BEC–BCS transition in excitonic systems

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Abstract. We consider quantum condensation in the electron–hole plasma of highly excited semiconductors. A theoretical approach applying the concept of time long range order in the framework of real-time Green’s functions is presented and non-equilibrium generalizations of the basic equations of quantum condensation are derived. For the quasi-equilibrium case, we solve the coupled system of number and gap equations in ladder approximation for a statically screened Coulomb potential. The resulting phase boundary shows a smooth crossover from BEC to BCS.

1. Introduction
In this paper we consider quantum condensation in electron–hole plasmas (EHPs) in excited semiconductors. Quantum condensation occurs in Bose systems well-known as Bose–Einstein condensation (BEC) and in Fermi systems as condensation of Cooper pairs into the BCS state. In this connection the question arises whether there are systems with both types of condensation. The answer is clear: BEC as well as BCS-type condensation may be expected in Fermi systems with Bose-like bound states, e.g., in

(i) nuclear matter [1]: \( p + n \rightleftharpoons D^+ \)
(ii) spin polarized hydrogen [2]: \( e + p \rightleftharpoons H \)
(iii) Fermi atoms in traps, currently intensively in the discussion [3, 4]: \( A + A \rightleftharpoons A_2 \)
(iv) EHPs in semiconductors [5, 6, 7]: \( e + h \rightleftharpoons X \)

The properties of an EHP are well investigated, see, e.g., Refs. [8, 9, 10]. Of particular interest is the formation of bound states, the excitons \((X)\). The thermodynamic equilibrium is connected with an ionization equilibrium \( e + h \rightleftharpoons X \) [11]. A special feature of the EHP is the screening of the Coulomb interaction and, therefore, a lowering of the coupling with increasing density. Due to various many-particle effects like self-energy and Pauli blocking one observes a lowering of the continuum edge (band gap renormalization) and, therefore, a lowering of the ionization energy [12]. Finally, at vanishing ionization energy, a breakup of the bound states at a certain density occurs referred to as Mott effect.

Some important properties of the EHP may be explained in the density–temperature \((n–T)\) plane, see Fig. 1. Here, in a schematic presentation, the border of the Bose condensation of ideal Bose particles as well as curves of constant degree of ionization are drawn. Due to the special behavior of these curves, the \(n–T\) plane is divided roughly into an area without bound states, i.e., a high-density \(e–h\) liquid (where also a phase of hole crystallization can occur, cf. [13]) and an area with bound states. Here, a partially ionized plasma with a strong dominance of excitons (and, possibly, biexcitons and trions) at lower temperatures may be found.
Since the excitons behave approximately like composite Bose particles, BEC in the region \( n\lambda^3 > 2.61 \) \([\lambda \text{ is the thermal de Broglie wavelength, } \lambda^2 = \frac{2\pi\hbar^2}{(mk_BT)}]\) may be expected if the chemical potential reaches the exciton 1s ground state energy \([14, 15, 16, 17]\). At higher densities, the region of BEC of excitons is, of course, limited by the Mott transition. However, we underline that the vanishing of the excitons does not imply a disappearance of the condensed phase. As proposed by Keldysh and Kopaev \([18]\) and others \([19, 20, 21]\), in the high-density highly degenerate \(e^-h^+\) liquid the formation of weakly bound cooperative Cooper pairs of electrons and holes and their Bose condensation to a BCS state may be expected. The whole condensed phase is sometimes referred to as excitonic insulator \([7]\).

The exciton gas as a system of interacting Bose-like particles implies the description as an interacting Bose gas. The latter one has been investigated in several “classical” papers \([22]\) as well as in more recent works (see, e.g., \([23]\)). It has further interesting physical properties like the occurrence of superfluidity \([24, 25]\). In the present work, however, the excitons are assumed to be noninteracting particles.

![Figure 1](image_url)

**Figure 1.** Example for a density–temperature plane. Parameters of germanium (Ge) are used.

An interesting problem is now the crossover from the BEC to the BCS state. It was shown by Eagles \([26]\) and by Leggett \([27]\) and generalized and extended to finite temperatures by Nozières and Schmitt-Rink \([5]\) that the crossover from the BEC to the BCS regime is smooth, despite the fact that the limits of BCS state and BEC of excitons are physically quite different. This is a general behavior of Fermi systems with Bose-like bound states and has been the subject of many papers mostly for Fermi atoms interacting via a contact potential.

