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# THERMODYNAMIC PROPERTIES OF SATURATED SEMICONDUCTORS

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The thermodynamic properties of a direct gap semiconducting system, under high intensity optical pumping are studied. The strong electromagnetic field of the pumping beam must have a frequency larger than the band gap. A Bose condensation of electron–hole pairs of zero momentum is found as the temperature goes to zero. This condensation persits even when the finite wavevector of the pump is taken into account.

IT HAS been shown[1] that high temperature superconductivity can be achieved in semiconducting systems with an inverted population of quasi particles. Such a system can be obtained by optical pumping on a direct gap semiconductor, with intensity high enough to insure that the probability of creating an electron–hole pair exceeds the recombination probability. For an electromagnetic wave whose frequency $\omega$ is larger than the band gap $\omega_g$, the bottom of the conduction band is filled with electrons and the top of the valence band with holes up to an energy $(1/m_e + 1/m_h)K_F^2/2 = \omega - \omega_g$. The energy spectrum, $\Omega(p)$, of the quasi particles in this system is found to be[2]

$$\Omega(p) = \tfrac{1}{2}[\epsilon_e(p) - \epsilon_h(p)] \pm \sqrt{\tfrac{1}{4}[\epsilon_e(p) + \epsilon_h(p)]^2 + \lambda_p^2} \quad (1)$$

with

$$\epsilon_{e(h)}(p) = \frac{p^2}{2\bar{m}_{e(h)}} + \frac{\omega_g - \omega}{2}. \quad (2)$$

Equation (1) shows a gap, $\lambda_p$, in this spectrum which depends on the field, the matrix element of **p** between the conduction and valence band and the angle between the direction of the field and the momentum of the electron.[3] Electric and magnetic properties of this system have been calculated by several authors by means of a canonical transformation.[3,4]

In order to reveal possible phase transtions in the system its thermodynamic properties must be known. No calculation of this kind is available to date. In the present work we undertake the calculation of the partition function for the aforementioned system using a mathematical method proposed by Eckmann and Guenin (EG) for solving fermion problems.[5] This method provides an extremely simple but exact solution to our problem making the present treatment superior to the previously used ones which yield numerical solutions. Our treatment predicts the existence of a condensed phase of electron–hole pairs, as $T$ goes to zero, which persists even when the finiteness of the wave vector of the pumping light is taken into account.

We consider a two band semiconductor in an electromagnetic field of vector potential

$$\mathbf{A} = \mathbf{A}_0 \cos(\omega t - \mathbf{q}\cdot\mathbf{r}), \quad \mathbf{A}\cdot\mathbf{q} = 0 \quad (3)$$

whose Hamiltonian, in the effective mass approximation, ignoring Coulomb interaction between electrons and holes, is given by:

$$H = \sum_p E_e(p)a_p^+a_p + E_h(p)b_{-p}b_{-p}^+ + \lambda_{p,q}a_p^+b_{-(p+q)}^+\,e^{-i\omega t} + \lambda_{p,q}^*b_{-(p+q)}a_p\,e^{i\omega t}, \quad (4)$$

here $E_e(p)$ and $E_h(p)$ are the energy of electrons and holes measured from the center of the band gap; $a_p^+(b_{-p}^+)$ and $a_p(b_{-p})$ are the creation and annihilation operators for electrons (holes), and $\lambda_{p,q}$ is the electric dipole matrix element for the interband transition. Performing the unitary transformation

$$U(t) = \exp\left\{-\frac{i\omega t}{2}\sum_p a_p^+ a_p + b_{-p}^+ b_{-p}\right\}, \quad (5)$$

the Hamiltonian becomes

$$H = \sum_p H_p = \sum_p \epsilon_e(p) a_p^+ a_p + \epsilon_h(p) b_{-p}^+ b_{-p} + \lambda_{p,q} a_p^+ b_{-(p+q)}^+ + \lambda_{p,q}^* b_{-(p+q)} a_p, \quad (6)$$

where $\epsilon_e$ and $\epsilon_p$ are given in equation (2).

