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Exchange–correlation correction to the dielectric function of the inhomogeneous electron gas

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Abstract. Exchange–correlation (XC) and band structure corrections to the dielectric matrix are investigated simultaneously within the framework of non-local density functional theory. The XC correction is calculated in the weighted density approximation and band structure effects are taken into account in second order in the pseudopotential. Particular attention is devoted to the question of whether or not the minimum in the plasmon dispersion in caesium is connected with the hump in the static structure factor of the homogeneous electron gas near $q = 2k_F$, as concluded in a previous paper using frequency–momentum analysis. It was found that such a hump may lead to anomalies (in alkaline metals most probably minima) at those q that are solutions of the equation $|G - q| = 2k_F$, where G is any reciprocal lattice vector and k_F is the Fermi momentum. In caesium, the location of the dominating minimum agrees with that of the experimental minimum, but its depth varies strongly for different homogeneous electron gas approximations.

1. Introduction

The random phase approximation (RPA) for the dielectric properties of the inhomogeneous electron gas (IHEG) gives satisfactory results for high densities and small wavevectors q (e.g. for optical properties of high-density simple metals and semiconductors). On the other hand, consideration of XC effects beyond the RPA within the homogeneous electron gas (HEG) model reveals a peak in the static structure factor near $q = 2k_F$ whose size differs in different treatments [1–7] and which is absent within the RPA. In principle the plasmon dispersion is a sensitive probe to XC effects, but the region $q \approx 2k_F$ is not accessible to the plasmon because it ceases to exist for $q > q_c$, the cut-off wavevector, which is of the order of k_F at metallic densities. Due to umklapp processes, however, this structure can influence the plasmon dispersion at small q . Therefore we have to consider XC effects and inhomogeneity simultaneously. In some previous work [8, 9] this has been done using frequency momentum analysis. In this way we obtained within the weighted density approximation (WDA) a simple formula for the centre of gravity of the loss function which illustrates the important role of umklapp processes. However, by frequency momentum analysis the frequency dependence of the dielectric function cannot be calculated explicitly. In the present paper we develop a theory for the dielectric

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function which goes over into the RPA in the high-density limit and is correct in the small- q and the large- q limit for vanishing inhomogeneity. This is achieved by using non-local density functional (DF) theory. Some previous treatments in the spirit of our goals used the local density approximation (LDA) [10, 11]. As shown below, this approximation fails qualitatively in some limiting cases.

We apply our theory to the plasmon dispersion of caesium which is a good candidate for pronounced XC effects because of its low valence electron density ($R_s = 5.62$). Indeed Cs exhibits a negative dispersion constant [25], which cannot be explained either within the RPA including the inhomogeneity or within the HEG model including XC effects. Instead both effects must be considered simultaneously.

This paper is organized as follows. In section 2 we review the theory of the dielectric function within DF theory, and in section 3 some approximations for the XC correction are discussed. The only one satisfying some rigorous constraints, namely the WDA, is applied in section 5 to the plasmon dispersion of caesium. In section 4 the calculation of the plasmon dispersion within second-order perturbation theory in the pseudopotential is described and in section 6 we summarize our results.

2. Non-local density functional theory of the exchange–correlation correction

2.1. Definitions

In linear response theory of the electron gas one has to distinguish between an external perturbation produced by a test charge (distinguishable from the electrons of the system) and by an electron (which causes exchange–correlation effects). Likewise, the particle that experiences the screened perturbation can be a test charge or an electron. We confine ourselves here to the case of a test charge as external perturbation. This includes electron loss spectroscopy, if the energy of the probe is so high that it may be considered as distinguishable from the sample electrons.

Thus we have one kind of external potential $\delta\Phi_{\text{ext}}(q)$ and two kinds of screened potentials $\delta\Phi_{\text{sc}}(q)$ and $\delta\Phi_{\text{sc}}^e(q)$, which act on test charges and electrons, respectively. Consequently we define two response functions

$$\delta n(q) = \sum_{q'} \alpha(q, q') \delta\Phi_{\text{ext}}(q') \quad \text{or} \quad \delta n = \alpha \delta\Phi_{\text{ext}} \quad (1)$$

$$\delta n(q) = \sum_{q'} \chi(q, q') \delta\Phi_{\text{sc}}^e(q') \quad \text{or} \quad \delta n = \chi \delta\Phi_{\text{sc}}^e. \quad (2)$$

The third possible relation which connects δn with $\delta\Phi_{\text{sc}}$ is not in general use. In the following we mainly use the matrix notation given on the right of (1) and (2). Response functions α, χ (and the later defined $\epsilon, \mathbf{F}, \mathbf{G}, \mathbf{V}$) denote matrices, whereas δn and $\delta\Phi$ are vectors. The q -sum runs over the fine mesh produced by periodic boundary conditions over the normalization volume \mathcal{V} . In case of lattice periodicity the sums over the fine q -mesh reduce to sums over reciprocal lattice vectors G and the arguments q, q' of the response functions have the form $k + G, k + G'$, where k lies within the first Brillouin zone.

Instead of α or χ , the system response can be characterized by dielectric matrices (DMs)

$$\delta\Phi_{\text{sc}} = \epsilon^{-1} \delta\Phi_{\text{ext}} \quad (3)$$

$$\delta\Phi_{\text{sc}}^e = (\epsilon^e)^{-1} \delta\Phi_{\text{ext}}. \quad (4)$$

Both DMs are appropriate for different physical quantities. Whereas ϵ can be applied to calculate phonons, optical properties (reflectivity etc) and loss functions for high-energy electrons and photons (Compton effect), ϵ^e has to be used for screened potentials which are to be inserted into the Schrödinger equation. In all these definitions the time or frequency dependence is not explicitly indicated.

2.2. Calculation of the dielectric matrices

The basic difference between $\delta\Phi_{sc}$ and $\delta\Phi_{sc}^e$ is that the latter comprises an induced XC potential having the form

$$\delta\Phi_{\mathbf{x}}(\mathbf{q}) = \sum_{\mathbf{q}'} F(\mathbf{q}, \mathbf{q}') \delta n(\mathbf{q}') \quad \text{or} \quad \delta\Phi_{\mathbf{x}} = \mathbf{F} \delta n. \quad (5)$$

In \mathbf{r} -space

$$\delta\Phi_{\mathbf{x}}(\mathbf{r}) = \int d\mathbf{r}' F(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}').$$

The matrix \mathbf{F} is determined below. Both quantities have in common the induced Hartree potential (atomic units $\hbar = m = e = 1$ are used)

$$\delta\Phi_{\text{H}}(\mathbf{q}) = (4\pi/q^2) \delta n(\mathbf{q}) \quad \text{or} \quad \delta\Phi_{\text{H}} = \mathbf{V} \delta n. \quad (6)$$

For convenience we defined a diagonal matrix \mathbf{V} with elements $v_q = 4\pi/q^2$. From their definition follows that

$$\delta\Phi_{sc} = \delta\Phi_{\text{ext}} + \delta\Phi_{\text{H}} \quad (7)$$

$$\delta\Phi_{sc}^e = \delta\Phi_{\text{ext}} + \delta\Phi_{\text{H}} + \delta\Phi_{\mathbf{x}} \quad (8)$$

and using (5) and (6)

$$\delta\Phi_{sc} = \delta\Phi_{\text{ext}} + \mathbf{V} \delta n. \quad (9)$$

$$\delta\Phi_{sc}^e = \delta\Phi_{\text{ext}} + (\mathbf{V} + \mathbf{F}) \delta n. \quad (10)$$

