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Reformulation of the Screened Heine-Abarenkov Model Potential*

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The screening of a generalized Heine-Abarenkov model potential is systematically reformulated. The electron density in a metal is calculated in terms of model-potential parameters. One contribution to this charge is a depletion hole, analogous to the orthogonalization hole in pseudopotential theory. A general expression for the depletion hole is derived. The screened form factor for the model potential is calculated, taking into account the nonlocality and energy dependence of the model potential. The long-wavelength limit of the form factor is evaluated and found to be $-\frac{2}{3}E_F$ at the Fermi surface, as for local potentials. It is found that the depletion-hole contribution cancels a term arising from the energy dependence of the potential at long wavelengths. Consequently, it is unnecessary to renormalize the dielectric constant as done by Heine and Animalu. The magnitude of the depletion hole is evaluated for several elements using the Heine-Abarenkov model potential. The expression for the depletion hole is also shown to be valid for a certain class of pseudopotentials.

1. INTRODUCTION

THE "model potential" was introduced by Abarenkov and Heine[1,2] in order to overcome the complexity of pseudopotential calculations from first principles. A simplification was achieved by calculating the model-potential parameters directly from atomic term values. It was hoped that by using experimental input it would be possible to account more accurately for the interaction of conduction electrons with the core. Animalu[3] first calculated the screening of the Heine-Abarenkov (HA) model potential, taking into account its nonlocality, but not its energy dependence. In a later paper, Animalu and Heine[4] introduced an orthogonalization hole from pseudopotential theory. The contribution of this additional charge in the screened form factor was eliminated by renormalizing the dielectric function.

The purpose of this paper is to reformulate the general model-potential problem in an internally consistent manner. We will show that the electron density can be computed exactly, and that a contribution to this density is a depletion hole at ion sites. We obtain an expression for this depletion hole in terms of experimentally determined model-potential parameters. In calculating the self-consistent screening of the model potential, we take account of both the nonlocality and the energy dependence of the model potential. An important feature of our reformulated theory is that it is no longer necessary to renormalize the dielectric function to obtain the correct long-wavelength limit for the model-potential form factor. Finally, we apply our general formulation to the HA model potential, calculate the size of the depletion hole for various elements, and compare the results to the orthogonalization hole of pseudopotential theory. We also note that our general expression for the depletion hole yields the correct orthogonalization hole for a certain class of pseudopotentials.

2. THE MODEL POTENTIAL

We will consider a model potential which is sufficiently general to include both the HA model potential and a limited class of pseudopotentials. We take the model-potential operator for an isolated atom to have the form

$$v_m = v - \sum_l A_l(E)|l\rangle\langle l| \,, \tag{2.1}$$

where the $|l\rangle$ are a set of angular-momentum eigenstates and E is the energy of the state under consideration. The label l serves only to designate the total angular-momentum quantum number but does not preclude the use of other quantum numbers (m for instance) in the sum.

The $\mathbf{r}$ representation of (2.1) is

$$\langle\mathbf{r}|v_m|\mathbf{r}'\rangle = v(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') - \sum_l A_l(r,E)\langle\mathbf{r}|l\rangle\langle l|\mathbf{r}'\rangle. \tag{2.2}$$

We have taken the potential $v(\mathbf{r})$ to be local (diagonal) in the $\mathbf{r}$ representation. It is clear, however, that the second term in (2.2) is not diagonal in the $\mathbf{r}$ representation and is consequently referred to as a nonlocal contribution.

To obtain the HA model potential for a single atom from (2.2) we simply set

$$v(r) = -(Ze^2/r)\quad \Theta(r-R_M)\,,$$
$$A_l(r,E) = A_l(E)\quad \Theta(R_M-r)\,,$$

where

$$\Theta(r)=0\,,\quad r<0$$
$$=1\,,\quad r>0$$

and let the set $|l\rangle$ be the spherical harmonics so that

$$\langle\mathbf{r}|l\rangle\langle l|\mathbf{r}'\rangle = \langle\Omega|l,m\rangle\langle l,m|\Omega'\rangle\delta(|\mathbf{r}|-|\mathbf{r}'|)\,.$$

A restricted class of pseudopotentials can also be written in the form (2.2) if we let $v(\mathbf{r})$ be the self-

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[1] I. V. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965).

[2] V. Heine and I. V. Abarenkov, Phil. Mag. **9**, 451 (1964).

[3] A. O. E. Animalu, Phil. Mag. **11**, 379 (1965).

[4] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

consistent Hartree core potential and let

$$\sum_l A_l(r,E)\langle \mathbf{r}|l\rangle\langle l|\mathbf{r}'\rangle = -\sum_\alpha f_\alpha(E)\langle \mathbf{r}|\alpha\rangle\langle\alpha|\mathbf{r}'\rangle,$$

where $\langle\mathbf{r}|\alpha\rangle$ is a core state of the free atom.

In the pseudopotential method, the pseudopotential is constructed such that the energy eigenvalue of the pseudowave equation for the metal is the same as that of the exact wave equation. However, the model potential is chosen to yield the correct energy eigenvalues of the free atom. Consequently, the $A_l(E)$ are known explicitly only at free-atom eigenvalues and must be extended to arbitrary energies by interpolation. Heine and Animalu[4] have given an approximate procedure for determining the energy at which $A_l(E)$ is to be evaluated when the model atoms are combined to form a metal.

We should point out that the metallic eigenvalues for the exact and model problems are the same only in the small-core approximation, that is when the sum of the valence-electron potential V_e, and the neighboring core potentials $\sum_{i\neq j} v(\mathbf{r}-\mathbf{r}_i)$, is nearly constant over the jth core. Then these simply shift the energy at which $A_l(E)$ is evaluated. The model potential then leads to correct energies and the unnormalized model wave function is equal to the exact wave function in the intercore region.

