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Screening of a Foreign Charge by an Electron Gas

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The random-phase approximation of the displaced density of an electron gas due to the presence of a foreign charge assumes a rather large error when the mean density of the gas is commensurate with that of conduction electrons in a metal. The assumption of a linear response is not quite valid. A modified formula, entailing little additional mathematical labor but treating the low-density problem more realistically, is proposed for the case of a negative foreign charge. For an arbitrary foreign-charge distribution, two expressions, each of which contains as special cases both the random-phase and the nonlinear Fermi-Thomas approximations. are examined. One of these comes quite close to reproducing the exact quantum-mechanical results in the hypothetical test case of a gas of noninteracting electrons.

To relate the charge density $-en(\mathbf{r})$ of an infinite system of electrons in the ground state to the potential $w(\mathbf{r})$ created by a foreign-charge distribution—which serves as a model for depicting impurity effects in metals and which bears on the study of electron correlations—is not a simple matter even with the disregard of exchange in an independent-particle approximation. A straightforward Hartree calculation for a point impurity charge would be comparable to that for an atom of infinite electrons.

The random-phase approximation[1] (RPA) of this relation may be expressed by

$$\Delta n = n(\mathbf{r}) - n_0 = (k_F/\pi^2 a_0 e) Q(k_F) u(\mathbf{r}) \tag{1}$$

in conjunction with Poisson's equation

$$4\pi e \Delta n = \nabla^2 v, \tag{2}$$

where n_0 is the mean value of $n(\mathbf{r})$, $k_F{}^3 = 3\pi^2 n_0$, a_0 is the Bohr radius, $v(\mathbf{r})$ represents the potential arising from the electrons in combination with the conventionally assumed neutralizing uniform distribution of fixed positive charge,

$$u(\mathbf{r}) = w(\mathbf{r}) + v(\mathbf{r}), \tag{3}$$

and, with $j_1(x) = (\sin x - x\cos x)/x^2$,

$$2\pi Q(k_F) u(\mathbf{r}) = k_F \int d\mathbf{r}'\, u(\mathbf{r}+\mathbf{r}') j_1(2k_F r')/r'^2. \tag{4}$$

The integral operator Q is commonly expressed through its Fourier transform inasmuch as

$$Q(k_F) e^{i\mathbf{k}\cdot\mathbf{r}} = \tfrac{1}{2} f(k^2/4k_F{}^2) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{5}$$

where

$$f(x^2) = 1 + \frac{1-x^2}{4x} \ln\left(\frac{1+x}{1-x}\right)^2. \tag{6}$$

Equation (1) is the first-order correction resulting from treating $w(\mathbf{r})$ in the Hartree equation as a perturbation upon a free electron gas. The question arises as to whether the nonlinear corrections of higher order can properly be neglected.

Physical interest tends to concentrate on a range of values of n_0 appropriate to the conduction electrons in metals, i.e., $1.8 \lesssim r_s \lesssim 5.5$, where $3/4\pi r_s{}^3 a_0{}^3 = n_0$. The foreign-charge distribution, on the other hand, must consist of a collection of point charges, each having a magnitude that is some multiple of e. For this n_0 range and for only a single point charge of $-e$ the linear approximation of $n(\mathbf{r})$ assumes, in defiance of reality, rather large negative values in the vicinity of the point charge. The consequent error in the potential energy from the interaction of the impurity charge with the displaced electronic charge is shown below to exceed 20%. It is the purpose of this paper to analyze certain nonlinear formulas which promise some improvement upon Eq. (1).

One well-known nonlinear expression is[2]

$$\begin{aligned} 3\pi^2 n(\mathbf{r}) &= [k_F{}^2 + (2/a_0 e) u(\mathbf{r})]^{3/2} && \text{for} \quad k_F{}^2 a_0 e \geq -2u \\ &= 0 && \text{for} \quad k_F{}^2 a_0 e < -2u, \end{aligned} \tag{7}$$

which, with Eq. (2), leads to the Fermi-Thomas equation. A linearized version[3]

$$\Delta n = (k_F/\pi^2 a_0 e) u(\mathbf{r}), \tag{8}$$

the result of preserving the first two terms of the expansion of the right-hand side of Eq. (7) for

$$2|u| \ll k_F{}^2 a_0 e, \tag{9}$$

has proven useful.

It is evident from Eqs. (5) and (6) that for $k \to 0$, $Q(k_F) \to 1$, rendering Eqs. (1) and (8) equivalent. In this circumstance Eq. (7) is preferable to Eq. (1), since condition (9), which justifies Eq. (1) as well, may not be met. A Coulomb potential, however, has important short-wavelength components. Equation (1), in contrast to Eqs. 7 and 8, admits[4] oscillations of the Friedel[5] kind.

