resistivity $\rho_T(\phi)$ (whose precise value is realizable neither experimentally nor theoretically).

[18] The calculations here have considered only the effect of residual scattering which is isotropic. Anisotropic relaxation of the electron distribution by dislocations, contraction voids, extrusion faults, and other possible sources of anisotropic residual scattering will serve only to further enhance the deviations resulting from the changing angular nature of the electron distribution (assuming, of course, that such anisotropy does not happen to exactly match the particular distortions generated by umklapp processes).

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[20] In Fig. 9, the pure reference sample's diameter is about 2.5 mm; complete diffuse surface scattering has been assumed in calculating the upper limit given.

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Charge Densities in the Presence of Strong Attractive Impurity Potentials

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The problem of calculating the induced charge density around a strong impurity potential is well known to be a most difficult one, and hence the need for approximate schemes. In this paper we show how to construct, in a simple manner, full self-consistent densities which may then be used to check an approximate procedure. We use these densities to check the accuracy of a method introduced by Sjölander and Stott to calculate positron annihilation rates. We rederive the Sjölander–Stott equation for a general attractive impurity potential and demonstrate that for infinite-mass impurities this equation gives very good results (far better than linear response) at small distances from the impurity, but long-range effects are not satisfactorily respresented. This conclusion seems to be independent of the electron density, the form of the impurity potential, and whether or not exchange and correlation effects are included. Finally, our analysis suggests that retention of only the first term of the Hohenberg–Kohn–Sham gradient expansion gives a good representation of exchange and correlation for the calculation of electron densities.

I. INTRODUCTION

The charge density surrounding an impurity placed in an electron gas is of considerable interest to many solid-state physicists, but unfortunately its calculation is usually a most formidable problem. Langer and Vosko[1] have provided the solution to the problem in the limit of weak impurity potentials using linear-response theory. But to go beyond linear response into the regime applicable to strong potentials is most difficult. Even the solution to the self-consistent Hartree equation for the system, let alone Hohenberg–Kohn–Sham[2] or Hartree–Fock schemes, requires prodigious effort, and hence it is of interest to develop approximate and simpler procedures which go beyond linear response. One such scheme has been developed recently by Sjölander and Stott[3] (referred to as SS) to calculate positron annihilation rates, though it can be applied to a much wider range of problems. The SS integral equation for the charge density is particularly interesting because the authors[3] demonstrate that it gives much better results than the linear-response method for a repulsive Coulomb potential using the Hartree approximation. Unfortunately, due to complications arising from the presence of bound states, they were unable to provide similar information for an attractive Coulomb potential. Nevertheless, the SS theory is sufficiently interesting to warrant further investigation and it is the purpose of this paper (a) to point out a relatively simple method for checking approximate schemes such as developed by SS and (b) to apply this method to the SS theory, in order to make a quantitative estimate of its validity for a wide range of attractive potentials.

In Sec. II we outline the derivation of the SS integral equation for a general impurity potential. We should point out that this equation is valid not only for an infinite-mass impurity (fixed impurity) but also for a finite-mass impurity such as a positron where recoil effects are important. In Sec. III, using an approach introduced by Geldart *et al.*,[4] we describe the procedure used to obtain the self-consistent Hartree charge distribution corresponding to an external potential. The power of this procedure lies not only in the ease with which the self-consistent Hartree solution is obtained, but also in the fact that any local exchange and correlation approximation may be introduced with virtually no further computation effort required. This enables us, then, not only to ascertain the accuracy with which the SS equation (or for that matter any other scheme) reproduces the exact Hartree solution, but also to provide an assessment of its ability to include exchange and correlation effects. We elaborate further on this point in Sec. III. Finally, in Sec. IV we summarize the results, which prompt us to conclude that the SS equation gives remarkably good results for small x (near the impurity) both with and without exchange and correlation, but that the results get progressively worse as x increases; in fact, the long-range oscillations are not reproduced satisfactorily.

II. INTEGRAL EQUATION FOR PAIR CORRELATION FUNCTION

Consider a two-component system where the elements comprising the two systems are not necessarily point charges. Let us write the general interaction between elements i and j of the same component or opposite components as

$$Z_\alpha Z_\beta e^2 \phi^{\alpha\beta}(\vec{r}_i - \vec{r}_j) \quad , \tag{1}$$

where α and β take the values 1 and 2 and refer to the two components. Z_1 and Z_2 are -1 or $+1$ depending on whether the interaction between components 1 and 2 is attractive or repulsive.

