

Static electronic susceptibility, $\chi(q_{\parallel}, z, z')$, of the Lang-Kohn jellium surface

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We present the first accurate values of $\chi(q_{\parallel}, z, z')$, the static susceptibility of a jellium surface, including (i) finite surface wave vector q_{\parallel} ; (ii) Friedel oscillations (from an exact kinetic energy functional); (iii) Kohn-Sham exchange-correlation effects (Wigner form); (iv) self-consistent screening; (v) realistic Lang-Kohn zero-order profile; and (vi) comparison, for $r_s = 2.07$, with a useful approximation.

The self-consistent and non-self-consistent susceptibilities $\chi(\bar{r} - \bar{r}')$ and $\chi^0(\bar{r} - \bar{r}')$ of the *uniform* electron gas have been quite thoroughly studied.^{1,2} Computation of their space Fourier transforms $\chi(q)$ and $\chi^0(q)$ [$\equiv \chi^{\text{Lindhard}}(q)$] is facilitated by translational invariance in \bar{r} space. For the jellium model of a metal surface,³ broken symmetry in the z direction leads one to consider susceptibilities $\chi(q_{\parallel}, z, z')$ and $\chi^0(q_{\parallel}, z, z')$ defined as follows:

$$\Delta n(\bar{r}) = \cos(\bar{q}_{\parallel} \cdot \bar{r}) \int_{-\infty}^{\infty} \chi(q_{\parallel}, z, z') \Delta V^{\text{ext}}(z') dz' + O((\Delta V^{\text{ext}})^2) \tag{1}$$

$$= \cos(\bar{q}_{\parallel} \cdot \bar{r}) \int_{-\infty}^{\infty} \chi^0(q_{\parallel}, z, z') \Delta V^{\text{sc}}(z') dz' + O((\Delta V^{\text{sc}})^2) \tag{2}$$

Here $\Delta n(\bar{r})$ is the change in electron number density at \bar{r} , induced by an *external* source yielding an electron potential energy

$$\Delta V^{\text{ext}}(\bar{r}) = \cos(\bar{q}_{\parallel} \cdot \bar{r}) \Delta V^{\text{ext}}(z)$$

where $\bar{q}_{\parallel} = q_x \hat{x} + q_y \hat{y}$. ΔV^{sc} is a *total* effective self-consistent potential which, in density functional theory, includes external, Hartree, and exchange-correlation terms.

It has recently been argued^{4,5} that $\chi(q_{\parallel}, z, z')$ is important in the study of static and lattice-dynamical properties of simple-metal surfaces within a pseudopotential model. Accurate results equivalent to values of $\chi(q_{\parallel} = 0, z, z')$ are already known within local density functional theory^{6,7} but no such results exist for finite q_{\parallel} , so that features arising from crystal surface structure cannot reliably be described. A number of workers⁸ have used finite step or barrier models, neglected exchange and correlation, used semi-classical approaches which omit Friedel oscillations, or have given expressions considered too complex for practical numerical evaluation. Our method, while similar to others, avoids these limitations. Full details of our formulas, which are related to ones for spin susceptibility and atomic polarizability,⁹ will appear elsewhere.⁴ A summary follows.

Consider electrons moving in an external potential $V_{\pm}^{\text{jell}}(z)$ due to a half-space $z < 0$ of uniform jellium background, plus an external three-dimensional perturbation $\Delta V^{\text{ext}}(\bar{r})$. The self-consistent Kohn-Sham equation¹⁰ is

$$[-\hbar^2 \nabla^2 / 2m + V_0^{\text{LK}}(z) + \Delta V^{\text{sc}}(\bar{r})] \Psi_{\bar{k}}(\bar{r}) = \epsilon_{\bar{k}} \Psi_{\bar{k}}(\bar{r}) \tag{3}$$

Here the total self-consistent potential energy is composed of external, exchange-correlation, and self-consistent Coulomb terms:

$$V_0^{\text{LK}}(z) + \Delta V^{\text{sc}}(\bar{r}) = V_{\pm}^{\text{jell}}(z) + \Delta V^{\text{ext}}(\bar{r}) + \mu_{\text{xc}}[n_{\text{LK}}(z) + \Delta n(\bar{r})] + e^2 \int d^3 r' \frac{n_{\text{LK}}(z') + \Delta n(\bar{r}')}{|\bar{r} - \bar{r}'|} \tag{4}$$

where $\mu_{\text{xc}}(n)$ is the exchange-correlation contribution to the chemical potential of a uniform gas of density n .

