New Approximation for Screened Exchange and the Dielectric Constant of Metals*

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Using self-consistent-field techniques, we derive the dynamic dielectric constants appropriate to electrons and to test charges which differ with the inclusion of screened Hartree-Fock exchange. For large wave vector (in the static limit), the exchange contributions exceed the Coulomb contributions, and the electronic dielectric constant becomes less than unity. We also derive a screened exchange potential linearly dependent on the charge density, which seems preferable to the Slater $\rho^{1/3}(\mathbf{r})$ approximation for energy-band calculations.

I. INTRODUCTION

IN a famous paper, Hubbard,[1] using complicated diagrammatic techniques, derived a formula for the exchange and correlation energy of a free-electron gas:

$$E^{\text{exch+corr}}=-\int_0^{e^2}\frac{d\lambda}{\lambda}\int_0^{\infty}\frac{\Omega d^3\kappa}{(2\pi)^3}\times\left\{\int_0^{\infty}\frac{\hbar d\omega}{2\pi}\,\mathrm{Im}\left[\frac{1}{\epsilon_t(\kappa,\omega)}\right]+\frac{2\pi N\lambda}{\kappa^2\Omega}\right\},\quad(1)$$

where N is the number of electrons in a gas of volume Ω and $\epsilon_t(\kappa,\omega)$, the dielectric constant, is defined in terms of an infinite sum of diagrams. Nozières and Pines[2] derived the same equation using only the definition of ϵ_t as the dielectric response function $V_t(\kappa,\omega)=V_0(\kappa,\omega)/\epsilon_t(\kappa,\omega)$, where $V_t(\kappa,\omega)$ is the potential seen by a test charge when an external potential $V_0(\kappa,\omega)=V_0e^{i\kappa\cdot\mathbf{r}}e^{i\omega t}$ is applied. By considering a single diagram Hubbard obtained ϵ in the random-phase approximation (RPA) $\epsilon(\kappa,\omega)=1+\chi(\kappa,\omega)$. By approximating the additional contribution of several exchange diagrams he obtained

$$\epsilon_t(\kappa,\omega)=1+\chi(\kappa,\omega)[1-\chi(\kappa,\omega)f_H(\kappa)]^{-1},\quad(2)$$

where

$$f_H(\kappa)=\tfrac{1}{2}\kappa^2[\kappa^2+k_F^2+K_s^2]^{-1},\quad(3)$$

with k_F the Fermi wave vector and K_s an inverse screening length which did not appear in Hubbard's original $f_H(\kappa)$, but which was suggested by him in private communications to several authors[3–5] and whose magnitude has varied from author to author.

Cohen and Phillips[6] were the first to point out that nearly self-consistent crystal potentials could be obtained by considering the ionic pseudopotential[7] to be screened by the valence electrons:

$$V_{\text{crystal}}=\sum_{\kappa}V_{\text{ion}}(\kappa)e^{i\kappa\cdot\mathbf{r}}/\epsilon_{\text{el}}(\kappa,0).$$

The dielectric constant for an electron differs from that for a test charge since the latter has no exchange interaction with the responding electron gas. We have $V_t(\kappa,\omega)=V_0(\kappa,\omega)+8\pi\rho_{\text{el}}(\kappa,\omega)/\kappa^2$ (which follows from Poisson's equation $\nabla^2V=8\pi\rho$) but $8\pi\rho_{\text{el}}(\kappa,\omega)=-V_{\text{el}}(\kappa,\omega)\kappa^2\chi(\kappa,\omega)$ follows from the definition of $\chi(\kappa,\omega)$, the electronic susceptibility, where V_{el} is the effective potential seen by the electrons, including exchange. From this and the definition of $\epsilon_t(\kappa,\omega)$ the relation $\epsilon_{\text{el}}(\kappa,\omega)=\chi(\kappa,\omega)\epsilon_t(\kappa,\omega)/[\epsilon_t(\kappa,\omega)-1]$ follows immediately. Substituting for ϵ_t from (2), we find

$$\epsilon_{\text{el}}(\kappa,\omega)=1+\chi(\kappa,\omega)[1-f_H(\kappa)].\quad(4)$$

This form of the dielectric constant has been used by Sham[3] and Vosko *et al.*[4] to calculate the cohesive energy and its derivatives which are needed in first-principles calculations of phonon-dispersion curves of metals.

We show in this paper from self-consistent-field considerations that $\epsilon_t(\kappa,\omega)$ and $\epsilon_{\text{el}}(\kappa,\omega)$ have the correct form in Eqs. (2) and (4) only in the static limit ($\omega\to0$) and that even then Hubbard's $f_H(\kappa)$ is completely incorrect for large κ. Note that $f_H(\kappa)\to\frac{1}{2}$ for large κ implies that the exchange interactions cancel out half the direct Coulomb interactions for large κ. This is what one might expect using very naive physical considerations, but as we shall show, only slightly more sophistication is required to demonstrate that the Coulomb contributions are negligible compared to the exchange for large κ. In Sec. II, on the way to deriving $\epsilon_{\text{el}}(\kappa,\omega)$, we find a new approximation for the exchange potential which we believe has practical as well as theoretical advantages for energy-band calculations over the now almost universally used Slater[8] approximation. In the Appendix we discuss the evaluation of the inverse screening length K_s.