Now let us apply weak external potentials $V^1(\vec{x}, t)$ and $V^2(\vec{x}, t)$, where $V^1(\vec{x}, t)$ acts only on component 1 and $V^2(\vec{x}, t)$ only on component 2. These two external fields introduce a new term in the Hamiltonian given by

$$H_I = \sum_{\beta=1}^{2} \int \hat{n}^\beta(\vec{x}, t) V^\beta(\vec{x}, t)\, d\vec{x} \quad , \tag{2}$$

where $\hat{n}^\beta(\vec{x}, t)$ is the density operator. From linear response, the induced density distributions of both components are given by the equation

$$n^\alpha(\vec{x}, t)_{\mathrm{ind}} = \frac{-i}{\hbar} \sum_{\beta=1}^{2} \int d\vec{x}' \times \int_{-\infty}^{t} dt' \langle [\hat{n}^\alpha(\vec{x}, t), \hat{n}^\beta(\vec{x}', t')] \rangle V^\beta(\vec{x}', t') \, . \tag{3}$$

The commutator of Eq. (3) is to be evaluated with the unperturbed ground state. The Fourier transform of Eq. (3) yields

$$n^\alpha(\vec{q}, \omega)_{\mathrm{ind}} = - \sum_{\beta=1}^{2} \chi^{\alpha\beta}(\vec{q}, \omega) V^\beta(\vec{q}, \omega) \quad , \tag{4}$$

where

$$\chi^{\alpha\beta}(\vec{q}, \omega) = (i/V\hbar) \int_0^\infty e^{i\omega t} \langle [\hat{n}^\alpha_{-\vec{q}}(t), \hat{n}^\beta_{\vec{q}}(0)] \rangle \, dt \quad . \tag{5}$$

V is the volume of the system and

$$\hat{n}^\alpha_{\vec{q}}(t) = \int e^{i\vec{q}\cdot\vec{x}} \hat{n}^\alpha(\vec{x}, t)\, d\vec{x} \quad .$$

Now the final interest is in the density distribution surrounding the elements of the two components. These are of course related to the pair correlation function $g^{\alpha\beta}(\vec{x})$, the Fourier transform of which can be written

$$g^{\alpha\beta}(\vec{q}) = (2\pi)^3 \delta(\vec{q}) + \gamma^{\alpha\beta}(\vec{q}) \quad , \tag{6}$$

where

$$\gamma^{\alpha\beta}(\vec{q}) = \frac{1}{n_\alpha n_\beta} \frac{1}{V} \langle \hat{n}^\alpha_{-\vec{q}}(0) \hat{n}^\beta_{\vec{q}}(0) \rangle - \frac{\delta_{\alpha\beta}}{n_\alpha} \quad . \tag{7}$$

In Eq. (7), $q \neq 0$. We have used the symbol n_α to denote the equilibrium density of the αth component. The static density-density correlation function $\langle \hat{n}^\alpha_{-\vec{q}}(0) \hat{n}^\beta_{\vec{q}}(0) \rangle$ is to be evaluated in the ground state. It is easily related to $\chi^{\alpha\beta}(\vec{q}, w)$ by[5]

$$\langle \hat{n}^\alpha_{-\vec{q}}(0) n^\beta_{\vec{q}}(0) \rangle = (\hbar/\pi) V \,\mathrm{Im} \int_0^\infty \chi^{\alpha\beta}(\vec{q}, \omega)\, d\omega \quad , \tag{8}$$

where again $q \neq 0$.

For arbitrary, small, external potentials $V^\alpha(\vec{x}, t)$, the induced densities are given exactly by Eq. (3) or (4). We may construct *approximate* induced densities corresponding to the same external potentials in the following manner. We introduce, as do SS, effective fields which act on the two components as if their elements were noninteracting and which take the form

$$V^\alpha_{\mathrm{eff}}(\vec{x}, t) = V^\alpha(\vec{x}, t) + \sum_{\beta=1}^{2} \psi^{\alpha\beta}(\vec{x} - \vec{x}') n^\beta(\vec{x}', t)_{\mathrm{ind}}\, d\vec{x}' \quad , \tag{9}$$

where $\psi^{\alpha\beta}(\vec{x})$ is an effective particle-particle interaction. The induced densities are then

$$n^{\alpha}(\vec{q},\omega)_{\mathrm{ind}} = -\chi_0^{\alpha}(\vec{q},\omega)V_{\mathrm{eff}}(\vec{q},\omega)$$

$$= -\chi_0^{\alpha}(\vec{q},\omega)\left(V^{\alpha}(\vec{q},\omega) + \sum_{\beta=1}^{2}\psi^{\alpha\beta}(\vec{q})n^{\beta}(\vec{q},\omega)_{\mathrm{ind}}\right), \tag{10}$$

