# ASYMPTOTIC DISPLACED CHARGE ROUND IMPURITIES IN METAL CRYSTALS WITH AND WITHOUT SURFACES

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Abstract—The displaced charge $\Delta\rho$ at distance $r$ from a localized perturbation $V$ in an inhomogeneous degenerate electron gas may be written in a linear response framework as

$$\Delta\rho(r) = \int V(r')F(rr')\,dr'.$$

The response function $F$ is expressed in terms of the Green function of the unperturbed system and attention is then focussed on two cases:
(i) A perfect periodic metal crystal, perturbed by $V$.
(ii) A metal lattice with a surface in which $V$ is embedded.
  A full discussion is given of the influence of Fermi surface topology on the anisotropy of $\Delta\rho$ in the asymptotic region far from the defect. Provided $V(r)$ has certain reasonable properties, it is shown that $\Delta\rho \sim r^{-n}x$ oscillatory function. For the bulk metal, $n$ can take values between 1 and 5 in different directions for Fermi surfaces with particular topologies. Possible experiments which bear on this anisotropy are briefly referred to. For a planar surface, the displaced charge is shorter range for $V$ embedded in the surface than for the bulk metal, in most, but not all cases. For a closed Fermi surface with non-zero curvature, $n = 5$ for the parallel configuration.

## 1. BACKGROUND

The purpose of this paper is to consider the asymptotic form of the displaced electron density $\Delta\rho(r)$ say, at distance $r$ relative to a localised perturbation $V(r)$. Special cases of this are well known, e.g. in a uniform Fermi gas, around a test charge, $\Delta\rho$ falls off as

$$\Delta\rho \sim \frac{A\cos 2k_f r}{r^3}, \qquad (1.1)$$

the so-called Friedel oscillations having wavelength $\pi/k_f$, $k_f$ being the Fermi momentum.

In the general case of a small perturbation $V$ embedded in an inhomogeneous electron gas we can write the displaced charge in a linear response framework as

$$\Delta\rho(r) = \int V(r')F(rr')\,dr'. \qquad (1.2)$$

The response function $F$ can be expressed in terms of the Green function of the unperturbed problem as

$$F = i\int dE\, G(rr'E)G(r'rE) \qquad (1.3)$$

which can be obtained, e.g. by performing an energy integration on the result given by Stoddart et al.[1].

Here, for $E$ less than the Fermi energy $E_f$, $G$ is the outgoing Green function, while for $E > E_f$, we take the incoming wave form (see eqns 2.1 and 2.2 below).

At this stage, we note that there are several situations arising in which the Friedel oscillations play a role:

(i) In determining electric field gradients induced by charged impurities in metals, as observed by nuclear magnetic resonance experiments.

(ii) In calculating the interaction between a pair of charged defects, say an impurity-vacancy complex, in a metal.

(iii) In affecting the long-range form of the effective interionic pair potential in solid and liquid metals.

Recently, Flores et al.[2] and Lau and Kohn [3] have studied the interaction between a pair of charged species placed parallel to a planar metal surface and within the spill-out electron density from the metal. Both these investigations lead to a form for the parallel configuration in which the interaction energy falls off like $\cos 2k_f r/r^5$; that is the interaction has a much shorter range than that given by (1.1) in the bulk metal. Reference should also be made to Einstein[4] for some comments on the limits of validity of this form $r^{-5}\cos 2k_f r$; this point will be touched on again in the discussion below. We must also refer here to the early work of Grimley et al.[5,6] on the oscillatory interaction between adsorbed atoms on a metal

surface. Another highly relevant study in the present context is that by Rudnick[7] on the static density response at a metal surface.

Though some discussion has been given of the form of the displaced charge in the presence of a more complex Fermi surface topology[8], there does not appear to be a very general treatment in the literature. Our object here is to supply this, treating both bulk metals, and metals with planar surfaces.

It will be convenient to start out from the case of the perfect periodic metal in Section 2 below. After discussing this case fully, we then turn in Section 3 to treat the metal with a surface, constructing the Green function required from the lattice Green function by appealing to image theory. We stress that throughout we work within the linear response framework afforded by eqns (1.2) and (1.3).

