

Electron-hole liquid as a true ground state

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Electron-hole-liquid (EHL) theory is shown to predict a first-order semiconductor-to-semimetal phase transition at a critical value of the fundamental (indirect) energy gap with a finite minimum value of the band overlap in the semimetallic phase. The consistency of this result with density-functional theory is discussed. The theory is applied to ScN. The ground-state density of the EHL is computed to be lower than 10^{20} cm^{-3} , which compares well with the smallest observed density of free carriers in this compound.

The electron-hole liquid (EHL) has been observed in a wide variety of semiconductors over the last 15 years, and the experimental binding energies and equilibrium densities are in good agreement with theoretical estimates based on the effective-mass approximation for electrons and holes.¹ In all materials considered so far the indirect band gap Δ for electronic excitations is considerably larger than the EHL binding energy E_B , and the system has to be excited by a laser beam in order for the new phase to appear. The number N of electron-hole pairs (EHP) is determined by the light intensity, and the EHL condenses to the equilibrium density by forming droplets surrounded by a gas of excitons and biexcitons. Within the droplets the energy gap is depressed with respect to its value in the absence of free carriers by the $\sim \mathbf{k}$ -independent exchange-correlation self-energy of the excited electrons and holes.¹ This suggests that, for Δ below a critical value Δ_{c1} , the system will spontaneously form an EHL to lower its ground-state energy.² Δ_{c1} can be obtained from the condition that the energy E_f for the EHL formation has to be zero or negative:

$$0 \geq E_f = N \left[\Delta + E_G \left(\frac{N}{\Omega} \right) \right], \quad (1)$$

where $E_G(N/\Omega)$ is the ground-state energy per EHP in the EHL phase as a function of the density N/Ω (Ω = volume). There are two cases to distinguish: Inequality (1) has only the solution $N=0$, as long as $\Delta > E_B$, where E_B is the EHL binding energy per EHP, defined as the negative of the minimum of the function $E_G(N/\Omega)$. But when the binding energy equals Δ , Eq. (1) also has the solution $\Delta = -E_G(N/\Omega)$, which corresponds to nonvanishing N ; the EHL phase is now stable and $\Delta_{c1} = E_B$. At Δ_{c1} , the electron-hole density will jump discontinuously from zero to the finite EHL ground-state density; this nonanalyticity is, in terms of Δ , a first-order semiconductor-semimetal transition.³ The band gap changes from the positive "upper critical value" Δ_{c1} to a negative "lower critical value" Δ_{c2} , with the implication that the real band gap (or overlap) cannot lie within the interval $[\Delta_{c2}, \Delta_{c1}]$.

The standard *ab initio* methods of band-structure calculation rely on density-functional theory, and one may wonder whether or not this theory is capable of reproducing the sudden change in ground-state character described above. The answer is yes,⁴ and the discontinuity is due to the

nonanalyticity of the *exact* exchange-correlation energy functional $E_{xc}[n]$, which also accounts for the fact that the density-functional ground-state formalism (DFGS) embodied in the Kohn-Sham equations is incapable of yielding the correct value for Δ .⁵ Experience shows that, for classical semiconductors the DFGS with the local-density approximation (LDA) for exchange and correlation typically underestimates the fundamental band gap by a factor of 2.⁶ In the opposite limit of a large overlap, self-consistent calculations for metals show that the predictions of DFGS in the LDA are rather accurate. As $\Delta_{\text{DFGS}}^{\text{LDA}}$ is reduced from these two extremes, the LDA, which makes $E_{xc}[n]$ a continuously differentiable functional of the density may produce arbitrarily small band gaps and overlaps. This feature makes it impossible to estimate the charge carrier concentration in very-narrow-gap (overlap) semiconductors (semimetals) using the band-structure approach. In what follows, we shall combine information from a self-consistent band-structure calculation, EHL theory, and optical experiments to obtain that quantity.

The total number N of EHP in the EHL phase is always adjusted in such a way that the total energy E of the solid is a minimum:

$$\frac{\partial E}{\partial N} = 0. \quad (2)$$

For E , we make the following simple ansatz for small N :

$$E = E^0 + N \Delta_{\text{DFGS}}^{\text{LDA}} + N E_G \left(\frac{N}{\Omega} \right),$$

where E^0 (independent of N) is the LDA density-functional energy, from which (for $\Delta_{\text{DFGS}}^{\text{LDA}} < 0$) the terms that will be reincluded as part of the EHL contribution have been subtracted. With this ansatz, Eq. (2) becomes

$$\Delta_{\text{DFGS}}^{\text{LDA}} + \mu \left(\frac{N}{\Omega} \right) = 0, \quad (3)$$

where $\mu(N/\Omega)$ is the chemical potential of the EHL:

$$\mu \left(\frac{N}{\Omega} \right) = E_G \left(\frac{N}{\Omega} \right) + \frac{N}{\Omega} \frac{\partial E_G}{\partial (N/\Omega)}.$$

