Variational Approach to the Ground State of the Electron-Hole Liquid

Tapash Chakraborty[a] and P. Pietiläinen
Department of Theoretical Physics, University of Oulu, SF-90570 Oulu 57, Finland

(Received 20 April 1982)

In the many-body variational approach, accurate results are obtained for the ground-state properties of the isotropic electron-hole liquid. With the increase in hole mass, the system undergoes a transition to a state with ordered heavy particles. In the case of Ge under a large [111] strain, it is predicted that the metallic state is not stable relative to free excitons. The density dependence of e-h correlation obtained here compares favorably with the experimental estimates.

PACS numbers: 71.45.Gm, 05.30.Fk, 71.35.+z.

At low temperatures, the excitons (bound electron-hole pairs) in semiconductors condense into electron-hole drops.[1] Several authors[1-5] have studied the ground-state properties of e-h liquids in Ge and Si. Those studies indicate that the multiplicity of the bands and their anisotropy stabilize the drop. The complexity of the band structure can either be avoided by considering the isotropic band structure with nondegenerate electron and hole bands (model), or can be greatly simplified by applying a large uniaxial stress. In the case of a stress in the [111] direction in Ge one deals with a single conduction band and one valence band. The system, in the high-stress limit, closely resembles the model system and has received much attention theoretically[1-4] and experimentally.[6,7]

In the earlier studies of the e-h liquid in Ge[111] or in the model system, Brinkman *et al.*[1,2] (BRAC) used the random-phase approximation as modified by Hubbard,[8] while Combescot and Nozières[3] (CN) employed the Nozières-Pines interpolation scheme.[9] Vashishta, Bhattacharyya, and Singwi[4] (VBS) used a self-consistent scheme based on the theory of electron correlations by Singwi *et al.*[10]

For the single-component electron gas, the many-body variational approach has proved to be very powerful.[11] A comparison with the exact Green's function–Monte Carlo results[11,12] reveals that, in the metallic density range, the hypernetted-chain variational upper bound obtained in the Lado approach[11,13] is only a few millirydbergs above the *exact* ground-state energy and of the order of one millirydberg above the *exact* expectation value of the variational Monte Carlo scheme (Table III of Ref. 11). The upper-bound property was found to be preserved at all densities. Furthermore, from the optimization procedure, one obtains the correct short- and long-range behavior for the pair-correlation functions.[11,14]

The many-body variational approach has recently been generalized for binary boson mixtures.[14] A further generalization of this method for the very interesting system of the e-h liquid is thus highly desirable. Besides the accurate variational upper bound, the present method would provide accurate values for the enhancement factor $g_{eh}(0)$, which is the ratio of the electron density on the hole to the mean density. An accurate evaluation of $g_{eh}(0)$ is essential for an interesting study of the decay kinetics of e-h drops in uniaxially deformed semiconductors.[6,15] Accurate values for the ground-state energy are also needed to resolve the interesting question of the existence of the e-h liquid in Ge[111]. In the limit of very large strain in Ge[111], BRAC obtained a small binding ($\sim 0.07E_x$), relative to free excitons E_x. CN do not find any binding of the metallic state. VBS obtained $\sim 0.1E_x$ and concluded that the metallic state is definitely bound.

We begin with a trial function of the form

$$\Psi = F_{11}F_{22}F_{12}\Phi_1\Phi_2 \qquad (1)$$

for the ground state of an uniform system of electrons (index 1) and holes (index 2). The charge neutrality of the system requires that the partial densities of the two species are equal. In Eq. (1), $F_{\alpha\beta} = \prod_{ij} f_{\alpha\beta}(|\vec{r}_{\alpha,i} - \vec{r}_{\beta,j}|)$ are the symmetric correlation factors, Φ_1 and Φ_2 are the determinants of the plane-wave states for electrons and holes, respectively. In the Lado approach[11,13] the squared Slater determinant is replaced by $\exp\sum_{ij} u_{\alpha\alpha}{}^0(r_{ij})$. In this case, one can closely follow the method proposed in Ref. 14. The pair-correlation functions $g_{\alpha\beta}(r)$ are then obtained by solving the following Euler-Lagrange equations,[14]

$$[-(\hbar^2/m_{\alpha\beta})\nabla^2 + v_{\alpha\beta}(r) + W_{\alpha\beta}{}^B(r) + W_{\alpha\beta}{}^x(r)]g_{\alpha\beta}{}^{1/2}(r) = 0, \qquad (2)$$

where $v_{\alpha\beta}(r)$ represents the bare Coulomb interaction for the three particle pairs 11, 22, 12. The induced potentials for the bosonic part $W_{\alpha\beta}{}^{B}(r)$ are given in momentum space,[14] for $\alpha \neq \beta$, by