where

$$\chi_0^{\alpha}(\vec{q},\omega) = \frac{i}{\hbar V}\int_0^{\infty}\langle[\hat{n}^{\alpha}_{-\vec{q}}(t),\hat{n}^{\alpha}_{\vec{q}}(0)]\rangle e^{i\omega t}\,dt$$

$$= 2\int \frac{f^0(\vec{k}) - f^0(\vec{k}+\vec{q})}{\epsilon(\vec{k}+\vec{q}) - \epsilon(\vec{k}) + \hbar\omega + i\delta}\,\frac{d\vec{k}}{(2\pi)^3}\;. \tag{11}$$

$f^0(\vec{k})$ is the zero-temperature Fermi function, $\epsilon(\vec{k}) = \hbar^2k^2/2m_{\alpha}$, and m_{α} is the mass of the element of the αth component.

So far, both Eqs. (4) and (10) are valid for arbitrary densities of the two components. We next restrict one component (component 1) to the limit of zero density. Comparing Eqs. (4) and (10) in that limit yields the following relation:

$$\chi^{12}(\vec{q},\omega) = -\chi_0^{1}(\vec{q},\omega)\psi^{12}(\vec{q})\chi^{22}(\vec{q},\omega)\;. \tag{12}$$

To complete the analysis in this section we must introduce some approximate form for the effective interaction $\psi^{12}(\vec{x})$. Following SS, we write

$$\nabla\psi^{12}(\vec{x}) = e^2Z_1Z_2g^{12}(\vec{x})\nabla\phi^{12}(\vec{x})\;, \tag{13}$$

where $g^{12}(\vec{x})$ is the pair correlation function between components 1 and 2. The errors introduced by the approximations in Eqs. (9) and (13) are not at all clear and we will attempt to investigate precisely these errors in Sec. III.

Using Eqs. (6)–(8), (12), and (13), we obtain the following integral equation for $\gamma^{12}(\vec{q})$:

$$\gamma^{12}(\vec{q}) = \frac{-\hbar e^2Z_1Z_2}{\pi n_1n_2}\left(\phi^{12}(\vec{q}) + \frac{1}{(2\pi)^3}\int\frac{\vec{q}\cdot\vec{q}\,'}{q^2}\gamma^{12}(\vec{q}-\vec{q}\,')\phi^{12}(\vec{q}\,')\,d\vec{q}\,'\right)\,\mathrm{Im}\int_0^{\infty}\chi_0^{1}(\vec{q},\omega)\chi^{22}(\vec{q},\omega)\,d\omega\;. \tag{14}$$

Equation (14) is sufficiently general to include any form of interaction between components 1 and 2 as well as between elements of component 2. If one were to evaluate $\chi^{22}(\vec{q},\omega)$ for a general interaction—say, via Feynman graphs—the only change from the electron-electron response function would be to replace the Coulomb interaction lines by lines appropriate to the desired interaction.

In Sec. III we concentrate on the case of an electron gas interacting with a general impurity potential. For that case $Z_2 = -1$, and $\chi^{22}(\vec{q},\omega)$ is simply the response function of an electron gas which can be written in terms of the dielectric function as

$$\chi^{22}(\vec{q},\omega) = \frac{q^2}{4\pi e^2}\left(1 - \frac{1}{\epsilon(q,\omega)}\right)\;. \tag{15}$$

Inserting this result into Eq. (14), we find

$$\gamma^{12}(\vec{q}) = \{q^2\phi^{12}(\vec{q}) + [1/(2\pi)^3] \times \int \vec{q}\cdot\vec{q}\,'\gamma^{12}(\vec{q}-\vec{q}\,')\phi^{12}(\vec{q}\,')\,d\vec{q}\,'\}f(\vec{q})\;, \tag{16}$$

where

$$f(\vec{q}) = \frac{\hbar Z_1}{4\pi^2n_1n_2}\,\mathrm{Im}\int_0^{\infty}\chi_0^{1}(\vec{q},\omega)\left(1 - \frac{1}{\epsilon(q,\omega)}\right)d\omega\;. \tag{17}$$

III. CALCULATION OF CHARGE DENSITIES FOR STRONG ATTRACTIVE POTENTIALS

Equation (16) is valid both for the case of infinite-mass and finite-mass impurities. It is especially useful in the case of finite-mass impurities, where the usual static nonlinear Hartree procedure is not applicable. However, in this paper we shall confine our attention to the infinite-mass or fixed impurity. It is most probable that our conclusions concerning the accuracy of the SS equation [Eq. (16)] will also apply to the finite-mass impurity.