The zero-order problem [$\Delta V^{\text{ext}} = 0 = \Delta V^{\text{sc}}, \Delta n(\bar{r}) = 0$] is the one-dimensional jellium problem solved by Lang and Kohn,³ with box-normalized eigenfunctions

$$\Psi_{\bar{k}}^0(\bar{r}) = (2/\Omega)^{1/2} \exp[i(k_x x + k_y y)] \psi_{kz}(z) \tag{5}$$

$$\psi_k(z) \underset{z \rightarrow -\infty}{\sim} \sin[kz - \gamma(k)] \tag{6}$$

(a) *Non-self-consistent susceptibility* $\chi^0(q_{\parallel}, z, z')$. We temporarily assume the total self-consistent potential-energy perturbation $\Delta V^{\text{sc}}(\bar{r})$ to be known, and to have a sinusoidal variation in the xy plane. Then the first-order correction $\Delta \Psi$, to the zero-order Lang-Kohn solution $\Psi_{\bar{k}}^0(\bar{r})$, satisfies

$$[-\hbar^2 \nabla^2 / 2m + V_0^{\text{LK}}(z) - \epsilon_{\bar{k}}] \Delta \Psi_{\bar{k}}(\bar{r}) = -\Delta V^{\text{sc}}(z) \cos(\bar{q}_{\parallel} \cdot \bar{r}) \Psi_{\bar{k}}^0(\bar{r}) \tag{7}$$

The solutions $\Delta \Psi_{\bar{k}}(\bar{r})$ have a surface-parallel position dependence $\exp[i(\bar{k}_{\parallel} \pm \bar{q}_{\parallel}) \cdot \bar{r}]$, leading to a

one-dimensional (1D) Schrödinger equation containing the zero-order potential $V_0^{LK}(z)$, with energy $E = \epsilon_{\vec{k}}^{(0)} - \hbar^2(\bar{k}_{\parallel} \pm \bar{q}_{\parallel})^2/2m$. [Note: E can lie below the minimum of $V_0^{LK}(z)$.] We solve the 1D equation via a Green function constructed from “right” and “left” zero-order solutions at energy E , thus avoiding infinite summations. This gives an expression for $\Delta n(\vec{r})$ in the form of Eq. (2) with

$$\chi^0(q_{\parallel}, z, z') = (8m/\pi\hbar^2) \int d^3k \Theta(k_F - k) \psi_{\vec{k}_z}^+(z) \psi_{\vec{k}_z}^+(z') \psi_p^+(z_{>}) \psi_p^-(z_{<}) / |p| . \quad (8)$$

Here, $p = (k_z^2 - 2k_x q_{\parallel} - q_{\parallel}^2)^{1/2}$ (which can be imaginary), while $\psi_{\vec{k}}^{\pm}$, $\psi_{\vec{k}}$ are solutions of

$$[-\hbar^2 d^2/(2mdz^2) + V_0^{LK}(z) - V_0^{LK}(-\infty) - \hbar^2 K^2/2m] \psi_K(z) = 0 , \quad (9)$$

satisfying the following boundary conditions:

(i) For K real,

$$\psi_K^+(z) \sim \begin{cases} \sin[Kz - \gamma(K)], & z \rightarrow -\infty \\ 0, & z \rightarrow \infty \end{cases}$$

$$\psi_K^{\hat{c}}(z) \sim \begin{cases} \cos[Kz - \gamma(K)], & z \rightarrow -\infty \\ \infty, & z \rightarrow +\infty \end{cases}$$

(ii) For K imaginary,

$$\psi_K^+(z) \sim \begin{cases} -\exp(-|K|z)/2, & z \rightarrow -\infty \\ 0, & z \rightarrow +\infty \end{cases}$$

$$\psi_K^{\hat{c}}(z) \sim \begin{cases} \exp(|K|z), & z \rightarrow -\infty \\ \infty, & z \rightarrow +\infty \end{cases}$$