II. EXCHANGE AND THE DIELECTRIC CONSTANT

We here derive $\epsilon_{\text{el}}{}^{\sigma}(\kappa,\omega)$ and $\epsilon_{\text{el}}{}^{\sigma}(\kappa,-\omega)$, from which we will be able to calculate $\epsilon_t(\kappa,\omega)=\epsilon_t{}^*(\kappa,-\omega)$. The

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[6] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961).
[7] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[8] J. C. Slater, Phys. Rev. **81**, 385 (1951).

latter equality holds because if we apply an external (real) potential

$$V_{\kappa\omega}{}^{0}(\mathbf{r},t)=(V_{\kappa\omega}{}^{0}e^{i\omega t}+V_{\kappa\omega}{}^{0*}e^{-i\omega t})(e^{i\kappa\cdot r}+e^{-i\kappa\cdot r})e^{\eta t}, \quad (5)$$

where η is a positive infinitesimal, a test charge will see a real potential

$$V_{\kappa\omega}{}^{t}(\mathbf{r},t)=\{[V_{\kappa\omega}{}^{0}/\epsilon_{t}(\kappa,\omega)]e^{i\omega t}+[V_{\kappa\omega}{}^{0*}/\epsilon_{t}{}^{*}(\kappa,\omega)]e^{-i\omega t}\}\times\{e^{i\kappa\cdot r}+e^{-i\kappa\cdot r}\}, \quad (6)$$

due to the real external potential and the real induced electronic charge density. On the other hand, the potential seen by an electron of wave vector $\mathbf{k}$ and spin σ,

$$V_{\kappa\omega\mathbf{k}\sigma}{}^{\mathrm{el}}(\mathbf{r},t)=V_{\kappa\omega}{}^{0}(\mathbf{r},t)+V_{\kappa\omega}{}^{\mathrm{Coul}}(\mathbf{r},t)+V_{\kappa\omega\mathbf{k}\sigma}{}^{\mathrm{exch}}(\mathbf{r},t)$$
$$=\{[V_{\kappa\omega}{}^{0}/\epsilon_{\mathrm{el}}{}^{\sigma}(\kappa,\mathbf{k},\omega)]e^{i\omega t}+[V_{\kappa\omega}{}^{0*}/\epsilon_{\mathrm{el}}{}^{\sigma}(\kappa,\mathbf{k},-\omega)]e^{-i\omega t}\}\times\{e^{i\kappa\cdot r}+e^{-i\kappa\cdot r}\}, \quad (7)$$

will in general be complex because the exchange charge density will be complex. (The potential will depend on $\mathbf{k}$ because the exchange operator is nonlocal.) Under the influence of the perturbation $V_{\kappa\omega\mathbf{k}\sigma}{}^{\mathrm{el}}(\mathbf{r},t)$ a typical electron wave function becomes (using standard first-order time-dependent perturbation theory)[9]

$$\varphi_{\mathbf{k}'\sigma}=\Omega^{-1/2}e^{-i\nu t}\{e^{i\mathbf{k}'\cdot r}+[a_{\mathbf{k}'+\kappa}{}^{\sigma}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma}(-\omega t)]e^{i(\mathbf{k}'+\kappa)\cdot r}+[a_{\mathbf{k}'-\kappa}{}^{\sigma}(\omega t)+a_{\mathbf{k}'-\kappa}{}^{\sigma}(-\omega t)]e^{i(\mathbf{k}'-\kappa)\cdot r}\}, \quad (8)$$

where

$$a_{\mathbf{k}'+\kappa}{}^{\sigma}(\omega t)=\frac{-V_{\kappa\omega\mathbf{k}'\sigma}{}^{(+)}e^{i\omega t}}{\omega+\kappa^{2}+2\mathbf{k}'\cdot\boldsymbol{\kappa}-i\eta},$$
$$a_{\mathbf{k}'+\kappa}{}^{\sigma}(-\omega t)=\frac{-V_{\kappa\omega\mathbf{k}'\sigma}{}^{(-)}e^{-i\omega t}}{-\omega+\kappa^{2}+2\mathbf{k}'\cdot\boldsymbol{\kappa}-i\eta},$$
$$a_{\mathbf{k}'-\kappa}{}^{\sigma}(\omega t)=\frac{-V_{\kappa\omega\mathbf{k}'\sigma}{}^{(+)}e^{i\omega t}}{\omega+\kappa^{2}-2\mathbf{k}'\cdot\boldsymbol{\kappa}-i\eta}, \quad (9)$$
$$a_{\mathbf{k}'-\kappa}{}^{\sigma}(-\omega t)=\frac{-V_{\kappa\omega\mathbf{k}'\sigma}{}^{(-)}e^{-i\omega t}}{-\omega+\kappa^{2}-2\mathbf{k}'\cdot\boldsymbol{\kappa}-i\eta},$$

with

$$V_{\kappa\omega\mathbf{k}'\sigma}{}^{(+)}=V_{\kappa\omega}{}^{0}/\epsilon_{\mathrm{el}}{}^{\sigma}(\kappa,\mathbf{k}',\omega)$$

and

$$V_{\kappa\omega\mathbf{k}'\sigma}{}^{(-)}=V_{\kappa\omega}{}^{0*}/\epsilon_{\mathrm{el}}{}^{\sigma}(\kappa,\mathbf{k}',-\omega). \quad (10)$$

We have assumed that the energy of the state $\mathbf{k}'$ is $\nu=k'^{2}$, i.e., we have neglected the $\mathbf{k}'$ dependence of the screened exchange interaction in the energy denominators of Eqs. (9). Note that

$$\sum_{\mathbf{k}'}a_{\mathbf{k}'+\kappa}{}^{\sigma}(\pm\omega t)=\sum_{\mathbf{k}'}a_{\mathbf{k}'-\kappa}{}^{\sigma}(\pm\omega t). \quad (11)$$