While the physics of the interacting exciton gas (BEC of excitons, superfluidity etc.) is an intensely investigated field (see, e.g., \([25]\)), for the BEC–BCS crossover in the EHP there exist only few papers. In spite of the fundamental importance of Ref. \([5]\), the special features of Coulomb systems mentioned above are not taken into account. Moreover, a separable potential was assumed. Further investigations to the crossover problem in the EHP have been carried out in Refs. \([6, 7]\). The first paper is restricted to the optical behavior at the crossover and the second one considers the crossover for Coulomb systems more in detail but a simultaneous consideration of the density is missing. In recent publications \([28]\) we elaborated a real-time Green’s functions approach to quantum condensation which is the basis of the following considerations.
2. Theory and basic relations

A convenient quantity for the unified theoretical description of quantum condensation is the real-time two-particle Green’s function defined on the two-time Keldysh contour by

\[ G_{ab}(12,1'2') = \frac{1}{(i\hbar)^2} \left\langle T_C \{ \Psi_a(1)\Psi_b(2)\Psi_b^\dagger(2')\Psi_a^\dagger(1') \} \right\rangle \quad (1 = \{r_1,t_1,s_1^{(3)}\}) \]

where \( T_C \) is the time ordering operator on the contour.

The two-particle Green’s function describes two-particle bound and scattering states and is a solution of the Bethe–Salpeter equation (BSE),

\[ \int d\vec{t} G_a^{-1}(1,\vec{t})G_{ab}(\vec{t}2,1'2') - i\hbar \int d\vec{t} d\vec{t}' G_b(2,3)W_{ab}(13,\vec{t}\vec{t}')G_{ab}(\vec{t}2,1'2') = G_b(2,2')\delta(1 - 1') \]

(2)

Here, \( W_{ab} \) is an effective two-particle interaction. In the following, we apply the so-called \( V^s \) approximation,

\[ W_{ab}(12,\vec{t}\vec{t}) = V^s_{ab}(1,2)\delta(1 - \vec{t})(2 - \vec{t}) \],

(3)

where \( V^s \) is the screened Coulomb potential.

In addition we need the Dyson equation for the determination of the one particle Green’s function

\[ \int d\vec{t} \left[ G_a^{-1}(1,\vec{t}) - \Sigma_a(1,\vec{t}) \right] G_a(\vec{t},1') = \delta(1 - 1') . \]

(4)

Now the important question arises: What is the signal of quantum condensation in terms of the two-particle Green’s function?

It can be shown [28] that quantum condensation occurs if \( G_{ab} \) has the structure

\[ G_{ab}(12,1'2') = \hat{G}_{ab}(12,1'2') + C_{ab}(12,1'2') , \]

(5)

where the normal phase term \( \hat{G}_{ab} \) vanishes if the difference of all primed and all unprimed variables tends to infinity,

\[ \lim_{\{t_1,t_2\} \rightarrow \infty} \hat{G}_{ab}(12,1'2') = 0 \]

(6)

and the time long range order (TLRO) contribution \( C_{ab} \) does not vanish in this limit but factorizes into the functions \( F_{ab} \) and \( F^s_{ab} \), i.e.,

\[ \lim_{\{t_1,t_2\} \rightarrow \infty} C_{ab}(12,1'2') \neq 0 , \quad C_{ab}(12,1'2') = G_{ab}(12)F_{ab}(1'2') . \]

(7)

Since \( G_{ab} \) is a solution of the BSE (2), \( F_{ab} \) must be a solution of the homogeneous BSE

\[ \int d\vec{t} G_a^{-1}(1,\vec{t})F_{ab}(\vec{t}) - \int d\vec{t} G_b(2,\vec{t})\Delta_{ab}(\vec{t}) = 0 . \]

(8)

Here, the important gap function is introduced, which is fundamental for the description of the condensate,

\[ \Delta_{ab}(\vec{t}) = i\hbar V^s_{ab}(1,2)F_{ab}(\vec{t}) . \]

(9)
The TLRO contribution in $G_{ab}$ induces TLRO terms in all quantities which are connected with the two-particle Green’s function, especially in the self-energy

$$
\int d\bar{t} \Sigma_a(1, \bar{1})G_a(\bar{1}, 1') = \sum_b \int d2V_{ab}(1 - 2)G_{ab}(12, 1'2^+) \\
= \int d\bar{t} \Sigma_a^{HF}(1, \bar{1})G_a(\bar{1}, 1') + \sum_b \int d2V_{ab}^*(1, 2)\Pi_{ab}(12, 1'2^+) \tag{10}
$$

with $\Sigma_a^{HF}$ being the Hartree–Fock self-energy and $\Pi_{ab}$ the polarization function.