We obtained ψ^+ and ψ^c numerically, using zero-order Lang-Kohn surface potentials $V_0^{LK}(z)$ generated by

Ferrante¹¹; these are self-consistent and employ local exchange-correlation potentials derived from the Wigner interpolation formula.¹² We performed the k_x integral in Eq. (8) analytically, and converted $\int dk_x$ to $\int dp$. There resulted a two-dimensional integral in the k_z, p plane involving [for $q_{\parallel} < 2k_F$ (bulk)] finite pieces on both the real- p and the imaginary- p sheets. The results for aluminium ($r_s = 2.07$) are shown in Fig. 1.

Features of the solution are as follows: (i) For $z \sim z' \ll -1$ a.u., χ^0 reduces to the bulk result

$$\chi^0(q_{\parallel}, z, z') \sim \chi^{0\text{bulk}}(q_{\parallel}, |z - z'|)$$

$$= (2\pi)^{-1} \int_{-\infty}^{\infty} \chi^{\text{Lindhard}}[(q_{\parallel}^2 + q^2)^{1/2}] \times \exp(iqz) dq . \quad (10)$$

(ii) For $z' \sim 0$ and $z \rightarrow -\infty$,

$$\chi^0(q_{\parallel}, z, z') \sim c |\xi|^{-2} \times \begin{cases} \sin[(4k_F^2 - q_{\parallel}^2)^{1/2} |\xi| - \phi], & q_{\parallel} < 2k_F \\ \exp[-(q_{\parallel}^2 - 4k_F^2)^{1/2} |\xi|], & q_{\parallel} > 2k_F \end{cases} , \quad (11)$$

where $\xi = z - z'$, and ϕ and c are independent of z . Thus Friedel oscillations appear only when $q_{\parallel} < 2k_F$.

(b) *Self-consistent screening.* From Eq. (1), the self-consistent susceptibility is just the linear response, at z , to an external perturbation

$$\Delta V^{\text{ext}}(\vec{r}) = \delta(z - z') \cos(\bar{q}_{\parallel} \cdot \vec{r}) .$$

We put this into the linearized form of Eq. (4) and performed the x - and y -Coulomb integrations analytically. Multiplying the resultant expression for $\Delta V^{\text{sc}}(z_1)$ by $\chi^0(q_{\parallel}, z, z_1)$, and using Eq. (2), we obtained

$$\chi(q_{\parallel}, z, z') = \chi^0(q_{\parallel}, z, z')$$

$$+ \int dz_1 Q(q_{\parallel}, z, z_1) \chi(q_{\parallel}, z_1, z') , \quad (12)$$

where

$$Q(q_{\parallel}, z, z_1) = \int [\mu'_{xc}(z_1) \delta(z_2 - z_1)$$

$$+ 2\pi e^2 \exp(-q_{\parallel} |z_1 - z_2|) / q_{\parallel}]$$

$$\times \chi^0(q_{\parallel}, z, z_2) dz_2 , \quad (13)$$

and $\mu'_{xc}(z_1)$ is the density derivative evaluated at the Lang-Kohn density $n_{LK}(z_1)$.

We discretized Eq. (12) and solved it iteratively, taking care with the Friedel oscillations for $q_{\parallel} < 2k_F$. The results appear in Figs. 1 and 2.

(c) *A simple approximation for χ .* The lack of Friedel oscillations for $q_{\parallel} > 2k_F$ does *not* indicate that our solutions in this regime are the Thomas-Fermi ones. A quasilocal approximation is available, however: Consider

$$\chi^{\text{ansatz}}(q_{\parallel}, z, z') = \chi^{\text{bulk}}(q_{\parallel}, |z - z'|, \bar{n}) , \quad (14)$$

where χ^{bulk} is the self-consistently screened version of Eq. (10), including exchange and correlation. The bulk density \bar{n} used in (14) is the average of zero-order jellium densities, $\bar{n} = [n_{LK}(z) + n_{LK}(z')]/2$. Figure 2 shows that, in the case of aluminum at least, this ansatz is very accurate for $q_{\parallel} > 2k_F$ and surprisingly good for $q_{\parallel} < 2k_F$, though the Friedel oscillations in the latter case are, of course, misrepresented. These results largely vindicate the use of χ^{ansatz} rather than χ in a recent calculation of the surface energy of Al.⁵