$$W_{\alpha\alpha}{}^{B}(k) = -[(\hbar^2k^2/4\rho)\{m_\alpha{}^{-1}(2S_{\alpha\alpha} + S_{\beta\beta}{}^2/D^2 - 3) + m_\beta{}^{-1}S_{\alpha\beta}{}^2/D^2\}],$$
$$W_{\alpha\beta}{}^{B}(k) = -[(\hbar^2k^2/4\rho)\{2m_{\alpha\beta}{}^{-1}S_{\alpha\beta} - S_{\alpha\beta}(m_\alpha{}^{-1}S_{\beta\beta} + m_\beta{}^{-1}S_{\alpha\alpha})/D^2\}],\quad m_{\alpha\beta}{}^{-1} = 0.5(m_\alpha{}^{-1} + m_\beta{}^{-1}). \tag{3}$$

Here, $S_{\alpha\beta}(k) - \delta_{\alpha\beta} = \rho\mathfrak{F}[g_{\alpha\beta}(r) - 1]$, where $\mathfrak{F}[f]$ denotes Fourier transform of f, ρ is the number density of electrons or holes, and $D(k) = S_{11}S_{22} - S_{12}{}^2$. The exchange parts of the induced potentials $W_{\alpha\beta}{}^{x}(r)$ are

$$W_{\alpha\beta}{}^{x}(r) = (\hbar^2\delta_{\alpha\beta}/4m_\alpha)[2\nabla^2u_{\alpha\beta}{}^{0}(r) + (\nabla u_{\alpha\beta}{}^{0})^2]. \tag{4}$$

A detailed study of the above equations for bosons, including the stability condition for the solutions, is given in Ref. 14.

We have solved the three coupled integro-differential equations for $g_{\alpha\beta}(r)$ using the linearization method of Ref. 14. In Fig. 1, we have plotted the three pair-correlation functions $g_{ee}(r)$, $g_{hh}(r)$, and $g_{eh}(r)$ for $m_h/m_e = 1$, 2, 10, and 50 at $r_s = 1$ (measured in units of exciton Bohr radius). As the hole mass increases, a hard-core-type behavior and an "overshoot" start developing in $g_{hh}(r)$, indicating that the system changes continuously to a state with ordered heavy particles. Figure 2 shows the enhancement factor as a function of r_s for $m_e/m_h = 1$ (solid line). Around $r_s = 2$, our values lie lower than those of VBS (dotted line). When compared with the case of one positron in the electron gas[16] (dashed line), based on the limiting case of the present method,[14,17] our values always lie lower. As Brinkman and Rice noted,[2] the electrons do not gain as much energy by clustering around the positrons as they would for a single positron. Therefore, on passing from one positron to the many-positron problem, the enhancement is reduced. Recent experimental estimates[6] for strained Ge indicate that $g_{eh}(0)$ increases rapidly with decreasing density. The behavior agrees qualitatively with our results.

In our calculation of the ground-state energy of the e-h liquid in Ge[111], we used the optically averaged masses[1,2] for electron and hole bands. The Hartree-Fock (HF) energy of the metallic state in Ge[111] can be written, using the results of the ellipsoidal bands,[3] as

$$\epsilon_{\rm HF} + 1.618/r_s{}^2 - 1.6594/r_s \tag{5}$$

expressed in units of exciton rydbergs. We have calculated the correlation energy with the assumption that the bands are isotropic with optically averaged masses. The relative simplicity of the band structure in Ge[111] allows us to do a scaling transformation[1,4] to that of an isotropic band. A reasonable estimate of the effect of anisotropy is also possible for the correlation energy.

In Fig. 3, we have plotted the ground-state energy (in units of exciton rydbergs) for Ge[111] as a function of r_s. The effect of anisotropy in the e-h bands is fully taken into account in the HF en-

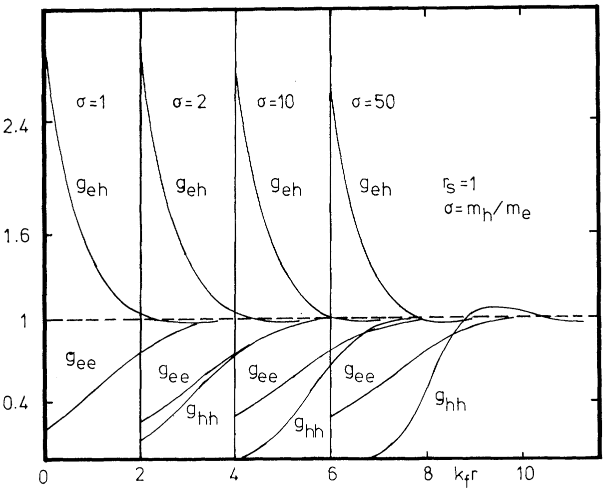

FIG. 1. Partial pair-correlation functions $g_{ee}(r)$, $g_{hh}(r)$, and $g_{eh}(r)$ vs $k_f r$ for $m_h/m_e = 1$, 2, 10, and 50 at $r_s = 1$.