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[1] D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1964), p. 146.

[2] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927); E. Fermi, Z. Physik **48**, 73 (1928).

[3] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[4] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1959).

[5] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

An expression which reduces to either Eqs. (1) or (7) under the circumstances that favor the use of that particular equation is

$$\begin{aligned} 3\pi^2 n(\mathbf{r}) &= [k_F{}^2+(2/a_0e)Q(k_F)u(\mathbf{r})]^{3/2} && \text{for} \quad k_F{}^2a_0e \geq -2Qu \\ &= 0 && \text{for} \quad k_F{}^2a_0 < e-2Qu. \quad (10) \end{aligned}$$

Now in the derivation of Eq. (4) the parameter k_F serves as the limit on the occupied states. In the Fermi-Thomas treatment, however, this limit depends on $n(\mathbf{r})$ rather than n_0. For instance, where w is positive one expects that $n(\mathbf{r}) > n_0$, thus providing for additional states to be occupied by electrons bound to this particular region. Hence, letting $\zeta^3 = n(\mathbf{r})/n_0$, one can perhaps refine Eq. (10) with

$$\begin{aligned} 3\pi^2 n(\mathbf{r}) &= [k_F{}^2+(2/a_0e)Q(\zeta k_F)u(\mathbf{r})]^{3/2} && \text{for} \quad k_F{}^2a_0e \geq -2Qu \\ &= 0 && \text{for} \quad k_F{}^2a_0e < -2Qu. \quad (11) \end{aligned}$$

These formulas are tested in a simple way by considering a hypothetical gas of electrons that are affected by a point impurity charge Ze, giving

$$w = Ze/r, \quad (12)$$

but do not interact with each other, i.e., $v=0$. Qualitatively, the resulting unscreened potential, $u=Ze/r$, resembles the screened potential, particularly in the critical region about $r=0$, where the contribution from v is not important. The exact quantum-mechanical result, derived from the known wave functions for this simple Coulomb potential, is given by

$$\begin{aligned} (\pi/2k_F{}^3)n(\mathbf{r}) &= G(Z/k_Fa_0, 2k_Fr) \\ &\quad + (Z/k_Fa_0)^3 g(2Zr/a_0) && \text{for} \quad Z>0 \\ &= G(Z/k_Fa_0, 2k_Fr) && \text{for} \quad Z<0, \quad (13) \end{aligned}$$

where, upon denoting by ${}_1F_1\ (\alpha,\beta,x)$ the confluent hypergeometric function,[6]

$$\rho G(s,\rho) = s\int_1^\infty dy\, y^{-2}(1-e^{-2\pi sy})^{-1} \times \int_0^{\rho/y} dx\, |{}_1F_1(isy,1,ix)|^2,$$

and, representing the contributions from the bound states,

$$g(\xi) = \sum_{n=1}^{\infty} \frac{e^{-\xi/n}}{n^4} \sum_{l=0}^{n-1} (2l+1)(n-l-1)!(n+l)!\left(\frac{\xi}{n}\right)^{2l} \times \left(\sum_{m=0}^{n-l-1} \frac{(-1)^m(\xi/n)^m}{m!(n-l-m-1)!(m+2l+1)!} \right)^2.$$

Equations (1), (7), (10), and (11) all give $\Delta n \to Zk_F/\pi^2a_0r$ as $r\to\infty$, in agreement with Eq. (13). Hence the errors in the predictions of these four formulas at $r=0$ provide some measure of their reliability inasmuch as $|\Delta n|$ assumes its maximum value at this point. Table I compares these predictions, with the exclusion of the result $n\to\infty$ for $Z>0$ and $n=0$ for $Z<0$ from Eq. (7), against that from Eq. (13) over a range of values of n_0.

In Table II other values of r within the region where $|\Delta n|$ is relatively large are considered for a value of n_0 which for $Z=\pm1$ lies near the middle of the metallic range. For $Z<0$ Eqs. (7), (10), and (11) yield only a small percent of error, as determined from Eq. (13), with respect to Δn.