Inserting (1) into (9) and (10) and comparing with (3) and (4) we obtain

$$\epsilon^{-1} = \mathbf{I} + \mathbf{V}\alpha \quad (11)$$

$$(\epsilon^e)^{-1} = \mathbf{I} + (\mathbf{V} + \mathbf{F})\alpha. \quad (12)$$

Because not α but χ is directly computable (see below), it is desirable to express the dielectric matrices in terms of χ instead. This is realized by insertion of (2) into (9) and (10) and by comparing with (50) and (6). We find

$$\epsilon = \mathbf{I} - \mathbf{V}(\mathbf{I} - \chi\mathbf{F})^{-1}\chi \quad (13)$$

$$\epsilon^e = \mathbf{I} - (\mathbf{V} + \mathbf{F})\chi. \quad (14)$$

For $\mathbf{F} = 0$ (neglect of XC effects) ϵ and ϵ^e are identical. Furthermore, in the limit of an HEG all matrices are diagonal and commonly known expressions are retained. Frequently, the XC correction of the HEG is expressed in terms of

$$G^0(q) = -(1/v_q) F^0(q, q) \equiv -(1/v_q) F^0(q). \quad (15)$$

Calculations of the dielectric properties of atoms, surfaces and other non-bulk systems are usually performed at least partly in \mathbf{r} -space. All formulae can be adapted to the corresponding case by Fourier-transform of some coordinates in \mathbf{r} -space.

2.3. Calculation of χ and F

The input quantities to this theory are F and χ , which are directly accessible in DF theory. χ reads [12]

$$\chi(\mathbf{q}, \mathbf{q}', \omega) = \frac{1}{\mathcal{V}} \sum_{k, k'} \frac{f(E_k) - f(E_{k'})}{E_k - E_{k'} + \omega^+} \langle k | e^{-i\mathbf{q}\mathbf{r}} | k' \rangle \langle k' | e^{i\mathbf{q}'\mathbf{r}} | k \rangle \quad (16)$$

where $|k\rangle$ and E_k are one-particle wavefunctions and energies, respectively, evaluated in DF theory, k comprises all quantum numbers, $f(E)$ is the Fermi distribution function, and $\omega^+ = \omega + 0i$. According to DF theory χ as given by (16) is *exact* in the static limit. The reason is that for the definition (2) of χ we need only the induced density. But the density is well defined in DF theory, despite the fact that χ contains the auxiliary quantities $|k\rangle$ and E_k , which have rigorously speaking no direct physical meaning.

Now we turn to the determination of F . The XC potential is a functional of the density. The change $\delta\Phi_{\mathbf{x}}$ of this functional under a variation δn of the density can be expressed in terms of the functional derivative

$$\delta\Phi_{\mathbf{x}}(\mathbf{r}) = \int d\mathbf{r}' \frac{\delta\Phi_{\mathbf{x}}(\mathbf{r}')}{\delta n(\mathbf{r}')} \delta n(\mathbf{r}').$$

Comparison with (5) gives the result we are looking for [10]

$$F(\mathbf{r}, \mathbf{r}') = \frac{\delta\Phi_{\mathbf{x}}(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta^2 E_{\mathbf{x}}}{\delta n(\mathbf{r}') \delta n(\mathbf{r})}. \quad (17)$$

The second equality considers the fact that $\Phi_{\mathbf{x}}$ itself is a functional derivative of the XC energy $E_{\mathbf{x}}$.

Even if we would have the exact XC energy functional, (17) would be correct in the static limit $\omega = 0$ only. The inclusion of the ω dependence might be possible within the time-dependent DF scheme (see [13]), but it is not straightforward and easy. For a homogeneous system, however, there are interpolation procedures for the inclusion of the ω dependence ([13]). But these schemes cannot be applied to the off-diagonal elements of F , which provide here the main effect (see section 5).

3. Some approximations for F

3.1. Rigorous boundary conditions

As seen from (17), each XC energy functional $E_{\mathbf{x}}[n]$ generates an XC-correction function F . On the basis of several approximations for $E_{\mathbf{x}}[n]$ found in the literature (for reviews see e.g. [16]–[18]) we calculate in this section the corresponding XC correction $F(\mathbf{q}, \mathbf{q}')$ and investigate whether this approximation obeys certain rigorous conditions. For *bulk* systems we require that in the HEG limit the XC correction function $G^0(\mathbf{q})$ as defined in (15) satisfies conditions known from HEG theory [14], in particular

$$\lim_{q \rightarrow 0} G^0(\mathbf{q}) = \gamma_0(\mathbf{q}/k_F)^2 \quad (18)$$

$$\lim_{q \rightarrow \infty} G^0(\mathbf{q}) = [1 - g(0)] \quad (19)$$

where $g(r)$ is the pair correlation function of the HEG. For finite frequencies a factor $\frac{2}{3}$ has to be added on the right hand side of (19) [15], but for the sake of internal consistency this is not considered here because we treat the XC correction F in the static limit.

For metal surfaces we have an additional rigorous condition for F . For convenience we discuss it in \mathbf{r} space. The XC potential far outside the metal must approach the classical image potential

$$v_{\text{xc}}(z) = -1/4z$$

where z is the coordinate perpendicular to the surface. Consequently v_{xc} is independent of $n(\mathbf{r})$ and $F(\mathbf{r}, \mathbf{r}')$ vanishes because of (17).

$$\lim_{z \rightarrow \infty} F(\mathbf{r}, \mathbf{r}') = 0. \quad (20)$$

Furthermore according to (17) $F(\mathbf{r}, \mathbf{r}')$ satisfies the symmetry relation $F(\mathbf{r}, \mathbf{r}') = F(\mathbf{r}', \mathbf{r})$.

Far outside an *atom* the XC potential must approach

$$v_{\text{xc}}(r) = -1/r$$

where r is the distance from the nucleus. This implies

$$\lim_{r \rightarrow \infty} F(\mathbf{r}, \mathbf{r}') = 0. \quad (21)$$

For atoms additionally the limit of having just one electron is of relevance. If we apply DF theory to this case, the Coulomb potential and the XC potential must cancel in order to retain the bare external potential, i.e.

$$v_{\text{xc}}(\mathbf{r}) = -v_{\text{Coul}}(\mathbf{r}) = - \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

giving

$$F(\mathbf{r}, \mathbf{r}') = -1/|\mathbf{r} - \mathbf{r}'|. \quad (22)$$

This condition is a test of whether self-interaction corrections are properly taken into account.

3.2. Local density approximation

The simplest and most widely used approximation is the local density approximation (LDA), in which the XC energy of the IHEG is constructed from the XC energy per particle ϵ_{xc}^0 of the HEG and the density $n(\mathbf{r})$, by replacing the constant density of the HEG by $n(\mathbf{r})$, i.e.

$$E_{\text{xc}} = \int_V d\mathbf{r} n(\mathbf{r}) \epsilon_{\text{xc}}^0(n(\mathbf{r})). \quad (23)$$

The second functional derivative reads

$$F(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \frac{d^2}{dn^2} [n \epsilon_{\text{xc}}^0(n)]_{n=n(\mathbf{r})} \equiv \delta(\mathbf{r} - \mathbf{r}') f(\mathbf{r}) \quad (24)$$

and the Fourier transform with respect to r and r' gives

$$F(q, q') = \frac{1}{V} \int_V d\mathbf{r} e^{-i(q'-q)\mathbf{r}} \frac{d^2}{dn^2} [n\epsilon_{\mathbf{x}\mathbf{x}}^0(n)]_{n=n(\mathbf{r})} = f(q' - q) \quad (25)$$

where $f(q)$ is the Fourier transform of $f(\mathbf{r})$.

