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Screening of a proton in an electron gas[*]

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Calculations are reported of the nonlinear screening of a proton in an electron gas of densities corresponding to $r_s = 1–6$. Results for charge densities and total energies are presented from self-consistent Kohn-Sham ground-state calculations. The results differ markedly from the case of linear screening, particularly at low densities. The occurrence of a bound state around the proton for $r_s > 1.9$ indicates that hydrogen in jellium is in the form of a screened H^- ion. It is also found that at metallic densities the induced polarization around the proton is insensitive to r_s, and the screening length is almost constant (0.65) for $2 < r_s < 6$.

I. INTRODUCTION

The problem of the screening of a point charge in an electron gas has attracted considerable attention. Linear screening of the impurity can be treated simply using the electron-gas dielectric function. Nonlinear response of the electron system to the presence of the impurity, which is a more difficult problem, has been considered recently by Sjölander and Stott[1] and by Bhattacharyya and Singwi.[2] Nonlinearity is particularly important in the case of attractive impurities where excessive charge pile up and bound states may occur, and the case of a proton in the electron gas was first studied by Friedel[3] who applied the results to the problem of hydrogen in metals.

More recently the density functional formalism of Hohenberg and Kohn[4] and Kohn and Sham[5] has been applied to the problem of a proton in an electron gas by Popovic and Stott[6] and by Almbladh and von Barth[7] using different calculational procedures. The results of these two different methods have been compared and found to be in complete agreement, and comprehensive results will be presented here for the metallic range of electron-gas densities.

A short description of the theory is followed by a review of the calculational procedures where differences between the two methods previously used[6,7] are emphasized. Results are then presented for the electron density around the proton and the relaxation energy for a range of electron-gas densities corresponding to $r_s = 1-6$ a.u.[8] Comparisons are made with the results of linear screening theory. The results are used to estimate hydrogen heats of solution for jellium. Finally, uncertainties in the results due to the use of the local-density approximation for exchange and correlation are discussed.

II. THEORY

We transform the many-body Hamiltonian of an electron gas in the external potential $-Z/r$ into an equivalent one-body Hamiltonian according to the prescription by Kohn and Sham[5]:

$$[-\tfrac{1}{2}\nabla^2 - Z/r + V_H(\vec{r}) + \mu_{xc}(\rho(\vec{r})) - \mu_{xc}(\rho_0)]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}). \quad (1)$$

$V_H(\vec{r})$, the Hartree potential, is given by

$$V_H(\vec{r}) = \int v(\vec{r} - \vec{r}\,')[\rho(\vec{r}\,') - \rho_0]d^3\vec{r}\,', \quad (2)$$

where $v(\vec{r}) = 1/r$ is the Coulomb interaction and ρ_0 is the density of the homogeneous gas with no external potential. We have used the local-density approximation[5] and $\mu_{xc}(\rho)$ is thus the exchange and correlation contribution to the chemical potential of an homogeneous gas of density ρ. In order to have a vanishing potential at infinity, the energy eigenvalues are shifted by the constant $\mu_{xc}^0 = \mu_{xc}(\rho_0)$. The electron density is obtained in the usual way

$$\rho(\vec{r}) = \sum_{\epsilon_i < \epsilon_F} |\phi_i(\vec{r})|^2, \quad (3)$$

and the equations (1), (2), and (3) are solved selfconsistently on a computer. Because the total self-consistent potential tends to zero faster than $1/r$, ϵ_F is the same as for the free electrons. Thus

$$\epsilon_F = \tfrac{1}{2}k_F^2 = \tfrac{1}{2}(3\pi^2\rho_0)^{2/3}. \tag{4}$$

In the local-density version of the Kohn-Sham theory, the total energy of the electron gas in an external potential w is given by

$$E[\rho] = \sum_{\epsilon_i<\epsilon_F} \epsilon_i - \frac{1}{2}\int\int \rho v \rho + \int \rho\epsilon_{xc} - \int \rho(\mu_{xc} - \mu_{xc}^0) + \frac{1}{2}\int\int \rho_0 v \rho_0 - \int \rho_0 w. \tag{5}$$