A formula like Eq. (11) in intent is available through the variational approach of Hohenberg and Kohn (HK).[7] Employing their Eq. (83), as subsequently amended,[8] gives, as the condition for an energy extremum under variation of $n(\mathbf{r})$,

$$(3\pi^2n)^{2/3} = k_F{}^2 + (2/a_0e)u + (2\pi^2/\zeta k_F) \times [1-Q^{-1}(\zeta k_F)]n + T, \quad (11')$$

where $T(\mathbf{r})$ is an integral expression of second order in the difference in the values of n at a variable and a fixed position. It arises from the fact that the kernel in Eq. (83) is also dependent on n. The use of Q as defined by Eq. (4) corresponds to the RPA approximation of the dielectric coefficient appearing in their formula. Of course, one could redefine Q so as to reflect exchange and correlation corrections.

In Eq. (83) of HK only terms up to the second order in the deviation of $n(\mathbf{r})$ from its value at a fixed position have been considered. This limits the expected accuracy of Eq. (11′) to first-order terms. While there is provision for extension to second-order terms and beyond—as one could obtain the second-order perturbation correction to Eq. (1) and modify Eq. (11) accordingly—the anticipated complexities give such a procedure little promise.

Now it can be shown that to the extent of terms that are linear in ∇n (or, therefore, in ∇u) the gradient expansions of Eqs. (11′) and (11) agree. With the aid of Eqs. (5) and (6), Eq. (11) may be rewritten as

$$(3\pi^2n)^{2/3} = k_F{}^2 + a_0{}^{-1}e^{-1}f(-\tfrac{1}{4}\zeta^{-2}k_F{}^{-2}\nabla^2)u.$$

Inasmuch as the expansion $\frac{1}{2}f(x^2) = 1-\frac{1}{3}x^2-\cdots$ converges for $x^2\leq1$, one obtains for relatively slow variations

$$(3\pi^2n)^{2/3} = k_F{}^2 + \frac{2}{a_0e}\left(1+\frac{1}{12\zeta^2k_F{}^2}\nabla^2 - \frac{1}{240\zeta^4k_F{}^4}\nabla^2\nabla^2+\cdots\right)u,$$

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[6] H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge U. P., Cambridge, England, 1950), 2nd ed., p. 607.

[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

TABLE I. Density $\zeta^3 k_F^3/3\pi^2$ of a gas of noninteracting electrons at the position of a point impurity charge Ze for various mean densities $k_F^3/3\pi^2$.

$2\pi Z/k_F a_0$	ζ^3			
	From Eq. (13)	From Eq. (11)	From Eq. (10)	From Eq. (1)
−10.0	0.000 106 5	0.007 14	⋯	−6.5
−5.0	0.013 22	0.043 16	⋯	−2.75
−2.0	0.199 3	0.236 1	⋯	−0.5
−1.0	0.458 5	0.476	0.354	0.25
−0.5	0.682	0.650	0.688	0.625
0.0	1.000	1.000	1.000	1.000
0.5	1.443	1.454	1.398	1.375
1.0	2.050	2.110	1.837	1.75
2.0	3.930	4.236	2.828	2.5
5.0	18.93	23.17	6.55	4.75
10.0	106.3	140.0	14.7	8.5
∞	$0.731(\pi Z/k_F a_0)^3$	$(\pi Z/k_F a_0)^3$		

or, to the same order in ∇u,

$$3\pi^2 n=\left(k_F^2+\frac{2}{a_0 e}u\right)^{3/2}$$

$$\times\left[1+\frac{1}{4a_0 e}\left(k_F^2+\frac{2}{a_0 e}u\right)^{-2}\nabla^2 u+\cdots\right],$$

which appears to be just that portion limited to linear terms in ∇u of the series that results from applying quantum corrections[9] (exclusive of exchange and correlation corrections) to the Fermi-Thomas model.

With respect to the remainder of the quantum corrections, Eq. (11′) does reproduce the term proportional to $\nabla u\cdot\nabla u$ by virtue of the function $T(\mathbf{r})$. Otherwise, neither Eq. (11) nor Eq. (11′) is faithful to the series.

However, they offer a more realistic response to rapid changes in u. In the example $u=Ze/r$, unlike the quantum-corrected statistical model they predict a bounded $n(\mathbf{r})$ for $Z>0$.

An additional shortcoming of the quantum corrections is their omission of the quantum-oscillatory terms. It has previously been remarked that Eq. (1) provides a quantum oscillation. However, in the example of $u=Ze/r$ one finds that Eqs. (1), (11), and (11′) all give such an oscillation which, while of the right wavelength, is not necessarily correct as to magnitude or phase.