First we consider the case $q = 0$, and a real $\lambda_p$ for simplicity. Then we can write

$$\exp\left\{-\sum_p H_p/kT\right\} = \prod_p \exp\{-H_p/kT\} \quad (7)$$

therefore the EG method is easily applicable to the problem. The vector basis, obtained by application of the EG method, given by

$$v_{n,A} = \langle\underbrace{H\ldots H}_{n-1}A\rangle \quad (8)$$

where $\langle\ldots\rangle$ means average over the ground state, has dimensionality four, and is

$$v_1 = 1$$

$$v_2 = \epsilon_e N_e + \epsilon_h N_h + \lambda(S^+ + S)$$

$$v_3 = (\epsilon_e^2 - \lambda^2)N_e + (\epsilon_h^2 - \lambda^2)N_h + \lambda^2 1 + \lambda(\epsilon_e + \epsilon_h)(S^+ + S) + 2(\epsilon_e\epsilon_h + \lambda^2)S^+S. \quad (9)$$

$$v_4 = \lambda^2(\epsilon_e + \epsilon_h)1 - \lambda^2(\epsilon_e + \epsilon_h)(N_e + N_h) + \epsilon_e^3 N_e + \epsilon_h^3 N_h + 3(\epsilon_e + \epsilon_h)(\epsilon_e\epsilon_h + \lambda^2)S^+S + \lambda\{(\epsilon_e + \epsilon_h)^2 + \lambda^2\}\cdot(S^+ + S)$$

where $N_e = a^+a$, $N_h = b^+b$, $S^+ = a^+b^+$ and $S = ba$ and we had dropped the index $p$ for simplicity. The fifth vector $v_5 = \langle HHHH\rangle$ is found to be a linear combination of the other four

$$v_5 = \lambda^2\epsilon_e\epsilon_h v_1 + (\epsilon_e + \epsilon_h)(\epsilon_e\epsilon_h - \lambda^2)v_2 + [\lambda^2 - \epsilon_e\epsilon_h - (\epsilon_e + \epsilon_h)^2]v_3 + 2(\epsilon_e + \epsilon_h)v_4 \quad (10)$$

and the matrix $L_{H,1}$, defined by

$$L_{H,A} v_A = HA$$

gives:[5]

$$L_{H,1} = \begin{bmatrix} 0 & 0 & 0 & \lambda^2\epsilon_e\epsilon_h \\ 1 & 0 & 0 & (\epsilon_e + \epsilon_h)(\epsilon_e\epsilon_h - \lambda^2) \\ 0 & 1 & 0 & \lambda^2 - \epsilon_e\epsilon_h - (\epsilon_e + \epsilon_h)^2 \\ 0 & 0 & 1 & 2(\epsilon_e + \epsilon_h) \end{bmatrix} \quad (11)$$

whose eigenvalues $\omega_k$, are: $\epsilon_e$, $\epsilon_h$ and $(\epsilon_e + \epsilon_h)/2 \pm \sqrt{(\epsilon_e + \epsilon_h/2)^2 + \lambda^2}$. Then

$$\exp(-H_p/kT) = \sum_{k=1}^{4} \mu_k x_k \exp(-\omega_k/kT) \quad (12)$$

where $\mu_k$ are the eigenvectors of $L_{H,1}$, and $x_k$ is defined by $v_1 = \sum_{k=1}^{4} \mu_k x_k$. Straightforward application of the EG method yields:[5]

$$Z = \prod_p Z(p) = 2\prod_p \exp\{-[\epsilon_e(p) + \epsilon_h(p)]/2kT\}\cdot\left\{ch\,\frac{\epsilon_e(p) - \epsilon_h(p)}{2kT} + ch\,\frac{\alpha(p)}{kT}\right\} \quad (13)$$

here $\alpha(p) = \sqrt{\lambda_p^2 + (\epsilon_e + \epsilon_h)^2/4}$. The number of electron–hole pairs is given by the thermal average of $\langle S^+S\rangle_T$, or

$$\langle S^+S\rangle_T = \frac{1}{2}\sum_p \frac{ch\left(\frac{\alpha(p)}{kT}\right) - \frac{\epsilon_e(p) + \epsilon_h(p)}{2\alpha(p)}\,sh\left(\frac{\alpha(p)}{kT}\right)}{ch\left(\frac{\epsilon_e(p) - \epsilon_h(p)}{2kT}\right) + ch\left(\frac{\alpha(p)}{kT}\right)} \quad (14)$$

$\langle S^+S\rangle_T$ tends to half the number of electrons plus holes[6] when $T \to 0$, near the quasi-particle Fermi surface, and we find pair condensation.