Using (8) and (11), we obtain

$$V_{\kappa\omega}{}^{\mathrm{Coul}}(t)=\Omega^{-1}\langle e^{i(\mathbf{k}+\kappa)\cdot r_1}|\sum_{\mathbf{k}'\sigma}\int d^{3}\mathbf{r}_{2}\varphi_{\mathbf{k}'\sigma}{}^{*}(\mathbf{r}_{2})\frac{2}{r_{12}}\varphi_{\mathbf{k}'\sigma}(\mathbf{r}_{2})|e^{i\mathbf{k}\cdot r_1}\rangle$$
$$=(8\pi/\Omega\kappa^{2})\sum_{\mathbf{k}',\sigma}[a_{\mathbf{k}'+\kappa}{}^{\sigma}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma}(-\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma*}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma*}(-\omega t)], \quad (12)$$

and

$$V_{\kappa\omega\mathbf{k}\sigma}{}^{\mathrm{exch}}(t)=-\Omega^{-1}\sum_{k'||}\langle e^{i(\mathbf{k}+\kappa)\cdot r_1}|\int\varphi_{\kappa'\sigma}{}^{*}(\mathbf{r}_{2})\frac{2}{r_{12}}e^{i\mathbf{k}\cdot r_2}d^{3}\mathbf{r}_{2}|\varphi_{\mathbf{k}'\sigma}(\mathbf{r}_{1})\rangle$$
$$=-(8\pi/\Omega)\sum_{k'||}[\{a_{\mathbf{k}'+\kappa}{}^{\sigma*}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma*}(-\omega t)\}(\mathbf{k}-\mathbf{k}'+\boldsymbol{\kappa})^{-2}+\{a_{\mathbf{k}'+\kappa}{}^{\sigma}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma}(-\omega t)\}(\mathbf{k}-\mathbf{k}')^{2}], \quad (13)$$

where the sum is over all electrons $\mathbf{k}'$ with spin parallel to σ.

If we now assume, as did Hubbard,[1] that $(\mathbf{k}-\mathbf{k}'+\boldsymbol{\kappa})^{2}$ may be approximated by $k_F{}^{2}+\kappa^{2}$ (eliminating the $\mathbf{k}$ dependence of $V_{\kappa\omega\mathbf{k}\sigma}{}^{\mathrm{exch}}$) and that the screening of the exchange may be included by replacing $(k_F{}^{2}+\kappa^{2})^{-1}$ by $(k_F{}^{2}+\kappa^{2}+K_s{}^{2})^{-1}$, we obtain

$$V_{\kappa\omega\sigma}{}^{\mathrm{exch}}(t)=-(8\pi/\Omega)\sum_{k'||}\left[\{a_{\mathbf{k}'+\kappa}{}^{\sigma*}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma*}(-\omega t)\}\frac{1}{k_F{}^{2}+\kappa^{2}+K_s{}^{2}}+\{a_{\mathbf{k}'+\kappa}{}^{\sigma}(\omega t)+a_{\mathbf{k}'+\kappa}{}^{\sigma}(-\omega t)\}\frac{1}{k_F{}^{2}+K_s{}^{2}}\right]. \quad (14)$$

In the static limit ($\omega=0$) one may take $\eta\equiv 0$ and $V_{\kappa\omega\sigma}{}^{(\pm)}$ real; then by examining $|\varphi_{\mathbf{k}'}|^{2}$, one sees that

$$\Omega^{-1}\sum_{\mathbf{k}'||}a_{\mathbf{k}'+\kappa}{}^{\sigma}(0)=\Omega^{-1}\sum_{\mathbf{k}'||}a_{\mathbf{k}'+\kappa}{}^{\sigma*}(0)=-\tfrac{1}{4}\rho_{\kappa\sigma},$$

where $\rho_{\kappa\sigma}$ is the coefficient of the κth fourier transform of the charge density with spin σ. We thus obtain a new approximation for exchange in terms of the charge density which is especially applicable to energy-band calculations:

$$V_{\kappa\sigma}{}^{\mathrm{exch}}=4\pi\rho_{\kappa\sigma}[(k_F{}^{2}+K_s{}^{2})^{-1}+(k_F{}^{2}+K_s{}^{2}+\kappa^{2})^{-1}]. \quad (15)$$

The linearity of this expression is a real, practical advantage over the Slater[8] $\rho^{1/3}(\mathbf{r})$ approximation. The latter leads to difficulty in tight-binding calculations with overlapping valence functions where one would like to express the crystal potential as a superposition of atomic potentials; it also leads to difficulty in plane-

[9] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 189.

wave expansions where one obtains $\rho_{\kappa\sigma}$ directly and is forced to calculate

$$\int[\sum_{\kappa}\rho_{\kappa\sigma}e^{i\kappa\cdot\mathbf{r}}]^{1/3}e^{-i\kappa\cdot\mathbf{r}}d^3\gamma$$