In the HEG limit with density n we obtain

$$F^0(q, q') = \delta_{q, q'} (d^2/dn^2) [n\epsilon_{\mathbf{x}\mathbf{x}}^0(n)] \equiv \delta_{q, q'} F^0(q). \quad (26)$$

Thus $F^0(q, q')$ is diagonal, $F^0(q)$ is constant (i.e. independent of q) and $G^0(q) = -(q^2/4\pi) F^0(q)$ is purely quadratic. $G^0(q)$ fulfills for small q the requirement (18), but it fails to obey the requirement for large q (19), which is important for our present application. Due to umklapp processes the HEG characteristics are necessary for $q > 2k_F$ also. It should be noted that the XC correction function always appears together with the factor $\chi^0(q, \omega)$. The total XC correction term reads

$$F^0(q)\chi^0(q, \omega) = -(4\pi/q^2) G^0(q)\chi^0(q, \omega).$$

The convergence of this term can be discussed easily in the limit $\omega = 0$ for the HEG. Because $\chi^0(q, 0)$ converges as q^{-2} for large q , the total XC term in the LDA converges, but only as q^{-2} and not as q^{-4} , as it should according to (19).

Far outside metal surfaces the density falls off exponentially: $n \propto \exp(-\alpha z)$. If we adopt the Slater or Kohn–Sham–Gaspar approximation with $\epsilon_{\mathbf{x}\mathbf{x}}^0 \propto n^{1/3}$, we obtain $v_{\mathbf{x}\mathbf{x}} \propto n^{1/3}$ and using (24) we have $f \propto n^{-2/3}$. In r -space this means that $v_{\mathbf{x}\mathbf{x}}(z) \propto \exp(-\frac{1}{3}\alpha z)$ and $f(z) \propto \exp(\frac{2}{3}\alpha z)$. Consequently, the LDA does not only fail in reproducing the image potential, but it also violates the boundary condition (20). Instead f diverges exponentially. But as already discussed in the HEG limit, this does not necessarily lead to divergences in measurable quantities.

3.3. Gradient expansion approximations

Just as the LDA, the gradient correction is not rigorous mathematically. For the calculation of the one-particle energies from the Kohn–Sham equations the lowest-order gradient correction usually gives no improvement over the LDA (see e.g. [16], [17]). Now we investigate how it influences the XC correction to the DMS. In the gradient approximation the following term

$$E_{\mathbf{x}\mathbf{x}} = E_{\mathbf{x}\mathbf{x}}^{\text{loc}} + \int_V d\mathbf{r} b(n(\mathbf{r})) |\nabla n(\mathbf{r})|^2 \quad (27)$$

is added to the LDA result. Because for the function $b(n)$ there are a lot of widely differing expressions [18], we leave it unspecified. Functional differentiation and Fourier transformation gives in the HEG limit [19]

$$\begin{aligned} F(q, q') &= F^{\text{loc}}(q, q') - a(q - q') + 2q \cdot q' b(q - q') \\ &= \delta_{q, q'} \left[\frac{d^2}{dn^2} n\epsilon_{\mathbf{x}\mathbf{x}}^0(n) + 2b(n)q^2 \right]. \end{aligned} \quad (28)$$

Using (15) we find

$$G^0(q) = -(1/4\pi) (d^2/dn^2) n\epsilon_{\mathbf{x}\mathbf{x}}^0(n)q^2 - (1/2\pi) b(n)q^4. \quad (29)$$

Because $b(n) > 0$ for all approximations available in the literature, the second term is negative, whereas the first one (LDA term) is positive. Therefore $G^0(q)$ starts quadratic in accordance with (18) but it tends to minus infinity as q^4 for large q and does not obey (19). In a sense, the gradient term is even worse than the LDA for large q . As mentioned above, the total XC correction term $F^0\chi^0$ must converge as q^{-4} . In the LDA convergence is reached, but as q^{-2} . Including the gradient term, $F^0\chi^0$ becomes constant and as a consequence ϵ^e does not converge to unity for $\omega = 0$ and large q as it should.

The simplest possible extension of the previously described gradient expansion is the additional inclusion of a term

$$- \int_{\mathcal{V}} d\mathbf{r} b(n(\mathbf{r}))n(\mathbf{r})\Delta n(\mathbf{r}).$$

This extra term modifies of course the detailed form of $F(q, q')$, but in the HEG limit it modifies only the prefactor of the q^4 term of $G^0(q)$ in (28). Because the form of $b(n)$ is very unclear, it is not possible to decide whether the additional term gives any improvement at all. At any rate, it does not produce the required limiting behaviour for large q .

In order to overcome the disadvantages of the gradient expansion regarding the energy spectrum, modified functionals have been developed [20,21], which include density gradients to all orders. We investigate here the functional by Langreth and Mehl [21]

$$E_{xc} = E_{xc}^{loc} + a \int_{\mathcal{V}} d\mathbf{r} n^{-4/3}(\mathbf{r})|\nabla n(\mathbf{r})|^2 \left[2 \exp(-dn^{-7/6}(\mathbf{r})|\nabla n(\mathbf{r})|) - \frac{7}{9} \right] \quad (30)$$

where a and d are constants. For $d=0$ and

$$\frac{11}{9}an^{-4/3} = b(n) \quad (31)$$

we recover the ordinary gradient expansion (27). The resulting formula for $F(q, q')$ is too lengthy to be given here. In the HEG limit, however, we obtain

$$F^0(q, q') = F^{0,loc}(q, q') + \frac{22}{9}an^{-4/3}q^2$$

which agrees completely with the ordinary gradient expansion (29), if (31) is fulfilled. Thus, the amendment by Langreth and Mehl does not remedy the defect of the LDA and of the ordinary gradient expansion with respect to the XC correction function for the DMS, although the energy spectrum is remarkably improved [21]. This may be understood as follows: if the first derivative of a functional $(v_{xc}(r))$ is satisfactory, this is not necessarily true for the second derivative $(F(r, r'))$.

3.4. Expansion for almost constant density

For almost constant density $E_{xc}[n(r)]$ can be expanded around the mean density n_0 as

$$E_{xc}[n] = E_{xc}[n_0] + \frac{1}{2} \int_{\mathcal{V}} d\mathbf{r} \int d\mathbf{r}' F^0(|\mathbf{r} - \mathbf{r}'|) \delta n(\mathbf{r}) \delta n(\mathbf{r}') \quad (32)$$

where $\delta n(\mathbf{r}) = n(\mathbf{r}) - n_0$. The second functional derivative reads

$$F(\mathbf{r}, \mathbf{r}') = (1/V) F_0 + F^0(|\mathbf{r} - \mathbf{r}'|) \quad (33)$$

where

$$F_0 = (1/V)(d^2/dn_0^2) E_{xc}[n_0] - F^0(q=0).$$

Fourier transformation with respect to \mathbf{r} and \mathbf{r}' results in

$$F(\mathbf{q}, \mathbf{q}') = \delta_{\mathbf{q},0} \delta_{\mathbf{q}',0} F_0 + \delta_{\mathbf{q},\mathbf{q}'} F^0(q) \quad (34)$$

where (the Fourier transform of quantities with finite range like $F^0(\mathbf{r})$ is defined without the factor $1/V$ contrary to the definition for bulk properties given in section 2.1)

$$F^0(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} F(\mathbf{r}).$$

The constant F_0 vanishes if $F^0(q)$ fulfils the compressibility sum rule. Obviously, F depends only on the mean density and therefore the HEG limit is identical with the general result (34). This is not surprising because we performed an expansion in second order around the HEG and then we took a second derivative with respect to the density. Therefore the boundary conditions (18) and (19) are fulfilled automatically. Because this type of expansion is reasonable for bulk material only, the other conditions cannot be imposed upon F . We did not make use of this approximation in our numerical calculations for bulk alkalis because it is essentially the zero-order contribution of the more general expression provided by the WDA discussed below.

