Mott transition in electron–hole plasmas

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Abstract. In connection with the ionization equilibrium of an electron–hole plasma in a highly excited semiconductor, the influence of many-particle effects on both the chemical potentials of carriers and the Mott transition of para-excitons in zinc selenide (ZnSe) is investigated over a wide range of temperatures and carrier densities. Special attention is directed to the determination of the region where an excitonic fraction can exist and, therefore, a possible Bose–Einstein condensate can occur at low temperatures.

1. Introduction
Collective quantum phenomena have been intensely investigated in semiconductor physics for many years. Such phenomena comprise Bose–Einstein condensation (BEC) of excitons as well as condensation of Cooper-like electron–hole pairs to a BCS state. According to the theory of the ideal Bose gas, the BEC of excitons should occur if their chemical potential reaches the exciton energy, either by reduction of the temperature or increase of the density. On the other hand, excitons are bound electron–hole pairs which are subject to an ionization equilibrium \( e + h \rightleftharpoons X \) and, therefore, form only a subsystem of the partially ionized electron–hole plasma (EHP). Due to many-particle effects like screening of the Coulomb interaction between the carriers, their coupling weakens with increasing density leading finally to a breakup of the excitons usually referred to as Mott effect (density ionization) \([1, 2, 3, 4, 5, 6]\). The existence of the excitonic fraction of the EHP (and, therefore, of a possible condensate) is limited by the Mott transition from an exciton gas to a fully ionized EHP as a consequence of the Mott effect.

In this paper we investigate the influence of many-particle effects on the composition of the partially ionized EHP in zinc selenide (ZnSe) beyond simple approximations \([7, 8]\). Concerning the phase diagram, we concentrate on the Mott transition; our aim is not the discussion of the full phase diagram including the occurrence of biexcitons, electron–hole liquid etc.

After a brief overview over the underlying theory \([9]\) in Sec. 2, the quasiparticle energies of the carriers and the exciton energies are analyzed in Secs. 3 and 4, respectively. Finally, in Sec. 5, the degree of ionization being a measure of the EHP composition is calculated.

2. Theory
A self-contained presentation of a quantum statistical description of thermodynamic properties of the EHP has been given in \([9]\). Only a brief outline shall be given here. Starting point is the
general quantum statistical relation

\[ n_e(\{\mu_e\}, T) = -i\hbar a \int \frac{dk}{(2\pi)^3} \int \frac{d\omega}{2\pi} G_a^< (k, \omega) = g_a \int \frac{dk}{(2\pi)^3} \int \frac{d\omega}{2\pi} A_a(k, \omega) f_a(\omega), \]

expressing the carrier density \( n_a \) of the species \( a \) via the single-particle correlation function \( G_a^< \) as a function of the chemical potentials \( \{\mu_e\} \) and the temperature \( T \). \( f_a(\omega) \) is a Fermi-like distribution, and \( g_a \) denotes the band multiplicity (including spin degeneracy) of species \( a \).

Using the spectral function in extended quasi-particle approximation [10] and the self-energy in screened ladder approximation, the electron density can be subdivided according to

\[ n_e(\mu_e, \mu_h, \mu_X, T) = \epsilon_e(k) + \int \frac{dK}{(2\pi)^3} n_X^B \left( \frac{h^2K^2}{2M} \right) \sum_{nl} (2l + 1) \int \frac{d\omega}{2\pi} n_{eh}(\omega) \Im F(\omega) \]

\[ + g_e g_h \int \frac{dK}{(2\pi)^3} n_X^B \left( \frac{h^2K^2}{2M} \right) \]

\[ = n_e^{QP} + n_e^{scatt} + n_X, \tag{2} \]

into “free” (quasiparticle \( n_e^{QP} \) and scattering \( n_e^{scatt} \)) and the bound (exciton) \( n_X \) contributions. Here, \( \epsilon_e(k) \) is the quasiparticle energy in random phase approximation (RPA) including the Hartree–Fock self-energy \( \Sigma_{HF}^a \),

\[ \epsilon_e(k) = \frac{h^2k^2}{2m_e} + \text{Re} \left[ \Sigma_{HF}^e(k, \omega) \right]_{\omega=\epsilon_e(k)}, \tag{3} \]