$\epsilon_{xc} = \epsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of the homogeneous electron gas of density ρ, and integrations are performed over all space. The relaxation energy (δE) of the infinite electron gas when an external charge Z is introduced is obtained by subtracting from $E[\rho]$ the energy $E[\rho_0]$, i.e., the energy when $w = 0$ and $\rho = \rho_0$

$$E[\rho_0] = \sum_{\epsilon_i<\epsilon_F} \epsilon_i^0 + \int \rho_0\epsilon_{x0}^0. \tag{6}$$

ϵ_i^0 are the free-electron energies and $\epsilon_{xc}^0 = \epsilon_{xc}(\rho_0)$. Using δ to denote differences in quantities with and without external potential we arrive at the formula ($w = -Zv$)

$$\delta E = \delta\Big(\sum_{\epsilon_i<\epsilon_F} \epsilon_i\Big) - \frac{1}{2}\int\int \delta\rho v \delta\rho + \int \delta(\rho\epsilon_{xc}) - \int \rho\delta\mu_{xc} + \int \rho_0\Big(Zv - \int v\,\delta\rho\Big). \tag{7}$$

From the one-particle equations it is straightforward to show that

$$\delta\Big(\sum_{\epsilon_i<\epsilon_F} \epsilon_i\Big) = Z_F(\epsilon_F)\epsilon_F - \int_0^{\epsilon_F} Z_F(\epsilon)\,d\epsilon + \sum_b \epsilon_b, \tag{8}$$

where

$$Z_F(\epsilon) = \frac{2}{\pi}\sum_{l=0}^{\infty}(2l+1)\delta_l(\epsilon). \tag{9}$$

$\delta_l(\epsilon)$ are the phase shifts (defined to be zero at infinite energy) of total self-consistent potential, and ϵ_b are the energies of possible bound states.

In the standard formulation of the Hohenberg-Kohn-Sham theory[4,5] one uses the minimal property of the functional $E[\rho]$ with the subsidiary condition of a constant number of particles. In our case we are treating the limiting case of an infinite system with a constant chemical potential $\mu = \epsilon_F + \mu_{xc}^0$. The functional with the minimal property is then $\Omega[\rho] = E[\rho] - \mu N[\rho]$, $N[\rho]$ being the number of particles. The number of particles is allowed to vary, and is in fact increased by Z after the introduction of the impurity, as required by the Friedel sum rule $Z = Z_F(\epsilon_F) - Z_F(0) + N_b$ (N_b is the number of occupied bound states). In all our fully converged calculations this relation is fulfilled within 0.01%.

An alternative approach for calculating the relaxation energy is based on Feynman's theorem. According to this theorem the relaxation free energy $\delta\Omega$ can be expressed in terms of the displaced density $\delta\rho(Z, r)$ as a function of Z

$$\delta\Omega = \int_0^Z \frac{d\zeta}{\zeta}\int d\vec{r}[-\zeta v(r)\delta\rho(\zeta, r)]. \tag{10}$$

Feynman's theorem in its usual form refers to the exact energy and the exact density rather than the corresponding local-density quantities. However, by taking the derivative of Eq. (7) with respect to Z it can easily be shown that Eq. (10) remains valid when local-density approximations are used. The two different approaches for calculating the relaxation energy are thus equivalent.

III. METHOD

Two different methods have been used to calculate the displaced density and relaxation energy. In the first[7] the parametrization of μ_{xc} by Hedin and Lundqvist[9] and modified by Arbman and von Barth[10] was used and the charge density and relaxation energy were iterated to self-consistency. The relaxation energy was computed using Eq. (7).

The second method achieves approximate self-consistency but is faster. The parametrization of Hedin and Lundqvist[9] was used for μ_{xc}. A trial potential was taken and two parameters were determined so that the correct amount of charge was displaced by the trial potential and also that the potential generated from that density again displaced the correct amount of charge. The relaxation energy was computed using Eq. (10) which is less sensitive to the displaced density far from the proton.

