SIZE EFFECTS IN SMALL ELECTRON-HOLE DROPS*

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The self-consistent formulation of density functional theory is used
to calculate the single-particle properties of electron-hole drop-
lets in Ge with between 10 and 120 pairs. Results are presented for
the recombination luminescence lineshape, the electron and hole
density profiles and the work function. As in the physics of the
nucleus there are strong effects associated with the filling of the
various electron and hole shells. In particular, the luminescence
line narrows and oscillates as N decreases for a drop with less than
120 pairs. If N = 70 the width is 70% of the bulk value; while for
N = 50 it is 80%. The density profiles and work functions for
different N are rather varied and show very strong shell effects.

I. Density functional theory has recently been applied to the study of small electron-hole drops[1] and bound multi-exciton complexes.[2,3] This paper continues the study of small electron-hole drops in unstrained Germanium at zero temperature. We emphasize here results which depend sensitively on the number of electron-hole pairs in the droplet for the range N=10 pairs to N=120 pairs.

As in the atomic nucleus, we may expect strong effects associated with the filling of the electron and hole energy levels. These shell effects can be seen in the luminescence radiation, the droplet density profiles and the work function. In order to simplify our study of these shell effects we have assumed that the complicated band structure of Germanium can be replaced by four spherical conduction bands and a single spherical valence band. We expect that the calculation should give a good idea of the nature of small droplets, and some of their interesting features, such as the general trend in energy level spacing and the relative importance of shell effects.

The structure of the paper is as follows. First we describe our calculational technique: the self consistent Kohn-Sham formulation of the density functional theory.[4] Next we describe the electron and hole energy level structure in section III. In IV results are presented for the work function; and density profiles are shown for the electrons and holes. We conclude with a discussion of the luminescence.

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

$$E[n_e(\vec{r}), n_h(\vec{r})] = T^e[n_e(\vec{r})] + T^h[n_h(\vec{r})]$$
$$+ \frac{1}{2} \int \frac{(n_e(\vec{r}) - n_h(\vec{r}))(n_e(\vec{r}') - n_h(\vec{r}'))d^3\vec{r}d^3\vec{r}'}{|\vec{r} - \vec{r}'|}$$
$$+ \int \varepsilon_{xc}(n_e(\vec{r}), n_h(\vec{r}))d^3\vec{r} \qquad (1)$$

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.[5] 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 the solving of the self-consistent Kohn-Sham equations which are written below for the electron component.

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

$$v^e_{eff}(r) =$$

$$-\int \frac{(n_h(r')-n_e(r')d^3r'}{|\vec{r'} - \vec{r}|} + \frac{d}{dn_e(r)} \, \varepsilon_{xc}(n_e,n_h)$$

$$(3)$$

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 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 states mass. The complicated valence 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 and the analogous equations for the holes are solved self-consistently, we obtain the kinetic energies T^e and T^h from

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

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.

We must in principle project out the center of mass motion of the droplet when performing a variational 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 center of mass). Hence the error in the energy per pair scales as $1/N^2$. For a single exciton, the error due to the center of mass motion is about one quarter of the exciton binding energy. For a drop with ten or more pairs, we expect the center of mass error to be less than .01 mev per pair.

Our spherical approximation to the band structure should give relatively good results for the total energy and density. It will also reveal the characteristic trends of spectroscopic quantities, such as the shifts and width of the luminescence line. However, the model's simplicity, leads to some errors. For example, we have an occupation of 2 for the S state of the holes. Symmetry indicates that the correct occupation must be four. Similarly the electron calculation ignores valley-orbit splitting. For these reasons we restrict our spectroscopic interpretation to general trends. Work is in progress to include the valence bands correctly and to take into account the small splitting in electron states.