The self-energy with TLRO is given by

$$\Sigma_a(1, 1') = \hat{\Sigma}_a(1, 1') + \Sigma_a^{LRO}(1, 1'), \tag{11}$$

$$\int d\bar{t} \Sigma_a^{LRO}(1, \bar{1})G_a(\bar{1}, 1') = \int d2\Delta_{ab}(12)\Phi_{ab}^*(1'2^+) \tag{12}$$

Therefore, the Dyson equation on the Keldysh contour $C$ including the quantum condensate takes the form

$$\left[ i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2 \nabla^2}{2m_a} + \epsilon_a \right] G_a(1, 1') - \int d\bar{t} \left[ \hat{\Sigma}_a(1, \bar{1}) + \Sigma_a^{LRO}(1, \bar{1}) \right] G_a(\bar{1}, 1') = \delta(1 - 1'), \tag{13}
$$

where $\epsilon_e - \epsilon_h = \epsilon_g$ is the energy gap.

From the considerations so far, we obtain the following conclusion:

**TLRO occurs if the coupled system of Dyson equation (13) and homogeneous BSE (8) has a solution.**

Let us consider the consequences of TLRO:

(i) Obviously, spatial off-diagonal long range order (ODLRO) [29, 30] as an important property of quantum condensation follows from TLRO. ODLRO is a property of the reduced density matrix,

$$g_{ab}(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}'_1\mathbf{r}'_2; t) = \hat{g}_{ab}(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}'_1\mathbf{r}'_2; t) + \Phi_{ab}(\mathbf{r}_1\mathbf{r}_2, t)\Phi_{ab}^*(\mathbf{r}'_1\mathbf{r}'_2), \tag{14}$$

where $\Phi_{ab}$ is the macroscopic wave function. ODLRO follows from TLRO since the two-particle density matrix is given by

$$g_{ab}(t_1 = t_2 = t'_1 = t'_2) = g_{ab}; \quad \Phi(\mathbf{r}_1\mathbf{r}_2, t_1) = i\hbar F_{ab}(12)|_{t_1=\tau_2} \tag{15}$$

(ii) In many cases it is more convenient to use instead of the two-particle Green’s function the T-matrix. The T-matrix is connected with $G_{ab}$ by the relation $T_{ab} = V_{ab}^* + V_{ab}^*G_{ab}V_{ab}^*$ and, therefore, has a TLRO term, too,

$$T_{ab}(12, 1'2') = \hat{T}_{ab}(12, 1'2') + \frac{1}{i\hbar}\Delta_{ab}(12)\Delta_{ab}^*(1'2'). \tag{16}$$

(iii) In the equilibrium case, Kwok and Schultz [31] have shown that TLRO modifies the spectral representation as follows

$$G_{ab}(\omega) = A_{ab}(\omega) \frac{\mathcal{P}}{e^{\beta(\hbar\omega - \mu_b - \mu_a)} - 1} + 2\pi\delta(\hbar\omega - \mu_b - \mu_a) F_{ab} F_{ab}^*, \tag{17}$$

$$\tilde{T}_{ab}(\omega) = 2\text{Im} T_{ab}(\omega) \frac{\mathcal{P}}{e^{\beta(\hbar\omega - \mu_b - \mu_a)} - 1} + 2\pi\delta(\hbar\omega - \mu_b - \mu_a) \Delta_{ab} \Delta_{ab}^*. \tag{18}$$
(iv) Finally, if we take into account the expression for $\Sigma^{LRO}$, Eq. (11), Dyson equation (13) and homogeneous BSE (8) are equivalent to the non-equilibrium Gorkov equations for $G_a$ and $F_{ab}$,

\[
\begin{align*}
\left[ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2 \nabla^2}{2m_a} + \epsilon_a \right] G_a(1,1') &= \int d\bar{\Gamma} \hat{\Sigma}_a(1,\bar{\Gamma}) G_a(\bar{\Gamma},1') - \int \frac{d\bar{\Gamma} \Delta_{ab}(\bar{\Gamma}) F_{ab}^R(1')}{\bar{\Gamma}} = \delta(1-1') \, , \quad (19) \\
\left[ i\hbar \frac{\partial}{\partial t_1} - \frac{\hbar^2 \nabla^2}{2m_b} - \epsilon_b \right] F_{ab}^R(1') &= \int \frac{d\bar{\Gamma} \hat{\Sigma}_b^R(1',\bar{\Gamma}) F_{ab}^A(\bar{\Gamma})}{\bar{\Gamma}} - \int \frac{d\bar{\Gamma} \Delta_{ab}^R(\bar{\Gamma}) G_a(\bar{\Gamma},1)}{\bar{\Gamma}} = 0 \, . \quad (20)
\end{align*}
\]