to obtain $V_{\kappa\sigma}{}^{\text{exch}}$. We also believe our expression to be somewhat preferable from a theoretical point of view to the Slater approximation, which, although derived for unscreened exchange, is known in at least one case[10] to give off-diagonal matrix elements in closer numerical agreement with the *screened* Hartree-Fock matrix elements. The "exchange hole," being of short range, seems intrinsically to contain screening, but in a disguised form which cannot be compared with current many-body theories. On the other hand, our Eq. (13) is exact for unscreened exchange; one may add screening in as highly sophisticated a manner as one wishes and then determine numerically, for several values of κ, what value of $k_F{}^2+K_s{}^2$ makes Eq. (15) [or Eq. (14) in the dynamic case] agree with the screened Eq. (13). The determination of $k_F{}^2+K_S{}^2$ as a function of κ is outlined in the Appendix. We should point out that ours is a linear approximation. That is, on going from Eq. (13) to Eq. (14), we assumed that those and only those states within the unperturbed Fermi sea were occupied. The external potential or ionic pseudopotential must be weak enough for this to be nearly the case. Of course one could try to account for nonlinear effects by replacing k_F in Eq. (14) with some k_F'. Besides the numerical difficulty in determining k_F' one would also have to face the fact that the averaging over the momentum dependence of the screened exchange becomes less valid for large k_F'. The Slater approximation is nowhere explicitly linear; on the other hand, it does explicitly assume a momentum-independent exchange potential and therefore it, too, is not completely free from these difficulties.

We now return to the evaluation of $V_{\kappa\omega}{}^{\text{Coul}}(t)$ and $V_{\kappa\omega\sigma}{}^{\text{exch}}(t)$. Let us define

$$\chi_\sigma(\kappa,\pm\omega)=\chi_{\sigma 1}(\kappa,\pm\omega)+i\chi_{\sigma 2}(\kappa,\pm\omega)=(32\pi/\Omega\kappa^2)\sum_{\mathbf{k}'}[\pm\omega+\kappa^2+2\mathbf{k}'\cdot\kappa-i\eta]^{-1}, \tag{16}$$

where the subscript σ means that the sum has been done over states $\mathbf{k}'$ with spin σ; thus $\chi(\kappa\pm\omega)=\frac{1}{2}[\chi_\sigma(\kappa,\pm\omega)+\chi_{\sigma'}(\kappa,\pm\omega)]$. We find

$$\chi_\sigma(\kappa,\pm\omega)=4(\pi\kappa)^{-2}\int_0^{k_{F\sigma}}d^3\mathbf{k}'[\pm\omega+\kappa^2+2\mathbf{k}'\cdot\kappa-i\eta]^{-1}$$

$$=\frac{2}{\pi\kappa^3}\left\{\left[k_{F\sigma}{}^2-\left(\frac{\kappa^2\pm\omega}{2\kappa}\right)^2\right]\ln\frac{\kappa^2\pm\omega+2\kappa k_{F\sigma}-i\eta}{\kappa^2\pm\omega-2\kappa k_{F\sigma}-i\eta}+\frac{k_{F\sigma}}{\kappa}(\kappa^2\pm\omega)\right\}, \tag{17}$$

so that[11]

$$\chi_{\sigma 1}(\kappa,\pm\omega)=\frac{2}{\pi\kappa^3}\left\{\left[k_{F\sigma}{}^2-\left(\frac{\kappa^2\pm\omega}{2\kappa}\right)^2\right]\ln\left|\frac{\kappa^2\pm\omega+2\kappa k_{F\sigma}}{\kappa^2\pm\omega-2\kappa k_{F\sigma}}\right|+\frac{k_{F\sigma}}{\kappa}(\kappa^2\pm\omega)\right\}, \tag{18a}$$

$$\chi_{\sigma 2}(\kappa,\omega)=\frac{2}{\kappa^3}\left[k_{F\sigma}{}^2-\left(\frac{\kappa^2+\omega}{2\kappa}\right)^2\right]\quad\text{if}\quad\omega<2\kappa k_{F\sigma}-\kappa^2;\quad 0\text{ otherwise} \tag{18b}$$

$$\chi_{\sigma 2}(\kappa,-\omega)=\frac{2}{\kappa^3}\left[k_{F\sigma}{}^2-\left(\frac{\kappa^2-\omega}{2\kappa}\right)^2\right]\quad\text{if}\quad\kappa^2-2\kappa k_{F\sigma}<\omega<\kappa^2+2\kappa k_{F\sigma};\quad 0\text{ otherwise}. \tag{18c}$$

We may now write

$$V_{\kappa\omega}{}^{\text{Coul}}(t)=-\tfrac{1}{4}\sum_\sigma\{[V_{\kappa\omega\sigma}{}^{(+)}\chi_\sigma(\kappa,\omega)+V_{\kappa\omega\sigma}{}^{(-)*}\chi_\sigma{}^*(\kappa,-\omega)]e^{i\omega t}$$

$$+[V_{\kappa\omega\sigma}{}^{(+)*}\chi_\sigma{}^*(\kappa,\omega)+V_{\kappa\omega\sigma}{}^{(-)}\chi_\sigma(\kappa,-\omega)]e^{-i\omega t}\}, \tag{19}$$

$$V_{\kappa\omega\sigma}{}^{\text{exch}}(t)=\frac{1}{4}\left[\frac{\kappa^2}{k_{F\sigma}{}^2+K_s{}^2}V_{\kappa\omega\sigma}{}^{(+)}\chi_\sigma(\kappa,\omega)+\frac{\kappa^2}{k_{F\sigma}{}^2+K_s{}^2+\kappa^2}V_{\kappa\omega\sigma}{}^{(-)*}\chi_\sigma{}^*(\kappa,-\omega)\right]e^{i\omega t}$$

$$+\frac{1}{4}\left[\frac{\kappa^2}{k_{F\sigma}{}^2+K_S{}^2+\kappa^2}V_{\kappa\omega\sigma}{}^{(+)*}\chi_\sigma{}^*(\kappa,\omega)+\frac{\kappa^2}{k_{F\sigma}{}^2+K_s{}^2}V_{\kappa\omega\sigma}{}^{(-)}\chi_\sigma(\kappa,-\omega)\right]e^{-i\omega t}. \tag{20}$$

[10] J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).