3.5. Weighted density approximation

There is an formally exact expression for E_{xc} which reads [23]

$$E_{xc} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{r} n(\mathbf{r}') n(\mathbf{r}' + \mathbf{r}) [\bar{g}(\mathbf{r}', \mathbf{r}' + \mathbf{r}) - 1] \quad (35)$$

where the pair correlation function $g(\mathbf{r}, \mathbf{r}')$ is usually unknown. The bar over g (and in the following also over other HEG quantities such as S and H) means averaging over the coupling constant λ between $\lambda = 0$ and $\lambda = e^2$ with density $n(\mathbf{r})$ held fixed. For g we make the following plausible approximation

$$g(\mathbf{r}, \mathbf{r}') \approx g^0(|\mathbf{r} - \mathbf{r}'|; \bar{n}(\mathbf{r}, \mathbf{r}')) \quad (36)$$

where $g^0(r; n)$ is the pair correlation function of the HEG with density n .

In the weighted density approximation (WDA) [22], $\bar{n}(\mathbf{r}, \mathbf{r}')$ is replaced by a single variable function $\hat{n}(\mathbf{r})$, which is determined by means of the sum rule for the xc hole. This leads to the implicit equation [8]

$$\hat{n}(\mathbf{r}) = n_0 + \sum_{\mathbf{G} \neq 0} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} [1 - S_{\mathbf{G}}(\hat{n}(\mathbf{r}))]. \quad (37)$$

S_q is the static structure factor of the HEG connected with $g^0(r)$ by

$$\frac{1}{n} [S_q(n) - 1] = \int d\mathbf{r} e^{i\mathbf{q}\mathbf{r}} [g^0(r; n) - 1]. \tag{38}$$

For the alkali metals all reciprocal lattice vectors G are larger than $2k_F$ and therefore we have $S_G \approx 1$ and because of (37) $\bar{n} \approx n_0$. In any bulk system $\bar{n} = n_0$ might be a useful first approximation because the factor $[1 - S_G]$ cuts off the higher Fourier coefficients and thus $\bar{n}(\mathbf{r})$ is always smoother than $n(\mathbf{r})$. It should be noted that $\bar{n} = n_0$ has to be inserted *after* the functional derivative has been taken.

For $\bar{n} = n_0$ (the result for general $\bar{n}(\mathbf{r})$ is given in appendix A) we obtain from (17),(35)–(37) and Fourier transform:

$$\begin{aligned} F(\mathbf{q}, \mathbf{q}') &= \bar{H}_q \delta_{\mathbf{q}, \mathbf{q}'} - (n_{\mathbf{q}-\mathbf{q}'} / n_0) [(\bar{S}_q + \bar{S}_{q'}) / 2 - 1] \hat{D}^{(1)} \bar{H}_{\mathbf{q}-\mathbf{q}'} \\ &\quad - (n_{\mathbf{q}-\mathbf{q}'} / n_0) (1/2) \left\{ [\bar{S}_{q'} - 1] \hat{D}^{(1)} \bar{H}_q + [\bar{S}_q - 1] \hat{D}^{(1)} \bar{H}_{q'} \right\} \\ &\quad + (1/2) \left\{ [\bar{S}_{q'} - 1] \hat{D}^{(1)} \bar{S}_q + [\bar{S}_q - 1] \hat{D}^{(1)} \bar{S}_{q'} \right\} A^{(1)} \\ &\quad + (1/2) [\bar{S}_q - 1] [\bar{S}_{q'} - 1] A^{(2)} \end{aligned} \tag{39}$$

where \bar{H}_q is defined by

$$\bar{H}_q = \int d\mathbf{r} e^{i\mathbf{q}\mathbf{r}} \frac{1}{r} [\bar{g}^0(r) - 1] = \frac{1}{n} \frac{1}{(2\pi)^3} \int d\mathbf{q}' \frac{4\pi}{|\mathbf{q} - \mathbf{q}'|^2} [\bar{S}_{q'} - 1] \tag{40}$$

the dimensionless operators $\hat{D}^{(m)}$ by

$$\hat{D}^{(m)} = n^m \frac{d^m}{dn^m}$$

and the constants $A^{(m)}$ by

$$A^{(m)} = \sum_{\mathbf{G}, \mathbf{G}'} \frac{n_{\mathbf{G}}}{n_0} \frac{n_{\mathbf{G}'}}{n_0} \hat{D}^{(m)} \bar{H}_{\mathbf{G}'} \delta_{\mathbf{G}+\mathbf{G}', \mathbf{q}-\mathbf{q}'}$$

All HEG-quantities must be taken at the density n_0 , which is not explicitly indicated.

For the HEG we obtain a diagonal matrix with elements

$$\begin{aligned} F^{(0)}(\mathbf{q}, \mathbf{q}) &= \bar{H}_q - [\bar{S}_q - 1] \hat{D}^{(1)} [\bar{H}_0 + \bar{H}_q] + [\bar{S}_q - 1] (\hat{D}^{(1)} \bar{S}_q) (\hat{D}^{(1)} \bar{H}_0) \\ &\quad + \frac{1}{2} [\bar{S}_q - 1]^2 \hat{D}^{(2)} \bar{H}_0. \end{aligned} \tag{41}$$

By means of (15) this formula defines $G^0(q)$. Once the dependence of S on the coupling constant e^2 is known, (41) can serve as the link between $G^0(q)$ and $S(q)$, which is necessary for a self-consistent determination of $G^0(q)$ according to Singwi *et al.* This has been done by Chacon and Tarazona [5] using a scaling assumption for the calculation of \bar{S} . Observe that the first term of (41) agrees with the corresponding

relation of Singwi *et al* [1] apart from the average over the coupling constant. Considering $\bar{H}_0 = (2/n)\epsilon_{\mathbf{x}}^0$, the $q = 0$ limit of (41) can be rewritten as

$$F^{(0)}(\mathbf{0}, 0) = (d^2/dn^2)[n\epsilon_{\mathbf{x}}^0]$$

what agrees exactly with the expression (27) for $F^{(0)}(q, q)$ in the LDA. In other words, in the LDA the function $F^{(0)}(q, q)$ is approximated by the constant value at $q = 0$ of the WDA result.

For any reasonable choice for \bar{S} , G^0 determined from (41) and (15) satisfies the boundary conditions (18) and (19). The conditions (20), (21), and (22) can be required for the general expression for $F(\mathbf{r}, \mathbf{r}')$ given in Appendix A only, because with the additional assumption $\bar{n}(\mathbf{r}) = n_0$ application is limited to bulk material. These constraints are guaranteed by the fact that the XC potential satisfies the corresponding conditions [22]. Because the WDA is the only approximation to fulfill all our boundary conditions (18–22), we will use it for the numerical calculation presented in section 5. In appendix B we discuss a semilocal approximation which is often used for the XC potential $v_{\mathbf{x}}(\mathbf{r})$ but which fails for $F(\mathbf{r}, \mathbf{r}')$ in the same way as the LDA.