\( n_X^B \) denotes the Bose distribution of ideal excitons,

\[ n_X^B \left( \frac{h^2K^2}{2M} \right) = \frac{1}{e^{\beta \left( \frac{h^2K^2}{2M} - \mu_X \right)} - 1}, \tag{4} \]

\( \beta = (k_B T)^{-1} \) and \( \Delta \) represents the lowering of the band (continuum) edge. In Eq. (2), we have introduced the so-called chemical picture, i.e., the bound electron–hole pairs are reinterpreted as a new particle species, the excitons, where the definition of the excitonic chemical potential

\[ \mu_X = \mu_e + \mu_h - E_{nl} \tag{5} \]

is just equivalent to the well-known thermodynamic condition for the chemical (ionization) equilibrium.

In the chemical picture, the EHP is characterized by the densities of free electrons \( n_e^* = n_e^{QP} + n_e^{scatt} \), free holes \( n_h^* \) (with \( n_h^* = n_e^* \)), and the density of excitons \( n_X \) (total electron density \( n_e = n_e^* + n_X \)). The ionization equilibrium \( e + h \leftrightarrow X \) is controlled by the relation (5) which determines the composition of the system described by the degree of ionization

\[ \alpha = \frac{n_e^*}{n_e} \tag{6} \]

and plays the role of a mass-action law (MAL).

The chemical potential of the excitons \( \mu_X \) is given by the inversion of

\[ n_X(\mu_X, T) = g_e g_h \int \frac{dK}{(2\pi)^3} \frac{1}{e^{\beta \left( \frac{h^2K^2}{2M} - \mu_X \right)} - 1}. \tag{7} \]
We should emphasize here, however, the limitations of the chemical picture or, more precisely, of the underlying extended quasiparticle approximation for the spectral function \( A_\alpha(k, \omega) \): While \( A_\alpha(k, \omega) \) exhibits, at lower densities, distinct bound state peaks and the pair continuum, the peaks broaden for higher densities due to the damping. Thus, a well defined distinction between bound and scattering states becomes problematic around the Mott density \([11, 5, 6]\). A quantitative demonstration of the effect for zinc oxide (ZnO) has been given by Klingshirn, see Fig. 24b in Ref. [12]. However, in ZnSe the excitonic linewidth is much smaller [13], as will be discussed in Sec. 4. Due to the damping of the two-particle states, the degree of ionization is not really a well defined quantity around the Mott density. It gives, however, a good qualitative measure for the state of the EHP.

The chemical potential of free carriers (neglecting scattering states) is given by

\[
\mu_a(n_e, T) = g_a \int \frac{dk}{(2\pi)^3} \frac{1}{e^{\beta(e_a(k) - \mu_a)} + 1}.
\]

An analytical determination of the chemical potential from Eq. (8) is possible at most in limiting cases (nondegenerate or highly degenerate, respectively). In the general case, knowing the RPA quasiparticle energy \( e_a(k) \), \( \mu_a \) can be obtained by numerical inversion of Eq. (8). The determination of \( e_a(k) \) according to Eq. (3) is, however, a numerically expensive task. As an alternative to the complete inversion of Eq. (8), one can split the chemical potential according to \([1, 14]\)

\[
\mu_a = \mu_a^{id} + \Delta \mu_a.
\]

Here, \( \mu_a^{id} \) is the ideal contribution, and \( \Delta \mu_a \) is the correlation part. The inversion of Eq. (8) with respect to the first order in \( \Delta \mu_a \) is usually referred to as incomplete inversion [15]. Then the ideal contribution, for arbitrary degeneracy, follows in well-known manner from

\[
n_a^*(\mu_a, T) = g_a \int \frac{dk}{(2\pi)^3} \frac{1}{e^{\beta(e_a(k) - \mu_a)} + 1}.
\]

Numerical calculations for the correlation part \( \Delta \mu_a \) have been performed, e.g., in Refs. [15, 16, 17, 2].