[11] The relationship between Hubbard's susceptibility (Ref. 1) and ours is

$$-A(\kappa,\omega)=\tfrac{1}{4}\textstyle\sum_\sigma[\chi_{\sigma 1}(\kappa,\omega)+\chi_{\sigma 1}(\kappa,-\omega)]$$

and

$$-\Sigma(\kappa,\omega)=\tfrac{1}{4}\textstyle\sum_\sigma[\chi_{\sigma 2}(\kappa,\omega)-\chi_{\sigma 2}(\kappa,-\omega)].$$

Now

$$V_{\kappa\omega\sigma}{}^{\rm el}(t)=V_{\kappa\omega\sigma}{}^{(+)}e^{i\omega t}+V_{\kappa\omega\sigma}{}^{(-)}e^{-i\omega t}=V_{\kappa\omega}{}^{0}(t)+V_{\kappa\omega}{}^{\rm Coul}(t)+V_{\kappa\omega\sigma}{}^{\rm exch}(t),$$

so that by equating coefficients of $e^{i\omega t}$ and of $e^{-i\omega t}$ we can obtain four coupled equations in $V_{\kappa\omega\sigma}{}^{(+)}$, $V_{\kappa\omega\sigma'}{}^{(+)}$, $V_{\kappa\omega\sigma}{}^{(-)}$, and $V_{\kappa\omega\sigma'}{}^{(-)}$. We shall simplify our work, however, by considering only the nonmagnetic case. Then we have the two coupled equations

$$V_{\kappa\omega}{}^{(+)}=V_{\kappa\omega}{}^{0}-\tfrac{1}{2}V_{\kappa\omega}{}^{(+)}\chi(\kappa,\omega)\left[1-\tfrac{1}{2}\frac{\kappa^2}{k_F{}^2+K_s{}^2}\right]-\tfrac{1}{2}V_{\kappa\omega}{}^{(-)*}\chi^*(\kappa,-\omega)\left[1-\tfrac{1}{2}\frac{\kappa^2}{k_F{}^2+K_s{}^2+\kappa^2}\right], \tag{21a}$$

$$V_{\kappa\omega}{}^{(-)}=V_{\kappa\omega}{}^{0*}-\tfrac{1}{2}V_{\kappa\omega}{}^{(-)}\chi(\kappa,-\omega)\left[1-\tfrac{1}{2}\frac{\kappa^2}{k_F{}^2+K_s{}^2}\right]-\tfrac{1}{2}V_{\kappa\omega}{}^{(+)*}\chi^*(\kappa,\omega)\left[1-\tfrac{1}{2}\frac{\kappa^2}{k_F{}^2+K_s{}^2+\kappa^2}\right]. \tag{21b}$$

Solving for $V_{\kappa\omega}{}^{(+)}=V_{\kappa\omega}{}^{0}/\epsilon_{\rm el}(\kappa,\omega)$ and $V_{\kappa\omega}{}^{(-)}=V_{\kappa\omega}{}^{0*}/\epsilon_{\rm el}(\kappa,-\omega)$, we find

$$\epsilon_{\rm el}(\kappa,\omega)=1+\frac{\alpha\chi(\kappa,\omega)+\beta\chi^*(\kappa,-\omega)+(\alpha^2-\beta^2)\chi(\kappa,\omega)\chi^*(\kappa,-\omega)}{1+(\alpha-\beta)\chi^*(\kappa,-\omega)} \tag{22a}$$

and

$$\epsilon_{\rm el}(\kappa,-\omega)=1+\frac{\alpha\chi(\kappa,-\omega)+\beta\chi^*(\kappa,\omega)+(\alpha^2-\beta^2)\chi(\kappa,-\omega)\chi^*(\kappa,\omega)}{1+(\alpha-\beta)\chi^*(\kappa,\omega)}, \tag{22b}$$

where

$$\begin{aligned}\beta&=\tfrac{1}{2}[1-\tfrac{1}{2}\kappa^2(k_F{}^2+K_s{}^2+\kappa^2)^{-1}],\\ \alpha&=\tfrac{1}{2}[1-\tfrac{1}{2}\kappa^2(k_F{}^2+K_s{}^2)^{-1}].\end{aligned} \tag{23}$$

It is interesting to examine Eq. (22) in the static limit $\omega=0$; then χ is real and

$$\epsilon_{\rm el}(\kappa,0)=1+\chi(\kappa,0)[1-f(\kappa)], \tag{24}$$

where

$$f(\kappa)=\frac{1}{4}\left[\frac{\kappa^2}{k_F{}^2+K_s{}^2+\kappa^2}+\frac{\kappa^2}{k_F{}^2+K_s{}^2}\right]. \tag{25}$$