The results of the two methods in the range of electron-gas densities $r_s = 1-3$ a.u. are in good agreement. The relaxation energies differ by less than 1%. The electron density at the proton calculated by the second method is slightly lower (1-2%) than the other. This small discrepancy may, at least in part, be due to the different parametrization of μ_{xc}, but at any rate the agreement is better than the expected accuracy of the local-density approximation. In view of this agreement the results of the first method are presented in Sec. IV, unless it is otherwise stated.

Linear screening results are presented along with the results of the nonlinear theory for comparison. In order that exchange and correlation are treated consistently in the linear and nonlinear theories the Kohn-Sham dielectric function

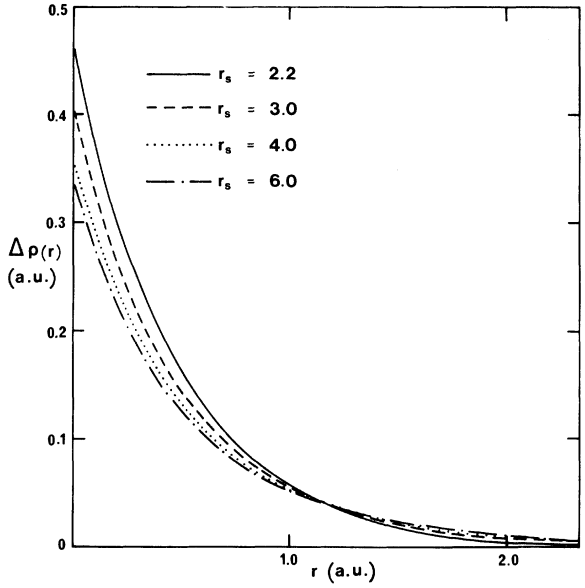

FIG. 1. Displaced electron densities [$\delta\rho(r)$] plotted against the distance from the proton for different values of r_s.

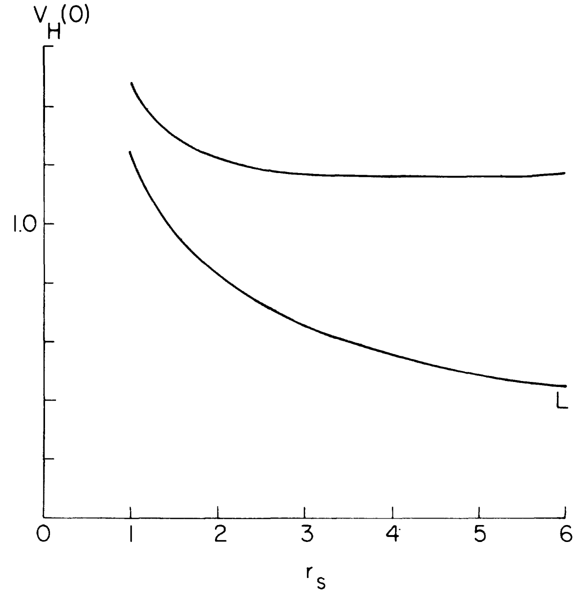

FIG. 2. The induced Hartree potential at the position of the proton [$V_H(0)$] plotted against r_s. L refers to the results from the linear theory. Atomic units used.

has been used where the local field factor is given by

$$G(q) = -\frac{d\mu_{xc}}{d\rho}\frac{q^2}{4\pi}. \tag{11}$$

IV. RESULTS AND DISCUSSION

Figure 1 illustrates the results for displaced electron density around the proton for the metallic range of electron-gas densities. At the highest mean densities where r_s is of the same order as the extent of the screening cloud the shape of the displaced density is sensitive to the mean electron density. However, at lower densities and throughout most of the metallic range the displaced density is insensitive to the mean density and the total density in the neighborhood of the proton is seen to consist of a contribution from the unperturbed electron density together with a polarization cloud which is somewhat rigid, being insensitive to the mean density.