To summarize, we have constructed a model for a metal in which the Hartree wave equation

$$[T+U]|\psi_k\rangle = E_k|\psi_k\rangle, \tag{2.3}$$

with U the self-consistent core potential plus the valence-electron potential, is replaced by a model wave equation

$$[T+W(E_k)]|\chi_k\rangle = E_k|\chi_k\rangle, \tag{2.4}$$

where the total model potential W is the sum of ionic-model potentials plus the same valence-electron potential V_e as in U. In the region between cores, $\langle\mathbf{r}|\psi_k\rangle \equiv \langle\mathbf{r}|\chi_k\rangle$. However, inside the core the behavior of $\langle\mathbf{r}|\psi_k\rangle = \psi_k(\mathbf{r})$ and $\langle\mathbf{r}|\chi_k\rangle = \chi_k(\mathbf{r})$ is quite different. The exact wave function oscillates as a result of the deep-core potential, whereas the model wave function is fairly smooth over the core region. Consequently, if we require that the $\psi_k(\mathbf{r})$ be orthonormal, then it is clear that the $\chi_k(\mathbf{r})$ can be neither normalized nor orthogonal. The situation is shown schematically in Fig. 1.

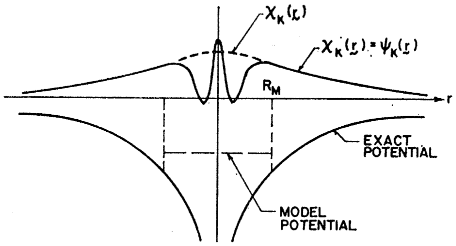

FIG. 1. Schematic drawing of the un-normalized model wave function $\chi_k(\mathbf{r})$ and the exact wave function $\psi_k(\mathbf{r})$. The wave functions are shown superimposed on a plot of the model and exact potentials.

3. THE DEPLETION HOLE

We wish to compute the exact electron density in the metal, $\psi_k^*(\mathbf{r})\psi_k(\mathbf{r})$. However, we have replaced the exact problem by a model wave equation, (2.4), which we solve for $\chi_k(\mathbf{r})$, the model wave function. Referring to Fig. 1, we see that the actual electron density can be regarded as the sum of two terms, a term $\chi_k^*(\mathbf{r})\chi_k(\mathbf{r})$ from the model wave function, and a contribution from the oscillating part of the real wave function localized in the core region. The total charge due to the core oscillations of the real wave function we define as the depletion hole ρ by analogy with the orthogonalization hole of pseudopotential theory:

$$\rho = \sum_{k\leq k_F}\int_{\Omega_M} d^3r\,[\psi_k^*(\mathbf{r})\,\psi_k(\mathbf{r}) - \chi_k^*(\mathbf{r})\chi_k(\mathbf{r})]. \tag{3.1}$$

The integral is over a single core volume Ω_M, so that ρ represents the depletion hole at a single ion site.

To evaluate ρ in terms of model-potential parameters we use a method similar to the one used in deriving the Friedel sum rule. We use the wave equations for $\psi_k(\mathbf{r})$ and $\chi_k(\mathbf{r})$,

$$\begin{aligned}\nabla^2\psi_k(\mathbf{r}) &= (2m/\hbar^2)U(r)\psi_k(\mathbf{r}) - (2m/\hbar^2)E_k\psi_k(\mathbf{r}),\\ \nabla^2\chi_k(\mathbf{r}) &= (2m/\hbar^2)W(E_k)\chi_k(\mathbf{r}) - (2m/\hbar^2)E_k\chi_k(\mathbf{r}),\end{aligned} \tag{3.2}$$

to write

$$\begin{aligned}\psi_k^*(\mathbf{r})\nabla^2\psi_{k'}(\mathbf{r}) - \psi_{k'}(\mathbf{r})\nabla^2\psi_k^*(\mathbf{r}) &= (2m/\hbar^2)\{\psi_k^*(\mathbf{r})U\psi_{k'}(\mathbf{r}) - \psi_{k'}(\mathbf{r})U\psi_k^*(\mathbf{r})\\ &\quad -[E_{k'}-E_k]\psi_k^*(\mathbf{r})\psi_{k'}(\mathbf{r})\},\end{aligned} \tag{3.3}$$

and

$$\begin{aligned}\chi_k^*(\mathbf{r})\nabla^2\chi_{k'}(\mathbf{r}) - \chi_{k'}(\mathbf{r})\nabla^2\chi_k^*(\mathbf{r}) &= (2m/\hbar^2)\{\chi_k^*(\mathbf{r})W(E_{k'})\chi_{k'}(\mathbf{r}) - \chi_{k'}(\mathbf{r})W^*(E_k)\chi_k^*(\mathbf{r})\\ &\quad -[E_{k'}-E_k]\chi_k^*(\mathbf{r})\chi_{k'}(\mathbf{r})\}.\end{aligned} \tag{3.4}$$

Now we let $\mathbf{k}'-\mathbf{k}=\mathbf{q}$ and take $\mathbf{q}$ to be small. Then expanding the functions of $\mathbf{k}'$ around $\mathbf{k}$ and keeping only lowest-order terms in $\mathbf{q}$, we obtain

$$\begin{aligned}\psi_k(\mathbf{r})\nabla^2\psi_k^*(\mathbf{r}) - \psi_k^*(\mathbf{r})\nabla^2\psi_k(\mathbf{r}) &+ \mathbf{q}\cdot\left[\frac{\partial\psi_k}{\partial\mathbf{k}}(\mathbf{r})\nabla^2\psi_k^*(\mathbf{r}) - \psi_k^*(\mathbf{r})\nabla^2\frac{\partial\psi_k}{\partial\mathbf{k}}(\mathbf{r})\right]\\ &= \frac{2m}{\hbar^2}\mathbf{q}\cdot\frac{\partial E_k}{\partial\mathbf{k}}\psi_k^*(\mathbf{r})\psi_k(\mathbf{r}),\end{aligned} \tag{3.5}$$