4. Plasmon dispersion in second-order perturbation theory

4.1. Macroscopic dielectric function

We now restrict ourselves to systems with lattice periodicity. As mentioned in Sect. 2.1, then all matrices in q -space have a form like this:

$$\epsilon_{q, q'} = \epsilon_{\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}'} \equiv \epsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{k})$$

i.e. all matrix elements are indexed by reciprocal lattice vectors \mathbf{G} and \mathbf{G}' . (The dependence on \mathbf{k} and ω will often not be indicated explicitly.) The macroscopic dielectric function follows from the microscopic DM using

$$\left[\epsilon_{\text{mac}}(\mathbf{k})\right]^{-1} = \left[\epsilon^{-1}\right]_{0,0}(\mathbf{k}). \quad (42)$$

It follows from (11) and (12) that

$$\epsilon^{-1} = \mathbf{I} + \mathbf{V}\chi(\epsilon^e)^{-1} \quad (43)$$

where ϵ^e is given by (14) in terms of χ and \mathbf{F} . If we assume the electrons are subject to a weak pseudopotential $W(\mathbf{r})$, the elements of the matrix χ can be calculated by perturbation theory. The explicit results are given elsewhere [24] and will not be repeated here. Here it suffices to mention, that all diagonal and off-diagonal elements are of zeroth and first order in W , respectively. Knowing this we can invert the matrix ϵ^e in second order in W and insert the result into (43) and (42). This procedure in the special case of the RPA is described in [24]. The result is

$$\epsilon_{\text{mac}} = \epsilon_{\text{mac}}^e/d + \mathcal{O}(W^3) \quad (44)$$

where

$$\epsilon_{\text{mac}}^e = \epsilon_{\alpha,0}^e - \sum_{\mathbf{G} \neq 0} \frac{\epsilon_{\mathbf{G},0}^e \epsilon_{0,\mathbf{G}}^e}{\epsilon_{\mathbf{G},\mathbf{G}}^{e,0}} \quad (45)$$

$$d = \epsilon_{0,0}^e + v_k \chi_{0,0} - \sum_{\mathbf{G} \neq 0} (\epsilon_{0,\mathbf{G}}^e + v_k \chi_{0,\mathbf{G}}) \frac{\epsilon_{0,\mathbf{G}}^e}{\epsilon_{\mathbf{G},\mathbf{G}}^{e,0}}. \quad (46)$$

$\epsilon_{\mathbf{G},\mathbf{G}}^{e,0}$ is identical with the dielectric function $\epsilon^e(\mathbf{k} + \mathbf{G})$ for the HEG. The numerator ϵ_{mac}^e can be interpreted as the macroscopic dielectric function resulting from ϵ^e using the analogue to (42) calculated in second order in W .

4.2. Plasmons

The electron energy loss function $P(q, \omega)$ can be calculated from ϵ_{mac} using

$$P(q, \omega) = -\text{Im}(1/\epsilon_{\text{mac}}(q, \omega)) = \text{Im}\epsilon_{\text{mac}} / ((\text{Re}\epsilon_{\text{mac}})^2 + (\text{Im}\epsilon_{\text{mac}})^2). \quad (47)$$

For weakly inhomogeneous systems and q smaller than the critical wavevector q_c , P versus ω is sharply peaked near the zero of $\text{Re}\epsilon_{\text{mac}}$. Therefore we define the plasmon frequency ω_q by

$$\text{Re}\epsilon_{\text{mac}}(q, \omega_q) = 0.$$

If we split up ω_q into the plasmon frequency of the HEG ω_q^0 defined by

$$\text{Re}\epsilon^0(q, \omega_q^0) = 0$$

and a correction $\delta\omega_q$ originating from the inhomogeneity, we have

$$\omega_q = \omega_q^0 + \delta\omega_q. \quad (48)$$

The correction can be calculated from [24]

$$\delta\omega_q = -[\text{Re}\epsilon_{\text{mac}}(q, \omega)/(d/d\omega)\text{Re}\epsilon^0(q, \omega)] \Big|_{\omega=\omega_q^0} + O(W^3). \quad (49)$$

Insertion of ϵ_{mac} from (44) into (49) leaves us with

$$\delta\omega_q = -[\text{Re}\epsilon_{\text{mac}}^e(q, \omega)/(d/d\omega)\text{Re}\epsilon^{e,0}(q, \omega)] \Big|_{\omega=\omega_q^0} + O(W^3). \quad (50)$$

Obviously, (50) differs from (49) only in replacing ϵ by ϵ^e .

5. Application to the plasmon dispersion of caesium

As a first test of the XC correction in the WDA described in section 3.5 we apply it to the plasmon dispersion of caesium. The essential contributions to ϵ are the one-particle susceptibility χ and the XC correction F . In order to make the calculations feasible we use the following approximations.

(i) For the calculation of χ , the inversion of ϵ , and the calculation of the plasmon frequency we use the formula derived in section 4 valid in second-order perturbation theory in the (local) pseudopotential. For simplicity only the (110) star of reciprocal lattice vectors is taken into account. The Fourier component $W_{110} = 2.57 \times 10^{-2}$ Hartree [26] was fitted to the Fermi surface. We are aware of the fact that because of low-lying unoccupied d bands, this simple picture may fail if excitations into these bands are important. Moreover, because V_{110}/E_F is 0.44, perturbation theory in second order is questionable. Furthermore, the idea cannot be excluded that the electron cores, which are increasingly polarizable with increasing shell number, modify the plasmon dispersion. It is not very likely, however, that the negative dispersion for Cs is caused by core polarization alone, because for Ba, which has the same type of core states, the dispersion of the (genuine) plasmon peak is positive. In view of these difficulties, the numerical results for Cs should be considered as a qualitative estimate only.

(ii) For the calculation of the XC correction F we need n_G , the Fourier transform of the electron density, and \bar{S}_q , the static structure factor of the HEG averaged over the coupling constant. For the sake of internal consistency n_G is evaluated in linear response theory from the same W_G that has been used for χ . Because its dependence on the coupling constant is usually not investigated or given, we were forced to replace \bar{S}_q by S_q . For S_q several approximations taken from the literature were used.

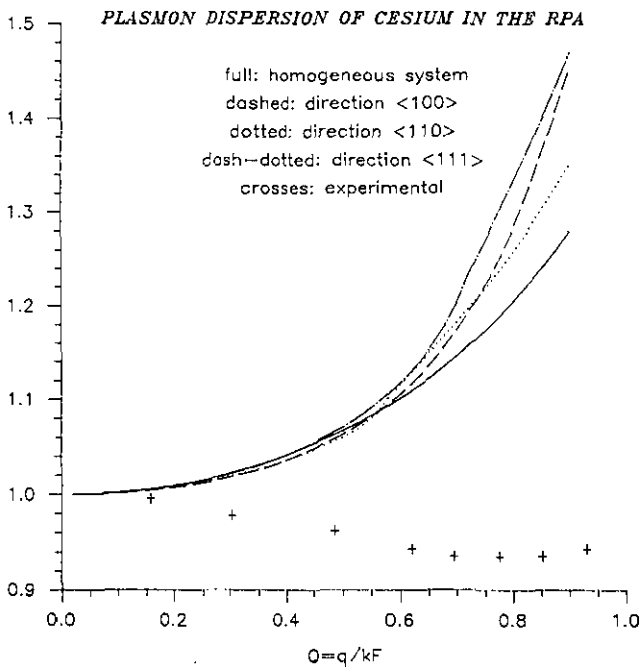


Figure 1. Anisotropy of the plasmon dispersion of Cs within the RPA for q parallel to $\langle 100 \rangle$ (dashed), $\langle 110 \rangle$ (dotted), and $\langle 111 \rangle$ (dash-dotted). The full line is the result for the HEG. Crosses indicate experimental values [25] for polycrystalline material. To get rid of the influence of the core polarization all dispersion curves are normalized to unity at $q = 0$, i.e. divided by the value at $q = 0$.

