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Nonlinear electron-density distribution around point defects in simple metals. I. Formulation*

A. K. Gupta and P. Jena
Physics Department and Materials Research Center, Northwestern University, Evanston, Illinois 60201

K. S. Singwi
Physics Department, Northwestern University, Evanston, Illinois 60201
and Argonne National Laboratory, Argonne, Illinois 60439
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A modification, which is exact in the limit of long wavelength, of the nonlinear theory of Sjölander and Stott of electron distribution around point defects is given. This modification consists in writing a nonlinear integral equation for the Fourier transform $\gamma_{12}(q)$ of the induced charge density surrounding the point defect, which includes a term involving the density derivative of $\gamma_{12}(q)$. A generalization of the Pauli-Feynman coupling-constant-integration method, together with the Kohn-Sham formalism, is used to exactly determine the coefficient of this derivative term in the long-wavelength limit. The theory is then used to calculate electron-density profiles around a vacancy, an eight-atom void, and a point ion. The results are compared with those of (i) a linear theory, (ii) Sjölander-Stott theory, and (iii) a fully self-consistent calculation based on the density-functional formalism of Kohn and Sham. It is found that in the case of a vacancy, the results of the present theory are in very good agreement with those based on Kohn-Sham formalism, whereas in the case of a singular attractive potential of a proton, the results are quite poor in the vicinity of the proton, but much better for larger distances. A critical discussion of the theory *vis à vis* the Kohn-Sham formalism is also given. Some applications of the theory are pointed out.

I. INTRODUCTION

During recent years, interest in the calculation of electron-density profiles around point defects (vacancies and impurities) in metals has been heightened because of the possibility of probing the density distribution through the measurements of the characteristics of positron annihilation[1] in vacancies and the electric field gradients[2] at host atom sites. The problem under consideration is a nonlinear one, since the perturbation of the defect on the electron gas is large and as such cannot be handled by a linear theory. An extreme example of nonlinearity is the electron distribution around a fixed proton in a metal. In most situations of interest, one uses some sort of pseudopotential for the defect, which is supposed to be weak. Even in this case, there has always been the nagging question of whether or not the often used linear screening theory is in fact adequate. This question can be resolved only through numerical calculations.

In the past, statistical methods such as the Thomas-Fermi[3] and nonlinear Hartree[4] have been used to calculate the electron-density distribution around a defect. None of these methods are satisfactory since they do not take the important effects of exchange and correlation into account. The former does not even give Friedel oscillations, which are an important feature of the polarization charge distribution. For these reasons we shall not discuss them here.

More recently the density-functional formalism of Kohn and Sham[5] has been used. In principle, this method is exact. In practice, one normally uses the local-density approximation for the exchange-correlation potential in the Kohn-Sham equation. A fully self-consistent numerical calculation of the electron density profile in the Kohn-Sham scheme is by no means a trivial matter. Besides, in this scheme it has not been found possible to treat the case of a moving impurity such as the screening of a positron in a metal.

An entirely different approach to treat the nonlinear problem at hand was given by Sjölander and Stott.[6] These authors derived an integral equation for the Fourier transform of the polarization charge around an impurity in an electron gas by extending the theory of electron correlations by Singwi *et al.*[7] to the case of a two-component plasma. On the basis of their theory, they were able to predict positron lifetimes in an electron gas for densities $r_s \leq 4$. For smaller densities $r_s \geq 5$ their method broke down because it gave a very large pileup of electrons on the positron. This defect was later rectified by Bhattacharya and Singwi[8] but in an *ad hoc* manner. For a fixed proton the Sjölander-Stott method also gave an unphysical pileup of electrons. This failure was attributed to the onset of an incipient bound state which the method could not handle.

The purpose of this paper is to generalize the Sjölander-Stott theory for a "two-component plasma" consisting of a static impurity and the electron gas such that it is exact in the long-wavelength limit, i.e., $q \rightarrow 0$. This modified version of the theory is used to calculate the electron distribution around a monovacancy corresponding to a spherical hole in a jellium. This distribution is then compared with that calculated in a fully self-consistent manner using the Kohn-Sham formalism. It turns out that the two distributions are very close to each other. This agreement, we find, becomes poorer as the size of the "void" is increased. A similar comparison is made for the case of a pseudoion in jellium. A critical examination of the generalized Sjölander-Stott scheme is made *vis a vis* the Kohn-Sham formalism. Although the present generalization marks a definite improvement over the earlier scheme and promises to be of wide applicability, it is still unsatisfactory for treating a singular attractive potential, e.g., that of a fixed proton in an electron gas.

II. MATHEMATICAL FORMULATION

For the sake of clarity and completeness, we shall divide this section into four subsections. In Sec. II A we generalize the local-field factor $G_{12}(q)$ in the Sjölander-Stott theory as applied to a single-impurity problem. This is done by introducing a density-derivative term with an unknown coefficient a_{12} exactly in the same way as is done in the Vashishta-Singwi[9] theory of a homogeneous electron gas. In Sec. II B we impose the requirement that the effective potentials appearing in the multicomponent generalization of Kohn-Sham theory be identical to those in the zero-frequency and long-wavelength limit of Sjölander-Stott theory. This gives us an exact relation between the small q limit of $G_{12}(q)$ and the density derivative of the correlation energy ϵ_c of a single impurity in an electron gas. In Sec. II C we derive an exact expression for the unknown coefficient a_{12} introduced in Sec. II A. We close this section with a brief description of the method by which a self-consistent value of a_{12} and the electron distribution surrounding the impurity are calculated. In Sec. II D we recapitulate the Kohn-Sham method for the determination of electron-density distribution around an impurity.

A. Extension of Sjölander-Stott theory

Consider a two-component system consisting of electrons with density n_1 and of impurities (mobile or fixed) with density n_2 on a uniform rigid positive background. Let us apply two arbitrarily weak external potentials $V^i_{\text{ext}}(\vec{r},t)$, which act only on the ith component of the plasma. Following the linear-response theory, we can write the induced density in the ith component as

$$\langle \delta n_i(\vec{q},\omega)\rangle = \sum_{j=1}^{2} \chi_{ij}(\vec{q},\omega) V^j_{\text{ext}}(\vec{q},\omega)\,, \tag{1}$$

where $\delta n_i(\vec{q},\omega)$ and $V^i_{\text{ext}}(\vec{q},\omega)$ are, respectively, the Fourier transforms of $\delta n_i(\vec{r},t)$ and $V^i_{\text{ext}}(\vec{r},t)$, and $\chi_{ij}(\vec{q},\omega)$ is the density-density response function.

