RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 2 15 JULY 1985

Two-component density-functional theory: Application to positron states

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(Received 28 January 1985)

A quantitative approach to calculating properties of inhomogeneous two-component Coulomb-Fermi systems is presented. As an application, the ground-state electronic structure of a jellium vacancy containing a trapped positron is calculated self-consistently. While the resulting density profiles and energetics are quite different from those obtained neglecting cross correlations, the conventional estimates for the annihilation rates are shown to remain valid, due to canceling effects of the increase in the mean electron density and the decrease in short-range screening.

Two-component Coulomb systems possess several intriguing properties derived from the interplay between attractive and repulsive long-range forces. In particular, the short-length-scale structure shows pronounced deviations (screening effects) from independent particle behavior. While the ground-state properties of homogeneous two-component fluids are being uncovered by detailed many-particle calculations, the theory of *inhomogeneous* systems is still in its infancy. Density-functional theory[1] (DFT) has proved extremely useful for the one-component inhomogeneous electron gas. In this Rapid Communication we report on the first full-scale density-functional calculation for an inhomogeneous, two-component Coulomb-Fermi system, incorporating all the exchange and correlation terms (including the all-important cross correlations) within the local-density approximation (LDA).

The most obvious condensed-matter realizations of a two-component Coulomb system are the electron-hole plasma in semiconductors[2–4] and the electron-positron systems in metals.[5] While the theory developed is quite general, we focus here on the latter example. The conventional way to treat positron states in solids is to first construct an unperturbed electronic ground state for the system and then to calculate the positron distribution by assuming the electron density to remain rigid, and by accounting for the electron-positron correlation in terms of a correlation (screening) potential[6] dependent on the electron density. Similarly, the experimentally observable electron-positron contact density (annihilation rate) is usually obtained from a local expression involving the unperturbed electron density profile and a density-dependent enhancement factor for a single positron in electron gas.[6] While this approach is a good one (apart from rather subtle momentum-dependent effects[7]) for delocalized positron states, it is much more questionable for localized (trapped) states. If a positron is trapped (typically at a lattice defect) it will have a severe effect on the electron states in its vicinity; the requirement of complete screening means that one additional electron will be pulled to the trap region and the assumption of a rigid electron density $n_-(\mathbf{r})$ cannot hold. On the other hand, the positron density $n_+(\mathbf{r})$ at the trap region is finite and can actually exceed the electron density. A situation involving a two-component plasma arises, and the picture of a single positron being screened in a locally homogeneous electron gas may break down. In what follows we stress the usefulness of the positron density as the basic variable.

The formal derivation of the density-functional equations for the two-component case is a generalization[8] from the familiar one-component case. Separating out the mean-field electrostatic Hartree terms, one can define exchange-correlation functionals accounting for the remaining electron-electron, electron-positron, and positron-positron interactions. If we assume that both the electrons and the positrons move in an external potential due to a (positive) background charge distribution $n_b(\mathbf{r})$, the DFT equations read (in atomic units)

$$-\frac{\nabla^2}{2}\psi_i(\mathbf{r})+\left[\frac{\delta E_{\rm xc}[n_-]}{\delta n_-(\mathbf{r})}+\phi(\mathbf{r})+\frac{\delta E_{\rm corr}[n_+,n_-]}{\delta n_-(\mathbf{r})}\right]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r}) \quad , \tag{1}$$

$$-\frac{\nabla^2}{2}\psi_+(\mathbf{r})+\left[\frac{\delta E_{\rm xc}[n_+]}{\delta n_+(\mathbf{r})}-\phi(\mathbf{r})+\frac{\delta E_{\rm corr}[n_+,n_-]}{\delta n_+(\mathbf{r})}\right]\psi_+(\mathbf{r})=\epsilon_+\psi_+(\mathbf{r}) \quad , \tag{2}$$

$$n_-(\mathbf{r})=\sum_i|\psi_i(\mathbf{r})|^2, \quad n_+(\mathbf{r})=|\psi_+(\mathbf{r})|^2 \quad , \tag{3}$$

$$\phi(\mathbf{r})=\int d\mathbf{r}'\frac{n_-(\mathbf{r}')-n_+(\mathbf{r}')-n_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad . \tag{4}$$

Here the functional derivatives $\delta E_{\rm xc}/\delta n_i (i=+,-)$ are the one-component exchange-correlation potentials for positrons and electrons, respectively, and

$$\delta E_{\rm corr}[n_+,n_-]/\delta n_i(\mathbf{r}), \quad i=+,-$$

is due to the cross-correlation. The ground-state densities and the total energy are obtained through the self-consistent solution of Eqs. (1)–(4).

In LDA,

$$E_{\rm xc}[n_i]=\int d\mathbf{r}\, n_i(\mathbf{r})\epsilon_{\rm xc}(n_i(\mathbf{r})) \quad , \tag{5}$$

where $\epsilon_{\rm xc}(n)$ is the exchange-correlation energy per particle in one-component gas.[9] Similarly, one can write

$$E_{\rm corr}[n_+,n_-]=\int d\mathbf{r}\, n_+(\mathbf{r})\epsilon_c(n_+(\mathbf{r}),n_-(\mathbf{r})) \quad , \tag{6}$$

where $\epsilon_c(n_+,n_-)$ is the (electron-positron) correlation en-

ergy per positron in a two-component gas with densities n_+, n_-.