## 2. LOCALISED PERTURBATION IN PERIODIC METAL CRYSTAL

Koster[9] has discussed the Green function in a perfect lattice and we shall utilise his results below. However, before doing so, let us summarise how the result (1.1) follows using the free-electron Green function in (1.3), at large distances from the localised perturbation. In this plane wave case we have

$$G^{out}(\mathbf{r r'} E) = \frac{\exp(ik|\mathbf{r} - \mathbf{r'}|)}{|\mathbf{r} - \mathbf{r'}|}, \quad E = \frac{1}{2}k^2 \quad (2.1)$$

and

$$G^{in}(\mathbf{r r'} E) = \frac{\exp(-ik|\mathbf{r} - \mathbf{r'}|)}{|\mathbf{r} - \mathbf{r'}|}. \quad (2.2)$$

The response function $F(\mathbf{r r'})$ given by eqn (1.3) then takes the form



Fig. 1. Shows vector $\mathbf{r} - \mathbf{r'}$ and stationary phase point $\mathbf{k}_0$ on constant energy surface $E(\mathbf{k})$. Point 0 is the centre of the Brillouin zone. The plane perpendicular to $\mathbf{r} - \mathbf{r'}$ and tangential to the constant energy surface is also shown.

of the surface. We note that

$$K = \left[ \frac{\partial^2 E(k_0)}{\partial k_1^2} \frac{\partial^2 E(k_0)}{\partial k_2^2} \right]^{1/2} \quad (2.5)$$

is the curvature at $k_0$ which is assumed here to be non-zero. Actually, the Green function whose asymptotic form we seek differs from (2.4) in that, in the numerator, Bloch waves $\psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$ replace the plane waves, where $u_k(\mathbf{r})$ is periodic with the period of the lattice. Using the reciprocal lattice vectors G one can therefore write the Fourier series

$$u_k(\mathbf{r}) = \sum_G V_{k+G} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.6)$$

where $v_{k+G}$ is the momentum eigenfunction. The desired modification to the asymptotic form (2.4) is then

$$G(\mathbf{r r'} E) = \frac{-4\pi^2}{|\mathbf{r} - \mathbf{r'}|} \frac{\exp\{i\mathbf{k}_0 \cdot (\mathbf{r} - \mathbf{r'})\} u_{\mathbf{k}_0}^*(\mathbf{r}) u_{\mathbf{k}_0}(\mathbf{r'})}{K}. \quad (2.7)$$

Forming the response function from eqn (1.3), one obtains at the Fermi surface, where $\mathbf{k}_0$ becomes $\mathbf{k}_{0f}$

$$F(\mathbf{r r'}) \sim \frac{[\exp\{2i\mathbf{k}_{0f} \cdot (\mathbf{r} - \mathbf{r'})\} u_{\mathbf{k}_{0f}}^{*2}(\mathbf{r}) u_{\mathbf{k}_{0f}}^2(\mathbf{r'}) + \exp\{-2i\mathbf{k}_{0f} \cdot (\mathbf{r} - \mathbf{r'})\} u_{\mathbf{k}_{0f}}^{*2}(\mathbf{r'})] |\nabla_{\mathbf{k}_{0f}} E|}{|\mathbf{r} - \mathbf{r'}|^3 K^2}. \quad (2.8)$$

$$F(\mathbf{r r'}) \sim i \int_0^{k_f} k \frac{\exp(2ikR)}{R^2} dk + i \int_{k_f}^{\infty} \frac{k \exp(-2ikR)}{R^2} dk$$

$$\sim \frac{\cos 2k_f R}{R^3} \quad (2.3)$$

where $R = |\mathbf{r} - \mathbf{r'}|$.