To show this one obtains for large r from Eq. (13)

$$\frac{3\pi^2}{k_F^3}n(\mathbf{r})=1+\frac{6s}{\rho}+\frac{6s^2}{\rho^2}-\frac{4s^3}{\rho^3}$$

$$+\frac{6\pi}{\rho^3\sinh\pi s}\operatorname{Re}\frac{e^{i(\rho+2s\ln\rho)}}{\Gamma^2(is)}+O(\rho^{-4}),$$

TABLE II. Density $\zeta^3 k_F^3/3\pi^2$ of a gas of noninteracting electrons at various distances r from a point impurity charge Ze for the mean density whereby $2\pi|Z|/k_F a_0=10$.

$\lvert Z\rvert r/a_0$	ζ^3				
	From Eq. (13)	From Eq. (11)	From Eq. (10)	From Eq. (7)	From Eq. (1)
		$Z>0$			
0	106.3	140.0	14.7	∞	8.5
1	16.32	16.06	10.19	14.94	6.55
2	6.28	6.755	6.80	6.64	4.885
3	4.51	4.33	4.63	4.41	3.67
4	3.42	3.385	3.43	3.41	2.91
		$Z<0$			
0	0.000 106 5	0.007 14	⋯	⋯	−6.5
1	0.000 678	0.008 33	⋯	⋯	−4.55
2	0.002 905	0.009 98	⋯	⋯	−2.89
3	0.009 15	0.012 43	⋯	⋯	−1.67
4	0.023 0	0.016 41	⋯	⋯	−0.91
5	0.048 5	0.024 0	0.000 65	⋯	−0.49
6	0.088 7	0.044 2	0.066 4	0.061 4	−0.25
7	0.144	0.129 1	0.141 2	0.145 2	−0.09
8	0.210	0.233 7	0.217 1	0.222 1	0.042
9	0.29	0.294 6	0.289 3	0.289	0.156

where $s=Z/k_F a_0$ and $\rho=2k_F r$, and from Eq. (11) as well as from Eq. (11′)

$$\frac{3\pi^2}{k_F^3}n(\mathbf{r})=1+\frac{6s}{\rho}+\frac{6s^2}{\rho^2}-\frac{4s^3}{\rho^3}-\frac{6s}{\rho^3}\cos\rho+O(\rho^{-4}).$$

Evidently, the two expressions agree only in the limit of $k_F\to\infty$.

This expansion also confirms the superiority of Eq. (11) [or of Eq. (10) since to this order one may set $\zeta=1$] with respect to Eq. (1), which fails to produce the nonoscillatory terms beyond $6s/\rho$. Eq. (7), by contrast, gives to the order shown just the nonoscillatory terms.

In this example Eqs. (11) and (11′) exhibit identical errors to the order considered. This suggests that the choice between them be governed by the greater simplicity of Eq. (11).

The apparent reasonableness of Eq. (10) for negative Z suggests as a modification of Eq. (1)

$$\begin{aligned}\Delta n&=(k_F/\pi^2 a_0 e)Q(k_F)u(\mathbf{r}) &&\text{for}\quad k_F^2 a_0 e\geq -3Qu\\ &=-k_F^3/3\pi^2 &&\text{for}\quad k_F^2 a_0 e< -3Qu,\end{aligned}\tag{14}$$

which satisfies Eq. (10) for $k_F^2 a_0 e\leq -2Qu$ and a linear version thereof for $k_F^2 a_0 e\geq -3Qu$ but disallows the negative values for $n(\mathbf{r})$ resulting from this linear version for $-2Qu<k_F^2 a_0 e<-3Qu$. The effect of this modification is seen in Tables I and II by substituting zeros for the negative values in the columns under Eq. (1).

Returning to the matter of screening in the case of the point impurity charge, one obtains from Eqs. (1)–(3) in connection with Eq. (12), for which $\nabla^2 w=0$ when $r\neq 0$,

$$\pi a_0\nabla^2 u=4k_F Q(k_F)u,\tag{15}$$

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[9] A. S. Kompaneets and E. S. Pavlovskii, Zh. Eksperim. i Teor. Fiz. **31**, 427 (1956) [Soviet Phys. JETP **4**, 328 (1957)]; D. A, Kirzhnits, *ibid.* **32**, 115 (1957) [**5**, 64 (1957)]; S. Golden, Phys. Rev. **105**, 604 (1957).