TABLE I. Electron density at the position of the proton relative to the background [$\rho(0)/\rho_0$], screening lengths (r_0), and the heat of solution of H_2 in jellium (ΔH_H) for different values of r_s. NL and L refer to the nonlinear and linear theories, respectively.

	r_0 (a.u.)		$\rho(0)/\rho_0$		
r_s (a.u.)	NL	L	NL	L	ΔH_H (eV)
1.0	0.543	0.616	5.16	2.67	28.5
1.4	0.595	0.731	8.73	3.23	11.3
1.9	0.630	0.858	15.7	3.90	4.5
2.0	0.632	0.881	17.5	4.03	3.9
3.0	0.648	1.090	45.6	5.31	1.2
4.0	0.641	1.264	97.4	6.54	0.8
6.0	0.621	1.542	303.2	9.03	0.9

Figure 1 also illustrates the excessive pile up of electrons around the proton. This point is illustrated by the values of the screening length r_0 defined by

$$\frac{Z}{r_0} - V_H(r_0) = \frac{1}{e}\frac{Z}{r_0}, \tag{12}$$

which is listed in Table I, and by the induced Hartree potential $V_H(0)$ at the position of the proton, which is shown in Fig. 2. The results are practically constant over the metallic range: $r_0 \sim 0.65$ a.u. and $V_H(0) \sim 1.2$ a.u. In contrast, the corresponding quantities from linear theory (also shown in Table I and Fig. 2) vary from 0.9 a.u. to 1.5 a.u. and from 0.8 a.u. to 0.5 a.u., respectively, indicating a polarization cloud which increases in extent as r_s increases.

The electron density at the proton varies little with mean electron-gas density over the metallic range, again illustrating the rigidity of the polarization cloud. The electron density at the proton is, however, greatly enhanced over the mean density as seen from the values for $\rho(0)/\rho_0$ in column 4 of the table. Corresponding values from the linear theory are also given in the table and it is seen that linear response grossly underestimates the charge pile up particularly for lower mean densities. A comparison of the charge densities

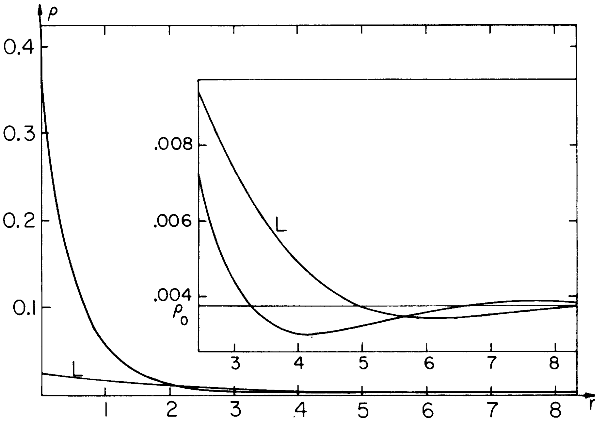

FIG. 3. Electron density [$\rho(r)$] plotted against the distance from the proton for $r_s = 4$. L refers to the results from the linear theory. Atomic units used.

calculated from linear and nonlinear theory for $r_s = 4$ is made in Fig. 3.

Not only does linear response underestimate the density near the proton, but it is also quite inadequate for treating the so-called Friedel density oscillation further from the proton. This point is also illustrated in Fig. 3. The phase of the Friedel oscillations is crucial for the interaction energy between the screened proton and neighboring ions entering detailed treatments of hydrogen in simple metals.[11] Linear response leads to zero phase for the Friedel oscillations, whereas in the nonlinear theory the oscillations are pulled in by about 90° in the metallic range.