### 2.1 General Fermi surface

We next consider the response function for a general Fermi surface. Then Koster[9] has shown that

$$\sum_k \frac{\exp\{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r'})\}}{E - E(\mathbf{k})} \sim -\frac{4\pi^2}{|\mathbf{r} - \mathbf{r'}|} + \frac{\exp\{i\mathbf{k}_0 \cdot (\mathbf{r} - \mathbf{r'})\}}{\left[ \frac{\partial^2 E(k_0)}{\partial k_1^2} \frac{\partial^2 E(k_0)}{\partial k_2^2} \right]^{1/2}} \quad (2.4)$$

where $k_0$ is shown in Fig. 1 and is defined as a point of stationary phase. The coordinates $(k_1)$ and $(k_2)$ are measured at $\mathbf{k}_0$ along the principal directions in the plane
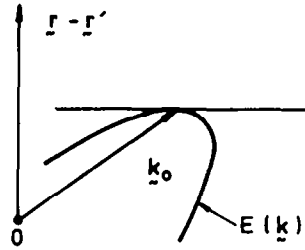
Two points are important here. The first is that the decay at large distances is as $|\mathbf{r} - \mathbf{r'}|^{-3}$ times an oscillatory function. For the important case when $\mathbf{r} - \mathbf{r'}$ is a direct lattice vector, the reciprocal lattice vectors G do not affect the wavelength, but only the amplitude. However, if one was dealing with the displaced charge round an impurity, or with the interaction between a pair of defects, around which appreciable lattice relaxation occurred, then one can expect that in a given direction there will be wavelengths associated not only with $\mathbf{k}_{0f}$ but also with $\mathbf{k}_{0f} + G$ where G is any reciprocal lattice vector. Naturally the weight of the wavelength associated with $\mathbf{k}_{0f} + G$ will not only depend on the extent of the relaxation of the lattice round the defect or the defect complex, but also on the magnitude of the momentum eigenfunction $v_{\mathbf{k}_{0f} + G}$. It is to be expected that, with an anisotropic Fermi surface, the wavelength in the presence of relaxation will not be a pure cosine form. Equation (2.8) shows also that the amplitude of the

response function, and hence of the displaced charge, is directly proportional to the group velocity at the point of stationary phase, as well as involving the periodic modulation $u$ at the same point in $k$ space.

We shall return to this form (2.8) of the response function when we discuss the interaction between surface adatoms in Section 3 below. However, before doing so, we wish to make the further point that the behaviour of $G(rr')$ as $\exp(ik_0 \cdot r - r')/|r - r'|$ depends on the Fermi surface properties. For instance, if the curvature $K$ in eqn (2.5) tends to zero, that is $\partial^2 E/\partial k_1^2$ or $\partial^2 E/\partial k_2^2$ tend to zero, the asymptotic behaviour of $G(rr')$ is altered. In the stationary phase argument given by Koster[9], what enters is the following integral

$$\int \exp\left\{\frac{i|r - r'|}{2|\nabla_k E|}\frac{\partial^2 E}{\partial k_1^2}k_1^2\right\} dk_1$$

which is proportional to $|\nabla_k E|^{1/2}/|r - r'|^{1/2}(\partial^2 E/\partial k_1^2)^{1/2}$.

Now if $\partial^2 E/\partial k_1^2 = 0$, then we have to replace this integral by one of the form

$$\int \exp\left\{\frac{i|r - r'|}{|\nabla_k E|}\left[\frac{1}{3!}\frac{\partial^3 E}{\partial k_1^3}k_1^3 + \frac{1}{4!}\frac{\partial^4 E}{\partial k_1^4}k_1^4 + \cdots\right]\right\} dk_1.$$

Here the most important term gives a contribution behaving as

$$\frac{1}{|r - r'|^{1/3}}\frac{1}{\{\partial^3 E/\partial k_1^3\}^{1/3}}$$

unless, for some specific reason, $\partial^3 E/\partial k_1^3$ were to vanish, in which case we would have to consider the next term. This implies, for $\partial^3 E/\partial k_1^3$ not equal to zero that