TABLE III. Variation of the displaced electron density Δn with distance r from a point impurity charge $-e$ for $r_s=3.0$.

k_Fr	$-\Delta n/k_F^3$ From Eq. (17) [a]	$-\Delta n/k_F^3$ From Eq. (20)
0.0	0.127 6	0.033 8
0.1	0.117 0	0.033 8
0.4	0.088 47	0.033 8
0.7	0.064 18	0.033 8
1.0	0.044 41	0.033 8
1.3	0.029 04	0.033 8
1.6	0.017 67	0.021 54
1.9	0.009 758	0.011 9
2.5	0.001 680	0.002 048
3.1	−0.000 294 5	−0.000 359
3.7	−0.000 064 59	−0.000 078 7

[a] See Ref. 4.

subject to the boundary conditions,

$$\lim_{r\to 0} ru = Ze \tag{16a}$$

and

$$\lim_{r\to\infty} ru = 0 \tag{16b}$$

(under the assumption that the system, comprising the electrons, impurity, and fixed positive charge, is electrically neutral). The consequent Δn is given by

$$\Delta n/k_F^3 = ZY(\gamma,2k_Fr), \tag{17}$$

where $\gamma=2\pi k_Fa_0$ and

$$\pi^2\rho Y(\gamma,\rho)=4\int_0^\infty dx\, xf(x^2)\sin\rho x/[\gamma x^2+f(x^2)].$$

The function $Y(\gamma,\rho)$ has been tabulated by Langer and Vosko[4] for several values of γ.

With the substitution of Eq. (14) for Eq. (1), Eq. (15) is replaced by

$$\begin{aligned}\pi a_0\nabla^2u &= 4k_FQ(k_F)u \quad \text{for} \quad r>r_0\\ &= -\tfrac{4}{3}k_F^3a_0e \quad \text{for} \quad r<r_0,\end{aligned} \tag{18}$$

where r_0 is the value of r for which $k_F^2a_0e=-3Qu$. For $r>r_0$, Eq. (18) and the boundary condition (16b) are satisfied by

$$u=4\pi\beta Zk_F^3er^{-1}\int_r^\infty ds\, s(s-r)Y(\gamma,2k_Fs);$$

for $r<r_0$, Eq. (18) and the boundary condition (16a), by

$$u=\alpha+Zer^{-1}-(2k_F^3e/9\pi)r^2.$$

One chooses α, β, and r_0 to give these two expressions the same value and the same first and second derivatives at $r=r_0$. This requires

$$3\pi^2\beta ZY(\gamma,2k_Fr_0)=-1$$

and

$$\beta\left(1-\tfrac{1}{2}\pi\int_0^{2k_Fr_0} d\rho\, \rho^2Y(\gamma,\rho)\right)=1-\frac{4k_F^3r_0^3}{9\pi}$$

when

$$3\pi^2ZY(\gamma,0) < -1. \tag{19}$$

Otherwise, one finds $\beta=1$ and $r_0=0$, representing the RPA. The resulting Δn is

$$\begin{aligned}\Delta n/k_F^3 &= \beta ZY(\gamma,2k_Fr) \quad \text{for} \quad r>r_0\\ &= -\tfrac{1}{3}\pi^{-2} \quad \text{for} \quad r<r_0.\end{aligned} \tag{20}$$

There is a particular value for γ above which condition (19) does not obtain. Consequently, since the RPA becomes exact in the high-density limit,[4] so must Eq. (18).

On the other hand, for $n_0\to 0$ when $Z=-1$, the above relations give $r_0\to r_sa_0$ while the expression for n deriving from Eq. (20) reduces to a step function:

$$\begin{aligned}3\pi^2n &= 0 \quad \text{for} \quad r<r_sa_0\\ &= k_F^3 \quad \text{for} \quad r>r_sa_0.\end{aligned} \tag{21}$$

Since the electrons in this limit may be regarded as static and have the same charge as the point impurity, Eq. (21) may be judged by how well it also serves as their pair function. To comply with Eq. (21)—to the extent of a spherical approximation of the Wigner-Seitz cell—the electrons must arrange themselves into a lattice, as depicted by Wigner.[10]

Hence, the modified RPA formula proposed here for negative values of Z is realistic at both density extremes.

In the metallic range of n_0 the difference in the results from Eqs. (17) and (20) for $Z=-1$ is quite pronounced. Table III shows this for $r_s=3.0$, which finds $\beta=1.219$ and $k_Fr_0=1.330$. The potential energy from the interaction of the impurity charge with the displaced electronic charge

$$4\pi e^2\int_0^\infty dr\, r\Delta n$$

turns out to be $-0.891\, k_Fe^2$ and $-0.733\, k_Fe^2$ according to the RPA and its modification, respectively. Inasmuch as even the latter, as deduced from Table II, exaggerates the screening at small r, the RPA error due to its presumption of a linear response must be larger yet than the difference between these values.

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[10] E. Wigner, Phys. Rev. 46, 1002 (1934).