and

$$\chi_k(\mathbf{r})\nabla^2\chi_k^*(\mathbf{r})-\chi_k^*(\mathbf{r})\nabla^2\chi_k(\mathbf{r}) +\mathbf{q}\cdot\left[\frac{\partial\chi_k(\mathbf{r})}{\partial\mathbf{k}}\nabla^2\chi_k^*(\mathbf{r})-\chi_k^*(\mathbf{r})\nabla^2\frac{\partial\chi_k(\mathbf{r})}{\partial\mathbf{k}}\right]$$
$$=\frac{2m}{\hbar^2}\mathbf{q}\cdot\left\{\frac{\partial E_k}{\partial\mathbf{k}}\chi_k^*(\mathbf{r})\chi_k(\mathbf{r})+\frac{\partial\chi_k(\mathbf{r})}{\partial\mathbf{k}}W(E_k)\chi_k^*(\mathbf{r}) -\chi_k^*(\mathbf{r})W^*(E_k)\frac{\partial\chi_k(\mathbf{r})}{\partial\mathbf{k}}-\chi_k^*(\mathbf{r})\frac{\partial E_k}{\partial\mathbf{k}}\frac{\partial W(E_k)}{\partial E_k}\chi_k(\mathbf{r})\right\}. \tag{3.6}$$

We subtract (3.6) from (3.5) and integrate over the volume Ω_M around one ion site. If we apply Green's theorem to the terms on the left-hand side of the resulting equation, we see that they sum to zero since $\chi_k(\mathbf{r})\equiv\psi_k(\mathbf{r})$ on the core boundary. Consequently the equation we obtain is simply

$$\int_{\Omega_M} d^3r[\psi_k^*(\mathbf{r})\psi_k(\mathbf{r})-\chi_k^*(\mathbf{r})\chi_k(\mathbf{r})] =-\int_{\Omega_M} d^3r\,\chi_k^*(\mathbf{r})\frac{\partial W(E_k)}{\partial E_k}\chi_k(\mathbf{r}). \tag{3.7}$$

The depletion hole can now be expressed in terms of the model potential and model wave functions[5]:

$$\rho=-\sum_{k\leq k_F}\int_{\Omega_M} d^3r\,\chi_k^*(\mathbf{r})\frac{\partial W(E_k)}{\partial E_k}\chi_k(\mathbf{r}). \tag{3.8}$$

This exact expression for the depletion hole is valid for any model potential of the form given by Eq. (2.1). It is clear that for a general structure, the depletion hole need not be the same at every ion site. However, we will show [Eq. (4.6)] that to lowest order in perturbation theory, ρ is the same at every site independent of ion configuration.

4. PERTURBATION THEORY AND SCREENING OF THE MODEL POTENTIAL

In order to calculate the self-consistent screening of the model potential, we must evaluate the electron potential, which is determined from the electron density by Poisson's equation. The total electron density can be written as the sum of two parts,

$$n(\mathbf{r})=\sum_{k\leq k_F}\psi_k^*(\mathbf{r})\psi_k(\mathbf{r}) =\sum_{k\leq k_F}\chi_k^*(\mathbf{r})\chi_k(\mathbf{r})+\sum_i\rho_i(\mathbf{r}-\mathbf{r}_i), \tag{4.1}$$

where $\rho_i(\mathbf{r})$ is the depletion-hole density at the ith ion site,

$$\rho_i=\int_{\Omega_{M_i}} d^3r\rho_i(\mathbf{r}-\mathbf{r}_i). \tag{4.2}$$

The density is nonzero only within the core volumes, since $\chi_k(\mathbf{r})\equiv\psi_k(\mathbf{r})$ outside. The last term in (4.1) is the sum of depletion-hole densities at all the ion sites in the crystal.

To evaluate (4.1) we solve the model wave equation for $\chi_k(\mathbf{r})$ by perturbation theory. For most applications of the model potential it is sufficient to know the energy eigenvalues to second order in W. Therefore, we obtain the wave function to first order. We expand the model wave function in plane waves,

$$|\chi_k\rangle=|\mathbf{k}\rangle+\sum_q a_q(\mathbf{k})|\mathbf{k}+\mathbf{q}\rangle, \tag{4.3}$$

where

$$\langle\mathbf{r}|\mathbf{k}\rangle=\Omega^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}.$$

From the perturbation calculation we obtain[6]

$$a_q(\mathbf{k})=\frac{\langle\mathbf{k}+\mathbf{q}|W(E_k)|\mathbf{k}\rangle}{(\hbar^2/2m)[\mathbf{k}^2-|\mathbf{k}+\mathbf{q}|^2]},\quad \mathbf{q}\neq0. \tag{4.4}$$

The coefficient $a_0(k)$ cannot be obtained by perturbation theory. However, if we substitute (4.3) into (4.1) and require that the exact wave function $\psi_k(\mathbf{r})$ be normalized then, by equating first-order coefficients, we find that

$$a_0(k)=\tfrac{1}{2}N\ \langle\mathbf{k}|\partial W(E_k)/\partial E_k|\mathbf{k}\rangle_{\Omega_M}, \tag{4.5}$$

where the integral is over a single core.

These results enable us to write a first-order expression for the electron density. Since $\partial W/\partial E$ is manifestly first order, the depletion hole becomes

$$\rho=-\sum_{k\leq k_F}\langle\mathbf{k}|\frac{\partial W(E_k)}{\partial E_k}|\mathbf{k}\rangle_{\Omega_M}, \tag{4.6}$$

to first order. The electron density is then

$$n(\mathbf{r})=\sum_{k\leq k_F}\left(\frac{1}{\Omega}\right)+\sum_{k\leq k_F}\frac{N}{\Omega}\langle\mathbf{k}|\frac{\partial W(E_k)}{\partial E_k}|\mathbf{k}\rangle_{\Omega_M} +2\sum_{k\leq k_F}\sum_q{}' a_q(k)e^{i\mathbf{q}\cdot\mathbf{r}}+\sum_i\rho(\mathbf{r}-\mathbf{r}_i), \tag{4.7}$$

where $\rho(\mathbf{r})$ is the first-order depletion-hole density and is the same at every site, since the first-order depletion hole (4.6) is independent of which Ω_M we choose. The first term in (4.7) is the uniform plane-wave density; the second is a uniform density, which, when integrated over the crystal, exactly cancels the integrated depletion hole (Fig. 2); the third term is the screening charge density.