Equation (24) is in the same form as Eq. (4), but $f(\kappa)$ differs markedly from Hubbard's $f_H(\kappa)$ in the limit of large κ. In the factor $[1-f(\kappa)]$, the 1 represents Coulomb contributions and the $f(\kappa)$ exchange. One supposes that the physical justification[3] for $f_H(\kappa)\to\frac{1}{2}$ as $\kappa\to\infty$ is that $\kappa\to\infty$ implies $\mathbf{r}\to 0$, and the exchange interaction expels $\frac{1}{2}$ the charge density from the point $\mathbf{r}=0$. This reasoning is fallacious; however, because the Coulomb interaction is long range, one must consider the entire exchange hole. As is well known,[8] the electrostatic energy of a point charge in the center of a hole of density ρ and radius such that it contains a total charge of just one, is proportional to $\rho^{1/3}$. Now if we expand

$$\rho^{1/3}=[\rho_0+\sum_\kappa \rho_\kappa e^{i\kappa\cdot\mathbf{r}}]^{1/3}\approx\rho_0{}^{1/3}+\tfrac{1}{3}\rho_0{}^{-2/3}\sum_\kappa \rho_\kappa e^{i\kappa\cdot\mathbf{r}},$$

we see that the κth Fourier component of exchange potential should be expected to be proportional to ρ_κ. On the other hand, the κth Fourier component of the Coulomb potential is proportional to ρ_κ/κ^2, so that the ratio of the exchange to Coulomb potentials is not $\frac{1}{2}$ but rather κ^2. This exchange-hole argument is of course approximate in that it contains an assumption of a square-shape exchange hole. Note though, that it leads to conclusions in agreement with Eq. (25) in both the large and small κ limits. This discussion is given for whatever physical insight it may provide, not to prove the correctness of either our approximation or the Slater exchange-hole approximation in the high-κ region. That our κ dependence is correct (for large κ) follows immediately from Eqs. (12) and (13), which are exact. If the approximations made in Eq. (14) are not done carefully, they affect the numerical results but leave the κ dependence unchanged. The same result may also be seen by forming an integral equation for $1/\epsilon(\kappa,0)$ from Eqs. (9), (10), (12), and (13), the latter either screened or unscreened. Solving this integral equation in the large-κ limit, one finds $\epsilon(\kappa,0)=1-\alpha\kappa^{-2}+\beta\kappa^{-4}$ (where α and β are numerical constants), in exact agreement with Eq. (24). Note also that because $f(\kappa)>1$ when $\kappa^2>4(k_F{}^2+K_s{}^2)$, the dielectric constant is less than unity throughout this range. Although $\chi(\kappa,0)$ is small in this range, so that $\epsilon_{\rm el}$ never drops appreciably below 1, this is, as far as we know, the first example of antiscreening of a static potential.

To obtain $\epsilon_t(\kappa,0)$ one needs only to substitute $f(\kappa)$ for $f_H(\kappa)$ in Eq. (2). It is not much more difficult to obtain $\epsilon_t(\kappa,\omega)$. Using

$$V_{\kappa\omega}{}^{t}(t)=V_{\kappa\omega}{}^{0}(t)/\epsilon_t(\kappa,\omega)=V_{\kappa\omega}{}^{0}(t)+V_{\kappa\omega}{}^{\rm Coul}(t),$$

substituting from Eq. (10) for the $V_{\kappa\omega}{}^{(+)}$ and $V_{\kappa\omega}{}^{(-)}$ which appear in the $V_{\kappa\omega}{}^{\rm Coul}(t)$ of Eq. (19), and equating separately the coefficients of the $e^{i\omega t}$ and $e^{-i\omega t}$ terms, one obtains

$$\frac{1}{\epsilon_t(\kappa,\omega)}=\frac{1}{\epsilon_t{}^*(\kappa,-\omega)}=1-\frac{1}{2}\left(\frac{\chi(\kappa,\omega)}{\epsilon_{\rm el}(\kappa,\omega)}+\frac{\chi^*(\kappa,-\omega)}{\epsilon_{\rm el}{}^*(\kappa,-\omega)}\right). \tag{26}$$

Note added in proof. Because in the limit $\kappa\to 0$ Eqs.

(18), (22), and (26) yield $\epsilon_t(0,\omega)=1-\omega_p^2(1+\Delta_0)/\omega^2$, where $\omega_p^2=16k_F^3/3\pi$ and $\Delta_0=\frac{1}{4}\omega_p^2(k_F^2+K_s^2)^{-2}$, in violation of a well-known theorem that $\epsilon_t(0,\omega)=1-\omega_p^2/\omega^2$, we have considered the effect of including the screened exchange self-energy in the energy denominators of Eq. (9). One has

$$\Delta=E_{\mathbf{k}+\boldsymbol{\kappa}}^{\text{exch}}-E_{\mathbf{k}}^{\text{exch}}$$
$$=-\frac{8\pi}{\Omega}\sum_{k'<k_F}\left(\frac{1}{(\mathbf{k}+\boldsymbol{\kappa}-\mathbf{k}')^2}-\frac{1}{(\mathbf{k}-\mathbf{k}')^2}\right). \quad (27)$$

And for screened exchange with our usual approximation

$$\Delta=\frac{4}{3\pi}k_F^2\frac{\kappa^2}{(k_F^2+\kappa^2+K_s^2)(k_F^2+K_s^2)}. \quad (28)$$

The inclusion of Δ in the denominators of (9) leads to the replacement of $\pm\omega$ by $\pm\omega+\Delta$ wherever it appears in Eq. (17) for $\chi_\sigma(\boldsymbol{\kappa},\pm\omega)$ and to no other changes in the theory. Note that for small κ, $\Delta\to\kappa^2\Delta_0$. A rather tedious expansion of Eq. (18a) yields

$$\chi(\kappa\to 0,\pm\omega)=\pm\frac{\omega_p^2}{\kappa^2\omega}-\frac{\omega_p^2(1+\Delta_0)}{\omega^2}\pm\frac{64}{15\pi}\frac{k_F^5}{\omega^3}$$
$$-\frac{16\kappa^2}{\pi\omega^2}\left[\frac{4}{5}\frac{k_F^5(1+\Delta_0)}{\omega^2}\mp\frac{k_F^3(1+\Delta_0)^2}{3\omega}\mp\frac{16}{35}\frac{k_F^7}{\omega^3}\right]. \quad (29)$$

