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The chemical potential of an ideal intrinsic semiconductor

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The standard result for the chemical potential μ of an ideal intrinsic semiconductor as calculated in the canonical ensemble indicates that μ goes to the middle of the band gap as the temperature T goes to zero. However, the definition of μ implies that μ goes to the bottom of the conduction band as $T \rightarrow 0$. The solution to this puzzle is that the Fermi–Dirac distribution function ceases to be accurate for the thermal occupation probabilities when the temperature is so low that the number of electrons in the conduction band is of order unity. The use of the correct occupation numbers results in μ going to the bottom of the conduction band as $T \rightarrow 0$. © 2004 American Association of Physics Teachers.
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I. INTRODUCTION

The ideal intrinsic semiconductor has proven to be useful for teaching several important concepts that are needed for the study of realistic semiconductors. These concepts include valence and conduction bands, the band gap, thermal occupation numbers, conductivity, and the chemical potential μ . Except for the low temperature behavior of the chemical potential, calculated in the canonical ensemble, these important concepts are covered in a number of excellent textbooks.

The standard result for the chemical potential calculated in the canonical ensemble suggests that μ goes to the middle of the band gap as the temperature T goes to zero. However, the chemical potential actually goes to the bottom of the conduction band as T goes to zero.¹ The reason that the standard treatment cannot be used to find the correct limit is not obvious and is somewhat surprising. Consequently, the study of the temperature dependence of the chemical potential of the ideal intrinsic semiconductor has much pedagogical value.

The principal purpose of this paper is to show that the standard result for μ as given in textbooks (see, for example, Refs. 2–11) cannot be used to obtain the correct behavior of μ as $T \rightarrow 0$; the correct form is given in Ref. 1. We will see that one of the assumptions made in the standard treatment breaks down as $T \rightarrow 0$. The nature of the incorrect assumption reminds us of the importance of checking assumptions—the incorrect assumption is seemingly so reasonable that it would appear to be beyond question.

Specifically, the Fermi–Dirac distribution function is used to calculate the thermal occupation numbers; careful analysis shows that the Fermi–Dirac distribution function breaks down for an ideal intrinsic semiconductor when the temperature is low enough that the number of electrons in the conduction band is of order unity.

II. STATEMENT OF THE PROBLEM AND THE STANDARD TREATMENT

The objective is to calculate the temperature dependence of the chemical potential μ of an ideal intrinsic semiconductor in the canonical ensemble. The definition of μ in the canonical ensemble is

$$\mu(N, T, V) = F(N+1, T, V) - F(N, T, V), \quad (1)$$

where $F(N, T, V)$ is the Helmholtz free energy for N particles in a volume V in thermal contact with a heat bath at

temperature T . The equation for μ is obtained in the canonical ensemble by equating the total number of electrons in the conduction band with the total number of holes in the valence band. The standard treatment leads to the following expression for μ , first obtained by Wilson¹² in 1931:

$$\mu = E_c - \frac{1}{2}E_g + \frac{3}{4}kT \ln\left(\frac{m_v}{m_c}\right), \quad (2)$$

where E_c is the energy at the bottom of the conduction band, E_g is the gap energy, and m_v and m_c are the effective masses for the valence band and the conduction band, respectively.¹³

In the limit $T \rightarrow 0$, Eq. (2) implies that μ goes to the middle of the band gap. However, the definition of μ leads to its interpretation in the $T \rightarrow 0$ limit as the work required to add one particle to the system, which would certainly seem to be E_c . We thus have an interesting quandary: does μ go to the middle of the band gap or to the bottom of the conduction band? If the former, why is the work required to add one more particle not equal to E_c ? If the latter, what is the reason that Eq. (2) breaks down as $T \rightarrow 0$?

The details that lead to the standard expression for μ in Eq. (2) have been presented and discussed previously (see, for example, Ref. 14). We will focus here on the main reason why Eq. (2) breaks down as $T \rightarrow 0$.

III. THE INCORRECT ASSUMPTION

The following expression is readily obtained in the canonical ensemble:¹⁵

$$f_i(N, T, V) = 1 - e^{[E_i - \mu(N, T, V)]/kT} f_i(N+1, T, V), \quad (3)$$

where $f_i(N, T, V)$ is the probability of a fermion (electron) being in the one-electron eigenstate $|i\rangle$ when there are N fermions in a volume V at temperature T , with E_i the energy of the state $|i\rangle$. If we assume that $f_i(N, T, V) \approx f_i(N+1, T, V)$, we obtain the Fermi–Dirac distribution function for $f_i(N, T, V)$:

$$f_i^{\text{FD}}(N, T, V) = (e^{[E_i - \mu(N, T, V)]/kT} + 1)^{-1}. \quad (4)$$

The assumption that $f_i(N, T, V) \approx f_i(N+1, T, V)$ seems to be beyond question. Because the electron number density is of order 10^{22} cm^{-3} , how could it possibly be that adding a single electron would lead to anything but a miniscule change in the occupation probability?