We can now proceed with the self-consistent screening calculation using the standard procedure.[6] Since each Fourier component (off-diagonal plane-wave matrix element in the case of a nonlocal potential) of the model potential is screened independently, we carry out the calculation in $\mathbf{k}$ space rather than in $\mathbf{r}$ space. The

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[5] In Sec. 7 we discuss the application of this result to pseudopotentials which have the form of Eq. (2.1).

[6] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

Fourier transform of the electron charge density,

$$n_q=\frac{1}{\Omega}\int d^3r\, e^{-i\mathbf{q}\cdot\mathbf{r}}n(\mathbf{r})\,, \tag{4.8}$$

can be obtained directly from Eq. (4.7). The result is

$$n_q=2\sum_{k\leq k_F} a_q(k)+S(q)\rho_q\,, \tag{4.9}$$

where ρ_q is the Fourier transform of the depletion-hole density at a single ion,

$$\rho_q=\frac{1}{\Omega_0}\int_{\Omega_M} d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}\rho(\mathbf{r})\,, \tag{4.10}$$

$$\Omega_0=\Omega/N=\text{volume per ion,}$$

and $S(q)$ is the structure factor for the system being considered,

$$S(q)=\frac{1}{N}\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i}. \tag{4.11}$$

We substitute (4.9) into Poisson's equation and solve self-consistently for the electron potential. Since W contains a nonlocal, energy-dependent term, the screening is not entirely local. We find that the screened form factor can be written

$$W_q(\mathbf{k})=\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle=(V_q+V_{dq})/\epsilon(q)+F(\mathbf{k},\mathbf{q})+G(q). \tag{4.12}$$

In this expression, $\epsilon(q)$ is the Hartree dielectric function,

$$\epsilon(q)=1+\frac{me^2}{2\pi k_F\hbar^2\eta^2}\left(\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|+1\right), \tag{4.13}$$

$$\eta=q/2k_F$$

V_q and $F(\mathbf{k},\mathbf{q})$ are, respectively, the matrix elements of the local and nonlocal parts of the unscreened model potential, $G(q)$ is given by

$$G(q)=\frac{2e^2}{\pi^2q^2\epsilon(q)}\int_{k\leq k_F} d^3k\frac{F(\mathbf{k},\mathbf{q})}{(\hbar^2/2m)[\mathbf{k}^2-|\mathbf{k}+\mathbf{q}|^2]}, \tag{4.14}$$

(we have converted the sum over occupied $\mathbf{k}$ into an integral), and V_{dq} is the depletion potential,

$$V_{dq}=(4\pi e^2/q^2)\rho_qS(q). \tag{4.15}$$

We can separate the information about the structure of the lattice out of Eq. (4.12) by noting that W can be written as a sum of potentials centered about individual ion sites,

$$W=\sum_i w_i\,,$$

so that we can write[6]

$$W_q(\mathbf{k})=NS(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle=S(q)w_q(\mathbf{k}). \tag{4.16}$$

The terms V_q and $F(\mathbf{k},\mathbf{q})$ are obtained directly from the bare model potential which is a sum of individual ion contributions. The depletion potential (4.15) contains the structure factor explicitly. Consequently, the form factor $w_q(\mathbf{k})$ can be written

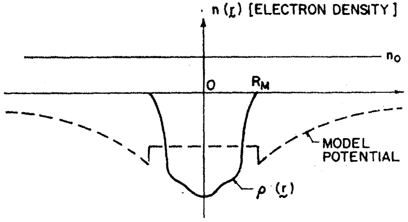

FIG. 2. A schematic plot of the uniform electron-depletion density

$$n_0=\sum_{k\leq k_F}\frac{N}{\Omega}\langle\mathbf{k}|\frac{\partial W(E_k)}{\partial E_k}|\mathbf{k}\rangle$$

and the depletion hole density $\rho(\mathbf{r})$ at a single model ion.

$$w_q(\mathbf{k})=(v_q+v_{dq})/\epsilon(q)+f(\mathbf{k},\mathbf{q})+g(q)\,, \tag{4.17}$$

with $v_{dq}=4\pi e^2\rho_q/q^2$ and all the other lower-case functions defined as in (4.16).

Equation (4.17) is a key result. It is valid for any potential of the form given in Eq. (2.1). In terms of that equation we have

$$v_q=N\langle\mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle\,,$$

and

$$f(\mathbf{k},\mathbf{q})=-N\sum_l\langle\mathbf{k}+\mathbf{q}|A_l(E_k,\mathbf{r})P_l|\mathbf{k}\rangle\,, \tag{4.18}$$

$$P_l=|l\rangle\langle l|\,.$$

Consequently, all the terms in (4.17) except v_{dq}, the depletion-hole contribution, can be evaluated explicitly for a given model potential.

To obtain v_{dq} we must know the distribution of the depletion hole in addition to its magnitude. We could in principle evaluate the Fourier transform

$$\rho_q=\frac{1}{\Omega_0}\sum_{k\leq k_F}\int_{\Omega_M} d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}[\psi_k^*(\mathbf{r})\psi_k(\mathbf{r})-\chi_k^*(\mathbf{r})\chi_k(\mathbf{r})] \tag{4.19}$$

by analytically continuing the wave functions into the model volume using the known magnitude and derivatives of these functions on the surface of Ω_M. However, such a computation turns out to be analytically intractable. The procedure used in Sec. 3 to evaluate similar integrals also breaks down since additional terms, which cannot be evaluated explicitly, enter due to the exponential in (4.19).