In the spirit of the generalized random-phase approximation (GRPA), the induced density is given by

$$\langle \delta n_i(\vec{q},\omega)\rangle = \chi^0_i(\vec{q},\omega)\left(V^i_{\text{ext}}(\vec{q},\omega) + \sum_{j=1}^{2} \psi_{ij}(\vec{q})\langle \delta n_j(\vec{q},\omega)\rangle\right), \tag{2}$$

where $\chi^0_i(\vec{q},\omega)$ is the noninteracting polarizability of the ith component and $\psi_{ij}(\vec{q})$ is the static effective interaction between the components i and j. The set of equations (2) can be trivially solved to give explicit expressions for $\langle \delta n_1(\vec{q},\omega)\rangle$ and $\langle \delta n_2(\vec{q},\omega)\rangle$. By comparing these equations with Eq. (1), we immediately obtain expressions for the response functions χ_{11}, χ_{12}, and χ_{22}. The elements of the dielectric tensor $\epsilon_{ij}(\vec{q},\omega)$ are defined by

$$1/\epsilon_{ij}(\vec{q},\omega) = \delta_{ij} + \Phi_{ij}(\vec{q})\chi_{ij}(\vec{q},\omega)\,, \tag{3}$$

where $\Phi_{ij}(\vec{q})$ is the bare interaction between the components i and j. We also define the Fourier transform of the static density-density correlation function $\langle n^i_{\vec{q}} n^j_{-\vec{q}}\rangle$ and the structure factor $\gamma_{ij}(\vec{q})$ which are related by the fluctuation-dissipation theorem to the imaginary part of $\chi_{ij}(\vec{q},\omega)$:

$$\begin{aligned}\langle n^i_{\vec{q}} n^j_{-\vec{q}}\rangle &= \Omega n_i\left(\delta_{ij} + \frac{n_j}{n_1}\gamma_{ij}(\vec{q})\right)\\ &= -\frac{\hbar\Omega}{\pi\Phi_{ij}}\int_0^\infty d\omega\,\mathrm{Im}\left(\frac{1}{\epsilon_{ij}(\vec{q},\omega)}\right),\end{aligned} \tag{4}$$

where Ω is the volume of the system. The partial pair-correlation function $g_{ij}(\vec{r})$ is related to $\gamma_{ij}(\vec{q})$:

$$g_{ij}(\vec{r}) = 1 + \frac{1}{(2\pi)^3}\frac{1}{n_1}\int d\vec{q}\, e^{i\vec{q}\cdot\vec{r}}\gamma_{ij}(\vec{q})\,. \tag{5}$$

In Eqs. (4) and (5), n_1 denotes the number density of electrons.

A fundamental assumption in the approach of Singwi *et al.*[7] is now introduced:

$$\vec{\nabla}\psi_{ij}(\vec{r}) = g_{ij}(\vec{r})\vec{\nabla}\Phi_{ij}(\vec{r})\,, \tag{6}$$

from which it follows that

$$\psi_{ij}(\vec{q}) = \Phi_{ij}(\vec{q})[1 - G_{ij}(\vec{q})]\,, \tag{7}$$

where the local-field factor $G_{ij}(\vec{q})$ is given by

$$G_{ij}(\vec{q}) = -\frac{1}{n_1}\frac{1}{\Phi_{ij}(\vec{q})}\int \frac{d\vec{q}\,'}{(2\pi)^3}\frac{\vec{q}\cdot\vec{q}\,'}{q^2}\Phi_{ij}(\vec{q}\,')\gamma_{ij}(\vec{q}-\vec{q}\,')\,. \tag{8}$$

In the limit of $n_2 \to 0$, i.e., small impurity concentration, the expressions for χ_{11} and χ_{12} become

$$\chi_{11}(\vec{q},\omega)=\frac{\chi_1^0(\vec{q},\omega)}{1-\psi_{11}(\vec{q})\chi_1^0(\vec{q},\omega)}\,, \tag{9}$$

$$\chi_{12}(\vec{q},\omega)=\chi_{11}(\vec{q},\omega)\chi_2^0(\vec{q},\omega)\psi_{12}(\vec{q})\Phi_{12}(\vec{q})/\Phi_{11}(\vec{q}) \tag{10}$$

($\chi_{12}=\chi_{21}$ and $\psi_{12}=\psi_{21}$ by symmetry). χ_{11} is nothing but the response function of the homogeneous interacting electron gas. Combining Eqs. (10), (3), and (4) gives

$$\gamma_{12}(\vec{q})=-\frac{\Phi_{12}(\vec{q})}{\Phi_{11}(\vec{q})}\int_0^\infty \chi_2^0(\vec{q},\omega)\,\mathrm{Im}\left(\frac{1}{\epsilon_{11}(\vec{q},\omega)}-1\right) \times d\omega[1-G_{12}(q)]\,. \tag{11}$$

Define

$$f(q)=\frac{\hbar}{\pi n_2}\int_0^\infty d\omega\chi_2^0(q,\omega)\,\mathrm{Im}\left(\frac{1}{\epsilon_{11}(q,\omega)}-1\right). \tag{12}$$

The free-particle response function χ_2^0 is given by

$$\chi_2^0(\vec{q},\omega)=\frac{n_2}{\hbar}\left(\frac{1}{\omega-\hbar q^2/2m_2+i\delta}-\frac{1}{\omega+\hbar q^2/2m_2+i\delta}\right), \tag{13}$$

where m_2 is the mass of the impurity particle. In the limit of $m_2\rightarrow\infty$ (i.e., fixed impurity), it is straightforward to show that

$$f(\vec{q})=-[1/\epsilon_{11}(\vec{q},0)-1]\,, \tag{14}$$

and hence

$$\gamma_{12}(\vec{q})=\frac{[1/\epsilon_{11}(\vec{q},0)-1]\Phi_{12}(\vec{q})[1-G_{12}(\vec{q})]}{\Phi_{11}(\vec{q})}. \tag{15}$$

Equations (15) and (8) together form an integral equation for $\gamma_{12}(\vec{q})$ which can be solved numerically, and the electron distribution $n_1g_{12}(\vec{r})$ around the impurity can be determined.

So far we have presented the standard Sjölander-Stott theory. The approximation given by Eq. (8) for $G_{12}(\vec{q})$ is a straightforward generalization of the approximation introduced by Singwi *et al.*[7] (hereafter referred to as STLS). In the one-component electron gas theory it is now known that STLS approximation can be made exact in the small q region by introducing an additional factor proportional to the deviative with respect to density. We refer the reader to the papers of Vashishta and Singwi[9] and Niklasson *et al.*[10] for a detailed discussion of this point.

We introduce here the following form for the local-field factor:

$$G_{12}(\vec{q})=\left(1+a_{12}n_1\frac{\partial}{\partial n_1}\right)\times\left(-\frac{1}{n_1\Phi_{12}(q)}\int\frac{d\vec{q}\,'}{(2\pi)^3}\frac{\vec{q}\cdot\vec{q}\,'}{q^2}\Phi_{12}(\vec{q}\,')\gamma_{12}(\vec{q}-\vec{q}\,')\right). \tag{16}$$

Analogous to the one-component electron gas theory, we shall now impose the requirement that the small q limit of $G_{12}(\vec{q})$ be exact, and use this condition to determine the unknown parameter a_{12}. This is done in the following section.