A quantitative assessment of Eq. (16) is possible if its solution can be compared to the exact self-consistent solution for some impurity potential. We obtain a self-consistent solution using a method introduced by Geldart *et al.*[4] Instead of starting with an external potential and constructing the corresponding self-consistent density distribution, we reverse the process and construct the external potential corresponding to a given self-consistent distribution using the following procedure. Suppose we solve the equation

$$[-(\hbar^2/2m)\nabla^2 + v(\vec{x})]\phi_i(\vec{x}) = \epsilon_i\phi_i(\vec{x})\;, \tag{18}$$

which is not a self-consistent equation and is easy to solve. Then we construct the density

$$\delta n(\vec{x}) = \sum_{i=1}^{N}\phi_i^*(\vec{x})\phi_i(\vec{x}) - n_0\;, \tag{19}$$

where n_0 is the unperturbed density. Now we may rewrite Eq. (18) in the form

$$[-(\hbar^2/2m)\nabla^2 + V_{\mathrm{ext}}(\vec{x}) + V_{\mathrm{eff}}(\vec{x})]\phi_i(\vec{x}) = \epsilon_i\phi_i(\vec{x})\;, \tag{20}$$

where

$$V_{\text{ext}}(\vec{x}) = v(\vec{x}) - V_{\text{eff}}(\vec{x}) \quad , \tag{21}$$

and we take $V_{\text{eff}}(\vec{x})$ to be some *local* self-consistent potential which is a functional of $\delta n(\vec{x})$. For example, in the Hohenberg–Kohn–Sham[2] (HKS) approach

$$V_{\text{eff}}(\vec{x}) = e^2 \int \frac{\delta n(\vec{x}\,')}{|\vec{x} - \vec{x}\,'|}\, d\vec{x}\,' + \frac{\delta E_{\text{xc}}(n)}{\delta n} \quad , \tag{22}$$

where the first term is the usual Hartree term and the second embodies the exchange and correlation effects. Thus by solving Eq. (18) and using Eq. (19), we have achieved the HKS self-consistent solution corresponding to the potential $V_{\text{ext}}(\vec{x})$ given by Eqs. (21) and (22). For the Hartree self-consistent solution it is only necessary to recalculate $V_{\text{ext}}(\vec{x})$ using just the first term of Eq. (22). Finally, we emphasize that the validity of the foregoing procedure depends on the maintenance of charge neutrality, which demands that

$$\int \delta n(\vec{x})\, d\vec{x} = \int [\nabla^2 V_{\text{ext}}(\vec{x})/4\pi e^2]\, d\vec{x} \quad .$$

This is satisfied for any neutral $v(\vec{x})$.

Note that with an arbitrary attractive $V_{\text{ext}}(\vec{x})$ we can easily eliminate the problem of bound states at all metallic densities simply by demanding that $v(\vec{x})$ has no bound states. Furthermore, the density $\delta n(\vec{x})$ is valid for any choice of a local $\delta E_{\text{xc}}(n)/\delta n$ in Eq. (22). Thus, if we expand this term in a gradient expansion, any order may be investigated without great effort.

For the calculations presented in this paper, we have chosen $v(\vec{x})$ to be of the form

$$v(\vec{x}) = v_0 e^{-x/a}/x \quad . \tag{23}$$

We chose this form because the resulting $V_{\text{ext}}(x)$ is of a nature similar to that of an ionic potential in that it has a Coulomb singularity at the origin coming from $v(\vec{x})$ and a Coulomb tail at large x coming from the Hartree term. In Fig. 1 we plot $V_{\text{ext}}(x)$ for two sets of the parameters v_0 and a and for the electron gas density parameter $r_s = 3$. For each choice of v_0 and a two versions of $V_{\text{ext}}(x)$ are displayed, one containing only the Hartree term and one including an exchange and correlation approximation which will be discussed later.

Let us now return to Eqs. (16) and (17). For a fixed impurity and vanishingly small density of component 1 ($m_1 \to \infty$ and $n_1 \to 0$), $\chi_0^1(\vec{q}, \omega)$ of Eq. (11) becomes

$$\chi_0^1(\vec{q}, \omega) = (\pi i n_1/\hbar)\delta(\omega) \quad , \tag{24}$$

and hence

$$f(q) = \frac{1}{4\pi n_0}\left(1 - \frac{1}{\epsilon(q, 0)}\right) \quad , \tag{25}$$

where we take $Z_1 = 1$, since our interest is in an attractive potential. In Eq. (16), $\phi^{12}(\vec{x})$ is related

