

ATTACHMENT OF AN ELECTRON-HOLE DROPLET TO A DONOR

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The attachment of an electron-hole droplet to a donor in Ge is considered using the density-functional method. We find the heat of solution of a donor in a droplet to be about 7 meV, and the electron density at the donor to be 32 times the carrier density in the droplet far from the donor. Effects on droplet pinning and recombination are discussed.

The emergence of the density functional technique<sup>1,2</sup> as a practical computational method has led to a new examination of many fundamental problems in the theory of interacting electron systems. Successful applications to the theory of metal surfaces are probably the best known example.<sup>3</sup> Recently several groups using the method have turned their attention to the simplest sort of impurity problem in the theory of metals, namely a point charge in a jellium background; self-consistent electron density distributions have been obtained.

Many obstacles lie between these theories and physical tests, however. For example the relaxation of a real metal lattice to the presence of the impurity has not been carefully considered, nor are there obvious ways to probe the density distribution experimentally. We have tried to apply similar techniques to a system which is much "cleaner" than ordinary metals: the electron-hole liquid in Germanium in the presence of a donor. For this case the condensed valence-band holes play the role of the metal lattice: their relaxation can be treated in exactly the same way as the electron system. Also, as we will see below, there exist "extra" probes for this system, notably the recombination radiation line-shape. And, of course, the influence of impurities on electron-hole liquid properties is of interest in its own right.

Our problem is the following: given a positive point charge fixed at the origin surrounded by electron-hole liquid

(EHL) find the self-consistent density distribution and binding energy.<sup>6</sup> We neglect effects due to the droplet surface: as long as the impurity is more than a few screening lengths from the surface this is a good approximation. (Note that even for small  $\alpha$ -drops the screening length is a small fraction of the drop radius.)

We must first state precisely what we mean by the binding energy. We define a quantity  $\Omega$  to be the energy of a droplet of  $N+1$  electrons,  $N$  holes, and an impurity charge inside minus the energy of a droplet of  $N$  electrons,  $N$  holes, an ionized impurity, and the extra electron, all well separated. The heat of solution of a neutral donor is:

$$H = (-\Omega) - |E_B| \quad (1)$$

where  $E_B$  is the donor binding energy.  $\Omega$  differs by a constant from the grand potential difference due to the donor. It is the quantity we minimize in our calculations.

The work is based on the Kohn-Sham formulation of density functional theory; we use the potential variation technique of Rose and Shore.<sup>7</sup> In this method the exchange-correlation energy is written in the local approximation. Together with the Hartree energy we have:

$$\begin{aligned} \Omega_1 = & \int [\epsilon_{xc}(n_e, n_h) - \epsilon_{xc}(n_o, n_o)] d^3r \\ & - \int \delta n(r)/r d^3r \\ & + \frac{1}{2} \int \delta n(r) \delta n(r') / |r-r'| d^3r' d^3r \\ \delta n = & n_e - n_h \end{aligned} \quad (2)$$

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In this expression  $n_{e,h}$  are the total electron (hole) densities, and the units are such that  $\mu = \hbar = e^2/\kappa = 1$ , where  $\mu$  is the exciton mass and  $\kappa$  the dielectric constants. The equilibrium EHL density is  $n_0 = 2.4 \times 10^{17} \text{ cm}^{-3}$ . The exchange - correlation energy per unit volume,  $\epsilon_{XC}$ , was calculated for the Germanium band structure. The exchange part is exact except for neglect of valence-band warping,<sup>8</sup> and the correlation part is the result of an RPA calculation for unequal  $n_e$  and  $n_h$ .<sup>9</sup>

The kinetic energy contribution to  $\Omega$  is:

$$\Omega_2 = - \sum_{l,i} \frac{2\pi+1}{\pi} \int k_F^i \delta^i(k) dk + \epsilon_F^e X_e + \epsilon_F^h X_h - \int V_e n_e d^3r - \int V_h n_h d^3e, \tag{3}$$

$$X_{e,h} = \int (n_{e,h} - n_0) d^3r.$$

Here the index  $i$  runs over the occupied bands,  $k_F^i$  is the Fermi wave vector, and  $\epsilon_F^i$  the Fermi energy. The functions  $V_{e,h}$  are the self-consistent potentials felt by the two species, and  $\delta_{\ell}^i(k)$  the associated scattering phase shifts. In the kinetic energy the light holes are neglected, and the  $\delta_{\ell}^i$  come from wave-equations involving density of states masses.

A third contribution to  $\Omega$  comes from the fact that the screening charges  $X_{e,h}$  corresponds to the transfer of charges from distant parts of the droplet; for each charge transferred a binding energy (chemical potential)  $\mu_{e,h}$  must be paid:

$$\Omega_3 = \mu_e(X_e - 1) - \mu_h X_h. \tag{4}$$

Alternatively, one may regard  $\Omega_3$  as the Lagrange multiplier term in a grand potential.