As a first approximation we ignore the exponential term in the integral and write

$$v_{dq}=(4\pi e^2/q^2\Omega_0)\rho\,, \tag{4.20}$$

which is equivalent to assuming that the depletion hole is a point charge at the ion position. Any spreading of the depletion hole will require that (4.20) be multiplied by a modulating function $M(q,R_M)$. It is probably reasonable to assume that $M(q,R_M)$ does not deviate much from unity over the range $0 \leq q \leq 2k_F$.

5. LONG-WAVELENGTH LIMIT OF THE FORM FACTOR

It is of particular interest to determine the behavior of the model-potential form factors in the long-wavelength limit. We consider first the local terms in (4.17). From (4.10) it is clear that

$$\rho_q \xrightarrow[q\to 0]{} \rho/\Omega_0 . \tag{5.1}$$

Using this result and the well known long-wavelength limit of the Hartree dielectric function we obtain immediately

$$\lim_{q\to 0} (v_q + v_{dq})/\epsilon(q) = -\tfrac{2}{3}E_F(1-\rho/Z), \tag{5.2}$$

where ρ is calculated in terms of the model potential of a single ion,

$$\rho = -\frac{2\Omega}{(2\pi)^3}\int_{k\leq k_F} d^3k \langle \mathbf{k} | \frac{\partial w(E_k)}{\partial E_k} | \mathbf{k} \rangle . \tag{5.3}$$

Next we consider the nonlocal terms in the form factor. For small $\mathbf{q}$ we shall expand the function $f(\mathbf{k},\mathbf{q})$ as

$$f(\mathbf{k},\mathbf{q}) = f(k) + \mathbf{q}\cdot \partial f(\mathbf{k},\mathbf{q})/\partial \mathbf{q}\,|_{q=0} + O(q^2),$$

where

$$f(k) = \lim_{q\to 0} f(\mathbf{k},\mathbf{q}).$$

Since

$$f(\mathbf{k},\mathbf{q}) = f\left(k, |\mathbf{k}+\mathbf{q}|, \hat{k}\cdot\frac{(\mathbf{k}+\mathbf{q})}{|\mathbf{k}+\mathbf{q}|}\right) = -N\sum_l \langle \mathbf{k}+\mathbf{q} | A_l(E_k)P_l | \mathbf{k} \rangle ,$$

we can, after some computation, rewrite the expansion as

$$f(\mathbf{k},\mathbf{q}) = f(k) - \frac{\mathbf{k}\cdot\mathbf{q}}{k} N \times \sum_l \frac{\partial}{\partial k'} \langle \mathbf{k}' | A_l(E_k)P_l | \mathbf{k} \rangle |_{k'=k} + O(q^2) . \tag{5.4}$$

Using this result we study the behavior of

$$g(q) = \frac{2e^2}{\pi^2 q^2 \epsilon(q)} \int_{k\leq k_F} d^3k \frac{f(\mathbf{k},\mathbf{q})}{(\hbar^2/2m)(k^2 - |\mathbf{k}+\mathbf{q}|^2)} \tag{5.5}$$

as q approaches zero. We substitute (5.4) into (5.5), carry out the angular integrations, and pass to the limit. The result we obtain after considerable manipulation [see the Appendix] is

$$g(q) \xrightarrow[q\to 0]{} -f(k_F) - \frac{N}{k_F}\sum_l \int_0^{k_F} dk\, k \langle \mathbf{k} | \frac{\partial A_l(E_k)}{\partial k} P_l | \mathbf{k} \rangle . \tag{5.6}$$

From Eq. (5.3) we can write $\frac{2}{3}E_F(\rho/Z)$ in the form

$$\tfrac{2}{3}E_F \frac{\rho}{Z} = \frac{N}{k_F}\sum_l \int_0^{k_F} dk\, k \langle \mathbf{k} | \frac{\partial A_l(E_k)}{\partial k} P_l | \mathbf{k} \rangle . \tag{5.7}$$

Consequently, the limit of $g(q)$ as q approaches zero is

$$g(q) \xrightarrow[q\to 0]{} -f(k_F) - \tfrac{2}{3}E_F(\rho/Z), \tag{5.8}$$

and the nonlocal contribution to the long-wavelength limit of the form factor is simply

$$\lim_{q\to 0} [f(\mathbf{k},\mathbf{q}) + g(q)] = f(k) - f(k_F) - \tfrac{2}{3}E_F(\rho/Z) . \tag{5.9}$$

When we combine Eqs. (5.2) and (5.9), we obtain

$$w_0(k) = \lim_{q\to 0} w_q(\mathbf{k}) = -\tfrac{2}{3}E_F + f(k) - f(k_F) . \tag{5.10}$$

It is clear that the long-wavelength limit of the form factor, evaluated at the Fermi surface, is

$$w_0(k_F) = -\tfrac{2}{3}E_F .$$

This is a well-known result for local potentials. Previously it had been assumed to hold for nonlocal potentials as well. We have now demonstrated that in fact it does. It should be emphasized, however, that (5.10) is a first-order result. Additional terms enter in higher order. Also, it is important to note that $-\frac{2}{3}E_F$ obtains only at the Fermi surface. For arbitrary $k \neq k_F$ we have the result given by (5.9).

We should point out the difference between our results and those obtained by Heine and Animalu.[4] Instead of calculating the true electron density, they introduced an orthogonalization hole of magnitude determined from orthogonalized-plane-wave (OPW) theory. In evaluating the long-wavelength limit they overlooked the energy dependence of the model-potential coefficients $A_l(E)$ and found that

$$\lim_{q\to 0} [f(\mathbf{k},\mathbf{q}) + g(q)] = 0 .$$

Therefore they obtained

$$-\tfrac{2}{3}E_F(1 - \rho^{\mathrm{OPW}}/Z)$$

for the long-wavelength limit of the form factor. In order to reduce this to the local limit, $-\frac{2}{3}E_F$, they renormalized the dielectric function with a constant factor $(1 - \rho^{\mathrm{OPW}}/Z)$.

We have shown that their renormalization procedure was not correct, that the depletion hole combines with the nonlocal contribution to the form factor to give $[f(k) - f(k_F)]$ in the long-wavelength limit.