This substituted in Eq. (22) gives

$$\epsilon_{el}(\kappa\to 0,\pm\omega)=1-\frac{\omega_p^2}{\omega^2}$$
$$+\kappa^2\left[\pm\left(\frac{\omega_p^2}{\omega^2}-1\right)\frac{\Delta_0}{\omega}+\text{terms of constant sign}\right]. \quad (30)$$

We have explicitly displayed terms vanishing as κ^2 because when combined in Eq. (26) with the κ^{-2} terms of χ they contribute to $\epsilon_t(0,\pm\omega)$, yielding

$$\epsilon_t(0,\pm\omega)=1-\omega_p^2/\omega^2. \quad (31)$$

It is of interest to examine the effect of these self-energy terms on the large κ dependence of $\epsilon_t(\boldsymbol{\kappa},0)$ and $\epsilon_{el}(\boldsymbol{\kappa},0)$. One has $\Delta\to\Delta_\infty=\frac{1}{4}\omega_p^2/(k_F^2+K_s^2)$. Expanding (18a) in this limit,

$$\chi(\kappa\to\infty,0)=\frac{\omega_p^2}{\kappa^4}\left(1-\frac{\Delta_\infty}{\kappa^2}\right), \quad (32)$$

where the only κ^{-6} terms included are the self-energy ones. Since we see from (24) that the regular exchange terms contribute to $\epsilon_{el}(\kappa\to\infty,0)$ as κ^{-2} and the Coulomb terms as κ^{-4}, the self-energy terms which go like κ^{-6} are completely negligible. We may determine the large κ dependence of ϵ_t by expanding Eq. (2) with $f_H(\boldsymbol{\kappa})$ replaced by $f(\boldsymbol{\kappa})$ to obtain

$$\epsilon_t(\kappa\to\infty,0)=1+\chi(1+f\chi)$$
$$=1+\frac{\omega_p^2}{\kappa^4}-\frac{\Delta_\infty\omega_p^2}{\kappa^6}+\left(\frac{\omega_p^2}{\kappa^4}\right)^2\frac{1}{4}\frac{\kappa^2}{k_F^2+K_s^2}$$
$$=1+\frac{\omega_p^2}{\kappa^4}. \quad (33)$$

Thus the self-energy term cancels the regular exchange term of order κ^{-6} (which of course is negligible anyway compared with the Coulomb term) and the leading exchange term will be of order κ^{-8}. This result was obtained by Geldart and Vosko, Can. J. Phys. **44**, 2137 (1966). I thank Dr. Vosko for calling it to my attention. It appears to be pure coincidence that Hubbard using the incorrect $f_H(\boldsymbol{\kappa})$ and neglecting self-energy corrections also gets the leading exchange term in $\epsilon_t(\kappa\to\infty,0)$ to be of order κ^{-8}.

Thus we see that our formulas for $\epsilon_{el}(\boldsymbol{\kappa},\pm\omega)$ and $\epsilon_t(\kappa,\pm\omega)$, which as far as we know are the only ones including exchange contributions ever derived in closed form for all values of $\boldsymbol{\kappa}$ and ω, yield results which are correct (to within ones ability to calculate K_s^2) in every limit in which one can test them.

APPENDIX

We here screen $V_{\kappa\omega\mathbf{k}}^{\text{exch}}(t)$ of Eq. (13), evaluate it numerically for the cases $\boldsymbol{\kappa}\to 0$ and $\boldsymbol{\kappa}\to\infty$, average over occupied states $\mathbf{k}$, and determine what values of $k_F^2+K_s^2$ are needed in Eq. (14) to make it agree with our screened averaged $V_{\kappa\omega\mathbf{k}}^{\text{exch}}$. We first examine the $\boldsymbol{\kappa}\to\infty$ case; then we may take the $a_{\mathbf{k}'+\boldsymbol{\kappa}}(\pm\omega t)$'s to be independent of $\mathbf{k}'$ and thus require

$$\left\langle\frac{1}{(\mathbf{k}-\mathbf{k}')^2}\operatorname{Re}\frac{1}{\epsilon(\mathbf{k}-\mathbf{k}',\nu_\kappa-\nu_{\kappa'})}\right\rangle_{\text{av}}=\frac{1}{k_F^2+K_s^2}, \quad (A1)$$

where we have screened the exchange interaction between a pair of electrons with wave vectors $\mathbf{k}$ and $\mathbf{k}'$ and energy $\nu_{\mathbf{k}}$ and $\nu_{\mathbf{k}'}$ with the real part of the RPA dielectric constant as suggested by Phillips[12] and by Nozières and Pines.[2] Since the screened exchange is a slowly varying function of $\mathbf{k}$ and $\mathbf{k}'$, we shall approximate the average in (A1) by merely substituting the average of $(\mathbf{k}-\mathbf{k}')^2$ and $|\nu_{\mathbf{k}}-\nu_{\mathbf{k}'}|=|\mathbf{k}^2-\mathbf{k}'^2|$ over the Fermi sphere. These are easily found to be

$$\langle(\mathbf{k}-\mathbf{k})^2\rangle_{\text{av}}=(6/5)k_F^2,\quad\langle|\nu_{\mathbf{k}}-\nu_{\mathbf{k}'}|\rangle_{\text{av}}=\tfrac{3}{10}k_F^2, \quad (A2)$$

so that

$$K_s^2(\boldsymbol{\kappa}\to\infty)$$
$$=\{(6/5)[\operatorname{Re}\epsilon^{-1}((6/5)^{1/2}k_F,\tfrac{3}{10}k_F^2)]^{-1}-1\}k_F^2. \quad (A3)$$

To determine $K_s^2(\boldsymbol{\kappa}\to 0)$ we note that we can let

[12] J. C. Phillips, Phys. Rev. **123**, 420 (1961).