While for a non-degenerate EHP, from Eq. (5), a Saha equation can be derived immediately [1, 18], the situation is more complicated in the case of arbitrary degeneracy. Then, the degree of ionization \( \alpha \) has to be determined directly from Eq. (5) which reads in terms of \( \alpha \) and \( n_e \)

\[
\mu_X[(1 - \alpha)n_e, T] = \mu_e[\alpha n_e, T] + \mu_h[\alpha n_e, T] - E_{nl}.
\]

Equation (11) represents a form of the MAL which allows for the determination of the degree of ionization \( \alpha \) as a function of density and temperature and, therefore, can be regarded as a generalized Saha equation. The degree of ionization is given implicitly by Eq. (11) and has to be obtained numerically [8, 9]. If an excitonic condensate is present, on the r.h.s. of Eq. (7) the density of condensed excitons occurs as an additional term, for the numerical treatment see Ref. [19].

3. Quasiparticle energies

The influence of many-particle effects on the composition of the partially ionized EHP according to the MAL [Eqs. (11) together with (8) and (7)] is contained in two quantities, namely (i) in the quasiparticle energies of the carriers \( e_a(k) \), and (ii) in the two-particle bound state (exciton) energy \( E_{nl} \). Both the quasiparticle energy of the carriers given by Eq. (3), and their damping \( \Gamma_a \),

\[
\Gamma_a(k, \omega) = -2\text{Im} \Sigma_a^\chi(k, \omega) = i \left[ \Sigma_a^>(k, \omega) - \Sigma_a^<(k, \omega) \right],
\]

3
are determined by the retarded RPA self-energy $\Sigma_a^r$ which can be split into a Hartree–Fock contribution $\Sigma_a^{\text{HF}}$ and a Montroll–Ward term $\Sigma_a^{\text{MW}}$ which considers the dynamical screening between carriers,

$$\Sigma_a^r(k, \omega) = \Sigma_a^{\text{HF}}(k) + \Sigma_a^{\text{MW}}(k, \omega),$$  \hspace{1cm} (13)

$$\Sigma_a^{\text{HF}}(k) = \int \frac{d\mathbf{q}}{(2\pi)^3} f_a(\varepsilon_a(\mathbf{q})) V_{aa}(k - \mathbf{q}),$$  \hspace{1cm} (14)

$$\Sigma_a^{\text{MW}}(k, \omega) = \int \frac{d\mathbf{q}}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \frac{1 - f_a(\varepsilon_a(\mathbf{q}))+ n^B(\omega')}{\hbar \omega - \varepsilon_a(\mathbf{q}) - \hbar \omega' + i\Gamma_a(\mathbf{q})/2}. $$  \hspace{1cm} (15)

The spectral function of the screened potential $\hat{V}(\mathbf{q}, \omega)$ appearing in the Eqs. (19) and (15) is related to the inverse retarded dielectric function $\varepsilon^{-1}(\mathbf{q}, \omega)$ via

$$\hat{V}(\mathbf{q}, \omega) = 2iV_{ab}(\mathbf{q}) \text{Im} \varepsilon^{-1}(\mathbf{q}, \omega).$$  \hspace{1cm} (16)

The function $n^B(\omega)$ represents the Bose distribution of the elementary excitations in the plasma (plasmons), and, in our calculations, we use the Lindhard dielectric function. Contributions of bound electron–hole pairs to the dielectric screening function in the sense of atomic (excitonic) polarizabilities [20] are small as compared to that of the free carriers and are neglected. This is justified if the description of the Mott transition is addressed, however, excitonic contributions to screening should be incorporated if the properties of the pure excitonic gas phase are investigated.