The self-energy of the normal phase will be considered in the following in screened ladder approximation [32]

\[
\hat{\Sigma}_a(1,1') = \pm i\hbar \sum_b \int d2d2 \left[ \hat{T}_{ab}(12,1'2) \pm \delta_{ab} \hat{T}_{ab}(12,21') \right. \\
\left. - V_{ab}^S(1,2) G_a(1,1') G_b(2,\bar{2}) \right] G_b(\bar{2},2) \, . \quad (21)
\]

Equations (19,20) are the basic equations for the description of the non-equilibrium behavior of a quantum many-particle system including the quantum condensate. From Eqs. (19,20), by time specialization on the Keldysh contour, there follow Kadanoff–Baym like equations for the correlation functions $F_{ab}^R$

\[
\begin{align*}
\left[ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2 \nabla^2}{2m_a} + \epsilon_a \right] g_a^R(1,1') &= \int d\bar{\Gamma} \left[ \hat{\Sigma}_a^R(1,\bar{\Gamma}) g_a^R(\bar{\Gamma},1') + \hat{\Sigma}_a^A(1,\bar{\Gamma}) g_a^A(\bar{\Gamma},1') \right] - \int d\bar{\Gamma} \Delta_{ab}(\bar{\Gamma}) F_{ab}^R(1') = 0 \, , \quad (22) \\
\left[ i\hbar \frac{\partial}{\partial t_1} - \frac{\hbar^2 \nabla^2}{2m_b} - \epsilon_b \right] F_{ab}^R(1') &= \int \frac{d\bar{\Gamma} \hat{\Sigma}_b^R(1',\bar{\Gamma}) F_{ab}^A(\bar{\Gamma})}{\bar{\Gamma}} - \int \frac{d\bar{\Gamma} \Delta_{ab}^R(\bar{\Gamma}) g_a^R(\bar{\Gamma},1)}{\bar{\Gamma}} = 0 \, . \quad (23)
\end{align*}
\]

The equations for the retarded and advanced Green’s functions follow easily from the definition and Eqs. (22,23) as

\[
\begin{align*}
\left[ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2 \nabla^2}{2m_a} + \epsilon_a \right] g_a^{R/A}(1,1') &= \int d\bar{\Gamma} \hat{\Sigma}_a^{R/A}(1,\bar{\Gamma}) g_a^{R/A}(\bar{\Gamma},1') \, - \int d\bar{\Gamma} \Delta_{ab}(\bar{\Gamma}) F_{ab}^{R/A}(1') = \delta(1-1') \, , \quad (24) \\
\left[ i\hbar \frac{\partial}{\partial t_1} - \frac{\hbar^2 \nabla^2}{2m_b} - \epsilon_b \right] F_{ab}^{R/A}(1') &= \int \frac{d\bar{\Gamma} \hat{\Sigma}_b^{R/A}(1',\bar{\Gamma}) F_{ab}^{R/A}(\bar{\Gamma})}{\bar{\Gamma}} - \int \frac{d\bar{\Gamma} \Delta_{ab}^{R/A}(\bar{\Gamma}) g_a^{R/A}(\bar{\Gamma},1)}{\bar{\Gamma}} = 0 \, . \quad (25)
\end{align*}
\]

From Eqs. (22–25), kinetic equations for the Wigner function (Boltzmann equation) and the macro wave function may be derived [28].