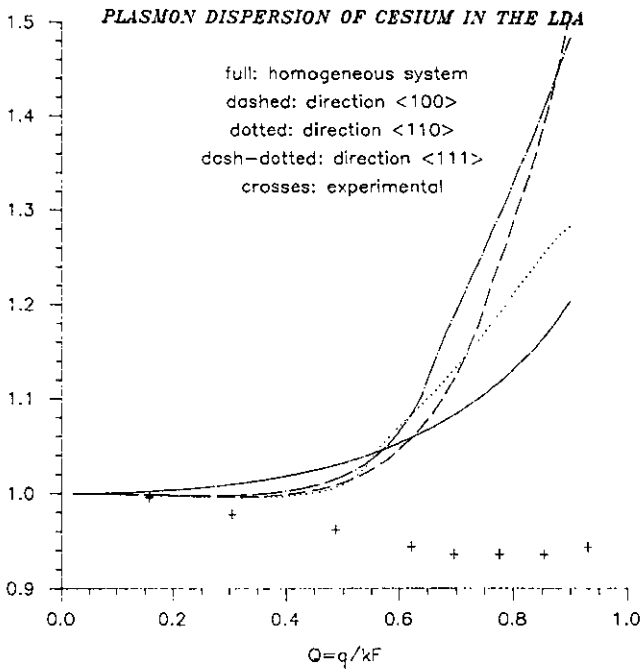


Figure 2. Plasmon dispersion of Cs as in figure 1, but XC corrections are included within the LDA.

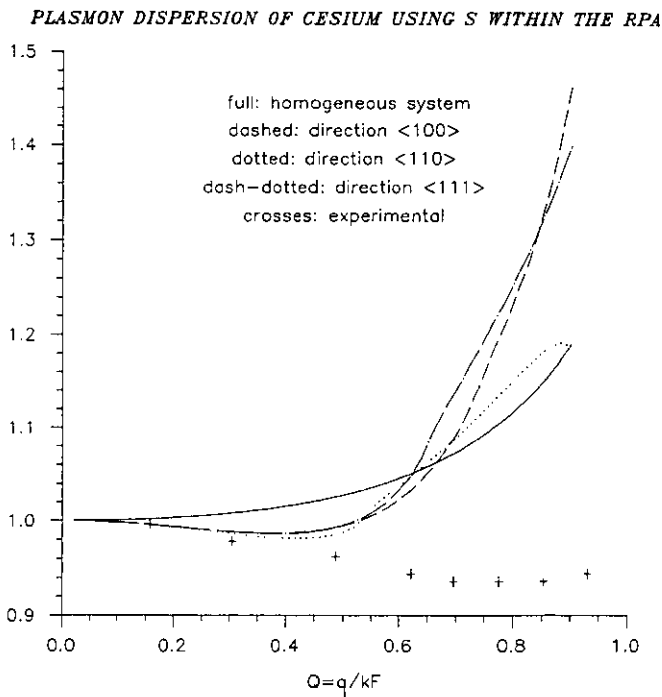


Figure 3. Anisotropy of the plasmon dispersion of Cs in the WDA using S_q and H_q in the RPA. The meaning of the line shapes is as in figure 1.

In figure 1 it is seen that the plasmon dispersion of Cs within the RPA does not agree with experiment. The XC corrections within the LDA, taken into account in figure 2, improve the agreement only slightly. The WDA, used in figures 3–7, gives rise to important XC corrections. This is mainly because $F(q, q')$ as given in (43) contains

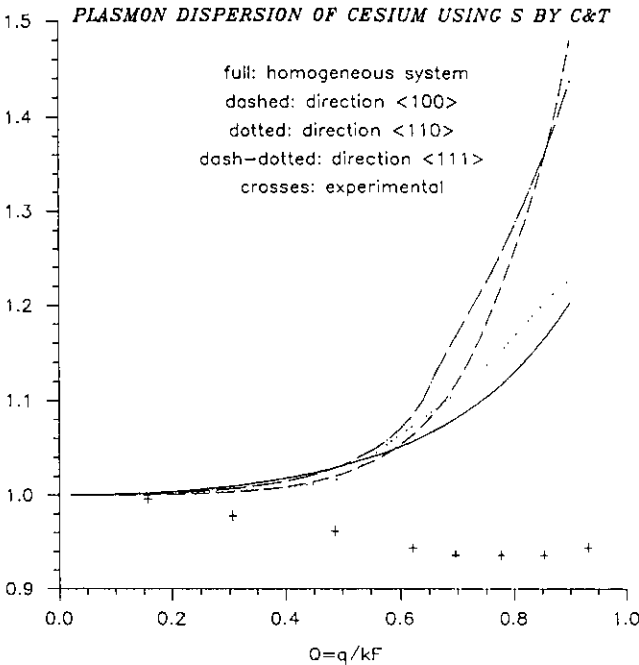


Figure 4. As figure 3, but the HEG functions S_q and H_q are calculated using the XC correction of Chacon and Tarazona [5].

density derivatives of S_q and H_q which become large near $q = 2k_F$, if S_q exhibits a peak near $q = 2k_F$ (see figures 5 and 6). Because the arguments of F decompose into sums over a reciprocal lattice vector G and the wavevector of the plasmon k , the peaks in the density derivatives become evident only near $|G + k| = 2k_F$. For given G and direction of k this is a quadratic equation for the modulus of k having zero, one or two solutions:

$$k = -G_{\parallel} \pm \sqrt{4k_F^2 - G_{\perp}^2} \tag{51}$$

where G_{\parallel} and G_{\perp} are the parallel and perpendicular components of G with respect to k , respectively. This equation must be solved for each reciprocal lattice vector to provide the location of anomalies in k -space. For k oriented along the principal symmetry directions we obtain the values given in table 2 of [8]. The values which are smaller than q_c are 0.43, 0.28, and 0.35 (in units of k_F) when k is parallel to $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$, respectively. Moreover, in the $\langle 110 \rangle$ direction we have a second solution at 0.82, which turns out to be the dominant one. The shape and strength of the anomalies cannot be anticipated completely without doing the full calculation. Some knowledge can be obtained from the behaviour of the centre of gravity which is predictable (see [8]). It should be mentioned that the anomalies produced by Fourier components beyond the $\langle 110 \rangle$ star (which are neglected in our numerical results) lie beyond the critical wavevector.