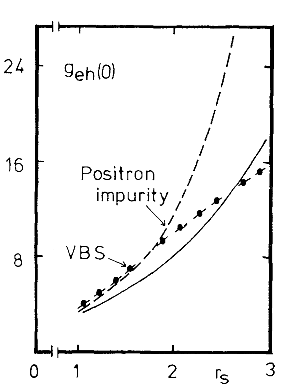

FIG. 2. The enhancement factor $g_{eh}(0)$ vs r_s for $m_h/m_e = 1$ (solid line), the VBS result (dotted line), and the case of positron impurity (dashed line).

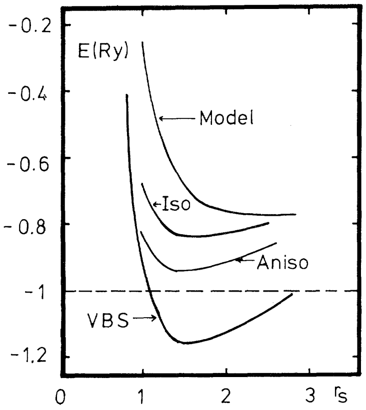

FIG. 3. Ground-state energy of Ge[111]. Model, Iso, and Aniso are the curves explained in the text. VBS: Ref. 4.

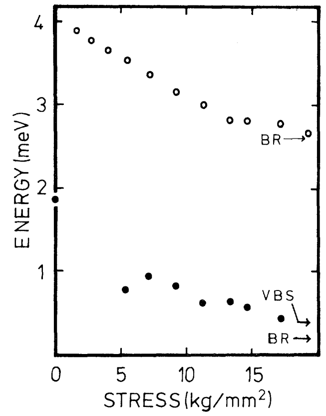

FIG. 4. Experimental results of Ref. 7 for the e-h drop binding energy φ (solid circles) and the free-exciton binding energy ϵ_x (open circles) vs uniform stress in [111] direction.

ergy contributions, but *not* in the correlation energy. The resulting curve (marked Iso) reveals the expected lowering of energy, when compared with the isotropic band model. However, taking the binding energy of an exciton[2] to be -1.002 Ry, we find that the metallic state is not stable relative to free excitons. As the curve is substantially above -1 Ry, it is highly unlikely that any improvements over the present scheme will lead to binding of the metallic state.

The major source of binding in Ge[111] might be the effect of *anisotropy in the correlation energy*. In Hubbard approximation this effect can be fully taken into account. This effect in Hubbard correlation energy[2,4] is now added to our total energy. The resulting curve is marked Aniso in Fig. 3, where the HF energy is exact. The VBS curve in Fig. 3 estimates the effect in the same way.

The experimental results[6,7] for Ge[111] indicate clearly that, on application of stress, the binding energy of the e-h drop decreases significantly with increasing stress along the [111] direction. In Fig. 4, we have plotted the experimental results of Feldman, Chou, and Wong[7] for the free-exciton binding energy ϵ_x and the e-h drop binding energy φ with respect to ϵ_x ($\varphi = |E| - \epsilon_x$). The free-exciton binding energy ϵ_x approaches a constant value of 2.6 ± 1.2 meV at higher stress,[7] close to the theoretical value of 2.65 meV in the high-stress limit.[2] The e-h drop binding, however, has the trend of decreasing with increasing stress.

Admittedly, the effect of anisotropy in the correlation energy is only an estimate in our present work. However, a stable e-h drop in Ge[111] would mean a large correction in our result. It is hardly conceivable that such a correction should come from the full anisotropic treatment in our work or from an improved scheme in the present variational approach. Therefore, within our scheme, we are led to predict that, in the limit of very large strain, the metallic phase probably disappears in Ge.

We wish to thank A. Kallio and L. J. Lantto for many helpful discussions. This work was supported in part by Nordisk Institut for Teoretisk Atomfysik and Teoreettisen Fysiikan Tutkimuslaitos, Helsingin Yliopisto.

---

[a] Present address: School of Physics and Astronomy, University of Minnesota, Minneapolis, Minn. 55455.

[1] For an excellent review, see T. M. Rice, Solid State Phys. 32, 1 (1977).

[2] W. F. Brinkman, T. M. Rice, P. W. Anderson, and S. T. Chui, Phys. Rev. Lett. 28, 961 (1972); W. F. Brinkman and T. M. Rice, Phys. Rev. B 7, 1508 (1973).

[3] M. Combescot and P. Nozières, J. Phys. C 5, 2369 (1972).