The Fermi distribution $f_a(\varepsilon_a(\mathbf{q}))$ appearing in Eqs. (14) and (15) contains the renormalized dispersion and the chemical potential $\mu_a$ of carriers being related to the carrier density $n^a$ by Eq. (8)

$$f_a(\varepsilon_a(\mathbf{q})) = \left[e^{(\varepsilon_a(\mathbf{q}) - \mu_a)/k_BT} + 1\right]^{-1}. $$  \hspace{1cm} (17)

In order to determine the quasiparticle energy and damping for a given carrier density and temperature, the Eqs. (3), (8), (13)–(15) have to be solved self-consistently, including the chemical potential. We start our numerical procedure with the calculation of the chemical potential $\mu_a^{\text{loc}}$ of free (non-correlated) carriers, cf. Eq. (10), considering only the kinetic energy part in (3) for the iteration of (8). This is used to iterate the whole system self-consistently. As a result we get the quasiparticle energy and damping which then are employed in the calculation of the carrier density of the correlated EHP with (8). In earlier papers the quasiparticle energy was approximated by the so-called Debye shift [1] or Coulomb-hole self-energy [21], given in excitonic units by $\Sigma^{\text{D}} = -\kappa a_X E_X^b$ ($\kappa$ – inverse screening length). We use the following parameters for ZnSe [13]: binding energy $E_X^b = 22.4$meV, Bohr radius $a_X = 3.65$nm, and effective electron and hole masses of $m_e = 0.15m^0$ and $m_h = 0.86m^0$, $m^0$ being the free electron mass. The real part of the self-energy for electrons and holes, resulting from our calculations (QPA) is compared in Fig. 1 to two approximations. For lower carrier densities, as considered in the figure, the deviation of the Debye self-energy (static screening) is obvious (note the factor 1/2 in $\Sigma^{\text{D}}$). Moreover, the influence of dynamical screening, following from the deviation of the QPA from the HF self-energies, is clearly demonstrated. One should remark that the Debye self-energy represents a rigid shift approximation, while the energy shifts in QPA and HF approximation, e.g., for the electrons, decrease for higher wave numbers. For comparison at different temperatures and densities the real part of the sum of the self-energies of electrons and holes at $k = 0$ ($\Sigma_0 = \Sigma_{e,0} + \Sigma_{h,0}$) is presented in Fig. 2. The quasiparticle energy increases with the density due to the many-body effects. The increase is larger for lower temperatures. Comparing our results (QPA) to simple approximations we find out that many-body effects are overestimated by the Debye self-energy, in particular for the intermediate density region and
Figure 1. Real part of the self-energy for electrons (e) and holes (h) in dependence of the wave vector. Comparison of our approach QPA (solid lines) with HF self-energy (14) (dashed) and Debye shift (dash-dotted).

Figure 2. Real part of the sum of self-energies for electrons and holes at \( k = 0 \) in dependence of the density of carriers. Comparison of our approach QPA (solid lines) with HF self-energy (14) (dashed) and Debye shift (dash-dotted).

for lower temperatures. As we will show later, this is the case for those densities at which the Mott transition of excitons occurs. Only for the higher densities beyond the Mott transition, the static screening approaches the QPA. On the other side, the HF contribution to the self-energy (13) is the dominant one for low temperatures. Here, screening effects play a minor role. Often \( \text{Re } \Sigma_0 \) was considered as the lowering of the band edge. At the crossing of lowered band edge and exciton binding energy, the Mott transition may be expected to occur due to the vanishing of the ionization energy. This will be discussed further in Sec. 4, and we will show that the real part of the interband self-energy (20) has to be considered instead of \( \text{Re } \Sigma_0 \). Nevertheless, for \( k = 0 \) and at the carrier dispersion both are identical. With regard to the crossing of energy shifts and exciton binding energy \( E_b^X \) in Fig. 2, one may expect the Mott density to be much higher in QPA than in Debye approximation. This effect will become even more pronounced in the discussion of the chemical potentials in the next section.