The answer emerges upon considering the N -dependence of the zero temperature limit of $\mu(N, T, V)$. Let N_{vb} denote the number of electrons needed to completely fill the valence band with no electrons in the conduction band at $T=0$. For $N=N_{vb}-1, N_{vb}-2, \dots$, the zero temperature limit of $\mu(N, T, V)$ will be near the top of the valence band. For $N=N_{vb}+1, N_{vb}+2, \dots$, the zero temperature limit of $\mu(N, T, V)$ will be near the bottom of the conduction band. Thus, the zero temperature limit of $\mu(N, T, V)$ goes from E_v , the energy at the top of the valence band, to E_c , the energy at the bottom of the conduction band, as N goes from $N_{vb}-1$ to $N_{vb}+1$. The implication is that the occupation probabilities, which depend sensitively on the value of the chemical potential, especially at low temperatures, change appreciably if a particle is added. The low temperature jump in μ occurs when the total number of particles is N_{vb} , that is, $f_i(N_{vb}-1, T, V)$ and $f_i(N_{vb}, T, V)$ differ appreciably as $T \rightarrow 0$.

The proof of this last statement is as follows. Take $N=N_{vb}-1$ in Eq. (3). For all states in the conduction band, for all T of interest, we have $f_i(N_{vb}-1, T, V) \ll 1$. Thus, the exact expression (3) gives, for all states in the conduction band,

$$f_i(N_{vb}, T, V) \approx e^{-[E_i - \mu(N_{vb}-1, T, V)]/kT}. \quad (5)$$

The Fermi-Dirac distribution function, Eq. (4), however, gives the following for all states in the conduction band:

$$f_i^{FD}(N_{vb}, T, V) \approx e^{-[E_i - \mu(N_{vb}, T, V)]/kT}. \quad (6)$$

We have already seen that $\mu(N_{vb}-1, T, V)$ and $\mu(N_{vb}, T, V)$ have drastically different values at low temperatures, which implies that Eqs. (5) and (6) give drastically different values for the occupation numbers f_i . The consequence is that the Fermi-Dirac distribution function, Eq. (4), breaks down for an ideal intrinsic semiconductor as $T \rightarrow 0$.

Equation (3) can be used to obtain the asymptotic form for the chemical potential $\mu(N_{vb}, T, V)$ in the canonical ensemble as $T \rightarrow 0$. Consider the occupation numbers $f_c(N, V, T)$ of the two states at the bottom of the conduction band, with energy E_c . We have $f_c(N_{vb}, V, T) \rightarrow 0$ as $T \rightarrow 0$ for $N=N_{vb}$, and $f_c(N_{vb}+1, V, T) \rightarrow 1/2$ as $T \rightarrow 0$ for $N=N_{vb}+1$. If we use these results in Eq. (3), we find

$$\mu(N_{vb}, T, V) \rightarrow E_c - kT \ln 2, \quad (7)$$

as $T \rightarrow 0$. Note that Eq. (7) holds for temperatures low enough that kT is much smaller than the spacing of the energy levels at the bottom of the conduction band. For temperatures higher than this spacing, but still low in that the number of electrons in the conduction band is of order unity, we need to use Eq. (3) to obtain the temperature dependence of μ . A full treatment gives the correct temperature dependence of the chemical potential in the canonical ensemble.¹ At temperatures where the number of electrons in the conduction band is large, the standard result, Eq. (2), is recovered. As the temperature drops low enough so that the number of electrons in the conduction band is not large, a new expression (given in the following) replaces Eq. (2). This equation for μ is

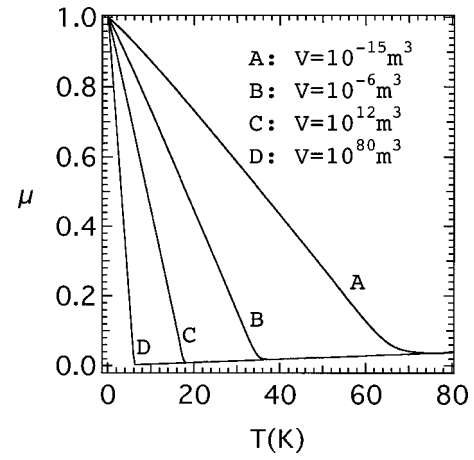


Fig. 1. The chemical potential μ of an ideal intrinsic semiconductor as a function of the temperature T for different volumes V : (a) 10^{-15} m^3 ; (b) 10^{-6} m^3 ; (c) 10^{12} m^3 ; (d) 10^{80} m^3 . $\mu=0$ corresponds to the middle of the band gap and $\mu=1$ is at the bottom of the conduction band. The effective masses have been chosen so that $(m_v/m_c)^{3/4}=2$ and $m_v m_c = m^2$.