[4] P. Vashishta, P. Bhattacharyya, and K. S. Singwi, Phys. Rev. Lett. 30, 1248 (1973), and Phys. Rev. B 10, 5108 (1974).

[5] M. Inoue and E. Hanamura, J. Phys. Soc. Jpn. 35, 643 (1973).

[6] H.-h. Chou and G. K. Wong, Phys. Rev. Lett. 41, 1677 (1978); T. Ohyama, T. Sanada, and E. Otsuka, Phys. Rev. Lett. 33, 647 (1974); G. A. Thomas and Ya. E. Pokrovskii, Phys. Rev. B 18, 864 (1978).

[7] B. J. Feldman, H.-h. Chou, and G. K. Wong, Solid State Commun. 26, 209 (1978).

[8] J. Hubbard, Proc. Roy. Soc. London, Ser. A 243,

336 (1957).

[9] P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958).

[10] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. 176, 589 (1968); P. Bhattacharjee and K. S. Singwi, Phys. Rev. Lett. 29, 22 (1972).

[11] J. G. Zabolitzky, Phys. Rev. B 22, 2353 (1980).

[12] D. Ceperley, in *Recent Progress in Many-Body Theory*, edited by J. Zabolitzky, Lecture Notes in Physics Vol. 142 (Springer-Verlag, Heidelberg, 1981), and Phys. Rev. B 18, 3126 (1978).

[13] J. G. Zabolitzky, Adv. Nucl. Phys. 12, 1 (1981); F. Lado, J. Chem. Phys. 47, 5369 (1967).

[14] Tapash Chakraborty, Phys. Rev. B 25, 3177 (1982), and J. Low Temp. Phys. 48, 151 (1982), and Phys. Rev. B, to be published.

[15] J. Wagner, A. Forchel, W. Schmid, and R. Sauer, Solid State Commun. 42, 275 (1982); P. L. Gourley and J. P. Wolfe, Phys. Rev. B 24, 5970 (1981).

[16] P. Pietiläinen and A. Kallio, Phys. Rev. B, to be published.

[17] J. C. Owen, Phys. Rev. Lett. 47, 586 (1981).

Evidence for Solitons in Conducting Organic Charge-Transfer Crystals

A. J. Epstein, J. W. Kaufer,[a] H. Rommelmann, I. A. Howard, and E. M. Conwell
Xerox Webster Research Center, Rochester, New York 14644

and

Joel S. Miller
Occidental Research Corporation, Irvine, California 92713

and

J. P. Pouget and R. Comès
Laboratoire de Physique des Solides, associé au Centre National de la Recherche Scientifique,
Université Paris-Sud, F-91405 Orsay, France

(Received 1 June 1982)

Magnetic susceptibility of (N-methylphenazinium)$_x$(phenazine)$_{1-x}$(tetracyanoquinodimethanide) [$(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$] shows the formation of defect states for $0.5 \lesssim x \lesssim 0.54$. Diffuse x-ray scattering and g-value studies indicate that these defects are solitons formed in the highly correlated quasi-one-dimensional system that occurs near the quarter-filled–band limit. A model for the decrease in the energy gap in the presence of large numbers of solitons is proposed to explain the excess conductivity.

PACS numbers: 71.50.+t, 71.30.+h, 72.60.+g, 72.80.Le

Quasi-one-dimensional (1D) conductors have been widely studied, both as crystalline charge-transfer salts, e.g., salts of TCNQ, and (doped) polymers, e.g., polyacetylene, $(\mathrm{CH})_x$.[1] The proper description of the electronic ground state of 1D conductors with nearly commensurate charge concentration (i.e., number of charges per unit cell close to a rational fraction) has been a central issue in the field. The suggestion[2,3] that a small excess or deficit of charge relative to the commensurate state is accommodated in $(\mathrm{CH})_x$ by the formation of solitons with charge $\pm e$, where e is the charge on the electron, is now well supported by experimental evidence.[1] Recent theoretical studies of highly correlated 1D charge-transfer salts near the quarter-filled-band limit have predicted the existence of solitons with fractional charge $\pm e/2$.[4] We report here the results of an experimental and theoretical study of such a salt, $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}$TCNQ with $x \simeq 0.5$, as a function of the concentration of conduction electrons. Our magnetic and diffuse x-ray scattering results are a direct demonstration that solitons are experimentally realized in charge-transfer salts. Effects of these solitons upon the temperature-dependent conductivity, $\sigma(T)$, are observed and can be understood within a model of a decreased gap caused by the presence of the solitons. The concentration regime for soliton formation is identified.

The system studied is based upon (NMP)(TCNQ), and is achieved by substituting neutral phenazine, Phen^0, for up to 50% of the NMP.[5,6] The Phen^0 is of similar size, shape, and polarizability to