The function $\epsilon_c(n_+, n_-)$ has been (approximately) known so far in the two limiting cases: $n_+ \to 0$ (single positron in electron gas[6,10]) and $n_+ = n_-$ (fully compensated plasma[3,10]). Recently, extensive variational many-body calculations[10,11] have provided accurate values for ϵ_c throughout the (n_+, n_-) plane. We have used these data to construct the cross-correlation functional and its derivatives,[12] which are of central importance for a successful application.

The physical implications of the two-component formulation are as follows: A localized positron will attract a screening electron into the trap region, whereby the average electron density there will be enhanced and the Friedel sum rule accordingly modified. The nonzero positron density, on the other hand, will lead to a locally weaker contact density increase and diminished local annihilation rate as compared with the dilute approximation; i.e., the proper local-density formula for the annihilation rate is

$$\lambda = \pi r_0^2 c \int d\mathbf{r}\, n_+(\mathbf{r}) n_-(\mathbf{r}) g_{12}(0; n_+(\mathbf{r}), n_-(\mathbf{r})) \quad . \quad (7)$$

Above, r_0 is the classical electron radius, c the speed of light, and $g_{12}(0; n_+, n_-)$ is the contact enhancement (the electron density increase at a positron or the value of the pair distribution function at the origin) in a homogeneous mixture of n_+ and n_-. For a delocalized positron, Eqs. (1)–(4) reduce to the conventional approach with no net effect of the positron on the electron states.[5]

Figure 1 shows the contact enhancement for concentration ratios $x = n_+/n_- = 0$, 0.5, and 1 for various values of the electron density parameter r_s. The variational many-body theory[10,11] employed here puts emphasis on the proper treatment of the short-range correlations, and hence we expect the results to be quite accurate. Also shown in Fig. 1 is the typical behavior of g_{12} as a function of x.

We have applied the full scheme to the case of positron trapping at a vacancy in a metal. We treat a well-studied model, a spherical monovacancy in jellium, i.e.,

$$n_b(\mathbf{r}) = \tfrac{3}{4}\pi r_s^3 \cdot \theta(r - R_{\mathrm{WS}})$$

(we take $r_s = 2.07$ for Al) and R_{WS} is the Wigner-Seitz radius. Furthermore, to obtain a realistic trapping potential for positrons, we mimic the repulsion of the positron from the true host ion cores[13] by an added square-well potential for a positron, with a depth of $E_0 = 4.8$ eV and a radius equal to R_{WS}.

Figure 2 first shows the self-consistent electron density for a jellium vacancy *without* a positron present. Using that as an input, the conventional calculation yields a trapped positron density as shown in Fig. 3 and a single-particle binding energy to the vacancy $E_B = 1.85$ eV. Using the conventional dilute-limit local-density formula [i.e., $g_{12}(0; n_+, n_-) \to g_{12}(0; 0, n_-)$ in Eq. (7)] the lifetime in the trap is calculated to be $(\lambda_v^0)^{-1} = 256$ psec. The same model gives the lifetime $(\lambda_b)^{-1} = 170$ psec for a delocalized positron in bulk metal. The positron trapping potential is also shown in Fig. 3.

The calculated lifetime values are actually in good agreement with experiment,[5] particularly if one adds the small correction due to annihilation with the tightly bound ion core electrons. However, it is clear that the description of the mean electron density at the trap cannot be satisfactory. Figure 2 also shows the results from the *self-consistent two-component* calculation. One immediately observes the increase of $n_-(r)$ inside the vacancy, amounting to the extra screening electron associated with the positron. The positron distribution and effective positron potential [see Eq. (1)] are also shown in Fig. 3. The positron distribution is slightly more spread out than in the non-self-consistent case, which reflects the slower asymptotic decay of the trapping potential. While the long tail is partly due to the local-density approximations employed, i.e., self-interaction effects, it also more faithfully reflects the nature of positron-dependent electron-positron correlations.

It is very interesting now to compare the lifetimes of the

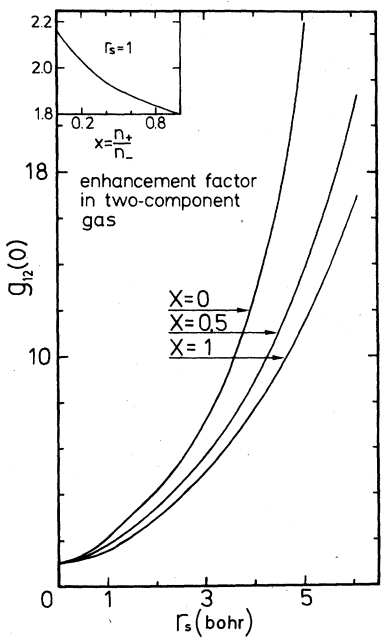

FIG. 1. The contact density enhancement $g_{12}(0)$ in a homogeneous two-component Coulomb-Fermi gas for different values of the density parameter r_s and the density ratio $x = n_+/n_-$.