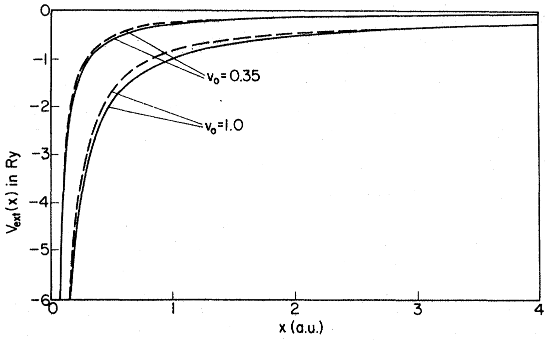

FIG. 1. The potentials $V_{\text{ext}}(x)$ [defined by (22)] used in this paper. In each case a [see (23)] was taken to be 1 Bohr radius and $r_s = 3$. Solid curve, inclusion of Hartree term only; dashed curve, inclusion of Hartree term and first term of the HKS gradient expansion.

to $V_{\text{ext}}(\vec{x})$ of Eq. (21) by

$$-e^2 \phi^{12}(\vec{q}) = V_{\text{ext}}(\vec{q}) \quad . \tag{26}$$

Using Eqs. (25) and (26), we can now solve Eq. (16) for $\gamma^{12}(q)$ or, equivalently, for $\delta n(q)$ and compare the result with that obtained from the full self-consistent solution. However, we feel that an easier and more accurate approach is to do the following. Since the density distribution of Eq. (19) is given in coordinate space, we prefer to transform Eq. (16) to yield the result

$$\delta n(\vec{x}) = \int f(\vec{x} - \vec{x}\,') \nabla_{x'}^2 \phi^{12}(\vec{x}\,')\, d\vec{x}\,' + (1/n_0) \int \nabla_x f(\vec{x} - \vec{x}\,') \cdot \nabla_{x'} \phi^{12}(\vec{x}\,') \delta n(\vec{x}\,')\, d\vec{x}\,' \quad , \tag{27}$$

where we have made use of the relation

$$\delta n(x) = \gamma^{12}(x)/n_0$$

and

$$f(\vec{x}) = \int f(\vec{q}) e^{i\vec{q}\cdot\vec{x}}\, d\vec{q}/(2\pi)^3 \quad . \tag{28}$$

At this point we could solve Eq. (27) directly for $\delta n(\vec{x})$ and compare the result with the full self-consistent solution which we shall refer to as $\delta n_s(\vec{x})$. However, since our objective in this paper is only to check the accuracy of this equation, we prefer to adopt the following approach. We simply insert the known $\delta n_s(\vec{x})$ into the right-hand side of (27) and determine the resulting $\delta n(\vec{x})$, which of course differs from $\delta n_s(\vec{x})$, the difference being a measure of the accuracy of (27). We do this for two self-consistent schemes, (a) the Hartree where we set $\delta E_{\text{xc}}(n)/\delta n = 0$ in Eq. (22) and (b) the HKS approach.

A. Nonlinear Hartree Approximation

In this case the density of Eq. (19) is the exact Hartree solution corresponding to $V_{\text{ext}}(x)$ [(21) and

(22)]. At first sight it is not completely clear whick dielectric function $\epsilon(q, 0)$ should be used in Eq. (25) to generate the solution of Eq. (27) corresponding to the Hartree case. However, in the limit of linear response $[V_{\text{ext}}(x) \rightarrow 0]$ the correct function is the random-phase-approximation (RPA) dielectric function given by

$$\epsilon(q, 0) = 1 + \frac{k_{\text{TF}}^2}{q^2}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln\left|\frac{q+2k_F}{q-2k_F}\right|\right) ,$$

where k_{TF} is the Thomas–Fermi screening parameter. Since Eq. (27) is independent of the strength of $\phi^{12}(\tilde{x})$, this same function should also be used in the nonlinear regime.

For the purposes of computation we chose to insert $\delta n_s(x)$ into the right-hand side of Eq. (27) and then write it as an explicit function of $v(x)$ and $\delta n_s(x)$. Using Eqs. (21), (22) $(\delta E_{\text{xc}}/\delta n = 0)$, and (26) in (27) with the fact that (27) is invariant under a rotation around the $\tilde{x}$ axis yields, after some algebra,

$$\delta n(x) = \delta n_L(x) + \delta n_{NL}(x) , \tag{29}$$

where

$$\delta n_L(x) = \frac{-1}{16\pi^3}\int_0^\infty \left(1 - \frac{1}{\epsilon(q, 0)}\right) v(q) j_0(qx) q^4\, dq - 16\pi^2 \int_0^\infty x'^2 \delta n_s(x') G(x, x')\, dx' ; \tag{30}$$