The imaginary part of the quasiparticle energy \( \Gamma_a(k) \) for electrons and holes is shown in Fig. 3 for different temperatures at a carrier density of \( n = 10^{16} \text{cm}^{-3} \). The results for electrons and holes differ due to their different effective masses. Just as the quasiparticle energies, the damping of the carrier states increases with the temperature. For the Mott density and at room temperature it reaches the order of the excitonic Rydberg energy. This is comparable
Figure 3. Imaginary part of the self-energy (damping) pairwise for electrons (lower curves) and holes (upper) in dependence of the wave vector for different temperatures.

to the results for the excitonic broadening discussed in the next section and suggests that the quasiparticle description becomes questionable at higher temperatures.

4. Exciton energies
Apart from the quasiparticle energy of the carriers, also the exciton energy contains the influence of many-particle effects on the properties of the EHP. It is well-known from both optical experiments [22] and from the theoretical point of view [3] that the exciton energy only weakly changes with increasing excitation, while the ionization is mainly generated by the lowering of the band edge, described in our approach by the quasiparticle energies of carriers. According to Ref. [3], this behavior can be described by an effective wave equation considering the influence of screening both by self-energies and by a renormalization of the Coulomb interaction.

Experimentally the influence of many-body effects in an excited semiconductor can be determined by measuring the optical spectrum detected with a weak probe pulse. A corresponding theoretical description is given by the semiconductor Bloch equations (SBE) [21]. If one considers the carriers to be in quasi-equilibrium, the carrier distributions are Fermi functions with given chemical potential and temperature, which are not affected by the weak probe pulse, and only the kinetic equation for the polarization has to be solved. In this case, the equation for the polarization \( p(k, \omega) \), generated by the probe pulse \( E(\omega) \) and coupled via the dipole matrix element \( d \) to the semiconductor, can be written in excitonic units as [23, 24, 25, 13, 26]

\[
\{ \omega - k^2 - \Delta^{\text{HF}}(k) - \Sigma'(k, \omega) \} p(k, \omega) + \int dq \frac{d}{(2\pi)^3} \{ N(k)V_{\text{ch}}(k - q) + \Theta(k, q, \omega) \} p(q, \omega) = N(k) d E(\omega) .
\]  

(18)

Many-body effects are contained (i) as Hartree–Fock (HF) renormalized carrier energies \( \Delta^{\text{HF}}(k) \) and Pauli blocking \( N(k) = 1 - f_e(k) - f_h(k) \), and (ii) as screening effects in the renormalized interaction matrix \( \Theta(k, q, \omega) \)

\[
\Theta(k, q, \omega) = \Delta V^{\text{eff}}(k, q, \omega) - i\Gamma(k, q, \omega)
\]

\[
= \sum_{a \neq b} \int \frac{d\omega}{2\pi} \frac{1 - f^a_0(\varepsilon_a(q)) + n^B(\omega')}{h\omega - \varepsilon_a(k) - \varepsilon_b(q) - \hbar \omega + i[\Gamma_a(k) + \Gamma_b(q)]/2},
\]

(19)

whose real and imaginary parts \( \Delta V^{\text{eff}}(k, q, \omega) \) and \( \Gamma(k, q, \omega) \) are the effective interaction and
the so-called off-diagonal dephasing, respectively, and in the interband self-energy $\Sigma^r(k,\omega)$

$$\Sigma^r(k,\omega) = \Delta e^{sc}(k,\omega) - i\Gamma(k,\omega) = \int \frac{dq}{(2\pi)^3} \Theta(q,k,\omega) = \Sigma^r_c(k,\omega - \epsilon_h) + \Sigma^r_h(k,\omega - \epsilon_e), \quad (20)$$

with its real and imaginary parts $\Delta e^{sc}(k,\omega)$ and $\Gamma(k,\omega)$ being the renormalized interband self-energy and the diagonal dephasing, respectively.