Once the functional form of  $\Omega = \Omega_1 + \Omega_2 + \Omega_3$  is known, the calculational procedure is as follows (see ref. 7 for more detail): choose a set of trial potentials  $V_{e,h}$ . Solve the wave-equation for many wave vectors within the Fermi seas of both species, and generate the densities  $n_e, n_h$  as a sum of squared wave functions. The phase shifts are also calculated, and all the quantities in  $\Omega$  can be numerically generated. The true densities are those which minimize  $\Omega$  subject to a constraint of charge neutrality. We required that the Friedel sum rule give the correct impurity charge.

In practice we followed the minimization procedure of ref. 5 for the electrons. (This is more rapid than the

original method of ref. 7):  $V_e$  was chosen at ten points and a potential was generated from the associated charge density:

$$\tilde{V}_e = \phi + \mu_e (n_e) - \epsilon_F^e(n_e) - (\mu_e(n_0) - \epsilon_F^e(n_0)), \tag{5}$$

where  $\phi$  is the electrostatic potential. The difference between  $V_e$  was minimized by varying the chosen ten values.

The holes give a small contribution to the final  $\Omega$  (about 5%): we simply used a trial potential with a few parameters for them. (Because of the weak dependence of  $\Omega$  on  $n_h$ , our results for  $n_h$  are probably less reliable than those for  $n_e$ .) Our technique was to set  $n_h = n_0$ , let the electrons relax, then "freeze"  $n_e$  and let the holes relax, freeze  $n_h$  and so on.

Our results for  $n_{e,h}$  are plotted in figure 1. Note the enormous build-up of electron density at the origin:  $n_e(0) =$

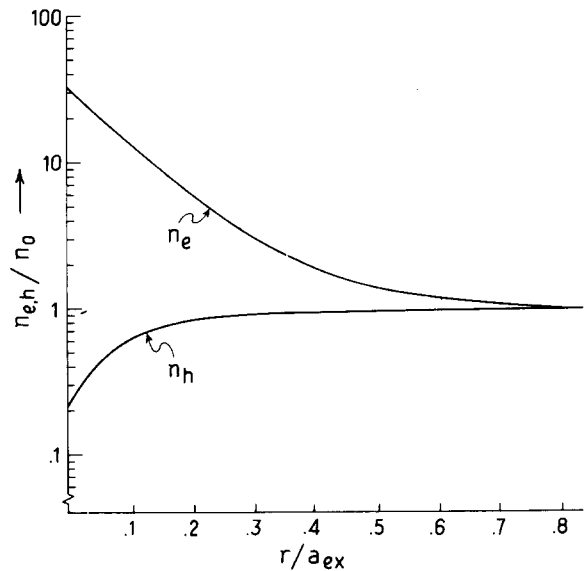


Figure 1. Electron and hole densities as a function of distance from the donor. Note the logarithmic scale.  $a_{ex} = 177\text{\AA}$

$32 n_0$ . This is to be expected: near the impurity the electron density should look very much like that of an ordinary donor (with a density of states mass). It is easy to show that for such a donor  $n_e(0)$  would be  $29 n_0$ . Our value for  $\Omega$  is

$-6.2$  exciton rydbergs =  $-16 \text{ meV}$ .

For a donor like Sb which has a small central cell correction, our results may be directly compared to those of Smith<sup>6</sup> for the heat of solution.

We find  $H = 7 \text{ meV} = 2.7 \text{ exciton rydbergs}$ , while Smith finds  $2.0 \text{ exciton rydbergs}$ . This difference is also to be expected because Smith uses linear response theory; in a case like the present one with very large charge buildup linear response underestimates energies. We disagree with Smith about the proper treatment of central-cell corrections for other impurities. All our theory so far has been in the effective mass approximation. Central cell effects increase  $|E_B|$ , but they should also increase  $-\Omega$  by about the same amount (cf. the discussion of  $n_e(0)$ , above). Thus,  $H$  which depends on their difference should be more or less independent of impurity type.

Evidence for large pinning energies of droplets to impurities has been given by Westervelt and Black<sup>10</sup> who measure a lower bound of about  $3 \text{ meV}$  for the activation energy for hopping of droplets off of nucleation centers (which are probably acceptors or donors). This is compatible with our value.

The EHL recombination radiation may be used as a more microscopic probe than the heat of solution. The linewidth is well known to be  $\epsilon_F^e + \epsilon_F^h$ . However the

phase shifts  $\delta_\ell(k)$  may be interpreted as a change in the energy  $\epsilon_\ell(k)$  of the level with wavevector  $k$  and angular momentum  $\ell$ :

$$\delta\epsilon_\ell/\epsilon_\ell = -\delta_\ell/2kR. \quad (6)$$

Here  $R$  is the radius of a sphere in which the particles are taken to be confined. For a doped sample with many impurities per drop, we estimate  $R$  as the mean distance between impurities: if there are  $10^{16} \text{ donors/cm}^3$ , we find at the Fermi surface the shift of an  $\ell=0$  state to be about  $5\%$ . (The phase shift  $\delta_0^e(k_F)$  is about  $.5$ ). A line narrowing of this order has been observed<sup>11</sup> and has been attributed to a change in density.<sup>6,11</sup> For  $\ell \neq 0$  the shifts are smaller, so that a redistribution of population among various  $\ell$  values may cancel this effect. A complete investigation of the effect of impurities on recombination line-shapes is in progress.<sup>12</sup>

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