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COMMENTS AND ADDENDA

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Insensitivity of the Infinite-Wavelength Surface Plasmon Frequency to the Electron Density Profile*

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Assuming that the ground-state electron density at a jellium-vacuum interface is the self-consistent Hartree density, and using the random-phase approximation to describe the electronic excitation spectrum, we show that the infinite-wavelength surface plasmon frequency is $1/\sqrt{2}$ times the bulk plasma frequency. This result is independent of the shape of the jellium background, and thus applies to a wide range of self-consistent electron density profiles.

INTRODUCTION

With the advent of reproducible experiments[1] on the scattering of low-energy electrons from metal surfaces, and new developments in the theory of such phenomena,[2] there has been a resurgence of interest in the theory of surface excitations in the electron gas. In particular, one would like to know what the measurement of the dispersion relation of the surface plasmon tells us about the structure of the electronic wave function in the surface region.

In a previous paper,[3] the author has shown that by making a high-frequency expansion of the random-phase approximation (RPA) it is possible to obtain the "classical" surface plasmon frequency,[4]

$$(1\sqrt{2})\omega_p,$$

in which

$$\omega_p = (4\pi e^2 n_\infty/m)^{1/2},$$

where n_∞ is the bulk electron density. However, in addition to the high-frequency expansion, it was necessary in I to replace the self-consistent ground-state electron density (the Hartree density) by a square density profile.

The purpose of the present note is to show that at infinite wavelength along the surface neither the high-frequency approximation nor the assumption of a square density profile is necessary to obtain the "classical" result. We obtain the classical surface plasmon frequency for the actual self-consistent electron density with no expansion in the RPA equation.

THEORY

We refer to I for the derivation of the RPA equation and quote in a slightly modified form Eq. (14) of that reference for $\varphi_{q\omega}(z)$, the fluctuating potential associated with an excitation of frequency ω, and wave vector $\vec{q}$ along the surface, as a function of z, the coordinate perpendicular to the surface ($q \equiv |\vec{q}\,|$):

$$\varphi_{q\omega}(z) = \frac{4\pi e^2}{q} \int \frac{d^2k}{(2\pi)^2} \sum_{nn'} \theta_{kn'}$$

$$\times \frac{(q^2 + 2\vec{k}\cdot\vec{q})/2m + \omega_n - \omega_{n'}}{\omega^2 - [(q^2 + 2\vec{k}\cdot\vec{q})/2m + \omega_n - \omega_{n'}]^2}$$

$$\times \int_{-\infty}^{\infty} dz'\, e^{-q|z-z'|}\, \psi_n(z')\, \psi_{n'}^*(z')$$

$$\times \int_{-\infty}^{\infty} dz''\, \psi_n^*(z'')\psi_{n'}(z'')\varphi_{q\omega}(z''). \tag{1}$$

In Eq. (1), θ_{kn} is the step function $\theta(\mathcal{E}_F - k^2/2m - \omega_n)$ with $\mathcal{E}_F$ the electron Fermi energy. The $\psi_n(z)$ are single-particle wave functions which satisfy

$$\left(\frac{1}{2m}\frac{d^2}{dz^2} + \omega_n - V_H(z)\right) \psi_n(z) = 0. \tag{2}$$

The Hartree potential $V_H(z) = -2\pi e^2 \int dz' \mid z - z \mid \times [n_0(z') - n_B(z')]$, where $n_0(z)$ is the self-consistent electron density and $n_B(z)$ is the jellium-background density. This expression for $V_H(z)$ is the only place in the theory where $n_B(z)$ enters. Therefore any result which bears no explicit dependence on $V_H(z)$ holds for any jellium-background density profile, and thus for a wide range of self-consistent electron densities.