It is important to notice that the various many-body quantities widely compensate each other pairwise in the case of bound states. This concerns on one hand the HF energies and the Pauli blocking, and the renormalized interband self-energy $\Delta e^{sc}(k,\omega)$ and the effective interaction $\Delta V_{eff}(k,q,\omega)$ on the other hand as well as the so-called diagonal and off-diagonal dephasing $\Gamma(k,\omega), \Theta(k,q,\omega)$, respectively. Moreover, there is an exact relation of the (two-particle) interband self-energy $\Sigma^r$ for an energy $\hbar\omega$ to the (single-particle) carrier self-energies $\Sigma^r_a$ at shifted energies $\hbar\omega - \epsilon_0$ given in Eq. (20). The appearance of this energy shift becomes physically clear if one looks at the energies in the denominator of the effective interaction matrix $\Theta(k,q,\omega)$. It becomes resonant if the incident photon with the energy $\hbar\omega$ generates an interband transition, described by the renormalized quasiparticle energies $\epsilon_p(k)$ and $\epsilon_h(q)$, accompanied by absorption or emission of a plasmon with the energy $\bar{\omega}$. The quasi-particle energies $\epsilon_p(k)$ and the quasi-particle damping $\Gamma(k,\omega)$ are determined from Eqs. (13)–(15).

For weak probe pulses the macroscopic polarization $P(\omega)$ depends linearly on the electric field

$$P(\omega) = \int \frac{dk}{(2\pi)^3} \rho(k,\omega) = \chi(\omega) E(\omega), \quad (21)$$

where the susceptibility $\chi(\omega)$ characterizes the dielectric properties of the semiconductor. The experimental verification of this approach was given in several optical experiments. In previous papers [23, 24, 25, 13] we have demonstrated how the influence of many-body effects on the exciton line, e.g., carrier-induced line broadening, shift of the exciton resonance and band gap shrinkage show up in the phase and amplitude of transmitted/reflected light.

The semiconductor Bloch equation approach sketched above describes systems with a band structure in an electromagnetic field. In general, the two-particle problem in a surrounding medium needs a careful analysis of the Bethe–Salpeter equation for the two-particle Green’s function. A first approach in this direction was given in Refs. [3, 4] using the dynamically screened ladder approximation. However, this result has some serious shortcomings, especially in the degenerate plasma. There, a static contribution in addition to the Hartree–Fock term, and, moreover, a division by the Pauli blocking factors $1 - f_a(k_1) - f_b(k_2)$ occur. In a subsequent paper [11] it was shown that these shortcomings are generated by using an inappropriate retarded Green’s function and by the treatment of the retardation of the screened potential by the Shindo approximation. The corrected effective Schrödinger equation was derived in Refs. [11, 27] and for the EHP in Refs. [25, 13]. For an electron–hole pair system, both approaches are in full agreement for zero center-of-mass momentum.

Numerical solutions for the pair spectrum have been given in Refs. [23, 24, 25, 13] using the SBE and in Refs. [3, 28, 29] using the effective Schrödinger equation in the nondegenerate case.

The two-particle spectrum shown in Fig. 4 exhibits the following peculiarities: (i) There is a lowering of the band (continuum) edge due to the many-body effects contained in the self-energy. (ii) The exciton ground state energy remains nearly constant up to higher densities. This follows from the approximate compensation of the many-particle effects for the bound states [3]. Moreover, at low temperatures, $\Theta(k,q,\omega)$ and, therefore, $\Sigma^r(k,\omega)$ are small, and Coulomb Hartree–Fock self-energy and Pauli blocking dominate. However, they nearly compensate each other at low densities, too, but lead to a weak shift for higher densities. (iii) The difference
between band edge and exciton energy defines the effective ionization energy $I_{\text{eff}}$ which is lowered with increasing density. (iv) For $I_{\text{eff}} = 0$, the bound state vanishes and merges into the scattering continuum. This process is referred to as Mott effect, and the corresponding density is called Mott density. Above that point, the bound state does not exist, and the bound state energy is no longer a meaningful quantity. (v) Finally, a small shift of the exciton energy appears with increasing carrier density, depending on the temperature [23]: a blue shift at low temperatures turns into a red shift for higher temperatures.