III. The electron and hole single particle eigenenergies are determined in the self-consistent procedure by Eq.2. The occupation of the eigenstates is determined by finding that configuration which yields the lowest self-consistent total energy. For the entire range of N considered, the order of filling the electron levels follows the scheme $1s^8;2p^{24}$; $3d^{40}2s^8;4f^{56}3p^{24}; \ldots$. The superscript denotes the number of states available for occupation. It takes into account the eight fold degeneracy which is due to the spin and the four equivalent electron valleys. The electron (and hole) occupation schemes suggest the following description. For small drops the levels are given primarily by a harmonic oscillator level ordering. In writing out the ordering of energy levels above, we have set off by semi-colons those states which would be degenerate for a three dimensional harmonic oscillator. We find in our detailed calculations that these energy levels generally lie close together. Now we have to describe the way these major groupings are split. Consider a very large droplet: its effective potential is constant over the interior of the droplet and then rises abruptly at the surface. Hence it looks like a rather deep square well with rounded edges, and we should expect the level ordering to be that of a harmonic oscillator split by a square well like perturbation, which becomes stronger as N increases. This is precisely what is found. The ordering of the electron states is that of non-interacting fermions in an infinitely deep spherical square well.

The level filling scheme for the holes is the same for N≥24 with a degeneracy factor of two, i.e. $1s^2;2p^6;3d^{10}$ etc. For N<24 there are two exceptions to this ordering. First for N=23, the 4f and 3p levels are reversed. Also, we find that for 10<N<18, the order of the 2s and 3d levels are reversed. The origin of the level reversals may be due to the much higher degeneracy factor for the electrons. As a result they have a smaller orbital angular momentum than the holes. Consequently the electrons tend to pile up more density near the origin. The hole density follows this pile up in electron density. Hence the holes prefer lower ℓ-values than they would otherwise; for example, the reversal of the expected $3d^{10}2s^2$ ordering for values of N between 10 and 18.

IV. The radial density profiles of the electrons and holes are shown in Fig. 1 for several different size droplets. The quantum oscillations in these density profiles are spectacular, exceeding 100% of the bulk density in some cases. The density profile for N=120 indicates that the density is beginning to approach that expected for a large droplet. That is, there is a large bulk like region with a rather sharp fall off in density at $r=2.8a^*_B$, indicating the surface of the droplet.[6]

The work function to remove an electron and a hole from the drop with N pairs is shown in Fig. 2. Here the shell effects can be seen clearly. The change in the value of the work function correlates directly with the level
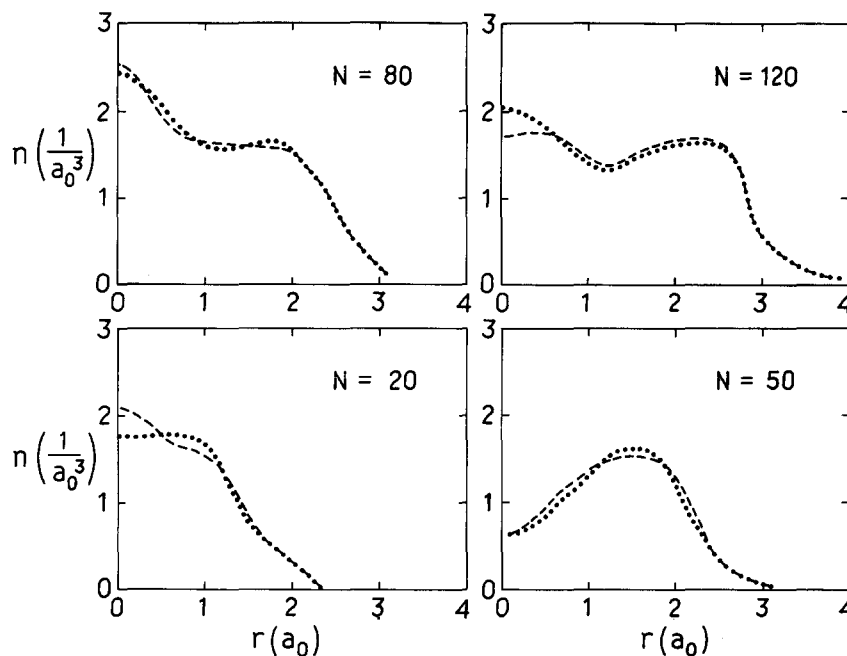
Fig. 1   Electron and hole density profiles. The _ _ _ line
is for holes and the . . . line is for electrons. Note
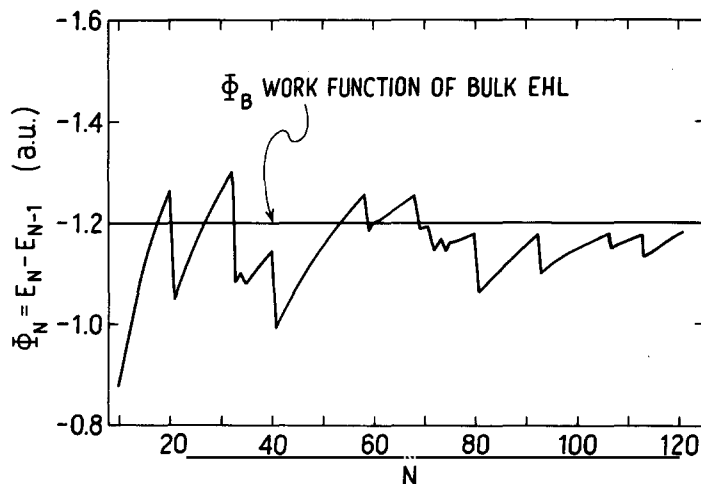the extremely large Fridel oscillations in the densities.

