GROUND STATE ENERGY OF SMALL ELECTRON-HOLE DROPS*

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The ground state energy of small electron-hole drops is calculated for droplets ranging in size from 10 to 10,000 pairs. A new value for the bending energy of 1.1×10^{-10} erg/cm is derived. We also give a simple highly accurate formula for the total energy per pair. The surface energy is extracted from the total energy and found to agree well with a previous self-consistent calculation. The density at the center of the drop remains essentially constant over the entire range of N, indicating that the drop is not dramatically compressed by the surface tension.

I. In the electron-hole liquid electrons and holes are metallic and delocalized. Hence the theory of the electron gas (suitably modified to account for bandstructure effects) can be used to determine the energetics of the droplets to a high precision in non-polar materials. Electron gas theory was first applied to the bulk energy of the EHL by several investigators, and good results for the ground state energy and density were obtained;[1] other investigators successfully applied the theory of the inhomogeneous electron gas to the EHL surface.[2] One area which has not been studied is the transition from large drops (where the number of pairs, N, is >10,000) to small drops (10<N<10,000) to exciton complexes (N<10). In this paper we use the density functional theory of the inhomogeneous electron gas to study small drops. This region is particularly interesting because it is here that quantum size effects begin to appear. Since there are no ion cores, the EHL provides a simple system in which to study the appearance of these effects.

We present calculations of the ground energy of small drops in unstrained Ge with N=10 to N=10,000. Self-consistent solutions of the Kohn-Sham[3] equations were obtained for N<120, while solutions for 10<N<10,000 were obtained using the gradient expansion for the kinetic energy.[4] Results of the calculation are a simple formula for the total energy per pair as a function of the number of pairs in a drop. We were able to use self-consistent results for N<120 to obtain an estimate of the surface energy. This value is consistent with an independent and quite different calculation of the surface energy by two of us (JHR and HBS).[5] We report a new and much larger value for the bending (curvature) energy. Finally it is

shown that there is no substantial compression of the droplet density due to the surface tension as has been suggested.[6] The self-consistent results are mainly used to provide a check on the gradient expansion calculation which forms the core of this paper. In a later paper we will discuss the self-consistent results including the level structure of small drops, shell effects, work function and variation in the recombination luminescence lineshape. The structure of this paper is as follows. We sketch the density functional theory, and the two forms of this theory which we have used in this paper. Then we present our results for the droplet energy, and the variation in density at the center of the drop.

II. The density functional theory for degenerate Fermi systems rests on constructing and minimizing the energy as a functional of the density.[3,4] The energy functional which we minimize here is given by

$$E[n_e(\vec{r}), n_h(\vec{r})] = T^e[n_e(\vec{r})] + T^h[n_h(\vec{r})]$$

$$+ \frac{1}{2} \int \frac{(n_e(\vec{r}) - n_h(\vec{r}))(n_e(\vec{r}') - n_h(\vec{r}')) d^3\vec{r} d^3\vec{r}'}{|\vec{r} - \vec{r}'|} \quad (1)$$

$$+ \int \epsilon_{xc}(n_e(\vec{r}), n_h(\vec{r})) d^3\vec{r}$$

The fourth term gives the exchange and correlation energy contribution to the total energy. Here ϵ_{xc} is a local approximation to the exchange and correlation energy per unit volume. The third term on the right is the electrostatic energy. The first two terms $T^e[n_e(\vec{r})]$ and $T^h[n_h(\vec{r})]$ are the kinetic energy of non-interacting electrons and holes with densities $n_e(r)$ and $n_h(r)$ respectively. T^e and T^h can be

determined (for a given model) by solving the self-consistent Kohn-Sham equations which are written below for the electron component.