B. Behavior of $G_{ij}(q)$ in the long-wavelength limit

The guiding principle in this section will be the exact sum rule (which is a generalization of the well-known compressibility sum rule) according to which the long-wavelength limit of the static density-density response function is related to a thermodynamic quantity, namely, the second (partial) density derivative of the total energy of the system. We shall essentially generalize the conclusions of Niklasson *et al.*[10] to a multicomponent system in this section.

We once again consider a two-component system of electrons and impurities in the presence of an external field $V^i_{\mathrm{ext}}(\vec{r})$, which is static. The ground-state energy of this system can be written

$$E=T_0[n_1,n_2]+\frac{1}{2}\sum_{i,j=1}^{2}\int d\vec{r}\int d\vec{r}\,'\,\Phi_{ij}(\vec{r}-\vec{r}\,')n_i(\vec{r})n_j(\vec{r}\,')+\sum_{i=1}^{2}\int d\vec{r}\,V^i_{\mathrm{ext}}(\vec{r})n_i(\vec{r})+E_{\mathrm{xc}}[n_1,n_2]\,, \tag{17}$$

where the first term is the kinetic energy of a system of noninteracting particles, the second term is the classical interaction energy, the third term is the interaction energy with the external fields, and the last term is the total exchange-correlation energy. Both T_0 and E_{xc} are functionals of $n_1(\vec{r})$ and $n_2(\vec{r})$. The exchange-correlation energy is given by

$$E_{\mathrm{xc}}[n_1,n_2]=\frac{1}{2}\sum_{ij}\int d\vec{r}\,d\vec{r}\,'\,\Phi_{ij}(\vec{r}-\vec{r}\,')\langle n_i(\vec{r})n_j(\vec{r}\,')\rangle_c+T[n_1,n_2]-T_0[n_1,n_2]\,. \tag{18}$$

$\langle\cdots\rangle_c$ denotes the correlated part and T is the interacting kinetic energy of the system. For a slightly inhomogeneous system, the exchange-correlation energy can be expanded in powers of $\tilde{n}_i(\vec{r})=n_i(\vec{r})-n_i^0$:

$$E_{\mathrm{xc}}[n_1,n_2]=E_{\mathrm{xc}}(n_1^0,n_2^0)+\frac{1}{2}\sum_{i,j}\int d\vec{r}\int d\vec{r}\,'K^{ij}_{\mathrm{xc}}(\vec{r}-\vec{r}\,';n_1^0,n_2^0)\times\tilde{n}_i(\vec{r})\tilde{n}_j(\vec{r}\,')+O(\tilde{n}^3)\,, \tag{19}$$

where $E_{\mathrm{xc}}(n_1^0,n_2^0)$ is the exchange-correlation energy in the homogeneous system, and K^{ij}_{xc} is a function of $|\vec{r}-\vec{r}\,'|$ and is determined completely by the properties of the homogeneous system. If the external potentials have a very long wavelength variation, then we can write

$$E_{\mathrm{xc}}[n_1,n_2]=E_{\mathrm{xc}}(n_1^0,n_2^0)+\frac{1}{2}\sum_{ij}K^{ij}(n_1^0,n_2^0)\int d\vec{r}\,\tilde{n}_i(\vec{r})\tilde{n}_j(\vec{r})\,, \tag{20}$$

where

$$K_{\mathrm{xc}}^{ij}(n_1^0,n_2^0)=\int d\vec{r}\,K_{\mathrm{xc}}^{ij}(\vec{r},n_1^0,n_2^0)\,. \tag{21}$$

In a similar manner we can write

$$T_0[n_1,n_2]=T_0(n_1^0,n_2^0)+\frac{1}{2}\sum_{ij}\int d\vec{r}\,d\vec{r}\,'\,K_0^{ij}(\vec{r}-\vec{r}\,';n_1^0,n_2^0)\times\tilde{n}_i(\vec{r})\tilde{n}_j(\vec{r}\,')+O(\tilde{n}^3)\,, \tag{22}$$

and in the long-wavelength limit

$$T_0[n_1,n_2]=T_0(n_1^0,n_2^0)+\frac{1}{2}\sum_{ij}K_0^{ij}(n_1^0,n_2^0)\int d\vec{r}\,\tilde{n}_i(\vec{r})\tilde{n}_j(\vec{r})\,. \tag{23}$$

According to Kohn-Sham theory the ground-state density $n_i(\vec{r})$ is determined by minimizing the energy functional (Eq. 17) with respect to $n_i(\vec{r})$, i.e.,

$$\frac{\delta T_0[n_1,n_2]}{\delta n_i}+\frac{\delta E_{\mathrm{xc}}[n_1,n_2]}{\delta n_i}+V_{\mathrm{ext}}^i(\vec{r})+\sum_j\int d\vec{r}\,'\Phi_{ij}(\vec{r}-\vec{r}\,')n_j(\vec{r}\,')=0\,. \tag{24}$$

We call the last term the Hartree potential, $V_{\mathrm{H}}^i(\vec{r})$; Eq. (24), using Eqs. (19) and (22), can be written in the following form:

$$\sum_j\int d\vec{r}\,'[K_0^{ij}(\vec{r}-\vec{r}\,';n_1^0,n_2^0)+K_{\mathrm{xc}}^{ij}(\vec{r}-\vec{r}\,';n_1^0,n_2^0)]\tilde{n}_j(\vec{r}\,')+V_{\mathrm{ext}}^i(\vec{r})+V_{\mathrm{H}}^i(\vec{r})=0\,. \tag{25}$$

The above equation determines the induced densities $\tilde{n}_1(\vec{r})$ and $\tilde{n}_2(\vec{r})$ under the influence of external potential and we would like to compare it with the GRPA expression.

After some simple arrangement of terms, Eqs. (2) and (7) can be written in the form

$$\left(-\frac{\delta n_i(\vec{q},\omega)}{\chi_i^0(\vec{q},\omega)}-\sum_j\Phi_{ij}(\vec{q})G_{ij}(\vec{q})\delta n_j(\vec{q},\omega)\right)+V_{\mathrm{ext}}^i(\vec{q},\omega)+V_{\mathrm{H}}^i(\vec{q},\omega)=0\,. \tag{26}$$

Comparison of Eq. (26) for $\omega=0$ with the Fourier transform of Eq. (25) leads to the following identification:

$$K_0^{ij}(q)=-\delta_{ij}/\chi_i^0(\vec{q},0)\,, \tag{27}$$

and

$$K_{\mathrm{xc}}^{ij}(\vec{q})=-\Phi_{ij}(\vec{q})G_{ij}(\vec{q})\,. \tag{28}$$

In the long-wavelength limit we have

$$\lim_{q\to0}\Phi_{ij}(\vec{q})G_{ij}(\vec{q})=-K_{\mathrm{xc}}^{ij}(0)=-\frac{1}{\Omega}\,\frac{\partial^2E_{\mathrm{xc}}(n_1^0,n_2^0)}{\partial n_i^0\partial n_j^0}\,. \tag{29}$$

The above equation gives us $q\to0$ limit of the local field factor $G_{ij}(\vec{q})$ and it is related to the second derivative of the exchange-correlation energy with respect to the densities. The above condition is the generalization of the compressibility sum rule to a multicomponent system and we seek to find a_{12} [Eq. (16)] such that $G_{12}(\vec{q})$ has the exact $(q\to0)$ limit given by Eq. (29).