Equation (3) should yield an upper bound to the true carrier density. This conclusion is obvious for the semiconductor

($\Delta > 0$) since, as discussed above, the actual excitation gap is larger than that resulting from the ground-state calculation. In the semimetallic ($\Delta < 0$) case, we argue that the part of the exchange-correlation self-energy appearing in μ is already present in Δ_{DFGS}^{DA} so that the ground-state calculation overestimates the overlap in the absence of EHL effects. We conjecture that the equilibrium density of the EHL obtained with Δ_{DFGS}^{DA} smoothly approaches the exact density from above as the system becomes truly metallic. The main problem here resides in the justification of Eq. (3) for the total energy of the crystal. A reasonable criterion for using this ansatz would be $\hbar\omega_p \ll \Delta_{DFGS}^{direct}$ where ω_p is the EHL plasma frequency screened by interband transitions, and Δ_{DFGS}^{direct} is the smallest direct gap produced by the band-structure calculation.

In the following, we shall illustrate our method by applying it to scandium nitride. ScN crystallizes in the rocksalt structure, with a room-temperature lattice constant of 4.50 Å.⁷ Band-structure calculations^{8,9} predict it to be a semimetal with an overlap between valence and conduction bands of ≈ 6 mRy. As seen in Fig. 1, the maximum of the valence band is a threefold-degenerate Γ_{15} level, and the conduction band has three equivalent anisotropic minima at the point X of the Brillouin zone. We fit the band curvatures by the standard effective-mass formulas,^{10,11} and eliminate the warping of the valence bands as in Ref. 1 by going over to the spherical model Hamiltonian of Baldereschi and Lipari,¹² which leads to a doubly degenerate band of heavy holes and a nondegenerate band of light holes. Their masses, m_H and m_L , and those of the electrons, $m_{||}$ and m_{\perp} , are listed in Table I.

The calculation of the ground-state energy of the EHL proceeds as usual. The unit of length is the excitonic Bohr radius $a_x = \epsilon_{\infty} \hbar^2 / m_0 e^2$ and the unit of energy is the excitonic Rydberg $E_R = e^2 / 2\epsilon_{\infty} a_x$, where ϵ_{∞} is the rigid-lattice dielectric constant in the absence of free carriers, and the optical mass m_0 is obtained as follows:

$$\begin{aligned} 1/m_0 &= 1/m_{0e} + 1/m_{0h} , \\ 1/m_{0e} &= 1/3(1/m_{||} + 2/m_{\perp}) , \\ 1/m_{0h} &= 1/3(1/m_L + 2/m_H) . \end{aligned} \quad (4)$$

In these reduced units, the kinetic energy per electron-hole

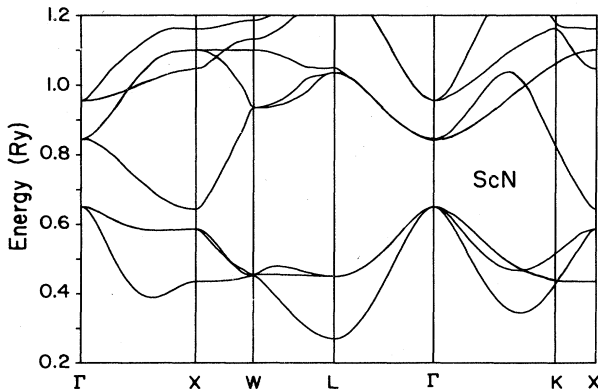


FIG. 1. Self-consistent band structure of ScN (Ref. 9).

TABLE I. Bare (first row) and polaron (second row) effective masses for electrons and holes in ScN. The bare Luttinger (Ref. 11) parameters for the holes are $\gamma_1=2.527$, $\gamma_2=0.692$, and $\gamma_3=0.221$.

$m_{ }$	m_{\perp}	m_H	m_L
1.550	0.130	0.585	0.240
1.568	0.131	0.608	0.253

pair is equal to

$$E_K = \frac{2.2099}{r_s^2} \left(\frac{m_0}{m_H [2 + (m_L/m_H)^{3/2}]^{2/3}} + \frac{m_0}{3^{2/3} (m_{||} m_{\perp}^2)^{1/3}} \right) , \quad (5)$$

where r_s is related to the density of electron-hole pairs by $4/3\pi(r_s a_x)^3 = n^{-1}$. In the rigid lattice, there are two more contributions to E_G , namely, the exchange and the correlation energy, the sum of which has recently been parametrized by Vashishta and Kalia¹³ in the form

$$E_{xc} = \frac{a + br_s}{c + dr_s + r_s^2} ,$$

with $a = -4.8316$, $b = -5.0879$, $c = 0.0152$, and $d = 3.0426$. The ground-state energy of the EHL obtained by adding Eqs. (4) and (5) is displayed in Fig. 2, together with the corresponding chemical potential. With the value of 10.8 for ϵ_{∞} quoted by Harbeke, Meier, and Dismukes,¹⁴ and a band overlap Δ_{DFGS} of $-6.06 E_R$, the total chemical potential vanishes at $r_s = 0.293$, which leads to a ground-state density of $1.0 \times 10^{20} \text{ cm}^{-3}$.