All diagonal elements consist of zeroth- and second-order contributions $F^{(0)}$ and $F^{(2)}$, respectively. $F^{(0)}$ is given in (45) and $F^{(2)}$ reads

$$F^{(2)}(q, q) = [S_q - 1] \left[\hat{D}^{(1)} S_q \right] \sum_{G \neq 0} \left| \frac{n_G}{n_0} \right|^2 \hat{D}^{(1)} H_G + \frac{1}{2} [S_q - 1]^2 \sum_{G \neq 0} \left| \frac{n_G}{n_0} \right|^2 \hat{D}^{(2)} H_G. \tag{52}$$

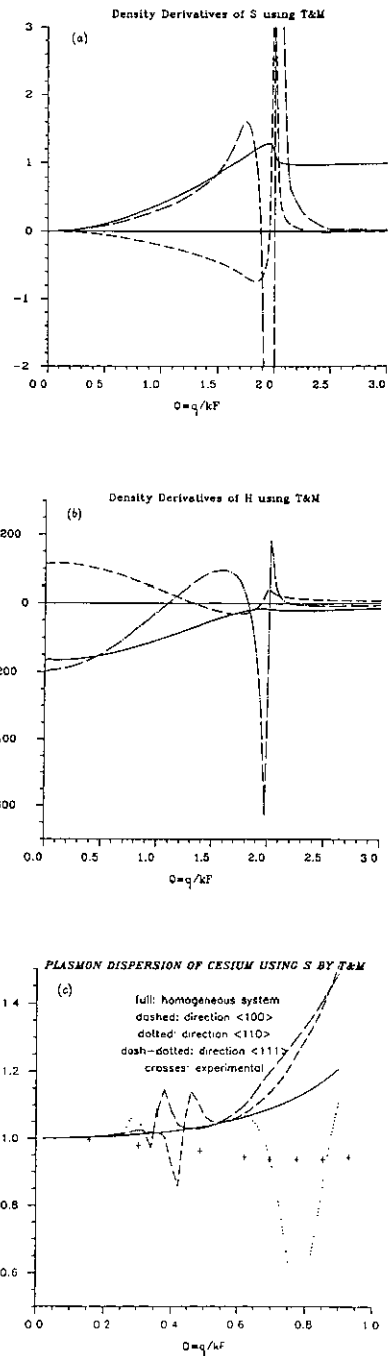
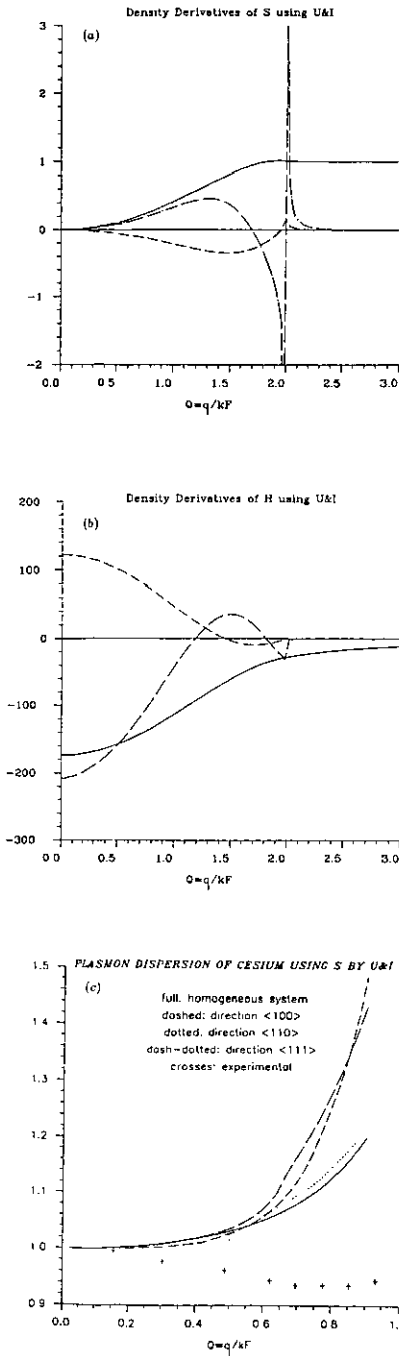


Figure 5. (a) Density derivatives $\dot{D}^{(m)}S_q$ using the XC correction of Utsumi and Ichimaru [3] for $m = 0$ (full line), $m = 1$ (dashed), and $m = 2$ (dash-dotted). (b) Density derivatives $\dot{D}^{(m)}H_q$ using the XC correction of Utsumi and Ichimaru [3] for $m = 0$ (full line), $m = 1$ (dashed), and $m = 2$ (dash-dotted). (c) Anisotropy of the plasmon dispersion of Cs in the wDA using S_q and H_q in the approximation of Utsumi and Ichimaru [3]. The meaning of the line shapes is as in figure 1.

Figure 6. As figure 5, but the HEG functions S_q and H_q are calculated using the XC correction of Tripathy and Mandal [4].

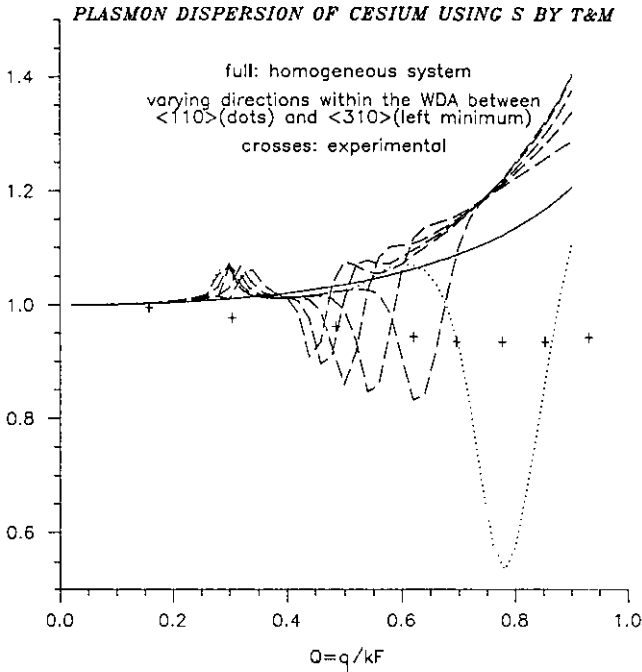


Figure 7. Anisotropy of the plasmon dispersion as in figure 6, but for some q directions close to $\langle 110 \rangle$. The full line is the result for the HEG and the crosses indicate the experimental result for polycrystalline Cs [25]. For the dashed lines the direction of q varies between $\langle 110 \rangle$ (dotted) and $\langle 310 \rangle$ (furthest left minimum).

In second-order perturbation theory, however, from all the diagonal elements of $F^{(2)}$, only the $G = G' = 0$ element appears in the result (see (49) and (50)). In this element the critical region near $2k_F$ can never be reached. Thus it is a smooth function of q and the anomaly influences the result only via the off-diagonal elements of F . Neglect of the off-diagonal elements of F (and χ) removes the anomalies.

Among all HEG approximations tested here that by Tripathy and Mandal [4] seems to be the only one which reproduces the experimentally observed anomaly at least qualitatively. Probably the minimum along $\langle 110 \rangle$ is too deep, i.e. the hump in S_q is too high. On the other hand, according to Utsumi and Ichimaru [3] there is a small hump in S_q , but its influence on the plasmon dispersion within the present treatment is too small (see figure 5). One has to take into account, however, that by the approximations additional to the WDA (see above) the influence of the anomaly is underestimated. This can be concluded by comparison of the present results with those using frequency momentum analysis [9], where the additional approximations in question are not necessary. Thus we cannot determine which of the HEG treatments is really the best. It is only clear that the hump in S_q may lead to a considerable minimum in the plasmon frequency at the experimentally observed frequency.

Moreover, the minimum in the plasmon frequency in figure 6 is too narrow. This discrepancy can be removed by consideration of directions in the vicinity of $\langle 110 \rangle$ as shown in figure 7. Obviously this minimum is shifted to lower frequencies if we turn the wavevector out of the $\langle 110 \rangle$ direction and the mean over all directions will have a broader minimum. However, this is a qualitative argument, because the plasmon frequency of a polycrystalline sample is not simply the mean over all directions. A second problem is the minor structure in the theoretical curves near $q/k_F = 0.4$ which is not seen in the experimental data. It is not clear to what extent this structure is smeared out by effects of the non-crystalline nature of the samples.

