A	$E_v[n]$	$\Delta E_v[n]$	$\delta E_v[n]$	Exact	
				$E_v[n]$	$\Delta E_v[n]$
0.05	-0.511 83 (-0.511 85)	-0.001 06 (-0.001 08)	-0.06 (-0.08)	-0.511 77	-0.001 00
0.1	-0.514 94 (-0.515 03)	-0.004 17 (-0.004 27)	-0.07 (-0.10)	-0.514 65	-0.003 88
0.15	-0.520 05 (-0.520 29)	-0.009 29 (-0.009 52)	-0.09 (-0.11)	-0.519 30	-0.008 54
0.3	-0.547 16 (-0.548 30)	-0.036 39 (-0.037 53)	-0.12 (-0.15)	-0.543 30	-0.032 53
0.5	-0.610 04 (-0.613 67)	-0.099 27 (-0.102 90)	-0.16 (-0.20)	-0.596 60	-0.085 84

**Table 2.** Ground-state total energies (in units of hartrees per electron) according to methods I and II (see the text) which are based upon the first-order perturbation theory. The contributions to the total energies due to the inhomogeneity of the external potential,  $\Delta E_v[n]$ , as well as the relative deviations of these,  $\delta E_v[n]$ , with respect to the Exact values are also given. The required  $\delta C$  and  $\delta \chi_0$  (see equation (39)) have been obtained through direct calculations of  $C^{(\lambda)}$  and  $\chi_0^{(\lambda)}$  at  $\lambda_0 = 0.0302$ ,  $\lambda_1 = 1.001\lambda_0$  (un-enclosed entries) and  $\lambda_0 = 0.01$ ,  $\lambda_1 = 1.01\lambda_0$  (entries enclosed by parentheses). The calculations have been carried out within a basis of 5 plane waves. For comparison with the Exact results, see table 1.

Method I			
A	$E_v[n]$	$\Delta E_v[n]$	$\delta E_v[n]$
0.05	-0.511 60 (-0.511 30)	-0.000 83 (-0.000 53)	0.17 (0.47)
0.1	-0.513 85 (-0.512 49)	-0.003 08 (-0.001 72)	0.21 (0.56)
0.15	-0.517 33 (-0.514 04)	-0.006 57 (-0.003 27)	0.23 (0.62)
0.3	-0.534 02 (-0.518 84)	-0.023 25 (-0.008 07)	0.29 (0.75)
0.5	-0.567 52 (-0.520 50)	-0.056 75 (-0.009 73)	0.34 (0.89)
Method II			
A	$E_v[n]$	$\Delta E_v[n]$	$\delta E_v[n]$
0.05	-0.511 67 (-0.511 53)	-0.000 90 (-0.000 76)	0.10 (0.25)
0.1	-0.514 21 (-0.513 66)	-0.003 44 (-0.002 89)	0.11 (0.26)
0.15	-0.518 29 (-0.517 05)	-0.007 52 (-0.006 28)	0.12 (0.26)
0.3	-0.539 15 (-0.534 23)	-0.028 38 (-0.023 46)	0.13 (0.28)
0.5	-0.585 59 (-0.572 18)	-0.074 82 (-0.061 42)	0.13 (0.28)

calculated according to methods I and II, with respect to the exactly evaluated  $\Delta E_v[n]$ s. From this table three immediate conclusions can be drawn: first, that method II is more reliable than method I—in particular notice that  $\delta E_v[n]$  according to method II is almost independent of A, unlike  $\delta E_v[n]$  according to method I; second, that within the framework of the first-order perturbation theory, method II, with  $\lambda_0 = 0.0302$ , accounts for about 90% of the total contribution of the inhomogeneous part of the external potential to the total energy; and finally, that it is important that  $\lambda_0$  is not chosen too small, a point to which we have referred in subsection 4.2. It is essential to mention that the difference between the

results based upon  $\lambda_0 = 0.0302$  and  $\lambda_0 = 0.01$  is *not* a consequence of the correspondingly different values for  $\lambda_1$ , as this only accounts for deviations less than 5 parts in  $10^6$ .