6. THE HA MODEL POTENTIAL

In this section we apply our results to a particular example of the general form given in Eq. (2.1), the

HA "model potential,"

$$\langle \mathbf{r}|v_m|\psi\rangle = -(Ze^2/r)\langle \mathbf{r}|\psi\rangle\,, \quad r>R_M$$

$$= -\sum_l A_l(E)\langle \mathbf{r}|l\rangle \int_{|\mathbf{r}|=|\mathbf{r}'|} d\Omega' \langle l|\mathbf{r}'\rangle\langle \mathbf{r}'|\psi\rangle\,, \quad r<R_M\,. \tag{6.1}$$

We compute the functions $f(\mathbf{k},\mathbf{q})$ and $g(q)$ and obtain

$$f(\mathbf{k},\mathbf{q}) = -3\left(\frac{R_M}{R_C}\right)^3 \sum_l (2l+1)A_l(E_k)P_l(\cos\theta) \times \int_0^1 dx\, x^2 j_l(k'R_M x)j_l(kR_M x)\,, \tag{6.2}$$

and

$$g(q) = \frac{12}{\pi^2 a_0 q^2 \epsilon(q)}\left(\frac{R_M}{R_C}\right)^3 \sum_l (2l+1)\int_{k\leq k_F} d^3k \times \left[P_l(\cos\theta)\frac{A_l(E_k)}{q^2+2\mathbf{k}\cdot\mathbf{q}}\int_0^1 dx\, x^2 j_l(k'R_M x)j_l(kR_M x)\right], \tag{6.3}$$

where

$a_0 =$ Bohr radius,
$\theta = \cos^{-1}\mathbf{k}\cdot\mathbf{k}'/kk'$,
$\mathbf{k}' = \mathbf{k}+\mathbf{q}$
$R_M =$ model radius, $\Omega_M = \frac{4}{3}\pi R_M{}^3$,
$R_C =$ cell radius, $\Omega_0 = \frac{4}{3}\pi R_C{}^3$.

The $q=0$ limit of $f(\mathbf{k},\mathbf{q})$, which appears in the long-wavelength form factor, is

$$f(k) = -3\left(\frac{R_M}{R_C}\right)^3 \sum_l (2l+1)A_l(E_k)\int_0^1 dx\, x^2 j_l{}^2(kR_M x)\,. \tag{6.4}$$

The x integrals in these expressions can be evaluated explicitly, but we leave the results in integral form for later convenience. These results are nearly identical to those given by Animalu[3] except that they display the energy dependence of the $A_l(E_k)$. In Sec. 5 we showed how this energy dependence is taken into account when the long-wavelength limit of the form factor is evaluated.

The general first-order expression for the depletion hole [Eqs. (4.6) and (5.7)] applied to the HA model potential gives

$$\tfrac{2}{3}E_F\frac{\rho}{Z} = \frac{4\pi}{\Omega_0}\sum (2l+1)\frac{1}{k_F} \times \int_0^{k_F} dk\, k\frac{\partial A_l(E_k)}{\partial k}\int_0^{R_M} dr\, r^2 j_l{}^2(kr)\,. \tag{6.5}$$

Animalu's[7] results indicate that the coefficients $A_l(E)$ are linear in E, so that we can write

$$A_l(E) = A_l(E_F) + (E-E_F)\partial A_l/\partial E|_{E_F}\,. \tag{6.6}$$

TABLE I. The depletion hole $(-\rho/Z)$ for several elements. A zero-order approximation for the depletion hole $[-(\partial A_0/\partial E)(R_M/R_C)^3]$ and the orthogonalization hole ρ^{OPW}/Z are given for comparison. The model radii R_M and cell radii R_C are values given by Animalu (Ref. 7).

Element	R_M	R_C	$-\dfrac{\partial A_0}{\partial E}\left(\dfrac{R_M}{R_C}\right)^3$	$-\rho/Z$	$-\rho^{\mathrm{OPW}}/Z$
Li	2.8	3.26	0.132	0.0605	0.068
Na	2.2	3.93	0.058	0.0564	0.074
Na	3.0	3.93	0.118	0.1006	
Na	3.4	3.93	0.161	0.1223	
Na	4.0	3.93	0.171	0.0950	
K	4.2	4.86	0.211	0.1699	0.144
Rb	4.4	5.20	0.224	0.1908	
Cs	4.8	5.63	0.258	0.2209	
Be	2.0	2.35	0.123	−0.0299	0.057
Mg	2.6	3.34	0.161	0.1082	0.079
Ba	3.4	4.66	0.183	0.1341	
Zn	2.2	2.90	0.147	0.1044	0.138
Hg	2.6	3.35	0.138	0.2042	
Al	2.0	2.98	0.118	0.0784	0.076
Ga	2.4	3.15	0.145	0.0869	
In	2.4	3.47	0.149	0.1186	
Tl	2.4	3.58	0.163	0.1459	
Si	2.0	3.18	0.092	0.0487	
Ge	2.0	3.33	0.090	0.0647	
Sn	2.0	3.51	0.096	0.0822	
Pb	2.1	3.65	0.111	0.1007	
Bi	2.0	3.85	0.080	0.0748	

The depletion charge can then be written

$$\frac{\rho}{Z} = 9\left(\frac{R_M}{R_C}\right)^3 \sum_l \frac{\partial A_l(E_F)}{\partial E}(2l+1) \times \int_0^1 dx\, x^2 \int_0^1 dy\, y^2 j_l{}^2(k_F R_M xy)\,. \tag{6.7}$$

We can make one further simplification. Following Heine and Abarenkov,[1] we let $A_l(E) = A_2(E)$ for $l>2$ and write

$$\partial A_i/\partial E = \partial A_2/\partial E + \partial\alpha_i/\partial E\,, \quad i=0,1\,. \tag{6.8}$$