C. Derivation of an exact expression for a_{12}

In this section we derive an exact expression for the correlation energy of an impurity in the electron gas using the familiar Pauli-Feynman method and relate it to a_{12} via Eq. (29).

The Hamiltonian of a system consisting of a single impurity in the electron gas is written

$$H=\sum_i\frac{p_i^2}{2m}+\frac{1}{2}\sum_{ij}\frac{e^2}{|r_{ij}|}+\sum_i w(\vec{r}_i-\vec{R})\,, \tag{30}$$

where $w(\vec{r}-\vec{R})$ $(\equiv\Phi_{12})$ is the interaction energy of the impurity at the position $\vec{R}$ and an electron at $\vec{r}$. We introduce two interaction parameters λ_1 and λ_2 such that

$$H=T+V(1,1)\,,$$

and

$$V(\lambda_1,\lambda_2)=\frac{1}{2}\sum_{ij}\lambda_1\frac{e^2}{|r_{ij}|}+\sum_i\lambda_2 w(\vec{r}_i-\vec{R})\,. \tag{31}$$

The ground-state energy E_0 is given by

$$E_0(\lambda_1,\lambda_2)=\langle\Psi_0|H(\lambda_1,\lambda_2)|\Psi_0\rangle\,, \tag{32}$$

where $|\Psi_0\rangle$ is the exact ground-state function of $H(\lambda_1,\lambda_2)$. Differentiating with respect to λ_1, we have

$$\frac{\partial E_0}{\partial\lambda_1}=\langle\Psi_0|\frac{\partial H}{\partial\lambda_1}|\Psi_0\rangle+\left\langle\frac{\partial\Psi_0}{\partial\lambda_1}\middle|H\middle|\Psi_0\right\rangle+\left\langle\Psi_0\middle|H\middle|\frac{\partial\Psi_0}{\partial\lambda_1}\right\rangle \tag{33}$$

$$=\langle\Psi_0|\frac{\partial H}{\partial\lambda_1}|\Psi_0\rangle+E_0\frac{\partial}{\partial\lambda_1}\langle\Psi_0|\Psi_0\rangle\,. \tag{34}$$

The second term on the right-hand side vanishes because the normalization of $|\Psi_0\rangle$ is chosen to be independent of λ_1, so that

$$\frac{\partial E_0}{\partial\lambda_1}=\frac{1}{2}\langle\Psi_0|\sum_{ij}\frac{e^2}{|\vec{r}_{ij}|}|\Psi\rangle\,. \tag{35}$$

Similarly,

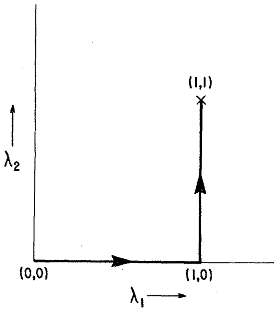

FIG. 1. Path of integration in the interaction parameter space for a two-component system. Point (0, 0) represents the noninteracting system while (1,1) represents the fully interacting system.

$$\frac{\partial E_0}{\partial \lambda_2} = \langle \Psi_0 | \sum_i w(\vec{r}_i - \vec{R}) | \Psi_0 \rangle . \tag{36}$$

The ground-state expectation value of the potential energy can also be written in the following form:

$$\langle \Psi_0 | V | \Psi_0 \rangle = \frac{1}{2} n_1^2 e^2 \Omega \int \frac{d\vec{r}}{|\vec{r}|} [g_{11}(\vec{r}) - 1] + n_1 \Omega \int d\vec{r} w(\vec{r}) [g_{12}(\vec{r}) - 1] , \tag{37}$$

where $g_{11}(\vec{r})$ and $g_{12}(\vec{r})$ are the partial pair-correlation functions. They have been defined earlier by Eq. (5); 1 refers to electrons and 2 to impurity. These pair-correlation functions will depend on the interaction parameters λ_1 and λ_2 in the system. Comparing Eq. (37) with

$$\langle \Psi_0 | V | \Psi_0 \rangle \doteq \langle \Psi_0 | \frac{1}{2} \sum_{ij} \frac{e^2}{|r_{ij}|} | \Psi_0 \rangle + \langle \Psi_0 | \sum_i w(\vec{r}_i - \vec{R}) | \Psi_0 \rangle , \tag{38}$$

and using Eqs. (35) and (36), we get

$$\left(\frac{\partial E_0}{\partial \lambda_1} \right)_{\lambda_2} = \frac{1}{2} n_1^2 e^2 \Omega \int \frac{d\vec{r}}{|\vec{r}|} [g_{11}(\vec{r}) - 1] , \tag{39}$$

and

$$\left(\frac{\partial E_0}{\partial \lambda_2} \right)_{\lambda_1} = n_1 \Omega \int d\vec{r} w(\vec{r}) [g_{12}(\vec{r}) - 1] . \tag{40}$$

Now E_0, the ground-state energy, is a unique function of the interaction strengths λ_1 and λ_2, so that

$$dE_0 = \left(\frac{\partial E_0}{\partial \lambda_1} \right)_{\lambda_2} d\lambda_1 + \left(\frac{\partial E_0}{\partial \lambda_2} \right)_{\lambda_1} d\lambda_2 . \tag{41}$$

We let the full interaction be switched on ($\lambda_1 = 1$, $\lambda_2 = 1$) and calculate the total interaction energy of the system in the following way. In the interaction parameter space (see Fig. 1) the point (0, 0) represents the noninteracting system and the point (1, 1) represents the full interacting system. The integral of dE_0 will depend only on the initial and final points of integration and will not depend on the path of integration. We choose the path as shown in Fig. 1. First integrating from (0, 0) to (1, 0), i.e.,

$$E(1,0) - E(0,0) = \int_0^1 d\lambda_1 \left(\frac{\partial E_0}{\partial \lambda_1} \right)_{\lambda_2 = 0} = \frac{1}{2} n_1^2 e^2 \Omega \int_0^1 d\lambda_1 \int \frac{d\vec{r}}{|\vec{r}|} [g_{11}(r; \lambda_1, 0) - 1] , \tag{42}$$

we get the interaction energy of the electron gas. $E(0, 0)$ is equal to the kinetic energy of free electrons. Further, integrating from (1, 0) to (1, 1) we get

$$E(1,1) - E(1,0) = \int_0^1 d\lambda_2 \left(\frac{\partial E_0}{\partial \lambda_2} \right)_{\lambda_1 = 1} = n_1 \Omega \int_0^1 d\lambda_2 \int d\vec{r} w(\vec{r}) [g_{12}(\vec{r}; 1, \lambda_2) - 1] . \tag{43}$$

We now know the total exchange-correlation energy of the system, i.e.,

$$E_{xc} = \frac{1}{2} n_1^2 e^2 \Omega \int_0^1 d\lambda_1 \int \frac{d\vec{r}}{|\vec{r}|} [g_{11}(\vec{r}; \lambda_1, 0) - 1] + n_1 \Omega \int_0^1 d\lambda_2 \int d\vec{r} w(\vec{r}) [g_{12}(\vec{r}; 1, \lambda_2) - 1] . \tag{44}$$