From table 2 the relative errors in the *total energies* (in relation to the Exact ones) according to method I are seen to range from 0.03% to 4.87%, for the cases corresponding to  $\lambda_0 = 0.0302$ ; 0.09% to 12.76%, for those corresponding to  $\lambda_0 = 0.01$ . According to method II for these ranges we have 0.02–1.84%, and 0.05–4.09%, corresponding to, respectively,  $\lambda_0 = 0.0302$  and  $\lambda_0 = 0.01$ . These are to be compared with the above-mentioned ranges as obtained through use of the zeroth-order perturbation theory. It appears that for  $A$  between 0 and approximately 0.3 the zeroth-order results are closer to the Exact results than the first-order results are [42]. This should not cause concern, as there is no *a priori* reason why the perturbation series under consideration should converge *uniformly*. Moreover, for  $A \gtrsim 0.3$  the results based upon method II turn out to be more accurate than those based upon the zeroth-order perturbation theory.

Since our calculations have only involved non-metallic systems, we may only reasonably compare the above-mentioned accuracies with those achieved by other approximate methods pertaining to semiconductors or insulators. Wang and Teter [12] present, amongst other things, two sets of results for the total energies of bulk Si in the diamond structure, as obtained from their first- and second-order expressions for  $T_s[n]$ ; see tables 1 and 2 in [12], in which in addition results obtained through the use of other approximate expressions for  $T_s[n]$  can be found. Taking the ratio of the LDA direct-band-gap energy to the LDA value for the valence bandwidth as a measure for characterizing a semiconductor, we can compare the results in these tables with our present results pertaining to  $A = 0.1$ . The relative errors in the *total energies* as calculated using the first- and second-order formulae of Wang and Teter, making use of the self-consistent Kohn–Sham charge density, amount to (the un-enclosed numbers are from table 1 in [12] and are obtained through use of some ‘smooth’ pseudopotential, while those enclosed by parentheses are from table 2 in [12] and correspond to some ‘sharp’ pseudopotential): 5.16% (2.96%) and 1.09% (0.72%), respectively; using a variational charge density, rather than the self-consistent Kohn–Sham one, leads to 3.24% (2.78%), and 0.45% (4.82%), respectively. These values should be compared with  $-0.06\%$ ,  $-0.07\%$  (if the zeroth-order perturbation theory is used, with  $\lambda_0 = 0.0302$  and  $\lambda_0 = 0.01$ , respectively), 0.16% (if method I is used with  $\lambda_0 = 0.0302$ ), 0.09% (method II,  $\lambda_0 = 0.0302$ ), 0.42% (method I,  $\lambda_0 = 0.01$ ), and 0.19% (method II,  $\lambda_0 = 0.01$ ). Although our presented results are obtained within the framework of the zeroth- and first-order perturbation theories (method II, however, incorporates some contributions to infinite order), these are by 1–2 order(s) of magnitude more accurate than those by Wang and Teter. For a precise comparison of the methods it is of course necessary that the calculations be performed on identical systems.

In table 3 we present the eigenvalues of  $\widehat{\mathcal{H}}$  corresponding to the external potential with  $A = 0.15$  Hartree, as calculated according to methods I and II. We present here also the weights  $\varrho_s$  of the corresponding eigenfunctions in the ensemble of which the average energy is equal to the ground-state total energy (the weights are identical for both of the *first-order* methods). The results in this table have been obtained within a space of 5 plane waves, and for making the inverses of  $\chi$  and  $\chi_0$  meaningful at appropriate instances we have worked within a four-dimensional subspace. One immediate feature that this table brings out is that almost the entire ensemble energy (i.e.  $\Delta E_v[n]$ ) is determined by the eigenstate of  $\widehat{\mathcal{H}}$  corresponding to the largest but one eigenvalue. This eigenvalue, moreover, does not seem to be sensitive to the dimensionality of the representation space: our calculation within a space spanned by 11 plane waves results in  $\varrho_{s=10} = 0.65959$ . Although this value is not quite equal to 0.65946 (see table 3), the values of other  $\varrho_s$ s and



**Table 3.** The eigenvalues of  $\widehat{\mathcal{H}}$ , i.e.  $\{e_s\}$  (in units of hartrees per electron), calculated according to methods I and II, and the weights of the eigenfunctions of  $\widehat{\mathcal{H}}$ , i.e.  $\{\varrho_s\}$ , in the ensemble of which the average energy is equal to the ground-state total energy of the interacting system (see section 2). The amplitude of the external potential  $A$  is chosen equal to 0.15 Hartree. The  $\delta C$  and  $\delta\chi_0$  employed have been derived through direct calculations at  $\lambda_0 = 0.0302$  and  $\lambda_1 = 1.001\lambda_0$  (for detailed specifications see the text, or table 2). For the calculations a basis of 5 plane waves has been employed.