Then using the result

$$\sum_l (2l+1)j_l{}^2(z) = 1\,,$$

we have

$$\frac{\rho}{Z} = \left(\frac{R_M}{R_C}\right)^3 \left[\frac{\partial A_2(E_F)}{\partial E} + 9\frac{\partial\alpha_0(E_F)}{\partial E} \times \int_0^1 dx\, x^2 \int_0^1 dy\, y^2 j_0{}^2(k_F R_M xy) + 27\frac{\partial\alpha_1(E_F)}{\partial E} \times \int_0^1 dx\, x^2 \int_0^1 dy y^2 j_1{}^2(k_F R_M xy)\right]. \tag{6.9}$$

Since $k_F = (1/R_C)(\frac{1}{4}9\pi Z)^{1/2}$ we find that to lowest order in R_M/R_C,

$$\frac{\rho}{Z} \cong \frac{\partial A_0(E_F)}{\partial E}\left(\frac{R_M}{R_C}\right)^3. \tag{6.10}$$

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[7] A. O. E. Animalu, Cavendish Laboratory Technical Report No. 4, Cambridge, England (unpublished).

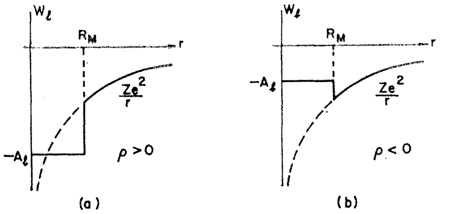

FIG. 3. Representative model potentials which lead to positive (a) and negative (b) depletion holes.

We have used Animalu's[7] results for $\partial A_l/\partial E$ to evaluate Eq. (6.9) to four places. The results are given in Table I along with values for the first-order expression, Eq. (6.10). For comparison we list also the OPW orthogonalization hole as given by Harrison.[6]

There are several results in Table I which deserve comment. We note that the first-order estimates for the depletion hole are always too large. When R_M/R_C can be regarded as a small parameter, the first-order expression does give reasonably accurate estimates. For Na we have values of ρ/Z for several R_M. One might expect an $R_M{}^3$ variation for ρ. However, it is clear from Table I that the variation is considerably less pronounced than this.

The negative depletion hole for Be given in Table I is not necessarily an incorrect result. For the HA model potential it is possible to obtain negative depletion holes. This becomes clear if we rewrite Eq. (3.1) for the depletion hole using Eqs. (3.2) and the virial theorem. We find

$$\rho=\frac{2\Omega}{(2\pi)^3}\sum(2l+1)\int_{k\leq k_F}d^3k\int_0^{R_M}r^2dr[\psi_l{}^2(k,r)-\chi_l{}^2(k,r)]$$

$$=\frac{2\Omega}{(2\pi)^3}\sum_l(2l+1)\int_{k\leq k_F}\frac{d^3k}{E(k)}\int_0^{R_M}r^2dr\times\left[A_l(k)\chi_l{}^2(k,r)-\frac{Ze^2}{2r}\psi_l{}^2(k,r)\right],\quad(6.11)$$

where we have written the wave functions in the form

$$\chi_k(r)=\sum_{l,m}\chi_l(k,r)Y_{lm}(\Theta,\varphi).$$

For A_l sufficiently large, the self-consistency of Eq. (6.11) requires that ρ (electron charge) be positive. Physically, this means that the constant potential well is considerably deeper than Ze^2/r over most of sphere of radius R_M, as shown in Fig. 3(a). Consequently, the model wave function will decrease more rapidly than the exact wave function for $r\lesssim R_M$. If A_l is large, then this condition will hold over most of the interval $(0,R_M)$. Since we choose $\chi_l(r)$ without nodes, it follows that it is possible for the first expression in (6.11) to be positive. For Be, the A_l given by Animalu[7] are large enough to give a negative depletion hole.

7. THE PSEUDOPOTENTIAL

As we indicated in Sec. 2, a restricted class of pseudopotentials,

$$W=V+\sum_\alpha f_\alpha(E)|\alpha\rangle\langle\alpha|\,,\quad(7.1)$$

have the same form as the general model potential we have considered. Consequently, we can apply our expression for the depletion hole to (7.1) and obtain

$$\rho=-\sum_{k\leq k_F}\sum_\alpha\frac{\partial f_\alpha(E_k)}{\partial E_k}\langle\chi_k|\alpha\rangle\langle\alpha|\chi_k\rangle.\quad(7.2)$$

Evidently, if f_α is independent of E_k, the depletion hole is zero. However, we know that the orthogonalization hole in pseudopotential theory is given exactly by

$$\rho^{\mathrm{OPW}}=-\sum_{k\leq k_F}\langle\chi_k|P|\chi_k\rangle,\quad(7.3)$$

$$P=\sum_\alpha|\alpha\rangle\langle\alpha|\,,$$

which is nonzero unless $|\chi_k\rangle$ is orthogonal to all the core states.

To resolve this apparent contradiction we will show that there is only one coefficient $f_\alpha(E)$ which yields a pseudowave function not identically equal to the true wave function, and that for this $f_\alpha(E)$, Eq. (7.2) is identical to (7.3).

If we take the inner product of the pseudowave equation,

$$(T+W)|\chi_k\rangle=E_k|\chi_k\rangle,\quad(7.4)$$

with a core state $\langle\beta|$, we obtain

$$\langle\beta|T+W|\chi_k\rangle=E_k\langle\beta|\chi_k\rangle$$

or

$$[f_\beta(E_k)-(E_k-E_\beta)]\langle\beta|\chi_k\rangle=0\,,\quad(7.5)$$

where E_β is the core-state energy. If $f_\beta(E_k)=E_k-E_\beta$ for all $\mathbf{k}$, then $|\chi_k\rangle$ need not be orthogonal to the core state $|\beta\rangle$. For all other choices of $f_\beta(E_k)$ it follows from (7.5) that

$$\langle\beta|\chi_k\rangle=0.\quad(7.6)$$

Since $|\chi_k\rangle=|\psi_k\rangle$ outside the core, the requirement of orthogonality to the core states means that $|\chi_k\rangle\equiv|\psi_k\rangle$ for all $\mathbf{k}$. Then by using the definition of the depletion hole, Eq. (3.1), or by substituting (7.6) into (7.2), we see that $\rho\equiv0$ for all pseudopotentials of the form (7.1), except

$$W=V+\sum_\alpha(E_k-E_\alpha)|\alpha\rangle\langle\alpha|\,.\quad(7.7)$$

Here E_k is the energy of the state $\mathbf{k}$ being considered. Our general expression for the depletion hole applied to this potential gives precisely the orthogonalization hole, Eq. (7.3).