$$-\frac{\nabla^2}{2m_e}\psi^e_{n\ell m}(\vec{r}) + v^e_{eff}(n_e(\vec{r}),n_h(\vec{r}))\psi^e_{n\ell m}(\vec{r})$$

$$= \varepsilon^e_{n\ell m}\psi^e_{n\ell m}(\vec{r}) \qquad (2)$$

$$v^e_{eff}(r) = -\int \frac{(n_h(\vec{r}')-n_e(\vec{r}'))d^3\vec{r}'}{|\vec{r}' - \vec{r}|}$$

$$\qquad (3)$$

$$+ \frac{d}{dn_e(r)} \varepsilon_{xc}(n_e,n_h)$$

and

$$n_e(r) = 8 \sum_{n\ell m}^{occ} |\psi_{n\ell m}(r)|^2 \qquad (4)$$

We use a spherical approximation in calculating the electron and hole dynamics, and hence we can use the quantum numbers n,ℓ,m. The electron eigenvalue given above are $\varepsilon^e_{n\ell m}$ and the eigen-function are $\psi_{n\ell m}(\vec{r})$. The factor of 8 appears in Eq. 4 to account for the electron degeneracy where we have four equivalent conduction minima and two spin states per minimum. The mass m_e is the density of state mass. The complicated va-lence band structure is replaced by a single spherical band whose mass is chosen to reproduce the density of states of the hole bands.

Once Eqs. 2-4 are solved self-consistently along with the analogous equations for the holes, we obtain the kinetic energies T^e and T^h from

$$T^e = 8 \sum_{n\ell m}^{occ} \varepsilon^e_{n\ell m} - \int v^e_{eff}(\vec{r})n_e(\vec{r})d^3\vec{r} \qquad (5)$$

and

$$T^h = 2 \sum_{n\ell m}^{occ} \varepsilon^h_{n\ell m} - \int v^h_{eff}(\vec{r})n_h(\vec{r})d^3\vec{r} \qquad (6)$$

Thus we determine Eq. 1 and the ground state energy and density of the droplets.

Several cautions are now in order. We must in principle project out the center of mass motion of the droplet when performing a varia-tional calculation. The error in the total energy, if we neglect to do this, is inversely proportional to the mass of the droplet ($\Delta E = P^2/2M$, P,M are the momentum and mass of the cen-ter of mass). Hence the error in the energy per pair scales $1/N^2$. For a single exciton, the error due to the center of mass motion is about one quarter of the exciton bending energy. For a drop with ten or more pairs, we expect the center of mass error to be less than .01 mev per pair.

A second caution arises from the fact that we have replaced the complicated band structure of Ge by a simple spherical model based on the density of states masses. Such a model gives rather good results for the surface energy of large drops ($N\rightarrow\infty$). However, for very small drops the complicated valence band structure may influence both the calculated energies and certain shell effects. An investigation of these effects is currently underway (primarily with

respect to the problem of the bound multi-exciton complex).

Finally, we have simplified the energy cal-culation in several ways from the more complete calculation.[5] Hence the results obtained here should not be regarded as supplanting the previous results in the limit as $N\rightarrow\infty$.

For $N>120$ we run into serious numerical problems. However, above $N\approx100$ the shell effects (i.e. the effects of the discreteness of the energy levels from the solution of Eq. 2) become much less pronounced and a statistical approximation provides a good description. Therefore we replace the self-consistent expressions for T^e and T^h with the gradient expansion of Reinecke and Ying.[7] For the density we use the approximation that $n_e(\vec{r}) = n_h(\vec{r}) \equiv n(\vec{r})$ and the following variational form

$$n(\vec{r}) = \begin{cases} n_o(1 - \frac{1}{2}e^{\beta(r-r_o)}) & r<r_o \\ n_o \frac{1}{2}e^{-\beta(r-r_o)} & r>r_o \end{cases} \qquad (7)$$

Using Eq. 7 and the Reinecke-Ying expressions for T^e and T^h we minimize the total energy of a droplet (Eq. 1) by varying the parameters n_o, β and r_o. Since we require that the droplet contain a fixed number of pairs, N, one of the variational parameters is constrained and we have two free parameters.

Some care is necessary in the numerical minimization since we are looking at the inter-play of surface and volume effects. Because of this, large changes in the parameters can correspond to small energy changes, and it is necessary that the energy be calculated very accurately. Since we are examining drops with up to 10,000 pairs in the gradient expansion, straight numerical integrations in evaluating Eq. 1 would be difficult. To avoid these problems we expand the energy for $r<r_o$ in a power series in terms of $\frac{1}{2}e^{\beta(r-r_o)}$. Once this expansion is made we can do the integration analytically and perform the sums. The requisite accuracy is obtained and the minimiza-tion proceeds straightforwardly.