In Sec. II B we have derived relation (29), which we rewrite

$$\lim_{q \to 0} w(\vec{q}) G_{12}(\vec{q}) = -K_{xc}^{12}(0) = -\frac{1}{\Omega} \frac{\partial^2 E_{xc}}{\partial n_1 \partial n_2} . \tag{45}$$

We define ϵ_c, the correlation energy of a single impurity, as

$$\epsilon_c = \frac{1}{\Omega} \left(\frac{\partial E_{xc}}{\partial n_2} \right)_{n_1} = n_1 \int_0^1 d\lambda_2 \int d\vec{r} w(\vec{r}) [g_{12}(\vec{r}; 1, \lambda_2) - 1] . \tag{46}$$

Then the following relation holds good:

$$\lim_{q \to 0} w(\vec{q}) G_{12}(\vec{q}) = -\frac{\partial \epsilon_c}{\partial n_1} . \tag{47}$$

We shall show later how to calculate ϵ_c numerically. First we consider the left-hand side of Eq. (47), which, on using Eq. (16), becomes

$$\lim_{q\to 0} w(\vec{q})G_{12}(\vec{q}) = -\lim_{q\to 0}\left(1+a_{12}n_1\frac{\partial}{\partial n_1}\right)\frac{1}{n_1}\int\frac{d\vec{q}\,'}{(2\pi)^3}\frac{\vec{q}\cdot\vec{q}\,'}{q^2}\,w(\vec{q}\,')\gamma_{12}(\vec{q}-\vec{q}\,')$$

$$= -\lim_{q\to 0}\left(1+a_{12}n_1\frac{\partial}{\partial n_1}\right)\frac{1}{4\pi^2 q^2 n_1}\int_0^\infty q'^2\,dq'\gamma_{12}(q')\int_{-1}^{+1} d\mu\,(q'q\mu+q^2)w(q^2+q'^2+2qq'\mu)^{1/2}\,. \tag{48}$$

It can be shown straightforwardly that

$$\lim_{q\to 0}\frac{1}{q^2}\int_{-1}^{+1} d\mu\,(qq'\mu+q^2)w(q^2+q'^2+2qq'\mu)^{1/2} = \frac{2}{3}\,q'\,\frac{dw(q')}{dq'}+2w(q')\,. \tag{49}$$

We define an integral

$$\mathcal{G}=\int_0^\infty q'^2\,dq'\gamma_{12}(q')\left(\frac{2}{3}\,q'\,\frac{dw(q')}{dq'}+2w(q')\right). \tag{50}$$

$\mathcal{G}$ will depend on the density of electron gas. Using Eq. (50), Eq. (48) becomes

$$\lim_{q=0} w(\vec{q})G_{12}(\vec{q}) = -\left(1+a_{12}n_1\frac{\partial}{\partial n_1}\right)\frac{\mathcal{G}}{4\pi^2 n_1}\,. \tag{51}$$

Noting that $(3\pi^2 n_1)=k_F{}^3$ and using Eq. (47), we get the following expression for a_{12}:

$$a_{12}=4\pi^2\left(k_F\frac{\partial\epsilon_c}{\partial k_F}-3\mathcal{G}(k_F)\right)\Big/\left(k_F\frac{\partial\mathcal{G}(k_F)}{\partial k_F}-3\mathcal{G}(k_F)\right). \tag{52}$$

The above expression for a_{12} forms an important result of this paper. ϵ_c can also be written in the following form:

$$\epsilon_c=\frac{1}{2\pi^2}\int_0^1 d\lambda_2\int_0^\infty q^2\,dq\,w(q)\gamma_{12}(q,\lambda_2)\,. \tag{53}$$

We now have all the equations necessary to do a self-consistent calculation, which we shall briefly describe in Sec. III.

D. Kohn-Sham scheme

According to the density-functional formalism developed by Hohenberg-Kohn-Sham,[5] the ground-state energy of the electron gas in the presence of an external potential (of the impurity) $w(\vec{r})$ is given by

$$E[n(\vec{r})]=\int w(\vec{r})n(\vec{r})\,d\vec{r}+T_0[n(\vec{r})] + \frac{1}{2}\int\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,'+E_{xc}[n(\vec{r})]\,, \tag{54}$$

where $n(\vec{r})$ is the electron density in the system, $T_0[n(\vec{r})]$ is the kinetic energy of a system of non-interacting electrons having density $n(\vec{r})$, and $E_{xc}[n(\vec{r})]$ is the exchange-correlation energy functional. The ground-state density $n(\vec{r})$ is the one which minimizes the energy functional $E[n(\vec{r})]$.

From this variational principle a set of self-consistent one-body equations are derived involving an effective one-body potential $v_{\text{eff}}[n(\vec{r});\vec{r}]$ given by

$$v_{\text{eff}}[n(\vec{r});\vec{r}]=w(\vec{r})+\int\frac{n(\vec{r}\,')\,d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}+\frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}\,. \tag{55}$$

The one-body Schrödinger-like equation

$$\{-(\hbar^2/2m)\nabla^2+v_{\text{eff}}[n(\vec{r});\vec{r}]\}\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}) \tag{56}$$

generates a set of wave functions $\psi_i(\vec{r})$ and energy eigenvalues ϵ_i from which the exact ground-state density of the system is calculated using

$$n(\vec{r})=\sum_{i=1}^{N}|\psi_i(\vec{r})|^2\,. \tag{57}$$

Although the formalism is exact up to this stage, we need some approximation for the exchange-correlation energy. For a slowly varying electron density the local-density approximation (LDA) can be used:

$$E_{xc}[n(\vec{r})]=\int\epsilon_{xc}(n(\vec{r}))n(\vec{r})\,d\vec{r}\,, \tag{58}$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy of a uniform electron gas of density n. The corrections to LDA have also recently received attention.[11] In view of recent estimates,[12] which show that the gradient corrections are not very significant in cases where the total exchange-correlation energy is not the dominant part of the total energy, we shall use LDA in this paper. The experience to date suggests that LDA gives good results even for systems of rapidly varying density. We have used the estimates of $\epsilon_{xc}(n)$ given by Vashishta and Singwi. In the LDA the exchange-correlation potential is given by

$$v_{xc}(\vec{r})=\frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}=\epsilon_{xc}(n(\vec{r}))+\left(\frac{n\,d\epsilon_{xc}}{dn}\right)_{n=n(\vec{r})}\,. \tag{59}$$

For a point impurity (like an ion or a vacancy), we can make use of spherical symmetry to write down the equation obeyed by radial wave function $R_{kl}(r)$:

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+v_{\text{eff}}(r)+\frac{l(l+1)}{r^2}\right)[rR_{kl}(r)]=\epsilon_k[rR_{kl}(r)]\,. \tag{60}$$

$v_{\text{eff}}(r)$ is chosen so that it is zero far away from the impurity. For continuum (scattering) states $\epsilon_k = \frac{1}{2}k^2$. Atomic units are used in the calculations.