$$\begin{aligned} \mu(N_{vb}, T, V) = E_c - \frac{1}{2} E_g + kT \ln \left[\left(\frac{m_v}{m_c} \right)^{3/4} \alpha(T, V) \right] \\ - kT N_i(T, V) [\alpha(T, V) + \alpha^{-1}(T, V) - 2], \end{aligned} \quad (8)$$

where

$$N_i(T, V) = \frac{1}{4} V \left(\frac{2kT}{\pi \hbar^2} \right)^{3/2} (m_v m_c)^{3/4} e^{-E_g/2kT}, \quad (9)$$

and

$$\alpha(T, V) = \frac{1 + \sqrt{1 + 4N_i^2(T, V)}}{2N_i(T, V)}, \quad (10)$$

with m_c and m_v the effective masses at the bottom of the conduction band and the top of the valence band.¹ Figure 1 shows $\mu(N_{vb}, T, V)$ as a function of T for various values of V .

The weak dependence of μ on the volume V at low temperatures can be understood as follows. From Eqs. (8) to (10), we see that the chemical potential begins to increase toward the conduction band when $N_i(T, V) \ll 1$, from which we find that V appears in the argument of the natural logarithm.

An interesting aspect of the logarithmic dependence of μ on V is the following. The statistically important quantity that determines the temperature, T_0 , at which μ starts to increase toward the conduction band, is the total number of electrons in the conduction band, N_{cb} . Consider increasing V and N without changing N/V and take V and N to be arbitrarily large but fixed. For any such value of V and N , there is a temperature T_0 at which N_{cb} is of order unity. For $T_0 > T \rightarrow 0$, $\mu \rightarrow E_c$. T_0 decreases with increasing V and N , but very slowly. Even for a volume of the order of 10^{80} m^3 as in Fig. 1(d), T_0 is still about 5 K.

The opposite extreme is to take T arbitrarily small but fixed, and then take $V \rightarrow \infty$ with N/V fixed. In this case Eq. (2) is recovered. Note that this recovery of Eq. (2) requires an enormous volume V . From Fig. 1 we see that for T

$=5\text{ K}$, V must be greater than 10^{80} m^3 , and for lower temperatures, V must be larger still. Further discussion of the volume dependence for large V and small T and related questions are given in Ref. 1.

IV. PEDAGOGICAL VALUE

Instructors might wish to use the material presented here to show students how important it is that assumptions be checked. There are a number of related problems, some of which can be given as problems for students.^{16–18} Some examples are as follows.

The most straightforward extension is to calculate the low temperature behavior of the chemical potential of the ideal intrinsic semiconductor with $N=N_{\text{vb}}-1, N_{\text{vb}}-2, \dots$; $N=N_{\text{vb}}+1, N_{\text{vb}}+2, \dots$.

Another challenging and interesting problem is to take into account the presence of N_d donor and N_a acceptor impurities. One can compare the chemical potential calculated using the Fermi–Dirac distribution function with the exact method outlined in this paper. One finds that the two differ negligibly whenever $N_d \gg 1$, $N_a \gg 1$, and $|N_d - N_a| \gg 1$, which makes sense, and explains why the incorrect result was not noticed for such a long time. The result is that there is, as expected, a noticeable difference between the Fermi–Dirac distribution function μ and the exact μ when $|N_d - N_a|$ is of order unity.

An instructive example for students is the case $N_d > N_a = 0$. Using the Fermi–Dirac distribution function gives $\mu \rightarrow (E_c + E_d)/2$ as $T \rightarrow 0$, whereas the correct treatment gives $\mu \rightarrow E_d$ as $T \rightarrow 0$ (E_d is the energy level of donors). This result can be extended to N_d and N_a of order unity: one finds that the Fermi–Dirac distribution function and the exact treatment give similar, but distinguishable results.

It is important to note that calculations can be solved in the canonical or the grand canonical ensemble. The same answers to the same physical questions can be found in either ensemble. For example, μ as given by Eq. (1) can be obtained by working in either ensemble, as was shown in Ref. 1.

V. DISCUSSION

A possible but unsatisfactory response to the low temperature behavior of the chemical potential of an ideal intrinsic semiconductor is to avoid the question by introducing a new quantity which we denote by ϕ . The quantity ϕ is taken to be the average of the chemical potential for adding one particle and the chemical potential for adding one hole in the canoni-

cal ensemble. Then using reasoning similar to that of the standard treatment of μ , it is found that as $T \rightarrow 0$, ϕ goes to the middle of the band gap. However, this response is inadequate. Introducing a new quantity begs the question addressed in this paper: the $T \rightarrow 0$ limit of ϕ does not explain what the $T \rightarrow 0$ limit of μ is. The result that ϕ goes to the middle of the gap would seem to suggest that μ goes to the bottom of the conduction band, and that the chemical potential for adding one hole goes to the top of the valence band. However, the introduction of ϕ does not explain why $\mu \rightarrow E_c$ as $T \rightarrow 0$, and does not give the low temperature behavior of μ .

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¹³Note that Wilson did not, in his 1931 paper, state that μ goes to the middle of the band gap as $T \rightarrow 0$.

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