$$G(rr') \sim \frac{\exp\{ik_0 \cdot (r - r')\}}{|r - r'|^{1/2}|r - r'|^{1/3}}$$

$$\times u_{k_0}^*(r)u_{k_0}(r')  \qquad (2.9)$$

while if the third derivative happened to vanish we would obtain

$$G(rr') \sim \frac{\exp\{ik_0 \cdot (r - r')\}}{|r - r'|^{1/2}|r - r'|^{1/4}}$$

$$\times u_{k_0}^*(r)u_{k_0}(r')  \qquad (2.10)$$

The corresponding forms of the response function $F$ in these two cases are

$$F(rr') \sim [\exp\{2ik_{0f} \cdot (r - r')\}u_{k_{0f}}^{*2}(r)u_{k_{0f}}^{\sim 2}(r')$$

$$+\text{complex conjugate}]$$

$$\times |\nabla_{k_{0f}}E|/|r - r'|^{8/3}  \qquad (2.11)$$

and for the case when $\partial^3 E/\partial k_1^3$ vanishes

$$F(rr') \sim [\exp\{2ik_{0f} \cdot (r - r')\}u_{k_{0f}}^{*2}(r)u_{k_{0f}}^2(r')$$

$$+\text{complex conjugate}]$$

$$\times |\nabla_{k_{0f}}E|/|r - r'|^{5/2}.  \qquad (2.12)$$

In the exceptional case when tall the derivatives

$\partial^n E/\partial k_1^n$ are zero, the response function decays in the direction perpendicular to the surface at the stationary phase point as $|r - r'|^{-2}$ times an oscillatory function. This, we stress, is the behaviour which will be found in the case when the Fermi surface is an ideal cylinder, as discussed quite explicitly in the Appendix. Further cases also treated there in relation to the range of the displaced charge can be found by having the second or higher derivatives with respect to $k_1$ zero. When derivatives with respect to both $k_1$ and $k_2$ are zero to all orders, which is the planar Fermi surface case, then the response function can have a range as great as $|r - r'|^{-1}$.

This leads us to comment on a Fermi surface having the schematic form shown in Fig. 2 which is appropriate to the noble metals. The new property here is that along some direction there is no point of stationary phase on the Fermi surface. We shall see, in contrast to the above cases, that this can lead to an asymptotic behaviour of the displaced charge corresponding to a more rapid decay than in any of the previous examples.
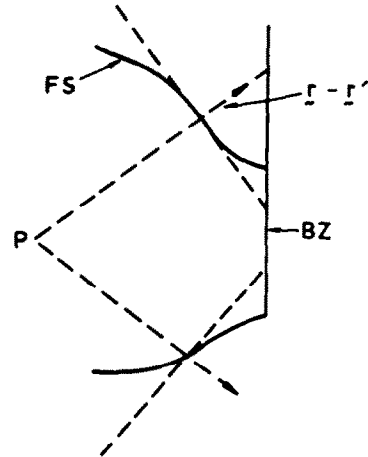


Fig. 2. Schematic form of a Fermi surface with necks such as in copper. BZ is the Brillouin zone boundary contacted by the Fermi surface. The vector $r - r'$ is again shown for the inflexion point. Rotation about a line through $P$ perpendicular to BZ generates the three-dimensional Fermi surface. The cone generated by the dashed arrowed lines divides the directions in coordinate space into the two regions discussed in the text.

As Fig. 2 shows, we can divide the directions in which to discuss the decay of the displaced charge $\Delta\rho$ into two regions separated by the cone shown there. The cone is defined by the points where the second derivative of the energy with respect to $k_1$ vanishes, that is points of inflexion. Outside the cone, the long distance behaviour of the displaced charge is as $r^{-3}$ times an oscillatory function, while over the surface of the cone this gives way to the form $r^{-8/3}$. The question then comes up as to the asymptotic form inside the surface of the cone. Applying the argument of Koster for obtaining $G(rr')$, one appears to have a situation that insofar as no stationary point exists, instead of a decay like

$$G(rr') \sim \frac{1}{|r - r'|} \times \text{oscillatory function}$$

one would have

$$G(rr') \sim \frac{1}{|r-r'|^2} \times \text{oscillatory function.}$$

This would then lead to a response function decaying in this region as

$$F(rr') \sim \frac{1}{|r-r'|^3} \times \text{oscillatory function.}$$

### 3. METAL SURFACE, WITH EMBEDDED IMPURITY

To deal now with the displaced charge round an adatom embedded in a metal surface, we note that, with an infinite barrier at the surface, and a plane of symmetry parallel to the surface coinciding with the infinite barrier position, the Green function can be constructed from the bulk Green function $G_b$ through

$$G(rr'E) = G_b(rr'E) - G_b(rr'_*E) \qquad (3.1)$$

where $r'_*$ is the image of $r'$ as shown in Fig. 3.