We should note that the gradient and self-consistent results are calculated in slightly different models; the gradient calculation contains corrections for the valence band coupling and the asphericity of the conduction bands. These small corrections were neglected in the self-consistent calculation.

III. Both the self-consistent and the gradient expansion technique yield estimates for the surface and the bending energy. After performing the summation procedure of the last section (and minimizing) we find that the following expression for the total energy of a droplet with N pairs:

$$E_N = \frac{4\pi R^3}{3} e^N_b + 4\pi R^2\sigma^N + 8\pi Re^N_c + const + (e^{-\beta R}). \qquad (8)$$

Here $R = (3N/4\pi n_o)^{1/3}$ is the radius of a uniform drop of uniform density, n_o, out to its boundary. The expansion coefficients e^N_b, σ^N and e^N_c have the following interpretation. For a given N there are a set of variational coefficients n_o, β, r_o which minimize the energy. Then ε^N_b is the bulk

TABLE 1. Values of the density at the center of the drop, n_o,
and the total energy per pair, E/N, are shown along with σ^N and
e_c^N. All values are shown in effective atomic units with the
effective Hartree = 5.28 mev and the effective Bohr orbit = 177Å.

N	n_o	E/N	σ^N	e_c^N
10	1.25	-1.03	.071	.015
30	1.34	-1.09	.072	.017
50	1.36	-1.11	.072	.018
100	1.37	-1.13	.072	.019
200	1.37	-1.15	.071	.019
500	1.36	-1.16	.070	.020
1,000	1.35	-1.17	.070	.020
10,000	1.32	-1.19	.070	.021
bulk	1.30	-1.20	.069	.022

energy per pair for a drop with density n_o.
Similarly σ^N and e_c^N are the surface and curvature
energies evaluated for the n_o, β and r_o of a
given drop with N pairs. When N→∞ we obtain the
volume energy ε_b, the surface energy σ and the
bending energy e_c. Table 1 gives values for σ^N
and e_c^N. We obtain

$$\sigma = 1.8(5) \times 10^{-4} \text{ ergs/cm}^2$$

and

$$e_c = 1.1 \times 10^{-10} \text{ ergs/cm .} \qquad (9)$$

In the large drop limit (N→∞) our calculation
for the surface energy reduces to the form of
the calculation of Reinecke and Ying who

considered a planar surface of the EHL. Our
value for σ is in very good agreement with their
most recent result.[8] The value of the bending
energy is much larger than the only other
calculation of this quantity by Buttner and
Gerlach.[9] However the difference between their
result and ours stems from the fact that we used
an improved correlation energy and the Reinecke-
Ying version of the gradient expansion.

An estimate of the surface energy can be
made from our self-consistent calculations for
N<120. First we re-express Eq. 8 in a way
which makes the N dependence explicit.

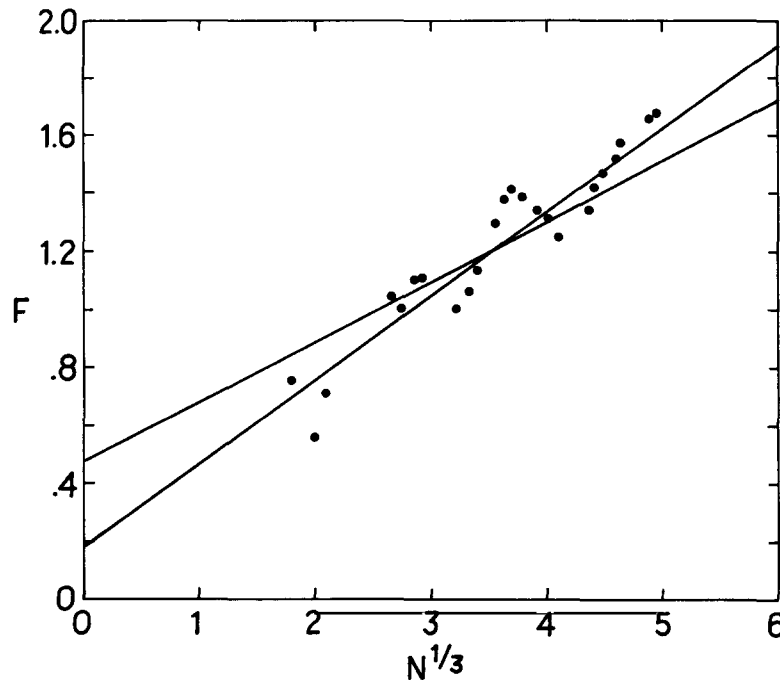$$E_N = \left(\frac{4\pi r_s^3}{3}\right) e_b^N N + (4\pi r_s^2)\sigma^N N^{2/3} + 8\pi r_s e_c^N N^{1/3} \qquad (10)$$