Fig. 2   The work function to remove a separated electron-hole
pair from a droplet. To obtain the work function to
remove an exciton from the droplet we must subtract the
exciton binding energy, .79 a.u.

scheme given in section III. The large changes
at N=32 and 80 are related to the closing of the
electron 2p and 2s levels respectively.

    V. The single particle occupations and
eigenenergies of the electrons and holes are
directly determined in our theory. The convo-
lution of these eigenspectra yields an approxi-
mate[7] luminescence spectrum which is shown in
Fig. 3 for N=19. The results are several groups
of sharp lines whose positions and heights
depend on N. If we compare this spectrum with
the smooth theoretical recombination line of the
bulk, we note several features. First the
harmonic oscillator nature of the spectrum is
evident: a pure harmonic oscillator potential
would give equally spaced lines without the
small splittings in Fig. 3. Also, the small
droplet line is shifted toward high energy and
the linewidth is reduced as compared to the
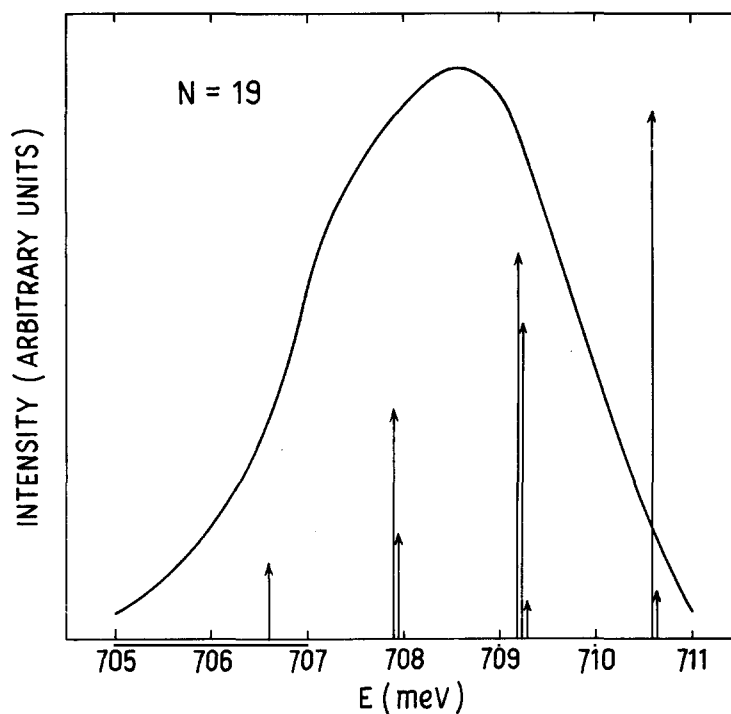large droplet case.