The asymptotic form of the radial wave functions is

$$R_{kl}(r) \rightarrow \cos\eta_{kl}\, j_l(kr) - \sin\eta_{kl}\, n_l(kr)\,, \tag{61}$$

where j_l and n_l are the spherical Bessel and Neuman functions, respectively, and η_{kl} is the phase shift. The induced charge density due to impurity potential is given by

$$\delta n(r) = \sum_{i=1}^{N} |\Psi_i(r)|^2 - n_1$$
$$= \frac{1}{\pi^2}\int_0^{k_F} dk\, k^2 \sum_{l=0}^{\infty}(2l+1)\,[R^2_{kl}(r) - j_l^2(kr)]. \tag{62}$$

In practice it is only necessary to take 7–8 partial waves. The Friedel sum rule, which states that the total displaced charge should equal the impurity charge for complete screening, is expressed

$$Z = \frac{2}{\pi}\sum_{l=0}^{\infty}(2l+1)\eta_l(k_F)\,. \tag{63}$$

III. METHOD OF CALCULATION

We have chosen two examples to illustrate the present theory. The first one is a model of vacancy in which it is represented by a spherical hole in the jellium, and the second is a metal ion represented by a model pseudopotential put in an electron gas of appropriate density. Both these calculations are done at $r_s = 2.07$ corresponding to Al metal. We shall take up realistic monovacancy calculations, positron annihilation rates in vacancies, and electric field gradients in dilute Al alloys in the following paper.[13]

The vacancy is described by a jellium density of the form

$$\rho_+(r) = n_1\theta(r - R_{\mathrm{WS}})\,, \tag{64}$$

where R_{WS} is given by

$$\tfrac{4}{3}\pi R^3_{\mathrm{WS}} = Z/n_1 \tag{65}$$

(n_1 is density of electron gas in this paper). The potential of the vacancy is then given (in a.u.) by

$$w_{\mathrm{vac}}(r) = \begin{cases} 4\pi n_1(R^2_{\mathrm{WS}} - \frac{1}{3}r^2), & r \leqslant R_{\mathrm{WS}} \\ \dfrac{8\pi n_1}{3}\dfrac{R^3_{\mathrm{WS}}}{r}\,, & r \geqslant R_{\mathrm{WS}} \end{cases} \tag{66}$$

and its Fourier transform is

$$w_{\mathrm{vac}}(q) = (32\pi^2 n_1/q^5)[\sin(qR_{\mathrm{WS}}) - qR_{\mathrm{WS}}\cos(qR_{\mathrm{WS}})]\,. \tag{67}$$

Substituting Eq. (16) in Eq. (15), we have

$$\gamma_{12}(\vec{q}) = \left(\frac{1}{\epsilon_{11}(q)} - 1\right)\frac{q^2}{4\pi e^2}\left[\Phi_{12}(\vec{q}) + \left(1 + a_{12}n_1\frac{d}{dn_1}\right)\times\left(\frac{1}{n_1}\int\frac{d^3k}{(2\pi)^3}\,\frac{\vec{k}\cdot\vec{q}}{q^2}\,\Phi_{12}(\vec{k})\gamma_{12}(\vec{k}-\vec{q})\right)\right]\,. \tag{68}$$

The linear theory result is obtained by letting $G_{12}(q) = 0$, i.e.,

$$\gamma^L_{12}(q) = \left(\frac{1}{\epsilon_{11}(q)} - 1\right)\frac{q^2}{4\pi e^2}\,\Phi_{12}(\vec{q})\,. \tag{69}$$

After some simple manipulations Eq. (68) becomes

$$\gamma_{12}(q) = \gamma^L_{12}(q) + (1 - a_{12})F(q)\int_0^{\infty} k\gamma_{12}(k)A(k,q)\,dk + \frac{a_{12}}{3}F(q)\int_0^{\infty} k\left(k_F\frac{\partial\gamma_{12}(k)}{\partial k_F}\right)A(k,q)\,dk\,, \tag{70}$$

where

$$F(q) = \left(\frac{1}{\epsilon_{11}(q)} - 1\right)\frac{3}{16\pi e^2 k_F^3}\,, \tag{71}$$

and

$$A(k,q) = \frac{1}{2q}\int_{|k-q|}^{(k+q)}[t^3 - (k^2 - q^2)t]\Phi_{12}(t)\,dt\,. \tag{72}$$

The expression for a_{12} is given by Eq. (52) combined with Eq. (53). The integral equation (70) for γ_{12} is solved by iteration requiring 10–15 iterations typically. The constant a_{12} is self-consistently determined as follows: We begin with $a_{12} = 0$, compute a new value of a_{12}, and then substitute it again in Eq. (70). Usually two to three such iterations lead to a value of a_{12} which is self-consistent to 1%. For evaluation of ϵ_c [Eq. (53)] a coupling-constant integration is required and it was found that the following method gives a very satisfactory answer in cases where the nonlinearity is not very large.

We define

$$\epsilon_c(\lambda_2) = \frac{1}{2\pi^2}\int_0^{\infty} q^2\,dq\,\Phi_{12}(q)\gamma_{12}(q_1\lambda_2) \tag{73}$$

such that

$$\epsilon_c = \int_0^{\lambda_2} d\lambda_2\,\epsilon_2(\lambda_2)\,. \tag{74}$$

We evaluate $\epsilon_c(0)$ (which is equal to zero, of course), $\epsilon_c(\frac{1}{2})$, and $\epsilon_c(1)$. In evaluating $\epsilon_c(\frac{1}{2})$ we approximate $\gamma_{12}(q_1, \frac{1}{2})$ by $\gamma^L_{12}(q, \frac{1}{2})$. $\epsilon_c(1)$ is evaluated using actual γ_{12} with full impurity potential. Now we fit the three points $\epsilon_c(0)$, $\epsilon_c(\frac{1}{2})$, and $\epsilon_c(1)$ by a parabola and for ϵ_c use the expression

$$\epsilon_c = \frac{0.5}{3}\,[\epsilon_c(0) + 4\epsilon_c(\tfrac{1}{2}) + \epsilon_c(1)]\,. \tag{75}$$

It is found that $\epsilon_c(1) = 2\epsilon_c(\frac{1}{2}) + \delta$, where δ is about

10%–15% of $\epsilon_c(1)$, implying that nonlinearity is not very large in cases we have considered.

The dielectric function $\epsilon_{11}(q)$ was taken from Vashishta and Singwi. We have checked the numerical accuracy of our procedure by varying various parameters in the computation, e.g., the integration mesh, upper cutoff limits in the integrals, Δk_F in numerical differentiation of ϵ_c and $\mathcal{G}$ in Eq. (52), etc. The self-consistency of a_{12} was typically 1%, while for $\gamma_{12}(q)$ it was typically 0.1%–0.2%.