Using Eq. (2), and integrating by parts, it is easy to prove the identity

$$\left(\omega_n - \omega_{n'} + \frac{q^2}{2m}\right)\int_{-\infty}^{\infty} dz'\, e^{-q|z-z'|}\, \psi_n(z')\psi_{n'}^*(z')$$

$$\equiv \frac{q}{m}\left[\psi_n(z)\psi_{n'}^*(z) - \int_{-\infty}^{\infty} dz' \operatorname{sgn}(z-z') \times e^{-q|z-z'|}\, \frac{d\psi_n}{dz'}\, \psi_{n'}^*(z')\right]. \tag{3}$$

This identity, together with the fact that any term in Eq. (1) odd in $\vec{k}\cdot\vec{q}$ contributes zero when we perform the integral on d^2k, enables us to convert Eq. (1) to the equivalent form

$$\varphi_{q\omega}(z) = \frac{4\pi e^2}{m}\int \frac{d^2k}{(2\pi)^2} \sum_{nn'} \theta_{kn'}\left[\omega^2 - \left(\frac{2\vec{k}\cdot\vec{q} + q^2}{2m} + \omega_n - \omega_{n'}\right)^2\right]^{-1}$$

$$\times\left(1 + \frac{2(\vec{k}\cdot\vec{q}/m)^2}{\omega^2 - (q^2/2m + \omega_n - \omega_{n'})^2 - (\vec{k}\cdot\vec{q}/m)^2}\right)\left[\psi_n(z)\psi_{n'}^*(z) - \int_{-\infty}^{\infty} dz' \operatorname{sgn}(z-z')e^{-q|z-z'|}\, \frac{d\psi_n}{dz'}\, \psi_{n'}^*(z')\right]$$

$$\times \int_{-\infty}^{\infty} dz''\, \psi_n^*(z'')\psi_{n'}(z'')\varphi_{q\omega}(z'') \quad .$$

We now allow q to approach zero. In the limit, we obtain

$$\varphi_{0\omega}(z) = \frac{4\pi e^2}{m}\int \frac{d^2k}{(2\pi)^2} \sum_{nn'} \theta_{kn'}\, \frac{1}{\omega^2 - (\omega_n - \omega_{n'})^2}$$

$$\times\left[\psi_n(z)\psi_{n'}^*(z) - \int_{-\infty}^{\infty} dz' \operatorname{sgn}(z-z')\, \frac{d\psi_n}{dz'}\, \psi_{n'}^*(z')\right]$$

$$\times \int_{-\infty}^{\infty} dz''\, \psi_n^*(z'')\psi_{n'}(z'')\varphi_{0\omega}(z''). \tag{5}$$

As an ansatz we try $\varphi_{0\omega}(z) = \text{const} = 1$. In this case Eq. (5) becomes

$$1 = \frac{2\pi e^2}{m\omega^2}\left(2n_0(z) - \int_{-\infty}^{\infty} dz' \operatorname{sgn}(z-z')\frac{dn_0}{dz'}\right), \tag{6}$$

where $n_0(z)$ is just the ground-state density,

$$n_0(z) \equiv \int \frac{d^2k}{(2\pi)^2} \sum_n \theta_{kn}\psi_n^*(z)\psi_n(z), \tag{7}$$

and where we have used the fact that

$$\int_{-\infty}^{\infty} dz''\, \psi_n^*(z'')\, \psi_{n'}(z'') = \delta_{nn'} \; .$$

Integrating by parts in Eq. (6), we see that $\varphi_{0\omega} = 1$ is a consistent solution of Eq. (5) if $1 = (2\pi e^2/m\omega^2) \times [n_0(+\infty) + n_0(-\infty)]$. Thus for a metal-vacuum interface, letting $n_0(\infty) = 0$, $n_0(-\infty) \equiv n_\infty$, we find the surface plasmon frequency $\omega^2 = 2\pi e^2 n_\infty/m = \frac{1}{2}\omega_p^2$; ω_p is the bulk plasma frequency.

We have made no assumption about the density $n_0(z)$ other than that it be the self-consistent Hartree density, given by Eq. (7). Since we can choose the shape of the jellium background in an essentially arbitrary manner, we conclude that the surface plasmon at $q = 0$ will have frequency $\frac{1}{2}\omega_p^2$ for a wide range of ground-state density shapes. This is somewhat unfortunate from the experimentalist's point of view, and provides an impetus for the theoretical study of the corrections due to finite q.