Figure 1. Plot of F versus $N^{1/3}$. A value of $\sigma \simeq 1.9 \times 10^{-4}$
ergs/cm^2 is extracted for the self-consistent value of
the surface energy. The solid lines are included to in-
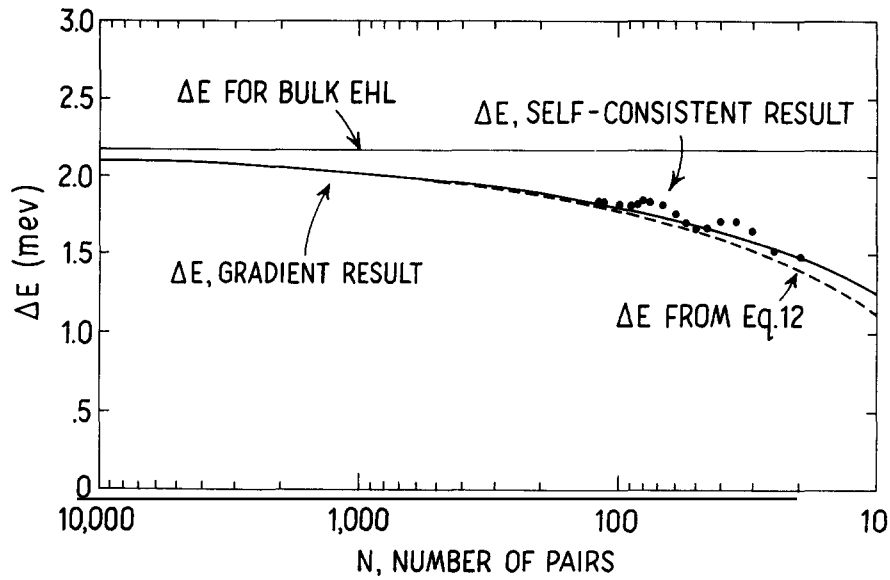dicate the uncertainty in the slope.

Figure 2. The gradient result for ΔE (solid line) compared to Eq. 12 (dashed line). The x's are the results of the self-consistent calculation. Their deviation from a smooth curve shows the importance of the shell effects in determining ΔE.
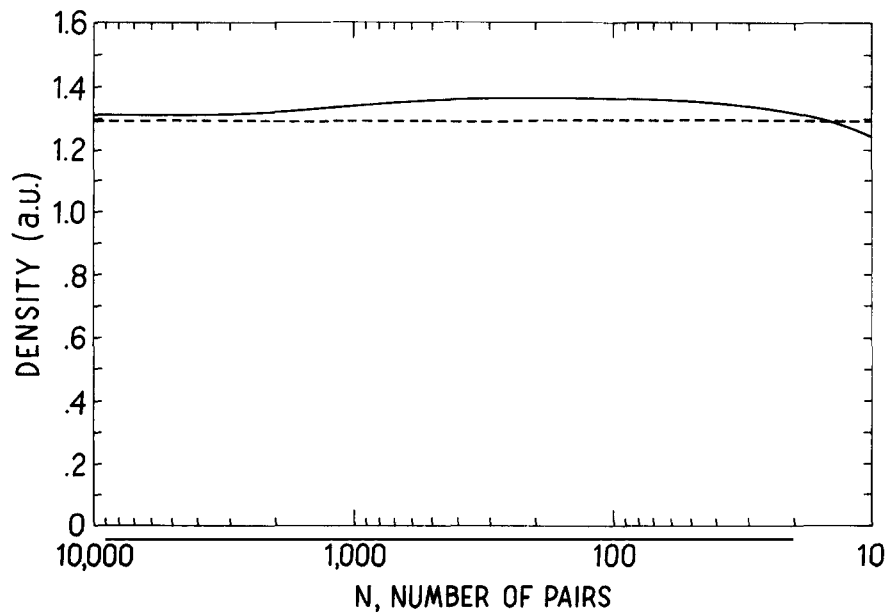