$$\begin{aligned} \delta n_{NL}(x) &= \frac{4\pi}{n_0}\int_0^\infty \left(\frac{x'^2}{2}\frac{\partial v(x')}{\partial x'} + Q(x')\right) \delta n_s(x') \frac{\partial G(x, x')}{\partial x'}\, dx' , \\ G(x, x') &= \frac{-1}{(2\pi)^3}\int_0^\infty \left(1 - \frac{1}{\epsilon(q, 0)}\right) j_0(qx) j_0(qx') q^2\, dq , \\ \frac{\partial G(x, x')}{\partial x'} &= \frac{1}{(2\pi)^3}\int_0^\infty \left(1 - \frac{1}{\epsilon(q, 0)}\right) j_0(qx) j_1(qx') q^3\, dq , \\ Q(x) &= 4\pi \int_0^x \delta n_s(x') x'^2\, dx' , \end{aligned} \tag{31}$$

and $j_0(qx)$ and $j_1(qx)$ are the usual spherical Bessel functions, $v(x)$ is in rydbergs, and all lengths in a.u.

The fact that $v(x)$ appears explicitly in Eqs. (30) and (31) and not $V_{\text{ext}}(x)$ arises because we have used Eqs. (21) and (22), where again $\delta E_{\text{xc}}(n)/\delta n = 0$. The term $\delta n_L(x)$ is simply the linear-response density for $V_{\text{ext}}(x)$ and $\delta n_{NL}(x)$ is the nonlinear correction.

Using the form (23) for $v(x)$ and taking $a = 1.0$ Bohr radii and values of $v_0 = -0.35$ and -1.00 Ry, we have evaluated Eq. (29) at $r_s = 3$. The results are displayed in Figs. 2 and 3, where we compare the linear-response term (30), the full nonlinear result (29), and the exact solution $\delta n_s(x)$. Also included in these figures is a plot of Eq. (29) evaluated using the Geldart–Taylor[6] dielectric function. The poor results obtained illustrate the importance of choosing the right dielectric function for the problem. It is interesting to note that as the strength of $V_{\text{ext}}(x)$ is increased (see Fig. 1 for a comparison of the two potentials), the linear-response term becomes completely unsatisfactory at small x. On the other hand, the nonlinear density agrees very well with the exact solution for both potentials. Unfortunately this very good agreement does not persist as x increases, and it is quite clear from the figures that the long-range oscillations show no improvement over the linear-response results. Essentially the same results where obtained at other electron gas densities and also with other forms of $v(x)$. Hence, we conclude that the use of the RPA dielectric function in the

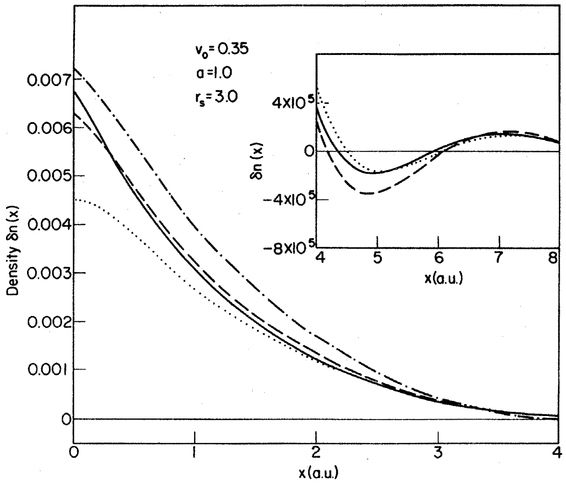

FIG. 2. Hartree densities calculated using the appropriate $V_{\text{ext}}(x)$, with $v_0 = -0.35$ Ry. Solid curve, full self-consistent Hartree density; dotted curve, linear-response density using RPA screening; dashed curve, density calculated using Eq. (29) and RPA screening; dot-dashed curve, density calculated using Eq. (29) and Geldart–Taylor screening.

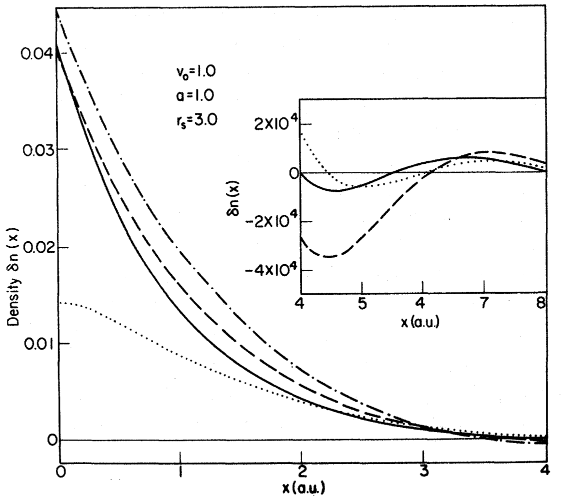

FIG. 3. See caption to Fig. 2. In this case $v_0 = -1.00$ Ry.