Though this assumption is somewhat specific, it is possible that it leads to results for the surface adatom interaction of wider generality; we believe in fact that this is so. But failing a proof of that, the results we obtain below for this case appear of sufficient interest to present in some detail.

Using the form (3.1) in the response function formula (1.3), the response function is evidently

$$F(rr') = i \int dE(G_b(rr') - G_b(rr'_*))[G_b(rr') - G_b(rr'_*)]$$

$$= i \int dE[G_b(rr')G_b(rr') + G_b(rr'_*)G_b(rr'_*)$$

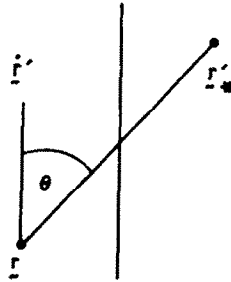$$-2G_b(rr')G_b(rr'_*)]. \qquad (3.2)$$

First of all, for free electrons, it is readily shown that



Fig. 3. Shows planar metal surface, with points $r$ and $r'$ defining direction in metal parallel to surface. Point $r'_*$ is the image of $r'$.

$$i \int dE G_b(rr')G_b(rr'_*) \sim i \int_0^{k_f} \frac{k \exp\{ik[|r-r'|+|r-r'_*|)\} dk}{|r-r'||r-r'_*|}$$

$$+ i \int_{k_f}^{\infty} \frac{k \exp\{-ik[|r-r'|+|r-r'_*|]\} dk}{|r-r'||r-r'_*|}$$

$$\approx \frac{2k_f \cos k_f\{|r-r'|+|r-r'_*|\}}{|r-r'||r-r'_*|\{|r-r'|+|r-r'_*|\}}.$$

Hence the free electron response function has the asymptotic form

$$F(rr') \sim \frac{\cos 2k_f|r-r'|}{|r-r'|^3} + \frac{\cos 2k_f|r-r'_*|}{|r-r'_*|^3}$$

$$- \frac{4\cos k_f\{|r-r'|+|r-r'_*|\}}{|r-r'||r-r'_*|\{|r-r'|+|r-r'_*|\}}. \qquad (3.3)$$

This decreases as $R^{-5} \times$ oscillatory function in the driection parallel to the planar surface, where $R = |r-r'|$.

### 3.1 Bloch wave case

We have now to consider the Bloch wave modifications in the terms involving $r-r'$ and $r-r'_*$ in eqn (3.3), the latter involving the image of $r'$. Corresponding to this, we have two different vectors describing the stationary phase point, $k_{0f}$ and $k'_{0f}$. The response function must then be generalised to

$$\frac{[\exp\{2ik_{0f}\cdot(r-r')\}u_{k_{0f}}^{*2}(r)u_{k_{0f}}^2(r')+c.c.]|\nabla_{k_{0f}}E|}{|r-r'|^3} + \frac{[\exp\{2ik'_{0f}\cdot(r-r'_*)\}u_{k'_{0f}}^{*2}(r)u_{k'_{0f}}^2(r'_*)+c.c.]|\nabla_{k'_{0f}}E|}{|r-r'_*|^3}$$

$$- \frac{4[\exp\{i[k_{0f}\cdot(r-r')+k'_{0f}\cdot(r-r'_*)]\}u_{k_{0f}}^*(r)u_{k_{0f}}(r')u_{k'_{0f}}^*(r)u_{k'_{0f}}(r')+c.c.]}{|r-r'||r-r'_*|\left\{\frac{|r-r'|}{|\nabla_{k_{0f}}E|}+\frac{|r-r'_*|}{|\nabla_{k'_{0f}}E|}\right\}}$$