Comparing the basic results of this theory with those obtained using frequency momentum analysis [9], we can state that in both treatments the hump in S_q gives rise to anomalous behaviour of the plasmon frequency in Cs. It must be remembered, however, that in the frequency momentum analysis we investigate the centre of gravity of the loss function, which differs greatly from the zero of $Re(\epsilon_{\text{mac}})$ when k is large or when the plasmon peak (on the frequency scale) is broad. This has the consequence that in the present calculation along the $\langle 110 \rangle$ direction the minimum at 0.82 is much more pronounced than the structure at 0.28, whereas in the frequency–momentum analysis the reverse is seen. The reason for this difference is that for large k the one-particle excitations, which are weakly influenced by electron correlations and which show no anomaly, contribute a lot to the centre of gravity, but not to the plasmon frequency as defined in this paper. Thus, for large k the anomalies in the centre of gravity are weaker than in the plasmon dispersion. There are two recent attempts to calculate the plasmon dispersion of the alkaline metals within the HEG model. Serra *et al* [27] obtained satisfactory results for the high-density metals Na and K, but failed for Cs. Kalman *et al* [28] obtained a negative dispersion for Cs treating it as a classical homogeneous plasma. They stressed that the frequency dependence of the XC correction is responsible for the minimum. The present investigations, however, showed that a minimum can be obtained without dynamical XC effects and that the frequency momentum analysis [9], which includes dynamical effects exactly, does not give qualitatively different results.

6. Summary

We have derived an XC correction matrix for the dielectric matrix of the inhomogeneous electron gas using non-local density functional theory. It is based on the WDA and it needs as input the Fourier transforms of the electron density as well as the static structure factor \tilde{S}_q from the theory of the homogeneous electron gas averaged over the coupling constant between 0 and e^2 . In the present application this average has been approximated by S_q for the full coupling constant.

The theory was applied to the plasmon dispersion of caesium, which exhibits a minimum near $q/k_F = 0.8$. We adopted a simple pseudopotential model considering one star of reciprocal lattice vectors. Within this model, the one-particle susceptibility χ and the macroscopic dielectric function ϵ_{mac} are calculated in second-order perturbation theory. It turns out that neither the RPA nor the XC corrections within the LDA nor more sophisticated XC corrections in the homogeneous electron gas can describe the plasmon dispersion in Cs. Within the WDA we obtain qualitative agreement with experiment, if we use a static structure factor S_q which exhibits a considerable hump near $2k_F$, e.g. that of Tripathy and Mandal [4]. Quantitative agreement could not be the goal for this work because the experimental values are for polycrystalline material and our results for single crystals are strongly anisotropic. Moreover, for quantitative comparison we should go beyond our simple potential model and calculate χ and ϵ_{mac} on the basis of a full band structure calculation. Possibly, we have to consider the average over the coupling constant in the static structure factor as well. Only if both problems were solved and experimental values for single crystals were available could we proceed to final conclusions as to which of the approximations for the XC correction in the HEG is most suitable and how well the WDA works.

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Appendix A. XC correction in r space within the WDA

From (17), (35), (36) and (37) we obtain:

$$\begin{aligned}
 F(r, r') = & \frac{1}{|r - r'|} \left[\frac{\tilde{g}^0(r - r'; \tilde{n}(r)) + \tilde{g}^0(r - r'; \tilde{n}(r'))}{2} - 1 \right] \\
 & - \frac{1}{2} \frac{C_1(r)}{D_1(r)} \left[\tilde{g}^0(r - r'; \tilde{n}(r)) - 1 \right] - \frac{1}{2} \frac{C_1(r')}{D_1(r')} \left[\tilde{g}^0(r - r'; \tilde{n}(r')) - 1 \right] \\
 & - \frac{1}{2} \int dr_1 n(r_1) \frac{1}{|r_1 - r|} \frac{1}{D_1(r_1)} \left[\tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) - 1 \right] \\
 & \times \frac{d}{d\tilde{n}} \tilde{g}^0(r_1 - r; \tilde{n}(r_1)) \\
 & - \frac{1}{2} \int dr_1 n(r_1) \frac{1}{|r_1 - r'|} \frac{1}{D_1(r_1)} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r_1)) - 1 \right] \\
 & \times \frac{d}{d\tilde{n}} \tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) \\
 & + \frac{1}{2} \int dr_1 n(r_1) \frac{C_1(r_1)}{[D_1(r_1)]^2} \left[\tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) - 1 \right] \frac{d}{d\tilde{n}} \tilde{g}^0(r_1 - r; \tilde{n}(r_1)) \\
 & + \frac{1}{2} \int dr_1 n(r_1) \frac{C_1(r_1)}{[D_1(r_1)]^2} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r_1)) - 1 \right] \frac{d}{d\tilde{n}} \tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) \\
 & - \frac{1}{2} \int dr_1 n(r_1) \frac{C_1(r_1) D_2(r_1)}{[D_1(r_1)]^3} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r_1)) - 1 \right] \\
 & \times \left[\tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) - 1 \right] \\
 & + \frac{1}{2} \int dr_1 n(r_1) \frac{C_2(r_1)}{[D_1(r_1)]^2} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r_1)) - 1 \right] \\
 & \times \left[\tilde{g}^0(r_1 - r'; \tilde{n}(r_1)) - 1 \right]
 \end{aligned} \tag{A1}$$

where

$$C_i(r) = \int dr_1 n(r_1) \frac{1}{|r_1 - r|} \frac{d^i}{d\tilde{n}^i} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r)) - 1 \right] \tag{A2}$$

$$D_i(r) = \int dr_1 n(r_1) \frac{d^i}{d\tilde{n}^i} \left[\tilde{g}^0(r_1 - r; \tilde{n}(r)) - 1 \right]. \tag{A3}$$

Observe that $D_0(r) = -1$ is the sum rule for the XC hole.

Appendix B. Semilocal approximation

Here we discuss an alternative procedure specifying the function $\tilde{n}(\mathbf{r}, \mathbf{r}')$ in (36). The *ansatz*

$$\tilde{n}(\mathbf{r}, \mathbf{r}') = n_0 + a \{ [n(\mathbf{r}) + n(\mathbf{r}')]/2 - n_0 \} \quad (\text{B1})$$

for (36) and (35) generates a family of semilocal approximations. The parameter a may be chosen so that the sum rule of the XC hole or any other requirement is optimally fulfilled. For $0 < a < 1$, $\tilde{n}(\mathbf{r}, \mathbf{r}')$ is smoother than $n(\mathbf{r})$. This trend agrees with the behaviour of the weighted density $\tilde{n}(\mathbf{r})$ discussed in section 3.5.

We give here the result in the HEG limit only

$$F^0(q, q') = \delta_{\mathbf{q}, \mathbf{q}'} \left\{ \left[1 + (a/2)n(d/dn) \right]^2 \tilde{H}_q^0(n) + an \left[1 + (a/2)d/dn \right] (d/dn) \tilde{H}_0^0 \right\} \\ + \delta_{\mathbf{q}, 0} \delta_{\mathbf{q}', 0} \times \text{constant}. \quad (\text{B2})$$

The first term in the bracket of (B2) has the required limiting behaviour whereas the second one is constant and therefore as wrong as the LDA is. Tracing back the origin of this defect leads us to the fact that $g(\mathbf{r}, \mathbf{r}')$ in our *ansatz* (B1) is a function of $n(\mathbf{r})$ and $n(\mathbf{r}')$. Thus some local character is retained leading to terms in F^0 which behave like the LDA. Only in the case $a = 0$, where $\tilde{n} = n_0$, and in the full WDA (see section 3.5), \tilde{n} and therefore g is a functional of $n(\mathbf{r})$ and therefore the correct behaviour in the HEG limit is obtained.

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