$\kappa \rightarrow -\kappa$ and $\mathbf{k}' \rightarrow \mathbf{k}'+\kappa$ in the first term of Eq. (13) to obtain

$$V_{\kappa\omega\mathbf{k}}{}^{\text{exch}} = \frac{-8\pi}{\Omega} \sum_{\mathbf{k}'|\mathrm{i}} \left[\frac{V_{\kappa\omega\mathbf{k}'}{}^{(+)} e^{i\omega t}}{-\omega+\kappa^2+2\mathbf{k}'\cdot\kappa+i\eta} + \frac{V_{\kappa\omega\mathbf{k}'}{}^{(-)} e^{-i\omega t}}{\omega+\kappa^2+2\mathbf{k}'\cdot\kappa+i\eta} \right] \left[\frac{n(\mathbf{k}'+\kappa)-n(\mathbf{k}')}{(\mathbf{k}-\mathbf{k}')^2} \right], \quad \text{(A4)}$$

where we have used the fact that $V_{\kappa\omega\mathbf{k}'}{}^{(+)*} = V_{\kappa\omega\mathbf{k}'}{}^{(-)}$ in the $\kappa \rightarrow 0$ limit. [This follows from Eqs. (10), (22), and (18).] Thus only states $\mathbf{k}'$ within κ of k_F contribute to $V_{\kappa\omega\mathbf{k}}{}^{\text{exch}}$. Now the dielectric constant [Eq. (22)] implicitly contains $V_{\kappa\omega\mathbf{k}}{}^{\text{exch}}$ integrated over all $\mathbf{k}$. However, to the extent that the $\mathbf{k}$ dependence of $V_{\kappa\omega\mathbf{k}}{}^{(+)}$ can be neglected, only those states $\mathbf{k}$ also within κ of k_F will contribute to the dielectric constant. Thus

$$(\mathbf{k}-\mathbf{k}')^2 = 2k_F{}^2(1-\cos\theta), \quad \nu_{\mathbf{k}}-\nu_{\mathbf{k}'}=0, \quad \text{(A5)}$$

so that

$$K_s{}^2(\kappa \rightarrow 0) = k_F{}^2 \left\{ \left\langle \frac{1}{2(1-\cos\theta)\epsilon[(2k_F{}^2(1-\cos\theta))^{1/2}, 0]} \right\rangle_{\text{av}}^{-1} - 1 \right\}. \quad \text{(A6)}$$

We have evaluated $K_s{}^2(\kappa \rightarrow 0)$ by averaging over the four values of $\theta = 0, \frac{1}{4}\pi, \frac{1}{2}\pi, \frac{3}{4}\pi$, for $k_F = 0.485$, the value for sodium. We have also evaluated $K_s{}^2(\kappa \rightarrow \infty)$ for the same value of k_F. We find $K_s{}^2(\kappa \rightarrow 0) = 0.553$, $K_s{}^2(\kappa \rightarrow \infty) = 0.604$; these should be compared with the range of values to be found in the literature,[5] $K_s{}^2 = 2k_F/\pi = 0.309$ to $K_s{}^2 = 4k_F/\pi = 0.618$.

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Dynamical Properties of Magnetic Impurities in Transition Metals*

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The dynamical properties of a magnetic impurity in a metallic host are studied. We employ the Wolff model, which describes an impurity of the 3*d* series placed in a nonmagnetic 4*d* or 5*d* host. We calculate the dynamical susceptibility of a material in which a single impurity is imbedded. We imagine the system is placed in an external magnetic field at the absolute zero of temperature. It is assumed that the ground-state wave function is well approximated by the Hartree-Fock ground state in the presence of the external field. A generalized random-phase approximation (RPA) is employed in the equation of motion for the two-particle Green's function; this allows us to find an approximate expression for the two-particle correlation function. The same result may be obtained by a diagrammatic analysis, in which the contribution from a certain subset of diagrams is summed. The dynamic susceptibility obtained in this manner exhibits a resonance for frequencies in the vicinity of the free-election spin resonance frequency. The total transverse magnetic moment that arises in the system from the application of a field of fixed frequency and arbitrary spatial variation exhibits a resonance response at the free-electron spin resonance frequency, with vanishing width. The short-wavelength components of the induced spin density exhibit a resonance of finite width, shifted from the free-electron resonance frequency. The *g* shift and width of the resonance in the short-wavelength response is independent of the wave vector of the component examined, so long as $v_F q$, $v_F q' \gg \Omega$, where v_F is the Fermi velocity of an electron at the Fermi surface, Ω and $\mathbf{q}'$ are the frequency and wave vector of the driving wave, and $\mathbf{q}$ is the wave vector of the component of the spin density in question.

I. INTRODUCTION

THE theoretical studies of magnetic impurity states in metals have involved several different approaches. In the theory of the formation of magnetic moments,[1–3] one employs a Hamiltonian which describes the perturbation produced on the Bloch states of the host metal by the impurity, including the intra-atomic Coulomb interaction between two electrons on the impurity site. If the intra-atomic Coulomb interaction is treated in the Hartree-Fock approximation, then the criteria for the appearance of a local moment may be obtained without difficulty. We should mention that the validity of the Hartree-Fock approach has recently been questioned.[4]

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