For the calculation of electron distribution around an impurity ion, we have for simplicity chosen the Animalu-Heine-model pseudopotential.[14] We cut off[15] the large q components (which are essentially unknown from empirical fitting procedures usually employed) by a suitable cutoff factor (in the case of Al ion reported in this paper we choose[12] $e^{-0.003(q/2k_F)}$ as the cutoff factor). A more important reason for doing this was to ignore the (unphysical) oscillations in the pseudopotential in q space. These oscillations are solely due to a sharp step in the r-space model potential.

An interesting feature of the calculations was that the self-consistent value of a_{12} was always found to be in the range 0.8–1.0. (It was found to be so for all vacancies and impurity ions we have studied, and also for the case of a proton and a positron in the electron gas.) a_{12} has very little dependence on the nature of the external potential and the density i.e., r_s) of the electron gas.

Lastly, it should be mentioned that in doing Kohn-Sham calculations we have followed the method for solving the Poisson's equation suggested by Manninen *et al.*[16] in the appendix of their paper.

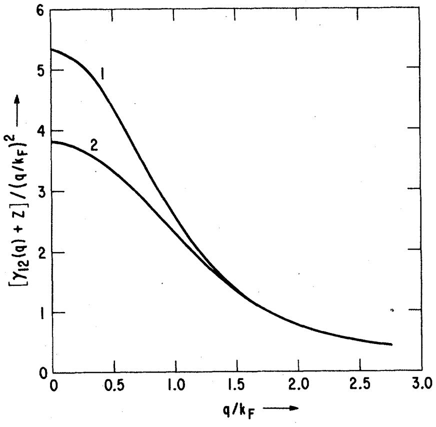

FIG. 2. The behavior of $\gamma_{12}(q)$ as a function of q/k_F for an Al vacancy (in the spherical hole model). Curve 1 corresponds to $a_{12}=0$, while curve 2 has $a_{12}=0.88$, its fully self-consistent value.

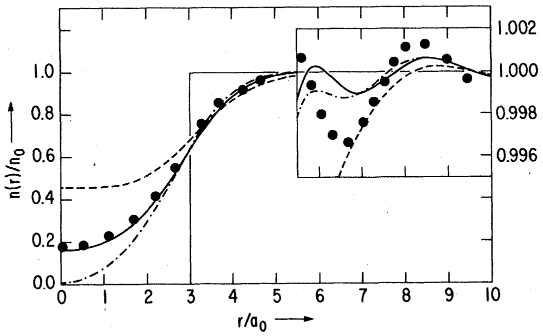

FIG. 3. The normalized electron density $n(r)/n_0$ around an Al vacancy in the spherical hole model as a function of r/a_0. The radius of the vacancy is $3a_0$. The dash-dot curve is due to the linear theory, while dashed curve corresponds to Sjölander-Stott theory ($a_{12}=0$). The result of fully self-consistent nonlinear theory with $a_{12}=0.88$ is shown by the solid curve. Values denoted by solid circles are based on a fully self-consistent Kohn-Sham calculation. The inset shows the Friedel oscillations on a magnified scale in each case.

IV. RESULTS

In Fig. 2 we have given as an illustration the behavior of $\gamma_{12}(q)$ for a vacancy in Al as a function of q for two cases: (i) when $a_{12}=0$, and (ii) when a_{12} has its fully self-consistent value (0.88). The value of $\gamma_{12}(0)$ is equal to $-Z$ in this case, and in order to bring out the large correction to the q^2 and q^4 terms of $\gamma_{12}(q)$, we have plotted $[\gamma_{12}(q)+Z]/(q/k_F)^2$ vs (q/k_F). This behavior is quite typical of all the cases we have studied.

In Fig. 3 we show the reduced electron density around a vacancy (spherical-hole model) in a jellium of $r_s=2.07$ as a function of distance in a.u. for various theories. The inset shows Friedel oscillations on a magnified scale. The solid circles are our results of a fully self-consistent Kohn-Sham calculation. There are several points to note: (a) Within the vacancy both the linear theory and the Sjölander-Stott theory ($a_{12}=0$) give results which are quite different from Kohn-Sham results. (b) Present nonlinear results ($a_{12}=0.88$) are quite close to Kohn-Sham results. It is to be noted that with the present generalization of Sjölander-Stott theory we achieve self-consistency of the charge density in the sense of Kohn-Sham theory. The "raw" Sjölander-Stott theory is clearly not self-consistent in this sense. This was earlier pointed out by Rasolt and Taylor.[17] (c) Except for the Sjölander-Stott theory, the differences both in the magnitude and phase of the Friedel oscillations between different theories are indeed small. From our numerical work it is clear that the slight differences between our results and those based on the Kohn-Sham method could be

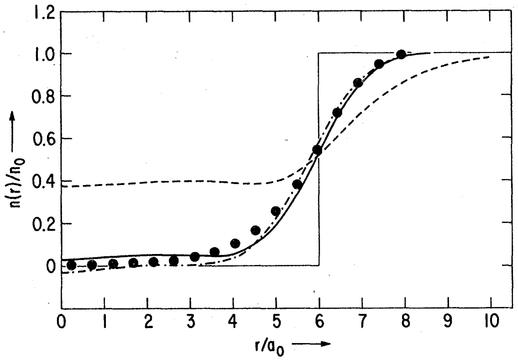

FIG. 4. Normalized electron density $n(r)/n_0$ around a spherical hole model of "eight-atom void" in Al (radius $=6a_0$). Different curves are labeled in the same way as in Fig. 3.

further reduced if we could push the numerical accuracy in solving self-consistently the Kohn-Sham equation. This we did not think necessary in view of the large computation time involved. However, some differences are bound to be there and these should be attributed to the neglect of the gradient corrections in the Kohn-Sham method and to an approximate treatment of kinetic energy in our scheme.

In Fig. 4 we have plotted similar results for the case of an eight-atom void (radius, 6 a.u.). Friedel oscillations have not been shown. The effective potential (not shown here) is much stronger (13.9 eV) and extends over a larger distance than that in the case of monovacancy. It is clear that the Sjölander-Stott theory gives a very poor density profile, which improves dramatically when a self-consistent value of the parameter a_{12} is used in solving the nonlinear integral equation (70).

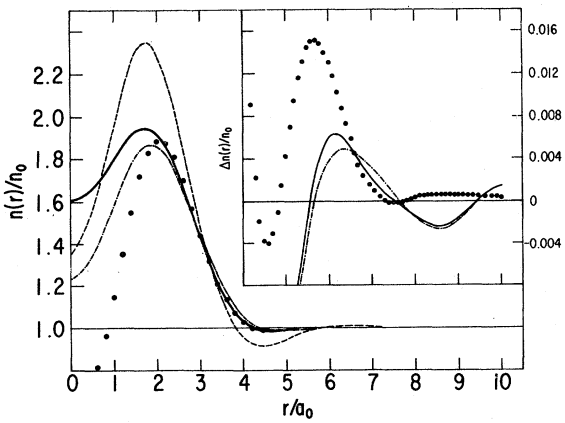

FIG. 5. Normalized electron density $n(r)/n_0$ around an Al ion represented by Animalu-Heine potential immersed in a jellium corresponding to Al($r_s=2.07$). The labeling of the curves is the same as in Fig. 3.