Concluding follows that the concept of TLRO is obviously very convenient for the description of quantum condensation in terms of real-time Green’s functions.
3. EHP in equilibrium

In the case of thermodynamic equilibrium, because of the spectral representation, the time dependence of the gap function is simply given by

$$\Delta_{ab}(\mathbf{p}, t) = e^{\frac{i}{\hbar}(\mu_a + \mu_b)t} \Delta_{ab}(\mathbf{p}).$$

Therefore, it is useful to introduce the substitutions

$$F_{ab}(t, t') = e^{\frac{i}{\hbar}(\mu_a + \mu_b)t} F_{ab}(t - t'), \quad G_{ab}(t, t') = e^{\frac{i}{\hbar}(\mu_a + \mu_b)t} G_{ab}(t - t'),$$

where the remaining functions depend only on the time difference. Therefore, the Fourier representation can be used and the Gorkov equations are algebraic equations only,

$$\left[\hbar \omega - E_a(\mathbf{p}) - \tilde{\Sigma}_a^R(\mathbf{p}, \omega)\right] g_a^{R/A}(\mathbf{p}, \omega) - \Delta_{ab}(\mathbf{p}) F_{ab}^{R/A}(-\mathbf{p}, -\omega) = 0,$$

with

$$\tilde{\Sigma}_a^L(\mathbf{p}, \omega) = \frac{|\Delta_{ab}(\mathbf{p})|^2}{\hbar \omega + E_a(\mathbf{p}) - \mu_a - \mu_b + \tilde{\Sigma}_b^R(\mathbf{p}, \omega)}$$

and

$$\Gamma_a(\mathbf{p}, \omega) = 2 \left( \text{Im} \tilde{\Sigma}_a^R(\mathbf{p}, \omega) + \text{Im} \tilde{\Sigma}_a^L(\mathbf{p}, \omega) \right).$$

In many cases, the spectral function is used in quasiparticle approximation, i.e., the damping $\Gamma$ is neglected and it follows simply that

$$a_a(\mathbf{p}, \omega) = 2\pi \left[ |u_p|^2 2 \delta (\hbar \omega - E_a^+(\mathbf{p})) + |v_p|^2 2 \delta (\hbar \omega - E_a^-(\mathbf{p})) \right].$$

This approximation is not in every case sufficient. Instead, we use an extended approximation obtained by an expansion with respect to the damping $\Gamma$ [33] called extended quasiparticle approximation

$$A_a(\mathbf{p}, \omega) = |u_p|^2 \left\{ \left[ 1 + |u_p|^2 \frac{\partial}{\partial \omega} \text{Re} \tilde{\Sigma}_a^R(\mathbf{p}, \omega)|_{\hbar \omega = E_a^+} \right] 2\pi \delta (\hbar \omega - E_a^+(\mathbf{p})) \right. \frac{\partial}{\partial \omega} \frac{\hbar \omega - E_a^+(\mathbf{p})}{P}$$

$$+ \left. |v_p|^2 \left\{ \left[ 1 + |v_p|^2 \frac{\partial}{\partial \omega} \text{Re} \tilde{\Sigma}_a^R(\mathbf{p}, \omega)|_{\hbar \omega = E_a^-} \right] 2\pi \delta (\hbar \omega - E_a^-(\mathbf{p})) \right\} \frac{\partial}{\partial \omega} \frac{\hbar \omega - E_a^-}{P}. \right. \right.$$
renormalization terms are linearized with respect to the normal self-energy. The second, off-pole, contribution describes the interaction between the quasiparticles.

The quasiparticle dispersion for the two-component EHP is given by

\[ E_{a}^{\pm}(\mathbf{p}) = \frac{1}{2} \left[ \varepsilon_a(\mathbf{p}, \omega) - \varepsilon_b(\mathbf{p}, \omega) \right] \pm \sqrt{\left[ \varepsilon_a(\mathbf{p}, \omega) + \varepsilon_b(\mathbf{p}, \omega) \right]^2 + 4 |\Delta_{ab}(\mathbf{p})|^2} \left. \right|_{\hbar \omega = E_{a}^{\pm}(\mathbf{p})} \]  

(34)

with the self-energy of the normal phase

\[ \varepsilon_a(\mathbf{p}, \omega) = \varepsilon_a(\mathbf{p}) + \text{Re} \Sigma_{aR}^{\text{LRO}}(\mathbf{p}, \omega), \quad \varepsilon_a(\mathbf{p}) = \frac{p^2}{2m_a} - \mu_a . \]  

(35)

Finally, the \( u_p \) and \( v_p \) are the spectral weights with the normalization \( |u_p|^2 + |v_p|^2 = 1 \). They are given by the renormalization terms with respect to the TLRO self-energy

\[ \left\{ \begin{array}{c}
|u_p|^2 \\
|v_p|^2
\end{array} \right\} = \frac{1}{1 - \frac{\partial}{\partial \omega} \text{Re} \Sigma_{ab}^{\text{LRO}}(\mathbf{p}, \omega)|_{\hbar \omega = E_{ab}(\mathbf{p})}} \left[ \begin{array}{c}
\varepsilon_a(\mathbf{p}, \omega) + \varepsilon_b(\mathbf{p}, \omega) \\
\sqrt{[\varepsilon_a(\mathbf{p}, \omega) + \varepsilon_b(\mathbf{p}, \omega)]^2 + 4 |\Delta_{ab}(\mathbf{p})|^2}
\end{array} \right] . \]  