$$= \frac{[\exp\{2ik_{0f}\cdot(r-r')\}u_{k_{0f}}^{*2}(r)u_{k_{0f}}^2(r')+c.c.]|\nabla_{k_{0f}}E|}{|r-r'|^3} + \frac{[\exp\{2ik'_{0f}\cdot(r-r'_*)\}u_{k'_{0f}}^{*2}(r)u_{k'_{0f}}^2(r')+c.c.]|\nabla_{k'_{0f}}E|}{|r-r'|^3}$$

$$- \frac{4[\exp\{i[k_{0f}\cdot(r-r')+k'_{0f}\cdot(r-r'_*)]\}u_{k_{0f}}^*(r)u_{k_{0f}}(r')u_{k'_{0f}}^*(r)u_{k'_{0f}}(r')+c.c.]}{|r-r'||r-r'_*|\left\{\frac{|r-r'|}{|\nabla_{k_{0f}}E|}+\frac{|r-r'_*|}{|\nabla_{k'_{0f}}E|}\right\}}.$$

since $u_k(r') = u_k(r'_*)$.

the separate terms have the asymptotic forms

$$i \int dE G_b(rr')G_b(rr') \sim \frac{k_f \cos 2k_f|r-r'|}{|r-r'|^3}$$

$$i \int dE G_b(rr'_*)G_b(rr'_*) \sim \frac{k_f \cos 2k_f|r-r'_*|}{|r-r'_*|^3}$$

The leading terms in the asymptotic forms then cancel again, as for free electrons, and we obtain an interaction between adatoms parallel to the planar surface having the form

$$\frac{1}{|r-r'|^3} \times \text{oscillatory function.}$$

Again, as in the bulk metal, if the adatoms cause appreciable relaxation of the metal atoms then it is possible for reciprocal lattice vectors to enter the wavelength.

In the bulk metal, we referred to some exceptional cases, and in particular to ideal cylindrical and to planar Fermi surfaces. In the former case, the interaction of adatoms parallel to the planar surface turns out to decay like $r^{-4}$ times an oscillatory function.

For the Fermi surface appropriate to the noble metals shown in Fig. 3, inside the cone depicted there the interaction between a pair of adatoms parallel to the surface decays as

$$|r - r'|^{-7} \times \text{oscillatory function.}$$

Along the surface of the cone, on the other hand, the interaction decreases as $|r - r'|^{-14/3}$ times an oscillatory function.

We wish to stress that there are circumstances which can occur when exceptional behaviour obtains. Thus, when $\partial^2 E / \partial k_1{}^2 = 0$ and $\partial^3 E / \partial k_1{}^3 \neq 0$, the Fermi surface region giving the most important contribution to the stationary phase integral has the length along $k_1$ of order $|r - r'|^{-1/3}$ and along $k_2$ of order $|r - r'|^{-1/2}$. But when the derivatives of different orders become zero, $\partial^3 E / \partial k_1{}^3 = \partial^4 E / \partial k_1{}^4, \ldots = 0$, the Fermi surface region becomes greater and greater, going along $k_1$ like $|r - r'|^{-1/n+1}$. In the limit when all the derivatives are zero, this region becomes the whole cylindrical Fermi surface. In order to obtain the result that the interaction between atoms decreases in an order $|r - r'|^{-2}$ with respect to the bulk, one must have that the region around the stationary phase point dominating the integral must be small compared with the whole Fermi surface. Such arguments, as elaborated a little below, and in the Appendix, do not apply to cylindrical or planar Fermi surfaces. If the Fermi surface has a very small curvature; that is, it is close to the cylindrical or planar forms, then $|r - r'|$ has to be very large indeed if we wish to apply the arguments of the paper. In other words, for relatively short distances, for an almost planar Fermi surface, the interaction will fall off like $1/r$, but for very large distances this will go over into the $r^{-5}$ form.

To summarise then, for a cylindrical Fermi surface, the interaction between ions in both bulk and surface

cases will fall off like $r^{-2}$. However, if one has a small curvature, rather than zero, then the bulk behaviour will be like $r^{-2}$ at shorter distances, but will go over into $r^{-3}$ at very large separations. For the surface case, the shorter distance behaviour of $r^{-2}$ will give way at sufficiently large distances to $r^{-5}$.