There is one exception to the above argument which requires special consideration. Suppose we let $f_\beta(E_k) = E_{k_0} - E_\beta$. Then for $\mathbf{k}=\mathbf{k}_0$, Eq. (7.5) is satisfied without requiring that $|\chi_{k_0}\rangle$ be orthogonal to the core states. In fact, $|\chi_{k_0}\rangle$ is arbitrary. Then from (3.1) we see that the $\mathbf{k}=\mathbf{k}_0$ component of ρ need not be identically zero. This possible deviation from zero for a single state constitutes a set of measure zero relative to the sum (or integration) over all occupied states and consequently does not alter the total depletion hole. However, we are led to ask why it is that from (3.1) the $\mathbf{k}_0$ component of ρ is not zero, whereas from (7.2) even the $\mathbf{k}=\mathbf{k}_0$ component of ρ is identically zero for the choice $f_\alpha(E_k) = E_{k_0} - E_\alpha$. The reason is that in deriving (7.2) we required that the pseudowave function be a smooth function of $\mathbf{k}$ in order that the expansion of $|\chi_k\rangle$ in Eq. (3.6) be valid. Now we have shown in (7.5) that for

$$W = V + \sum_\alpha (E_{k_0} - E_\alpha)|\alpha\rangle\langle\alpha|\,, \tag{7.8}$$

$|\chi_k\rangle \equiv |\psi_k\rangle$ for all $\mathbf{k}\neq\mathbf{k}_0$. For $\mathbf{k}=\mathbf{k}_0$, $|\chi_{k_0}\rangle$ is arbitrary. To insure the smoothness of $|\chi_k\rangle$ in k space, which is required to obtain (7.2), we must set $|\chi_{k_0}\rangle = |\psi_{k_0}\rangle$ (which we are free to do since $|\chi_{k_0}\rangle$ is arbitrary). With this choice for $|\chi_{k_0}\rangle$, Eq. (3.1) gives $\rho\equiv 0$, as does (7.2). If we do not choose $|\chi_{k_0}\rangle = |\psi_{k_0}\rangle$, then we cannot use (7.2) to compute ρ and we see from (3.1) that the $\mathbf{k}=\mathbf{k}_0$ component of ρ is nonzero, though the total depletion hole remains essentially zero.

It is possible[8] to obtain an expression analogous to (3.8) for the depletion hole associated with a general pseudopotential of the form[6,9]

$$W|\mathbf{k}\rangle = V|\mathbf{k}\rangle + \sum_\alpha f_\alpha(\mathbf{k})|\alpha\rangle\langle\alpha|\mathbf{k}\rangle. \tag{7.9}$$

However, this expression yields the well-known result (7.3) for the orthogonalization hole.

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APPENDIX

Our result for the long-wavelength limit of the form factors depends critically on Eq. (5.6). Therefore, it is important that we provide some details of the calculation leading to this equation, particularly since it differs from the result obtained by Animalu.[3]

When we substitute Eq. (5.4) into (5.5) and do the angle integrations we obtain

$$g(q) \underset{q\to 0}{\longrightarrow} \frac{N}{k_F}\int_0^{k_F} dk \sum_l \left[\frac{k}{q}\ln\left|\frac{2k+q}{2k-q}\right| \langle\mathbf{k}|A_l(E_k)P_l|\mathbf{k}\rangle + 2k\frac{\partial}{\partial k'}\langle\mathbf{k}'|A_l(E_k)P_l|\mathbf{k}\rangle|_{k'=k}\right]. \tag{A1}$$

The limit of the first term can be determined by writing $f(k) = d\xi/dk$, integrating by parts, splitting the integral into two regions around the singularity, and finally integrating by parts once more. The result is

$$-\frac{1}{k_F}\int_0^{k_F} dk f(k)\,, \tag{A2}$$

which is precisely what is obtained by evaluating the limit before integrating.

We can rewrite the second term in (A1) by noting that the derivative acts only on the wave function:

$$\begin{aligned} 2k\frac{\partial}{\partial k'}\langle\mathbf{k}'|A_l(E_k)P_l|\mathbf{k}\rangle|_{k'=k} &= k\frac{\partial}{\partial k'}\langle\mathbf{k}'|A_l(E_k)P_l|\mathbf{k}\rangle|_{k'=k} \\ +k\frac{\partial}{\partial k'}\langle\mathbf{k}|A_l(E_k)P_l|\mathbf{k}'\rangle|_{k'=k} &= k\frac{\partial}{\partial k}\langle\mathbf{k}|A_l(E_k)P_l|\mathbf{k}\rangle \\ &\quad -k\langle\mathbf{k}|[\partial A_l(E_k)/\partial k]P_l|\mathbf{k}\rangle. \end{aligned} \tag{A3}$$

Using Eq. (A2) and (A3) in (A1), we find that

$$g(q) \underset{q\to 0}{\longrightarrow} -\frac{1}{k_F}\int_0^{k_F} dk\left[f(k) + k\frac{\partial f(k)}{\partial k}\right] - \frac{N}{k_F}\sum_l \int_0^{k_F} dk\, k\langle\mathbf{k}|\frac{\partial A_l(E_k)}{\partial k}P_l|\mathbf{k}\rangle. \tag{A4}$$

Integrating the first term in (A4) by parts leads us directly to Eq. (5.6).

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[8] R. W. Shaw, Jr., thesis (unpublished).

[9] J. B. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).