(36)

The crucial quantity in the theory is the gap function \( \Delta_{ab} \). From the definition and the homogeneous BSE (8), approximating the dynamically screened potential by the statically screened one (denoted again by \( V_{ab}^{R} \)), the following integral equation for \( \Delta_{ab} \) may be obtained,

\[ \Delta_{ab}(\mathbf{p}) = i \hbar \int \frac{d\mathbf{p}'}{(2\pi \hbar)^3} V_{ab}(\mathbf{p} - \mathbf{p}') G_{ab}^{R}(\mathbf{p}', -\mathbf{p}; \omega)|_{\hbar \omega = \mu_a + \mu_b} \Delta_{ab}(\mathbf{p}') , \]  

(37)

where \( V_{ab}^{R} \) is the statically screened Coulomb potential. For the determination of the free pair propagator \( G_{ab}^{R}(\omega) \) entering the gap equation

\[ G_{ab}^{R}(\omega) = \int \frac{d\omega}{2\pi} \int \frac{d\omega}{2\pi} g_a^{\diamond}(\omega) g_b^{\diamond}(\overline{\omega}) - g_a^{\diamond}(\overline{\omega}) g_b^{\diamond}(\omega) \omega - \omega - \overline{\omega} + i\epsilon \]  

in this case it is sufficient to use the quasiparticle spectral function (32). Then the following nonlinear gap equation for an EHP is obtained (\( e_{ab} = \frac{1}{2}(e_a + e_b) \), \( e_a = E_a - \mu_a \))

\[ \Delta_{ab}(\mathbf{p}) = \frac{e^2}{\epsilon_0 c_r} \int \frac{d\mathbf{p}}{(2\pi \hbar)^3} \frac{h^2}{(\mathbf{p} - \mathbf{p}')^2 + h^2 \kappa^2} \frac{\Delta_{ab}(\mathbf{p})}{2 \sqrt{(e_{ab}(\mathbf{p}) - f(E_{a}^{+}(\mathbf{p})))^2 + |\Delta_{ab}(\mathbf{p})|^2}} . \]  

(38)

A central problem in the theory of quantum condensation is the determination of the critical temperature \( T_c \) as a function of the chemical potential and the density, i.e., the phase boundary of the condensate. This boundary is determined by the vanishing of the gap. Under this condition, the gap equation is reduced to the linearized form

\[ \Delta_{ab}(\mathbf{p}) = -\frac{e^2}{\epsilon_0 c_r} \int \frac{d\mathbf{p}}{(2\pi \hbar)^3} \frac{h^2}{(\mathbf{p} - \mathbf{p}')^2 + h^2 \kappa^2} \frac{\Delta_{ab}(\mathbf{p})}{e_{ab}(\mathbf{p})} \left[ 1 - f(e_a(\mathbf{p})) - f(e_b(\mathbf{p})) \right] . \]  

(39)

The critical temperature of quantum condensation is obtained by numerical solution of Eq. (39) (for details see Ref. [28]). The result for the model case \( m_e = m_h \) is shown in Fig. 6.

We find the onset of the Bose condensation of excitons at \( \mu_e + \mu_h = E_{1s} = -1 \) and \( T = 0 \). With increasing chemical potential, the critical temperature increases and reaches a maximum.
Figure 2. Critical temperature vs. chemical potential for a model semiconductor with \( m_e = m_h \). Result of the solution of the gap equation under the condition of vanishing gap [28]. \( R_X \) denotes the excitonic Rydberg.

The region of Bose condensation of excitons is limited by the Mott transition and we observe a smooth crossover to the phase boundary of a BCS state.

In many cases it more convenient to know the critical temperature as a function of the density. The determination of \( T_c \) vs. density requires the coupled solution of gap and density equations,

\[
n_a(\mu, T) = \int \frac{dP}{(2\pi\hbar)^3} \frac{d\omega}{2\pi} A_a(p, \omega) f_a(\omega).
\]  

(40)

By inversion \( \mu = \mu(n, T) \) we are able to eliminate the chemical potential from \( T_c \).