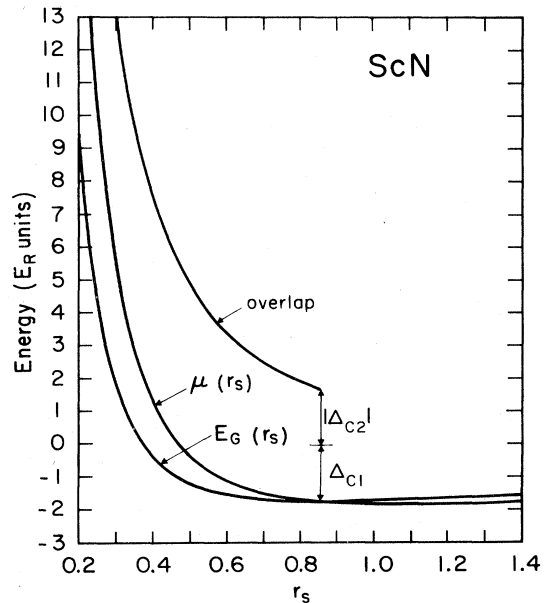


FIG. 2. Ground-state energy and chemical potential plotted against r_s for ScN in the rigid-lattice approximation. The unit of length is $a_x = 45.0$ Å and the unit of energy is $E_R = 14.8$ meV. Also shown is the overlap in the effective-mass approximation, as a function of r_s , with the two critical values of the gap: Δ_{c1} and Δ_{c2} .

In a polar semiconductor, the coupling of the charge carriers to the LO phonons is known to stabilize the EHL.¹ In the ϵ_0^* approximation, valid at low densities, this effect is accounted for by replacing ϵ_∞ by ϵ_0 , the static dielectric functions, in the Coulomb interaction between the carriers, and allowing for a shift of the bottom of the electron and hole bands and a renormalization of the electron and hole masses as given by the intermediate coupling polaron theory.^{15,16} The strength of the interaction is measured by the dimensionless coupling constant:

$$\alpha = \frac{e^2}{\hbar} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left(\frac{m}{2\hbar\omega_{LO}} \right)^{1/2},$$

where m is the free-electron mass. Since no information is available on ϵ_0 and ω_{LO} in ScN, we have used the phonon spectrum of TiC to obtain these quantities.¹⁷ Owing to the screening by the free carriers, the LO-TO splitting vanishes at the Γ point. Away from the center of the Brillouin zone, however, it becomes apparent again, and we can deduce the following estimates for the LO and TO frequencies: $\hbar\omega_{LO} \approx 79$ meV, $\hbar\omega_{TO} \approx 67$ meV, which, when inserted in the Lyddane-Sachs-Teller relationship¹⁸ yield a value ≈ 15 for the static dielectric constant. With these parameters, we find that, in the ϵ_0^* approximation, the chemical potential vanishes at the same density as in the rigid lattice, within our numerical accuracy. Since the two models represent two extreme situations, we expect the true ground-state density to be rather close to, but smaller than 10^{20} cm⁻³. The corresponding screened plasma frequency is $\hbar\omega_p \approx 0.27$ eV, which is about one-third of Δ_{Dirac} . Our results are summarized in Table II.

A quantitative comparison of our results with experiment

TABLE II. Equilibrium density, ground-state energy, electron and hole Fermi energies for the electron-hole liquid in ScN. First row, rigid lattice, second row, ϵ_0^* approximation.

n_0 (cm ⁻³)	$E_G(n_0)$ (meV)	E_F^e (meV)	E_F^h (meV)
1.0×10^{20}	-57	129	80
1.0×10^{20}	-59	126	72

is hampered by the apparent impossibility of growing crystals of ScN without vacancies¹⁹ or impurities⁶ acting as donors. As a consequence, the Hall-effect measurements of Ref. 7 lead to n -type carrier densities varying between 8.6×10^{19} and 4.7×10^{21} cm⁻³, depending on the sample preparation conditions. By fitting infrared reflectivity data to a Drude formula and using the values of Ref. 7 for n_{eff} , Harbeke *et al.*¹⁴ find an optical mass between $0.1m$ and $0.2m$ at the lowest carrier concentrations. Our calculation yields $0.13m$, which suggests that in the low density limit n_{eff} is close to the true n , the latter being remarkably well predicted by our theory.

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