Fig. 3   The sharp lines indicate the calculated luminescence
          from a drop with 19 pairs. The grouping of the sharp
          lines and the approximately equal spacing of the groups
          indicate the harmonic oscillator like nature of the
          effective potential. The bulk luminescence is given for
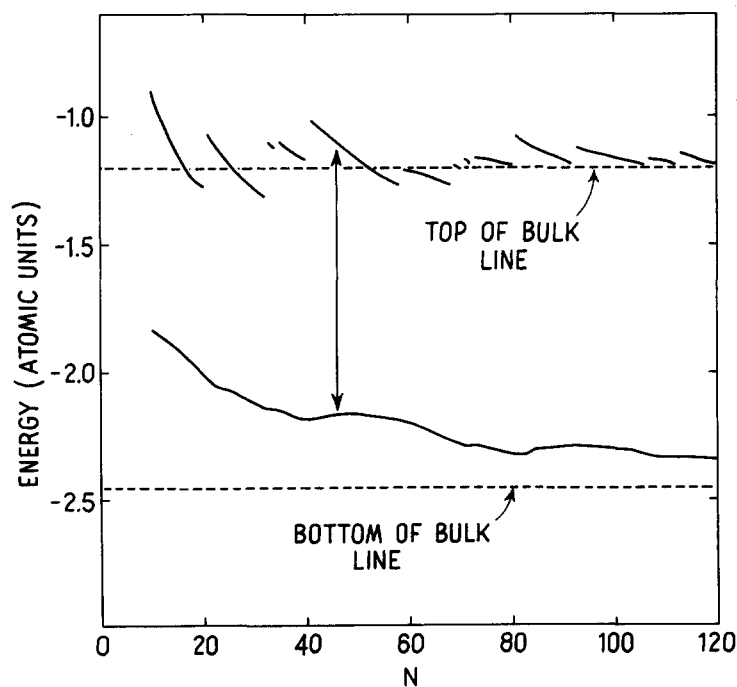   comparison.

Fig. 4   The position of the highest and lowest energy recombination
          lines with respect to the luminescence from a non-interacting
          pair, i.e. the indirect phonon assisted energy gap of Ge.

In order to give these results compactly we make some arbitrary assignments. For a given N we take the top of the recombination line to be that sharp line with least negative energy. Similarly we associate the bottom of the line with that sharp line which has the greatest negative energy. We plot these values for the top and bottom of the line in Fig. 4. Taking the linewidth to be the difference between the top and bottom of the line, we see that the linewidth decreases in an oscillating fashion as N decreases.

The variation of the top of the luminescence line with droplet size has been observed, and the shift has been used to estimate the surface tension of the electron hole liquid in Ge.[8] Fig. 4 shows that for droplets with N<120, the shell effects should make such observations very difficult to interpret. For a drop with N∼100 the shift in the top of the line is appoximately 0.1 a.u.* Hence the measurements related to surface tension should be made for much smaller observed shifts (as has indeed

been done by Benoit, et al.).[8] It should be remarked that even for larger drops, the interpretation of the lineshift in terms of surface energy could be complicated.

Perhaps the most interesting features of Fig. 3 are the narrowing of the overall luminescence band and the appearance of groups of sharp lines. As far as we know these effects have never been observed. Two factors would complicate such an observation. First, typical luminescence measurements have an energy resolution of 1-2 mev (see Fig. 3), and a measurement presumably includes a collection of many droplets with differing numbers of pairs, which would smear out the structure.

We would like to point out that the various qualitative features discussed above are expected to hold for the EHL in Si. In Si it may be easier to make measurements in the small droplet regime. We suggest that the EHL in Si is a good system in which to investigate the effects we have described here.

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6. We have used effective atomic units, $a_B^* = 177Å$ and a.u.* = 5.28 mev.

7. For a finite drop the intensity of the various sharp lines may be changed somewhat from the results obtained by a simple convolution of eigenvalues because the various electrons and holes are not uniformly distributed throughout the volume of the droplet.

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