SS integral equation for a general attractive potential $-e^2\phi^{12}(x)$, with no bound states, will reproduce very reliable nonlinear Hartree charge densities at small x.

B. Nonlinear Hohenberg-Kohn-Sham Approximation

It is of considerable interest to see whether the SS approach manages to handle exchange and correlation as well as the Hartree case. We include this in the self-consistent calculation of $\delta n_s(x)$ via the HKS approach. We emphasize that no recalculation of $\delta n_s(x)$ is necessary; we simply have to include the term $\delta E_{xc}(n)/\delta n$ in Eq. (22). The question is what should we choose for this term. HKS have suggested that $\delta E_{xc}(n)/\delta n$ can be expanded in a power series of the gradient operator with respect to density and the series terminated at hopefully some low order. And Geldart *et al.*[4] have shown that for the case of small $V_{ext}(x)$ (linear response) best results are obtained if only the first term in the gradient expansion is retained. We assume that this is still true for large $V_{ext}(x)$, where nonlinear effects are important. Thus we choose

$$\frac{\delta E_{xc}(n)}{\delta n} = \frac{\partial}{\partial n}[\epsilon_{xc}(n)n] , \tag{32}$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy of the uniform electron gas. The resulting $V_{ext}(x)$ is illustrated in Fig. 1 for two combinations of v_0 and a, and for $r_s = 3$. The effect of further terms in the gradient expansion can of course be investigated without great difficulty, if the need arises, simply by adding these terms into Eq. (32); $\delta n_s(x)$ will be unaltered.

The insertion of Eq. (32) into (22) yields, after some algebra, an additional term to the right of Eq. (29):

$$\delta n_A(x) = (\pi/x)\int_0^\infty [(x+x')f'(x+x') - |x-x'|f'(|x-x'|) + f(x+x') - f(|x-x'|)]H(\delta n_s(x'))x'\,dx' , \tag{33}$$

where

$$H(\delta n) = \frac{1}{n_0}\int_{n_0}^{n_0+\delta n} \frac{\partial^2 E_{xc}(n)}{\partial n^2}\, n\, dn , \tag{34}$$

$f(x)$ is given by Eq. (28), and the prime indicates

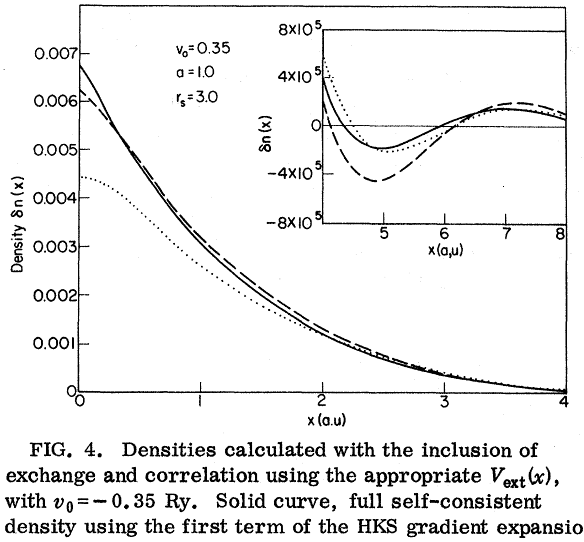

FIG. 4. Densities calculated with the inclusion of exchange and correlation using the appropriate $V_{ext}(x)$, with $v_0 = -0.35$ Ry. Solid curve, full self-consistent density using the first term of the HKS gradient expansion to represent exchange and correlation; dotted curve, linear-response density using Geldart–Taylor screening; dashed curve, density calculated using Eqs. (29) and (33) and Geldart–Taylor screening.