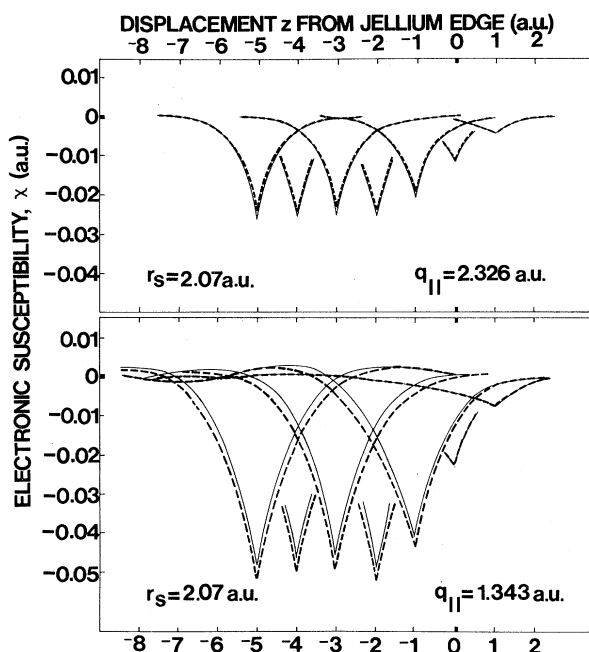


FIG. 1. Electronic susceptibilities of the Lang-Kohn jellium surface with Fermi wave number $k_F = 0.927$ (aluminum), for two nonzero surface wave vectors $q_{||}$. The dashed line represents the non-self-consistent susceptibility $\chi^0(q_{||}, z, z')$ from Eq. (8). The solid line represents the self-consistent susceptibility χ from Eq. (12). All quantities are in a.u. (atomic units, $e = \hbar = m_e = 1$). The cusps indicate the location of z' .

In practice, we suggest the use of Eq. (14) for z and z' both near the surface, or both deep in the metal, in the case $q_{||} < 2k_F$, and for all z, z' in the case $q_{||} > 2k_F$. We have developed efficient algorithms for $\chi^{\text{bulk}}(q_{||}, |z - z'|, \bar{n})$. Equations (11), together with other results which we are developing to deal with asymptotic reflection and interference terms, should then reduce the amount of tabulation required to give a complete summary of χ . Detailed calculations based on wave functions may therefore

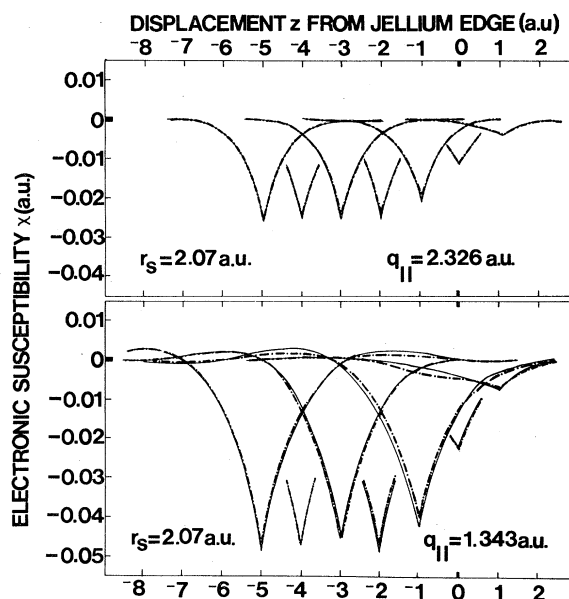


FIG. 2. Comparison between the self-consistent susceptibility $\chi(q_{||}, z, z')$ from Eq. (8) (solid line) and the average-density approximation $\chi^{\text{ansatz}}(q_{||}, z, z')$ from Eq. (14) (dash-dotted line).

be unnecessary in the future. We should also point out that, because of the simple way in which μ_{xc} enters this theory [see Eq. (13)], improved and even nonlocal density functionals can easily be included. We can thus hope that, shortly, lack of a reliable static jellium surface susceptibility will no longer be an obstacle in the theory of simple-metal surfaces.

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