Here it is not sufficient to use the spectral function in quasiparticle approximation. In order to take into account correlated states, especially the important bound states, \( A_a \) has to be taken in extended quasiparticle approximation, Eq. (33). However, on the phase boundary of the quantum condensate it is sufficient to consider the relation (40) for the normal phase, i.e., to use Eq. (33) with \( v_p \to 0 \) and \( u_p \to 1 \) [33, 8],

\[
n_a(\mu_a, T) = \int \frac{dP}{(2\pi\hbar)^3} f(\epsilon^{\text{RPA}}_a) + \sum_{nl} (2l + 1) \int \frac{dP}{(2\pi\hbar)^3} n_{ab}^R \left( \frac{P^2}{2M} + E_{nl} \right) \\
+ \int_0^\infty \frac{d\omega}{2\pi} n_{ab}^R(\omega) \text{Im} \text{Tr}_{12} \left[ \frac{d}{d\omega} g_{ab}^R(\omega) T_{ab}^R(\omega) \right] .
\]  

(41)

Obviously, for the application of this relation we need the solution of the two-particle bound and scattering problem. Quantum mechanics determines the properties of a two-particle system from the stationary Schrödinger equation. In a dense plasma, the influence of the surrounding medium has to be taken into account, i.e., (i) influence of the Pauli blocking or phase space occupation effect, (ii) self-energy corrections to the kinetic energy, (iii) screening of the interaction between the two particles.

A solution of this problem needs a careful analysis of the Bethe–Salpeter equation for the two-time two-particle Green’s function in dynamically screened ladder approximation [12, 34, 35]. The result of such investigations is an effective Schrödinger equation for the determination of the two-particle properties of the EHP following from the homogeneous BSE [12, 34, 36],

\[
\left( H_{ab}^{0} + V_{ab} - E_\alpha P(\omega, t) + H_{ab}^{R}(\omega, t) \right) |\psi_\alpha P(\omega, t)\rangle = 0 .
\]  

(42)
An equivalent approach applicable in the EHP are the semiconductor Bloch equations [37, 38, 39, 40, 41]. For an electron–hole pair system, both approaches are in full agreement for zero center-of-mass momentum.

The influence of the surrounding plasma on the two-particle properties is described in Eq. (42) by the in-medium part $H_{ab}^m(\omega,t)$, explicitly given in Refs. [32, 34].

$$\begin{align*}
\text{Figure 3. Two-particle spectrum vs. density: band (continuum) edge (upper curves), ground state energy } E_b \text{ (lower curves) in zinc selenide (ZnSe) (in units of excitonic Rydberg) [42].}
\end{align*}$$

The resulting two-particle spectrum, following by extensive numerical work, is presented in Fig. 3 [42] which shows that the plasma modifies the electron–hole pair in the following way [12, 37, 38, 39, 40, 42]:

(i) There is a lowering of the band (continuum) edge

$$\Delta E_{ab} = \Sigma_a^{\text{HF}} + \Sigma_b^{\text{HF}} + \Delta, \quad \Delta = \Delta_a + \Delta_b. \quad (43)$$

(ii) The exciton ground state energy is nearly independent of the density

$$E_b = E_b^0 + \delta. \quad (44)$$

It changes by the small quantity $\delta$, but it shows a weaker density dependence as compared to the continuum edge. This follows from an approximative compensation of the many-particle effects [12].

(iii) The influence of the plasma leads to a lowering of the ionization energy,

$$I^{\text{eff}} = |E_b| + \Delta E_{eh} = |E_b^0| - \delta + \Delta E_{eh}. \quad (45)$$

In statically screened approximation is $\Delta = -\kappa e^2$. In general, $\Delta$ and $\delta$ follow from the numerical solution of the effective Schrödinger equation with dynamically screened potential or, analogously, the semiconductor Bloch equations.

(iv) For $I^{\text{eff}} = 0$, the bound state vanishes and merges into the scattering continuum (Fig. 3). This is usually referred to as the Mott effect.