We turn now to the validity of this calculation for finite $q$. In order to do so, we write the vector potential $A(q) = A(0) + [A(q) - A(0)]$, and calculate the change in the thermodynamic potential $\Omega$. This we do by using the Green's function method. We define the Green's functions $G_e(x, x') = -i\langle T\psi_e(x)\psi_e^+(x')\rangle$ and $F^+(x, x') = \langle T\psi_h^+(x)\psi_e^+(x')\rangle$. If we write $G_e = G_e^{(0)} + G_e^{(1)}$, $F^+ = F^{+(0)} + F^{+(1)}$ and keep first order terms in $A(q) - A(0)$ we find[7]

$$\begin{pmatrix} G^{(1)}(x,x') \\ F^{+(1)}(x,x') \end{pmatrix} = \begin{pmatrix} G^{(0)}(x-x') & F^{+(0)}(x-x') \\ F^{+(0)}(x-x') & -G^{(0)}(x-x') \end{pmatrix} \begin{pmatrix} \frac{e}{mc}(\mathbf{A}-\mathbf{A}_0)\cdot\nabla F^{+(0)} \\ -\frac{e}{mc}(\mathbf{A}-\mathbf{A}_0)\cdot\nabla G^{(0)} \end{pmatrix} \quad (15)$$

where $G^{(0)}$ and $F^{+(0)}$ are the Green's functions for the unperturbed system. The change in the thermodynamic potential turns out to be:

$$\Delta\Omega = \pm\pi VT \sum_{\omega_n} \int d^3p \frac{ie}{mc}(\mathbf{A}_0\cdot\mathbf{p}) \Big\{ F^{+(0)}(\mathbf{p}-\mathbf{q}, \omega_n-\omega) - F^{+(0)}(\mathbf{p},\omega_n-\omega) - F^{+(0)}(p,\omega_n) \times \left( \frac{G^{(0)}(\mathbf{p}-\mathbf{q},\omega_n-\omega)}{G^{(0)}(\mathbf{p},\omega_n)} - \frac{G^{(0)}(\mathbf{p},\omega_n-\omega)}{G^{(0)}(\mathbf{p},\omega_n)} \right) \Big\}; \quad (16)$$

to estimate this expression for $q \to 0$, we use $G^{(0)}(p,\omega)$ and $F^{+(0)}(p,\omega)$ found by Elesin[3] (for $m_e = m_h$), and find

$$\Delta\Omega = \frac{V\pi\omega}{4} \int d^3p \frac{e}{mc}(\mathbf{A}_0\cdot\mathbf{p})\lambda_p \frac{\mathbf{p}\cdot\mathbf{q}}{m} \frac{\epsilon(p)}{\alpha(p)[\alpha(p)-i\delta]} \times \left\{ \frac{\delta[\omega+\alpha(p-q)]}{\epsilon(p)-\omega-\alpha(p-q)+i\delta} + \frac{\delta[\omega-\alpha(p-q)]}{\epsilon(p)-\omega+\alpha(p-q)-i\delta} \right\}$$

which goes to zero for $q \to 0$.

We have succeeded in calculating the partition function for a saturated semiconductor by a method which is at the same simple and exact. We have found a Bose condensation of pairs, near the Fermi surface when $T$ goes to zero, brought about by the interaction between electron–hole pairs via electromagnetic fields. Work is under way to find out if there exists a finite temperature $T_c > 0$ at which this condensation occurs including many body effects and a more realistic many band model. This condensation should lead to important changes in some observable quantities of which optical absorption and Raman scattering are being considered. These extensions of the present work will be published elsewhere.

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6. $N_{el} + N_{\text{holes}} = -kT \sum_p [1/Z(p)]\,[\partial Z(p)/\partial\epsilon_e(p) + \partial Z(p)/\partial\epsilon_h(p)]$.
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