For $r_s > 1.9$ a.u. a bound state is found. This 1s state, which is doubly occupied, remains very shallow being deepest at $r_s = 4$ a.u. for which the binding energy is 0.3 eV. The relevance of these bound states to the excitation spectrum is uncertain because the Kohn-Sham formalism applies strictly only to the ground-state energy and density. The local-density approximations for the ground-state exchange-correlation potential[5] and the nonlocal energy-dependent quasiparticle potential are, however, very similar.[9,12] They should thus produce similar wave functions at the same energy. In any case no distinction between such weakly bound states and incipient bound states near the bottom of the continuum can be made because of the energy broadening due to lifetime effects.[13] The presence of the doubly occupied 1s state therefore suggests that for $r_s > 1.9$ the hydrogen atom in jellium is actually in the form of a screened H^- ion. This is reasonable in view of the stability of the free H^- ion which is the correct low mean electron density limit.[14] The calculated densities and the relaxation energies appear to be continuous in this region of mean densities where this bound state appears, this is in accordance with the theorem of Kohn and Majumdar[15] for noninteracting systems.

The relaxation energies calculated from the nonlinear and linear theories are illustrated in Fig. 4. The linear theory considerably underestimates the magnitude of the energies throughout the metallic range, which is consistent with the reduced charge pile up near the proton. The results for the nonlinear theory flatten off at larger r_s and appear to approach asymptotically the value for the Kohn-Sham H$^-$ ion.[14,16]

The calculated relaxation energies for the proton can be used to estimate hydrogen heats of solution for jellium which have some relevance to simple metals.[11] The heat of solution per hydrogen atom is given by

$$\Delta H_H = E_M + E_I + \mu_0 + \delta\Omega, \qquad (13)$$

where E_M is the binding energy per electron of the hydrogen molecules and E_I is the hydrogen-atom ionization energy. Results for ΔH_H are given in the final column of the table where for consistency the Kohn-Sham values $E_M = 2.40$ eV,[17] and $E_I = 13.38$ eV,[18] have been taken. Even though lattice corrections to ΔH_H are liable to be substantial the overall picture is that of positive heats of solution which is consistent with the simple metals which dissolve only very small quantities of hydrogen.

The local-density approximation is expected to work only for small density gradients. However, on not too light atoms the theory reproduces the charge density within 2%, and the obvious reason is that v_{xc} is small compared to the Hartree potential. Even in the case of helium the local approximation gives a density which agrees within 2.8% with the density from a correlated wave

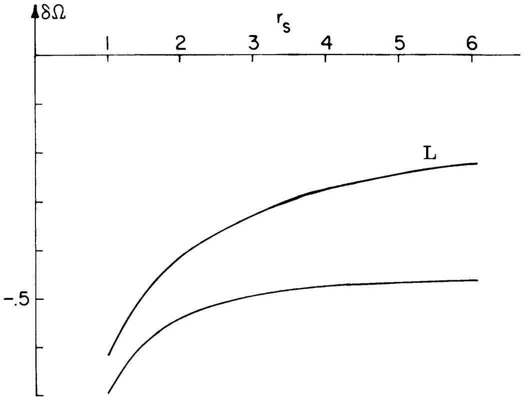

FIG. 4. Relaxation energy (δΩ) plotted against r_s. L refers to the results from the linear theory. Atomic units used.

function.[19] The worst case is the hydrogen atom where the true v_{xc} exactly cancels the Hartree potential. In this purely ferromagnetic case the spin-polarized version of the Kohn-Sham theory must be applied,[20] which gives only a 5% error. In the range of metallic densities, where we have two bound electrons, the error estimate obtained from the helium atom is more relevant, and our accuracy for $\rho(r)$ should be within 3% here. For $r_s = 2$ we get $\rho(0)/\rho_0 = 17.4 \pm 0.5$ compared to 21 obtained by Bhattacharyya and Singwi.[2] This discrepancy is probably a consequence of stretching their theory into the region of bound states where it does not apply. The error might also be due to an inadequate treatment of the nonlinear effects in their theory. In the limit $r_s \to 0$ our results tend to the results of the linear theory using the Kohn-Sham dielectric function, and the theory of Ref. 2 will in this regime be better owing to a better dielectric function. In order for the linear theory to work the induced charge density at the origin $[\delta\rho(0)]$ probably has to be one order of magnitude smaller than the background density. Since $\delta\rho(0)$ obtained by different dielectric functions agree to within 5% in this regime they should thus agree on $\rho(0)/\rho_0$ within 0.5%.

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