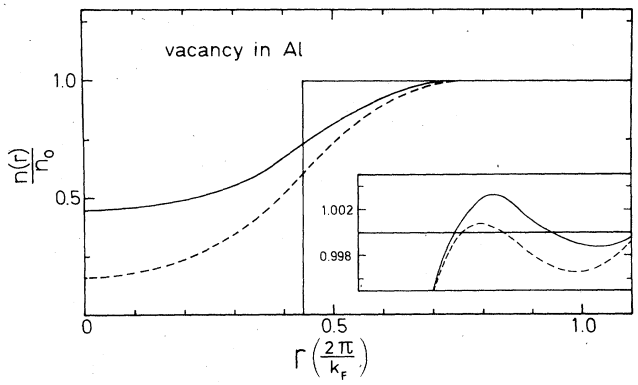

FIG. 2. The electron density at a jellium vacancy. Full curve: two-component density-functional theory; dotted curve: electron density in absence of the positron. The distance is in units of the Fermi wavelength corresponding to $r_s = 2.07$. The density is given in units of the bulk density $n_0 = 0.027$ a.u.

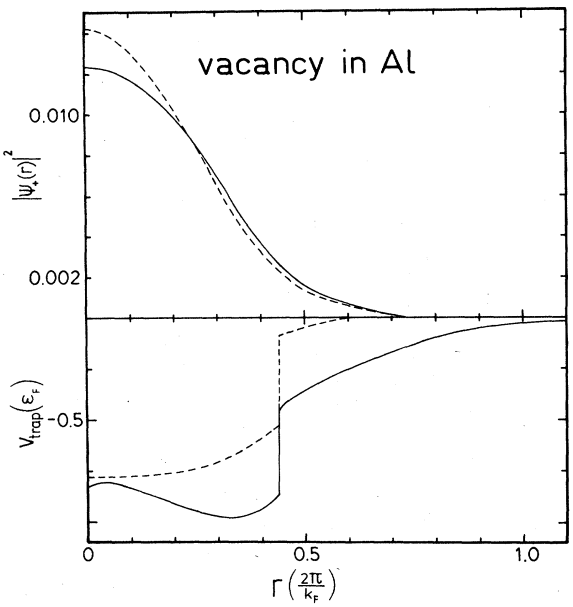

FIG. 3. The positron probability distribution $|\psi_+(\mathbf{r})|^2$ and the effective trapping potential $V_{\text{trap}}(\mathbf{r})$. Full curve: two-component density-functional theory; dotted curve: assuming no electron density response to the entering positron. The potentials are given in units of the Fermi energy (11.7 eV).

values of the two approaches. The two-component calculation using Eq. (7) gives $(\lambda_v^0)^{-1}=245$ psec, i.e., a value only 4% different from the first estimate. This signals that, as far as rates of annihilation are concerned, there is a cancellation between (i) the electron pileup in the trap due to the presence of the positron and (ii) the diminished "local" annihilation rate due to the nonzero positron density. The results from this model calculation give strong *a posteriori* support for the wealth of lifetime calculations reported in literature which are based on the conventional approach.

The binding energy of a positron to the trap must, in the self-consistent case, be calculated from the *difference* between two total energies. This gives a value of $E_B=2.65$ eV, i.e., considerably larger than the old value, even if the positron distribution is actually less localized. This signals that the previous one-particle calculations for the positron binding energies are subject to criticism, and should be considered with suspicion, at least for quantitative purposes.

In summary, we have developed a two-component density-functional theory applicable to nonuniform interpenetrating charged Coulomb-Fermi systems, such as electron-hole plasmas or liquid metallic hydrogen. Here we have applied the quantitative method to electron-positron systems realized at defect-bound positron states.[14] The results show the correct electron and positron densities when the cross-correlations are truly accounted for and thus transcend all previous ones. We show that, due to cancellation effects, the conventional estimates for the lifetime values remain accurate. This, of course, is good news from the viewpoint of positron-defect spectroscopy by lifetime analysis, since the two-component calculations are substantially heavier than the conventional ones. On the other hand, the earlier estimates for the binding energy are much less reliable.

One should also note that the present LDA calculation includes the self-interaction effects, which can lead to considerable errors for the trapped positron energy. This can be remedied by introducing self-interaction corrections,[15] which actually are a step from the true density-functional theory back to the direction of the original formulation. We shall report on these and the full details of the present work in a forthcoming publication.[12]

We have benefited from discussions with Matti Manninen. One of us (E.B.) is grateful to International Atomic Energy Agency for financial support.

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[14] With the development of intense slow-positron beams, the laboratory realization of *many*-positron-many-electron plasmas is becoming a possibility [P. Platzman and A. P. Mills, Jr. (private communication)].

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