The density derivative term in this equation acts as a negative feedback reducing the density within the void and increasing it outside the void. Although the present theory gives results which are quite close to those based on the Kohn-Sham method, the quantitative differences here are more than those in the case of a monovacancy. The linear theory gives an unphysical result near the center of the void. If one disregards this, the electron density in linear theory is reasonably close to a nonlinear Kohn-Sham density. The same situation persists even for a void of radius 9 a.u. for which we have performed similar calculations. In the last two cases the height of the effective potential is more or less the same (13.9 and 15.7 eV), the only difference being that the potential in one case is more extended than in the other.

In Fig. 5 are shown the density distributions around a positive Al pseudoion (Heine-Aberenkov type with cutoff) in a jellium with $r_s=2.07$ in four different theories. Again we see that the present theory gives results which are different from those of the linear theory and the Sjölander-Stott theory. The differences between the results in Kohn-Sham theory and our present nonlinear formulation are greater than the corresponding situation in vacancies. This could be due to the fact that while there is no limit to the extent that charges can pile up around an ion, the maximum charge repulsion in the vacancy case is always limited to n_0. Thus the effect of kinetic energy term may be more important in the screening of an ion than a vacancy and this term is not properly treated in the mean-field approach.

In Fig. 6 is shown the reduced electron density $n(r)/n_0$ around a proton as a function of distance in three cases: (i) Kohn-Sham (local-density approximation), (ii) present theory (self-consistent value of $a_{12}=0.85$), and (iii) Sjölander-Stott theory ($a_{12}=0$). Here we wish to make several points. Our Kohn-Sham results are the outcome of a fully self-consistent calculation and they agree very well with those of Popovic *et al.*,[18] who used a parametrized form for the effective potential in the Kohn-Sham equation. Present theory gives an enhancement factor $n(0)/n_0$, which is a factor of 3 smaller than that given by Kohn-Sham theory, whereas the Sjölander-Stott theory gives a value which is larger by a factor of 3. Thus in the vicinity of the proton, results of both theories when compared to those of Kohn-Sham theory are unsatisfactory. We attribute this poor behavior to two causes: (i) improper treatment of the kinetic energy and (ii) incorrect form of $G_{12}(q)$ for large values of q. It should be mentioned here that if one is interested in getting only the correct enhancement factor, we can achieve this by treating

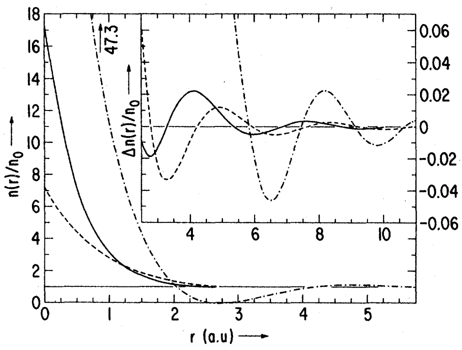

FIG. 6. Normalized electron density around a proton immersed in a jellium of $r_s = 2.07$. The dash-dot curve corresponds to the Sjolander-Stott theory ($a_{12} = 0$), while the dashed curve corresponds to the self-consistent nonlinear theory. The result of a self-consistent Kohn-Sham calculation is the solid curve. The inset shows the Friedel oscillations on a magnified scale.

a_{12} as a parameter as was done earlier by Bhattacharyya and Singwi.[8] We have here refrained from doing so. It may also be mentioned that although Bhattacharyya and Singwi were able to get a reasonable value of $n(0)/n_0$, their values of $\Delta n(r)/n_0$ in the region of Friedel oscillations were quite poor. One also notices from the inset of Fig. 6, where $\Delta n(r)/n_0$ is shown, that the present theory results, except for a small phase shift, are in reasonable accord with those of Kohn and Sham, whereas the "raw" Sjölander-Stott theory results are indeed extremely poor. The conclusion then is that the present modification of the Sjölander-Stott theory is still inadequate to treat properly the electron-density distribution around a singular attractive potential of a proton.

V. DISCUSSION AND CONCLUSIONS

From the results of Sec. IV, it is clear that the present generalization of the Sjölander-Stott theory, although only exact in the long-wavelength limit, goes a long way to improve the results for the electron-density distribution both around a vacancy and a pseudoion in an electron gas. The agreement between the Kohn-Sham and our calculated charge densities around a vacancy is rather remarkable. However, we have seen that as one goes to a bigger vacancy (eight-atom void), i.e., with increasing strength of the perturbing potential, the quality of this agreement gets somewhat poorer. This we attribute to the fact that it is not enough to correct only the small q behavior of the local field factor $G_{12}(q)$; one needs to improve it for both intermediate and large values of q. Besides, as the void gets bigger the density profile becomes much steeper (in fact for a void of radius 10 Å and bigger, it almost approaches the profile for a surface) and in that case it is essential to treat the kinetic energy exactly. In other words in Eq. (22) one needs to take higher-order terms, of order $[\tilde{n}(r)]^3$ and higher. This is not accomplished in the present formulation, whereas in the Kohn-Sham formalism the kinetic energy changes arising as a result of rapid density variations are properly accounted for through the ∇^2 operator in the one-particle equation. This seems to be the weakness of the present formulation. In fact it is this inadequacy in the theory which leads to an enhancement of electron density at the proton in an electron gas ($r_s = 2.07$), which is much smaller than what we obtain using the Kohn-Sham method. It should be mentioned here that in an earlier calculation by Bhattacharyya and Singwi[8] the value of the parameter a_{12} was not a self-consistent one [i.e., given by Eq. (52)] but was adjusted to fit the experimental values of the positron lifetime for $r_s = 6$.

From our present study, we draw the conclusions that the generalized version of the Sjölander-Stott theory should be adequate in situations where the density variation is such that one can neglect terms of order $[\tilde{n}(r)]^3$ and higher in the kinetic energy functional $T_0[n_1 n_2]$ of Eq. (22). In this particular situation, the present theory has the advantage that it takes into account all gradient corrections to the exchange-correlation energy functional. Present generalization can be easily extended to a multicomponent plasma such as electron-hole liquid in semiconductors and to a spin-polarized electron gas, and we have done so. In the latter case it should be possible to calculate the ground-state energy beyond the random-phase approximation and also the gradient correction to the exchange-correlation energy functional. These results should be useful in treating the surface of a spin-polarized electron gas within the Kohn-Sham formalism. Hitherto, the calculations of the energetics of the electron-hole liquid by Vashishta *et al.*[19] have been based on the raw Sjölander-Stott theory. It would be interesting to repeat those calculations using the generalized version of the Sjölander-Stott theory at least in the simplest situation of Ge under a very large [111] strain. We do not expect any significant change either in the values of the ground-state energy or the equilibrium density, but would not be surprised if there are important changes in the value of the enhancement factor and in the magnitude of the coefficients of the gradient term of the exchange-correlation energy functional. This needs to be confirmed through a detailed numerical computation.

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