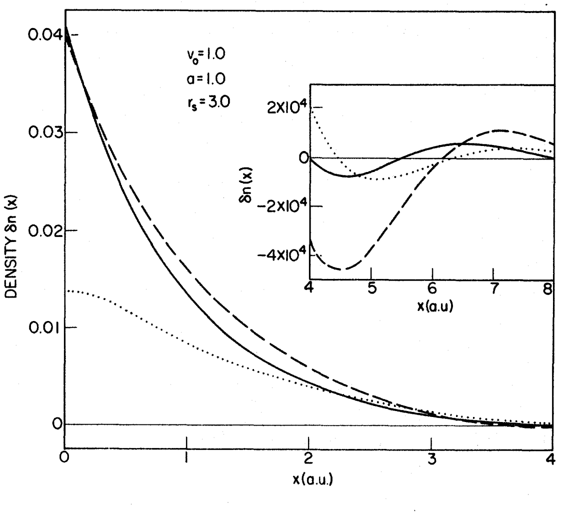

FIG. 5. See caption to Fig. 4. In this case $v_0 = -1.00$ Ry.

derivative with respect to the argument of the function. δn_A arises solely from the fact that $V_{\text{ext}}(x)$ has been redefined. Using the Nozières–Pines[7] expression for the correlation energy, we get

$$\frac{\partial E_{xc}(n)}{\delta n}=\frac{-2(3\pi^2 n)^{1/3}}{\pi}-\frac{0.031}{3}\ln(n)+C\ ,$$

which when inserted into Eq. (34) yields

$$H(\delta n)=-\frac{1}{2\pi}\frac{(3\pi^2)^{1/3}}{n_0}\left[(n_0+\delta n)^{4/3}-n_0^{4/3}\right]-\frac{0.031}{3}\frac{\delta n}{n_0}\ . \qquad (35)$$

Now by evaluating Eq. (29) with the additional term (33) and $H(\delta n)$ defined by (35) we obtain a density which can be compared to $\delta n_s(x)$. We again emphasize that in this case $\delta n_s(x)$ is the self-consistent density induced by $V_{\text{ext}}(x)$ and defined by Eqs. (22) and (32). It should also be stressed that exchange and correlation have been treated in an *approximate* way by retaining only the first term of the HKS gradient expansion. Therefore, by comparing the density calculated from Eqs. (29) and (33) with $\delta n_s(x)$, we are really comparing one approximate method with another.

The correct type of dielectric function to be used to evaluate Eqs. (29) and (33) can be established, as in the Hartree case, by examining the limit of small $V_{\text{ext}}(x)$, where it is clear that all exchange and correlation effects should be included in the dielectric function. In Figs. 4 and 5 we display the results obtained using the Geldart–Taylor[6] version of the dielectric function, which contains exchange and correlation. These calculations were performed at $r_s=3$ and we have used the same two potentials $v(x)$ as before, but of course $V_{\text{ext}}(x)$ is different, as can be seen from Fig. 1.

Similar results were obtained for other electron gas densities and other forms of $v(x)$. It is most interesting to note that Figs. 4 and 5 show a very close resemblance to Figs. 2 and 3. Just as in the Hartree case the linear-response result is completely unsatisfactory, whereas the nonlinear density gives very good agreement with $\delta n_s(x)$ for small x, this agreement getting progressively worse as x increases, culminating in very poor long-range oscillations. The particularly interesting feature is that the differences between the curves in Figs. 4 and 5 appear to be just about the same as in Figs. 2 and 3. This shows then that the inclusion of exchange and correlation in the general SS integral equation (27) produces a density differing from the approximate HKS density to the same degree that the Hartree SS density differs from the exact Hartree density. It seems likely, therefore, that (i) the retention of only the first term in the HKS gradient expansion gives a good representation of exchange and correlation in the presence of a strong potential and (ii) the general SS integral equation for the density $\delta n(x)$ includes exchange and correlation effects satisfactorily.

IV. SUMMARY

The main purpose of this paper has been to assess the accuracy of the SS integral equation for the density in the presence of a general, attractive impurity potential with no bound states. This is given by Eq. (27). We emphasize, though, that the same methods used here can be applied to test any similar approximate scheme in the limit of infinite mass. We have shown that for the particular potentials illustrated in Fig. 1 the SS integral equation gives very reliable results for small x, whereas use of linear response is most unsatisfactory. Unfortunately, for larger distances, particularly in the long-range oscillation region, the SS equation is not an improvement over linear response. This conclusion appears to be independent of whether or not exchange and correlation effects are included. Since the potentials in Fig. 1 are ionic in character and since we obtained similar results using other forms of $v(x)$ and at other densities, we expect the same sort of accuracy for any reasonable impurity potential.

Finally, the SS integral equation does not depend upon, in any way, a finite power series in $\vec{q}$ or, equivalently, a terminated gradient expansion. Hence, the good agreement between the two procedures (i.e., the SS and the HKS) suggests that correlation and exchange are well represented in the HKS formalism by retaining the first term in the gradient expansion.

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