While the exciton energy is shown in Fig. 4 as a well-defined line, in fact, with increasing carrier density the exciton is broadened due to screening of the Coulomb interaction between carriers. This broadening, being described in Eq. (18) by the diagonal and off-diagonal dephasing, strongly increases at higher carrier densities. At low temperatures, this broadening is small: the excitonic full width at half maximum is $\gamma = 0.012$ Ryd for 3 K and $\gamma = 0.07$ Ryd for 30 K just below the Mott density, respectively. However, at room temperature it reaches the order of the excitonic Rydberg. This is shown in Fig. 4 by the grey area. For corresponding experimental results see [30, 12].

In addition to our results from the solution of the full SBE (18), in Fig. 4 we show a comparison to two approximations: That is (i) a solution with screening effects being neglected in the SBE and only the HF energies and the Pauli blocking considered, i.e., $\Theta(k, q, \omega) = 0$ and $\Sigma(k, \omega) = 0$ (Hartree–Fock approximation). (ii) A further frequently used approximation is the static limit of $\Theta(k, q, \omega)$. It follows from Eq. (19) if $\omega$ exceeds all other terms in the denominator. If furthermore, for $\Delta e_{\text{sc}}(k, \omega)$ [cf. Eq. (20)] the classical limit is applied, it leads to the Debye shift $\Sigma_D$. Figure 4 shows that this approximation provides an inadequate description of both bound state energy and band edge even at room temperature. In particular, the Mott effect occurs at far too low densities. Static screening becomes a convenient approximation far above room

**Figure 4.** Two-particle spectrum vs. density in ZnSe: band edge (upper curves) and exciton ground state energy (lower curves). Solid lines: solution of the full SBE, dashed lines: Hartree–Fock approximation, dotted lines: Debye approximation. The grey area marks the width (full width at half maximum) of the exciton. Ryd denotes the excitonic Rydberg.
temperature but completely fails at low temperatures.

5. Degree of ionization
A quantitative measure for the ionization state of the EHP is given by the degree of ionization \( \alpha \) defined by Eq. (6). For an overview of the ionization state it is convenient to consider isolines \( \alpha(n_e, T) = \text{const.} \) in the density–temperature plane. Such “ionization maps” are presented in Figs. 5–7 which differ in the approximations for the chemical potential of the carriers. All cases have in common that, with increasing temperature at fixed density, thermal ionization takes place quite smoothly, while at fixed temperature with increasing density, the Mott transition appears as an abrupt jump from \( \alpha = 0 \) to \( \alpha = 1 \).

**Figure 5.** Isolines of the degree of ionization in the density–temperature plane for ZnSe. Solution of the MAL using self-consistent quasiparticle energies for the carriers and the SBE results for the exciton energies. The dashed triangle at the bottom borders the region where BEC of excitons is possible, cf. Eq. (22).

**Figure 6.** Same representation as in Fig. 5, but using the Padé formula from [16] for the carrier chemical potentials.

**Figure 7.** Same representation as in Fig. 5, but using carrier chemical potentials in Debye approximation.

However, the position as well as temperature dependence of the Mott density is entirely different. Especially the Debye approximation overestimates the Mott effect drastically so that the Mott transition occurs at more than two orders of magnitude too low densities. Already the application of the Padé formulas [16] shifts the Mott density considerably. Only our self-consistent calculations, however, exhibit a window for a possible Bose–Einstein condensation (BEC) of excitons in the depicted temperature range: Looking at the area of strong dominance
of the excitons \( (\alpha \approx 0) \) and regarding them as noninteracting bosons, BEC may be expected under the condition

\[
(1 - \alpha)n_e A_X^3 \geq \zeta (3/2) \approx 2.61 .
\]  

(22)

This condition is given in Fig. 5 by the triangle bordered by the dashed line at the bottom. Note that the breakup of excitons at the Mott density does not mean a disappearance of the condensate. Instead, a closer investigation shows a smooth crossover to a BCS-type condensate at high densities \([31, 32, 33]\). Thus, the physical nature of the condensed particles changes, i.e., we find excitons below the Mott density, and Cooper-like electron–hole pairs far above it. To which extent the survival of the excitons as resonances just above the Mott density plays a role has still to be investigated.

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