For the planar Fermi surface, in contrast, the bulk and surface interactions fall off as $r^{-1}$. However, the introduction of a small curvature leads to shorter distance behaviour in the bulk as $r^{-1}$, giving way at large distances to $r^{-3}$. In the surface, the shorter distance behaviour of $r^{-1}$ eventually goes over into $r^{-5}$.

## 4. DISCUSSION

The effects of an anisotropic Fermi surface on the screening of a charged impurity in a metal will be accessible, in favourable cases, from nuclear magnetic resonance experiments. Unfortunately, to date we can find but one experiment of this kind which bears on the anisotropy of the screening charge round an impurity in a metal. Thus Drain[10] has observed structure due to nuclear quadrupole interaction in the $^{27}$Al magnetic resonance from dilute alloys of zinc in Al. These results support the existence of an oscillatory displaced charge round the zinc impurity atoms, as do other examples. But the point to be made here is that Drain can demonstrate from his measurements the necessity to consider departures from spherical symmetry of the displaced charge round the Zn atoms.

There are, of course, a number of points to be made immediately. First, the effects he sees may not be sufficiently well represented by appeal to merely the asymptotic form of the displaced charge. Secondly, the Zn atom, having a different core from the matrix Al atoms, may well be poorly treated in linear response. Also, since Al is normally discussed as a rather free electron metal, the Brillouin zone effects discussed here, while undoubtedly present, may be quite small in this case. Nevertheless, we think it of interest that anisotropic effects can be demonstrated by NMR in the dilute AlZn alloys, and this may be an interesting area for further work, using matrices with more anisotropic Fermi surfaces than Al.

Regarding area (ii) referred to in Section 1, it seems also possible that there will be different interaction energies in different orientations for charged complexes of defects in metals with highly non-spherical Fermi surfaces.

The third area referred to above concerns force fields in pure metals. Johnson[11] has pointed out that it appears to be difficult to describe the lattice properties of gold by means of central pair potentials. It is tempting to associate this with the necks on the Fermi surface (see Fig. 2), and the corresponding anisotropic screening of Au$^+$ ion itself in the pure metal. But, of course this will involve a full investigation of the electron screening, and perhaps also consideration of relativistic effects quite carefully. Nevertheless, we anticipate that, in the future, such departures from sphericity in the screening clouds will have to be incorporated into the lattice dynamical treatment of not only a noble metal such as gold but in
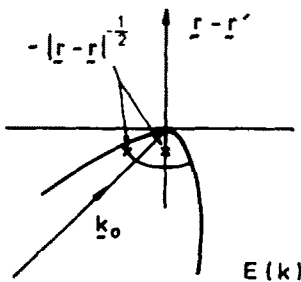


Fig. 4. As in Fig. 1 except that region contributing to stationary phase integral is shown by the new curve. The linear dimension of this region, i.e. the distance between the two crosses, is of order $|r - r'|^{-1/2}$.

numerous transition metals. However, we need to caution the reader that before the quantitative discussion could be made in this general area, self-consistency would have to be imposed between the displaced charge $\Delta\rho$ and the localised perturbation $V(r)$ and this goes beyond the scope of the present paper. That such self-consistency is important quantitatively is clear, e.g. from the work of Rudnick and Stern[12].

Our other main comments concern our findings for adatoms in a metal surface. Here, provided the Fermi surface is spherical, the displaced charge out along a direction parallel to the plane surface will be short-ranged compared with eqn (1.1). But we have seen again how Fermi surface topology can affect the range. While these results are in principle relevant to area (ii); e.g. to the interaction between suitable adsorbed atoms on the surface of high electron density transition metals, some additional comments are called for here. Thus, Einstein[4] has cautioned against assuming that the asymptotic regime treated here is necessarily going to be directly reflected in the interaction between chemisorbed atoms at the small separations at which it is significant.