$s$	$e_s$ (method I)	$e_s$ (method II)	$\varrho_s$
1	-0.014 64	-0.014 62	0.0
2	-0.013 45	-0.013 54	0.000 87
3	-0.010 79	-0.011 81	0.0
4	-0.009 94	-0.011 39	0.659 46
5	0.0	0.0	0.339 67

$e_s$ ,  $s$  corresponding to  $s = 1, 2, \dots, 9$ , are such that the ensemble energy  $\Delta E_v[n]$  within the accuracy of our calculations retains the value corresponding to the 5-plane-wave basis set. Furthermore, within the larger basis all of the eigenstates  $|s\rangle$  turn out to be either exactly or nearly doubly degenerate, and interestingly, in each multiplet of (nearly) degenerate states, only *one* of the two  $\varrho_s$  turns out to be non-vanishing. This apparent redundancy in the dimensionality of the representation space, at least as far as the value for  $\Delta E_v[n]$  is concerned, is computationally a very attractive feature. In particular it is important that the dominant contributions to  $\Delta E_v[n]$  are due to those single-particle states (i.e.  $|s\rangle$ ) that correspond to the few *smallest*  $|\varrho_s|$ s: problems involving a subspace of eigenvectors whose eigenvalues are near one of the extrema of the eigenvalues are easily handled by means of the Lanczos method [43], especially when the eigenproblem concerns a band matrix (recall that  $\widehat{\mathcal{H}}$  is a band matrix).

Further investigation of the formalism presented in this paper will be subject of our future work. In particular we will investigate to what extent the conclusions arrived at in this paper are model independent.

## 6. Summary and concluding remarks

In this paper we have derived an expression for the ground-state total energy of an interacting system that consists of two contributions: one that is determined entirely by the average value of the charge density in the system, and the other that is only non-vanishing if the external potential deviates from a constant. At a first glance, the most interesting aspect of this second contribution is that it has an *explicit* quadratic dependence upon the external potential so that an  $m$ th-order perturbation expansion with respect to the external potential of the kernel in this contribution (i.e.,  $\chi_{eff}$ ) gives rise to an  $m + 2$ nd-order expression for the ground-state total energy. More importantly, by employing the available ‘exact’ results for the uniform-electron-gas system obtained through the quantum Monte Carlo calculations, our expression yields total energies that in so far as the electron–electron interaction effects are concerned are ‘exact’ up to and including the second order in the external potential.

Furthermore, we have provided an exact mapping of the Hamiltonian of a fully interacting system onto an effective one, of which a well-specified ensemble of eigenvectors has an energy identical to the ground-state total energy of the fully interacting system. In a way our result shows similarities with the result that one obtains formally by applying

the Hubbard–Stratonovich transformation [44] to the partition function pertaining to an interacting system. Here one also obtains an *effective* Hamiltonian that contains terms that couple to some fluctuating auxiliary fields. We recall that the eigenfunctions of  $\chi$  are directly related to the fluctuation of electronic charge (plasmons) in an interacting system [45]. We have not investigated whether formally one can relate the two mappings by taking a zero-temperature limit of the grand potential as obtained from the functional-integral representation of the partition function to which the Hubbard–Stratonovich transformation has been applied. If indeed such a formal link between the two transformations can be established, it will then be of interest to investigate whether such a connection can be of use in obtaining novel controlled approximation techniques for evaluating the functional-integral representation for partition functions.

In applying the perturbation theory within the present formalism, we encounter a coupling-constant integration over the strength of the external potential, i.e. over the  $\lambda$ . As this coupling constant occurs in the inverse of some operator (cf. equation (41)), one may consider approximating this inverse operator by a series expansion that is truncated at the same order in  $\lambda$  as the order of the perturbation expansion employed for the operator in question (cf. equation (43)). Although a valid approach, we have shown that it is not necessary to proceed in this way: through employing a spectral representation for the operator concerned (cf. equation (46)), the required coupling-constant integral can be evaluated exactly, giving rise to a non-perturbative result that in real applications can prove valuable. Our numerical results in the previous section indicate this to be indeed the case. In view of our statement in the first paragraph of this section, it is clear that the thus-calculated non-perturbative terms also take into account some non-perturbative electron–electron interaction effects that can be incorporated '*exactly*' up to and including the second order in the external potential. We have presented the mathematical details leading to the above-mentioned non-perturbative result within the framework of the first-order perturbation theory and outlined the required procedure when a higher-than-first-order perturbation expansion is attempted. The effort for an exact evaluation of the above-mentioned coupling-constant integral amounts to one matrix diagonalization for each order of the perturbation theory. In the context of the present work this operation is not computationally demanding as it can be shown that in the momentum representation the matrices to be diagonalized are band matrices, with the bandwidths being determined directly, but not entirely, by the rate of decrease in the magnitude of the Fourier components of the *screened* external potential (i.e., in the magnitude of  $\tilde{v}_{eff}$ , as presented in the text following equation (28)) for increasing magnitudes of the reciprocal-lattice vectors. We have pointed out that even if the matrices to be diagonalized are diagonalized perturbatively, with their off-diagonal elements playing the role of the perturbations, the results for the ground-state total energy retain their non-perturbative character.