Due to the lowering of the ionization energy it may be expected that the bound state part of the density has discontinuities at the critical values of the coupling parameter connected with drastic changes in the thermodynamic functions. However, one can show that the total density...
is a smooth function of the coupling parameter [43, 32] because there is a compensation of the discontinuities by contributions of the scattering part. By application of the higher order Levinson theorems [32], these parts may be transferred into the bound state contribution. This renormalized bound state contribution is a generalization of the Planck–Larkin sum of states to degenerate systems and can be written as [33]

$$n_{\text{bound}} = (2s + 1)^2 \int \frac{dP}{(2\pi \hbar)^3} \left\{ n_B \left( \frac{P^2}{2M} + I_{\text{eff}}(\zeta_e, \zeta_h) - \zeta_e - \zeta_h \right) 
- n_B \left( \frac{P^2}{2M} - \zeta_e - \zeta_h \right) - \frac{M}{P^2} I_{\text{eff}}(\zeta_e, \zeta_h) n_B \left( \frac{P^2}{2M} - \zeta_e - \zeta_h \right) \right\}$$  \hspace{1cm} (46)$$

where $n_B$ is the Bose function and $\zeta_a = \mu_a - \Delta_a$.

**Figure 4.** Electron density as a function of the effective chemical potential: total density $n_e$ (dotted line), quasiparticle contribution $n_{\text{QP}}$ (dashed line), bound state contribution $n_{\text{bound}}$ (solid line) for a model semiconductor with $m_e = m_h$ [28]. $a_X$ denotes the excitonic Bohr radius.

At lower temperatures, the remaining scattering part in Eq. (41) is small and can be neglected. Therefore, the total density can be subdivided into two parts

$$n_{\text{tot}}(\mu, T) = n_{\text{QP}}(\mu, T) + n_{\text{bound}}(\mu, T).$$  \hspace{1cm} (47)$$

The resulting total electron density is shown in Fig. 4 vs. the effective chemical potential. Here and in all subsequent figures, results are shown for a model semiconductor with equal masses of electrons and holes and a background dielectric constant of $\epsilon_r = 7$ corresponding approximately to the parameters of cuprous oxide ($\text{Cu}_2\text{O}$).

With the subdivision of the density according to Eq. (47), the degree of ionization can be defined,

$$\alpha(\mu, T) = \frac{n_{\text{QP}}(\mu, T)}{n_{\text{tot}}(\mu, T)}. \hspace{1cm} (48)$$

Isotherms of the degree of ionization as a function of the density are shown in Fig. 5. We observe a very strong increase of the degree of ionization up to $\alpha = 1$ due to the lowering of the ionization energy [11, 43]. This behavior is usually referred to as Mott transition as a consequence of the Mott effect. The detailed properties of $\alpha$, however, are strongly modified by including exciton–exciton interaction and the possible formation of biexcitons and trions, known already from experiences from gaseous plasmas (atom–atom interaction and molecule formation) [32] and recently confirmed in first-principle numerical simulations [44].
With the density relations (41) and (46), the critical temperature may be determined as a function of the density. The result is shown in Fig. 6. At lower densities, the critical temperature agrees with the condition for Bose condensation of ideal excitons, \( n \lambda^3 \geq 2.61 \), as a consequence of the neglect of the exciton–exciton interaction in our model. With increasing density, we observe a strong deviation from the ideal behavior due to the lowering of the ionization energy and further a smooth crossover to the BCS regime.

This behavior is confirmed in Fig. 7 where the critical temperature is given in units of the Fermi energy vs. inverse Fermi momentum. This curve is qualitatively in agreement with corresponding curves of the crossover of Fermi atom systems in traps [4].

4. Conclusion
Summarizing our investigations, we have presented a description of quantum condensation in the EHP of highly excited semiconductors.

In the framework of real-time Green’s functions applying the concept of time long range order for the two-particle Green’s function we have derived nonequilibrium Gorkov equations on the Keldysh time contour. In order to consider the EHP, the theory has been specified to systems with Coulomb interaction using the screened ladder approximation.
In thermodynamic quasiequilibrium, we have obtained the usual BCS scheme of equations in terms of the screened potential for the two-component case including the influence of the normal phase.

For a complete solution of the problem we solved the coupled system of gap and density equations in extended quasiparticle approximation. The analysis of the density in screened ladder approximation and the associated two-particle problem in a plasma environment shows a lowering of the ionization energy and finally a breakup of bound states with increasing density, the Mott effect. Therefore, we observe a transition from a partially ionized EHP to a high density $e^{-}h$ liquid connected with a change of the physical nature of the quantum condensate (BEC–BCS crossover).

The phase boundary of the quantum condensate arises from the condition of vanishing gap function. Therefore, we have determined the critical temperature as a function of the chemical potential by solution of the linearized gap equation with a screened Coulomb potential. The result shows a smooth crossover from the Bose–Einstein condensate of excitons to BCS states at high densities driven by lowering of ionization energy and Mott effect.

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