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Comments on the Knight Shift in Bismuth and Other p-Band Diamagnetic Metals

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The role of p-polarization and conduction-electron diamagnetism in some diamagnetic metals and intermetallic compounds, which have negative Knight shifts, is examined.

It has been known for some time that the diamagnetic susceptibility contributes a negative term, $\kappa_{\rm dia}$, to the Knight shift $\mathcal{K}$. The first expression was given by Das and Sondheimer[1] and applied particularly to Be. They obtained, in the free-electron approximation,

$$\mathcal{K}_{\rm dia} = \frac{8\pi}{3}\chi_{\rm dia} \tag{1a}$$

$$= -\frac{8\pi}{3}\left(\tfrac{1}{3}\chi_p\right)\left\langle\frac{m}{m^*}\right\rangle^2 , \tag{1b}$$

where the symbols have their usual meanings. The Pauli and diamagnetic conduction-band susceptibilities χ_p and $\chi_{\rm dia}$ are in volume units. One purpose of this paper is to point out that the above term may be significant in diamagnetic metals and semimetals other than Be, such as Bi, Te, $\mathrm{Na\underline{Tl}}$, and $\mathrm{Bi\underline{In}}$, which have a negative $\mathcal{K}$ (the p-electron atom sites sampled by $\mathcal{K}$ are underlined). Now, there exist mechanisms other than $\mathcal{K}_{\rm dia}$, which may make negative contributions to $\mathcal{K}$. One of these is p-electron core polarization, and it has recently been fashionable to attribute the above and certain other negative Knight shifts to this term. The purpose of the present comment is to indicate that there are quantitative difficulties with this attribution. It appears likely that $\mathcal{K}_{\rm dia}$ predominates at least in Bi and Be, and that this and other mechanisms are important to certain compounds. It will also become clear that the understanding of p-core polarization effects is grossly inadequate, the situation being far worse than that for d-core polarization effects in transition metals.

Subsequent to the work of Das and Sonheimer, Das and co-workers made energy band estimates[2] of a number of the Knight-shift contributions in Be. These calculations emphasized the contribution of p-core polarization to the negative Knight shift. Recently it has been concluded[3] that the p term, as deduced from the calculations, cannot be responsible for the observed negative $\mathcal{K}$ and that $\mathcal{K}_{\rm dia}$ must predominate. Be is a somewhat special case in that its $\mathcal{K}$ is small (-0.0025%)[4] as well as negative. The other materials which we will consider have significantly larger negative $\mathcal{K}$ values. In the remainder of this comment we will inspect $\mathcal{K}_{\rm dia}$, p-core polarization, and other negative terms. This will be followed by consideration of the experimental situation for Bi and some of the compounds.

It has been pointed out[5] that the Knight shift arising from the orbital electronic currents can be conveniently divided into two parts: One including Eq. (1) and a second one associated with the short-range part of the orbital hyperfine interaction. Using the tight-binding scheme, Clogston *et al.* obtained,[6] an alternative description of the short-range part which includes the Van Vleck or orbital Knight shift, and a term of the form

$$\mathcal{K}_2 = \frac{8\pi}{3}\chi_{\rm dia}\frac{\langle r^{-1}\rangle}{\langle r^2\rangle} r_{\rm WS}^3 , \tag{2}$$

where $\chi_{\rm dia}$ is the single-site diamagnetism and $r_{\rm WS}$ the Wigner-Seitz radius. For the tight-binding wave functions involved, the $\langle r^{-1}\rangle r_{\rm WS}^3/\langle r^2\rangle$ factor will generally have a value in excess of 10 thus enhancing the diamagnetic Knight shift. It is, of course, not clear that such a tight-binding description is relevant to a p-band metal. There are additional terms, in either the Clogston[6] or Hebborn[5] description, whose behaviors are not clearly discernible.[7] We will em-