We should also point out that the procedure presented in this paper for obtaining an effective Hamiltonian with the above-mentioned property can equally well be applied to the case in which the coupling constant involved in the formalism (i.e.  $\lambda$ ) represents the strength of the electron–electron interaction, rather than that of the electron–ion interaction. The coupling-constant-integration method for obtaining the correlation part of the total energy [46] has, to the best of the present author's knowledge, only been applied to the uniform-electron-gas system. With the procedure presented in this paper (making use of the spectral representation of the appropriate operators), the required coupling-constant integral for the correlation energy corresponding to an inhomogeneous system can be evaluated explicitly and in this way one arrives at an effective Hamiltonian of which a well-specified ensemble of eigenvectors yields the correlation energy of the interacting system.

Although perturbation theory can fruitfully be employed within the framework of the formalism presented in this paper (with the external potential playing the role of the perturbation), we have indicated that use of some of the existing approximate expressions for the dielectric response function of inhomogeneous systems can be equally advantageous. On the other hand, since most of the reliable models for this function require an *a priori* knowledge concerning some other properties of the inhomogeneous system (such as the average value of the gap), use of such models is only feasible when the above-mentioned properties are in turn evaluated within the framework of the perturbation theory.

## Acknowledgments

The author would like to thank Professors Volker Heine and Lars Hedin for a discussion and Girton College, Cambridge, for partial support. The hospitality of Max-Planck-Institut für Festkörperforschung, Stuttgart, is gratefully acknowledged.

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- [27] From figure 5 in [25] in which  $\tilde{\chi}(q; [n])$  is displayed, one can observe the way in which different Fourier components of the external potential, within the present zeroth-order approximation of  $\chi_{eff}$ , contribute to the ground-state total energy.
- [28] In fact these expressions concern  $\epsilon_{TC}$  or  $\epsilon_{TC}^{-1}$ , but since  $\epsilon_{TC}^{-1} = I + v_c\chi$ —see subsection 4.2— $\chi$  can easily be deduced from these.
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- [35] This function, i.e.  $\epsilon_{TC}$ , determines the screened potential through which the electrons in the system interact; see, e.g., [25].
- [36] As one term in this expression is exact and the other a local approximation, we refer to this as a *hybrid* expression.
- [37] The procedure to be described does not depend upon  $D$  being diagonal;  $D$  must, however, be symmetric. Further, the transition from the homogeneous to inhomogeneous systems gives rise to  $D$  in the momentum representation transforming from a diagonal to a band matrix, the width of the band increasing in accordance with the number of non-vanishing Fourier components of the external potential. Note that for  $D$  not positive definite,  $D^{1/2}$  is essentially complex valued.
- [38] As the system is almost uniform, plane waves are an ideal choice for use as basis functions. When  $\lambda_0 \rightarrow 0$ , we propose that the results of explicit calculations within a small set of plane waves be complemented with the corresponding results pertaining to the uniform-electron-gas system in the following way. For definiteness, suppose we are dealing with  $\chi_0^{(\lambda_0)}$  which has explicitly been evaluated within a basis of  $N_{pw}$  plane waves. This  $N_{pw} \times N_{pw}$  matrix is *complemented* by considering it as a sub-matrix of a larger  $N \times N$  matrix, of which all entries *except* those pertaining to the  $N_{pw} \times N_{pw}$  sub-matrix *and* the diagonal elements are identically vanishing. In this larger matrix we propose the diagonal elements not belonging to the sub-matrix to be those of the uniform electron gas corresponding to the average charge density.
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- [41] The reciprocal-lattice vectors involved are of the form  $G_j^\pm = \pm 2\pi j/a_c$ , with  $j = 0, 1, 2$  in the first case and  $j = 0, 1, \dots, 5$ , in the second.
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