Furthermore we want to stress that the surface calculations reported here can only be applied to:

(i) *Neutral covalently*, bonded impurities with relatively weak adatom-substrate coupling. Einstein's work[4] indicates that with strong coupling between the adatom and the substrate the law $r^{-5} \times$ oscillatory function can be strongly modified.

(ii) *Impurities embedded in the metal*; i.e. with the impurities located in a region with high electronic density. Indeed, for ions outside the surface the most relevant interaction is the dipole–dipole one as discussed by Kohn and Lau[13]. The role of elastic interactions must also be kept in mind at large separations[14, 15].

The problem of the Ruderman–Kittel indirect interaction between localised spins in metallic matrices[16] has many similarities with the problem of displcaced charge treated in the present paper. Work on magnetic interactions by Caroli[17] should also be referred to in this context. We can, e.g. expect different ranges of exchange interactions between localised spins embedded in a metal surface and the same spins treated in the bulk. Indeed, for a closed Fermi surface and the case of a bulk metal, the approach of Roth *et al.*[18] for spin polarization could be applied to obtain similar results to the ones given here for the displaced charge, for this particular case.

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## APPENDIX

*Relation to other models*

In this Appendix, we make more explicit the relation of the general method employed in this paper to specific models, and especially to that of Lau and Kohn[3]. We shall find it convenient to return to the cases of (i) a planar Fermi surface and (ii) a cylindrical Fermi surface, on which we commented in the main text.

(i) *Planar Fermi surface.* Let the $x$ direction be perpendicular to the planar Fermi surface. For the Green function

$$G \sim \sum_k \psi_k^*(r)\psi_k(r')/(E - E_k)$$

we note that $E_k$ depends only on $k_x$. Thus, introducing the Bloch wave function we can write

$$G(rr'E) = \sum_{k_x} \frac{\exp(ik_x X)}{E - E_{k_x}} \sum_{k_y k_z} \exp(ik_y Y)$$
$$\times \exp(ik_z Z) u_k^*(r) u_k(r') \qquad (A1)$$

with $X = x - x'$, $Y = y - y'$ and $Z = z - z'$.

For $Y = Z = 0$, this shows that

$$G(rr'E) \sim \exp(ik_{x0} X) \qquad (A2)$$

where $E(k_{x0}) = E$, while for $Y$ and $Z$ going to infinity

$$G(rr'E) \sim \exp(ik_{x0} X) \frac{1}{Y} \frac{1}{Z}$$
$$\times \text{oscillatory functions in } Y \text{ and } Z. \qquad (A3)$$

This demonstrates, by means of eqn (1.3), that for the response function we have

$$F(rr') \sim \frac{\cos 2k_{x0f} X}{X} \frac{1}{Y^2} \frac{1}{Z^2}$$
$$\times \text{oscillatory functions in } Y \text{ and } Z$$
$$\text{for } X, Y, Z \rightarrow \infty \qquad (A4)$$

or

$$\frac{\cos 2k_{x0f} X}{X} \quad \text{for} \quad x \rightarrow \infty, \quad Y = Z = 0. \qquad (A5)$$

From these results, and using the arguments of Section 3, it is straightforward to show that the interaction between two impurities placed on the surface containing the $x$-direction behaves

asymptotically as

$$\frac{\cos 2k_{x0f}X}{X} \qquad (A6)$$

which is in agreement with the model calculation of Lau and Kohn.

(ii) *Cylindrical Fermi surface.* For a cylindrical Fermi surface, we can follow again the above line of argument to show that

$$G(\mathbf{rr}'E) \sim \frac{\exp(ik_{x0}X)}{X^{1/2}} \frac{1}{Z} \times \text{oscillatory function in } Z \qquad (A7)$$

$Z$ being along the axis of the cylinder. Then the response function has the form

$$F(\mathbf{rr}') \sim \frac{\cos 2k_{x0f}X}{X^2} \frac{1}{Z^2} \times \text{oscillatory function in } Z. \qquad (A8)$$

These results are appropriate to the bulk metal.

For a model of a surface corresponding to the Green function (3.1), the interaction between two adatoms parallel to the planar surface goes like

$$\frac{1}{X^2} \cos 2k_{x0f}X. \qquad (A9).$$