Figure 3. Variations of density at the center of the drop in the gradient expansion.

Here r_s is the radius of a sphere containing one pair at density n_0, $(4\pi r_s^3/3 = 1/n_0)$. If we assume that r_s and the coefficients of $N, N^{2/3}$, $N^{1/2}$ are relatively constant as a function of N, we can replace them by their limit as $N \rightarrow \infty$. Then we define a function F

$$F \equiv \frac{E_N - Ne_B\left(\frac{4\pi r_s}{3}\right)}{N^{1/3}} = (4\pi r_s)\sigma N^{1/3} + 8\pi r_s e_c \qquad (11)$$

We plot F versus $N^{1/3}$ and obtain σ and e_c as

shown in Fig. 1. The resulting value for the surface energy σ is $\approx 1.9 \times 10^{-4}$ ergs/cm^2. This is in acceptable agreement with a value of $\sigma = 1.6 \times 10^{-4}$ which can be obtained from the self-consistent surface calculation of Rose and Shore who considered the case of an EHL surface at a semi-infinite half-space.[5] The relevant comparison is with model B of that paper, when the Reinecke-Ying correction, $\Delta\sigma_s$, is subtracted. The value of the bending energy deduced from the above analysis is quite uncertain but is consistent with $e_c = 1.1 \times 10^{-10}$ ergs/cm obtained using the gradient expansion.

In Fig. 2, we plot a binding energy, ΔE, as a function of N. ΔE is defined as the total energy per pair minus the binding energy, e_{ex}, of the exciton (4.15 mev). The solid line gives the result for the gradient expansion. The self-consistent results are denoted by the crosses. The relative importance of shell effects in determining the binding energy can be seen in the scatter of the self-consistent results.

An interesting question is: how well can we predict the binding energy of small droplets knowing the properties of the large drop limits (N→∞)? Using Eq. 8 obtain (N→∞)

$$\Delta E = \varepsilon_b - \varepsilon_{ex} + 4\pi\bar{R}^2\sigma/N + 8\pi\bar{R}\,e_c/N \qquad (12)$$

Here $\bar{R}$ is the droplet radius determine using the density $\bar{n}_o$ of the bulk EHL. The first term on the right hand side is the bulk energy per pair. Eq. 12 gives essentially exact agreement with the results of the numerical calculation for N>150 and even agrees within 10% down to N=10. The small discrepancy for N<150 can be traced primarily to the fact that $8\pi\bar{R}e_c^N/N$ varies with N. The discrepancy would be removed if we had used e_c^N instead of e_c.

There has been some speculation concerning the possible compression of the EHD by the surface tension. Using a simple phenomenological model Benoit et al.[6] have predicted that substantial compression of the droplet might occur. However, in experimentally analyzing the effect of droplet size on the recombination luminescence, they found that the proposed effect apparently did not occur. In Fig. 3 we plot the gradient expansion result for the density at the center of the drop. We see that the droplet is only very slightly compressed, and has a maximum central density for a drop with about ∿100–200 pairs. For smaller numbers of pairs our theory predicts that the central density decreases. The results of the gradient expansion technique are only approximate for the density profile since the gradient expansion theory leaves out Friedel oscillations and related effects. Nonetheless, the results do indicate that there is no dramatic compression of droplets for a small number of pairs, in agreement with the experiments mentioned above.

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