RADIATIVE TRANSITIONS IN SEMICONDUCTORS

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A basis system of functions, whose set of quantum numbers includes the occupation numbers, is introduced, in the two-band approximation, for an excited radiation system consisting of a semiconductor and radiation field. A criterion for occurrence of interband multiphoton transitions is found with help of an appropriate perturbation-theory series. The absorption coefficient is calculated in the "one-photon" approximation and is found to be the same as that calculated by Bardeen, Blatt and Hall.[4]

1. INTRODUCTION

ALEKSEEV, Vdovin, and Galitskiĭ[1] have investigated the photon density oscillations in a system of two-level molecules. It has turned out that the system radiates in a strongly bound state, starting with a definite instant of time which depends in turn on the molecule density. The interaction of radiating objects with one another can also be described by expanding the system evolution operator F(t) in a perturbation-theory series[2]. A perfectly analogous approach will be applied below to a system consisting of an intrinsic semiconductor and a radiation field, contained in a volume V which constitutes the physical volume of the entire system.

In analogy with the earlier procedure[2], we can introduce a basis system of functions of the unperturbed Hamiltonian H_0 of the semiconductor and the radiation field, such that the set of quantum numbers of the functions include also the occupation numbers of the bands and of the field oscillators. In the interaction representation, the state of the system at the instant of time t is determined by the action of the time-shift operator[3] S on the wave function of the initial state of the unperturbed system:

$$\Psi(t) = S(t)\Psi_i(0). \tag{1}$$

On the other hand, we can write two expansions; one for Ψ:

$$\Psi(t) = \sum_l C_l(t)\Psi_l(0), \tag{2}$$

and another for S(t)

$$S(t) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} T \int_0^t H^{int}(t_1)\dots H^{int}(t_n)\,dt_1\dots dt_n. \tag{3}$$

From (2) and (3), taking into account the fact that $C_i(0) = 1$, it follows that

$$C_m(t) = \sum_{k=0} \frac{(-i)^{m+2k}}{(2k+m)!} \times \left\langle m \left| T \int_0 H^{int}(t_1)\dots H^{int}(t_{|m-i|+2k}) \right| i \right\rangle. \tag{4}$$

Here we have retained in the series (3) only the terms with "reabsorption" of photons, which lead to the same final state. If there are i photons in the initial state and m photons in the final state, we call this an (m − i)-photon transition (with emission or absorption).

The transitions defined in this manner are real, that is, they conserve energy, and must be distinguished from the well-known virtual processes. Unlike the latter, the former exist only in excited many- or single-particle systems. For example, for one molecule excited at the initial instant of time, in the absence of a radiation field, and in the presence of only one type of oscillation, formula (4) takes the form

$$C_{2,0}(t) = \sum_{l=0} \frac{(-i)^{2l}}{(2l)!} \times \left\langle 2,0 \left| T \int_0^t H^{int}\dots H^{int}(t_{2l})\,dt_1\dots dt_{2l} \right| 2,0 \right\rangle,$$

$$C_{1,1}(t) = \sum_{l=0} \frac{(-i)^{2l+1}}{(2l+1)!} \times \left\langle 1,1 \left| T \int_0 H^{int}(t_1)\dots H^{int}(t_{2l+1})\,dt_1\dots dt_{2l+1} \right| 2,0 \right\rangle,$$

where $C_{2,0}(t)$ is the amplitude of the initial state and $C_{1,1}(t)$ is the amplitude of the final state $[C_{2,0}(0) = 1]$.

We confine ourselves below to the modest problem of estimating the relative probability of excitation of multiphoton states in a semiconductor, if at the initial instant there is no radiation field and part of the electrons is transferred from the valence band to the conduction band. The absorption coefficient which we calculate in the "single-photon" approximation (linear in the time), confining ourselves only to the term $S^{(1)}$ in (3), coincides with that obtained by Bardeen, Blatt, and Hall[4].

To clarify the qualitative aspects of the phenomena, we confine ourselves to direct allowed transitions in an intrinsic semiconductor with spherical equal-energy surfaces. We consider the interaction of the carriers with the free radiation field, without account of the interaction with the phonons. The distribution function at the initial instant of time is chosen in the form of "step functions":

$$f_{c,v}(p) = \begin{cases} 1, & p \leqslant p^F_{c,v} \\ 0, & p > p^F_{c,v} \end{cases},$$

where $p^F_{c,v}$ are the Fermi momenta of the carriers in the conduction band c and in the valence band v, respectively.

To carry out the program we must find the Hamiltonian for the interaction between the carriers and the radiation field. The expression obtained below for H is very similar to the corresponding one obtained from other physical considerations by Bonch-Bruevich and Rozman[5].

2. HAMILTONIAN OF THE SYSTEM

We assume for the unperturbed Hamiltonian H_0 the sum of the Hamiltonian of the atomic conduction electron in the field of an ideal crystal lattice, and the Hamiltonian of the free radiation field.

Without taking into account the Coulomb interaction of the electrons and holes with each other, or their interaction with the lattice vibrations and with the additional Coulomb field in the case of a lattice with an ionic bond, we start with the well-known expression for H^{int}

$$H^{int} = c^{-1}\mathbf{jA}. \tag{5}$$

Here j is the operator of current density in the semiconductor crystal, A the vector potential of the free radiation field, and c the velocity of light in vacuum. For the single-particle functions we choose Bloch functions normalized in the ground-state and satisfying the well-known periodic conditions

$$\sum_s \int_V \varphi^*_{lp\sigma}(\mathbf{r}, s)\,\varphi_{l'p'\sigma'}(\mathbf{r}, s)\,dV = \delta_{ll'}\delta_{pp'}\delta_{\sigma\sigma'},$$
$$\varphi_{lp\sigma}(\mathbf{r} + \mathbf{a}_m, s) = \varphi_{lp\sigma}(\mathbf{r}, s). \tag{6}$$

Here l is the number of the band, p the quasi-momentum of the electron, and σ the index of the spin state. We shall also need the formula

$$\sum_m \exp[i(\mathbf{p} - \mathbf{p}')\mathbf{a}_m] = \delta_{pp'}G^3, \tag{7}$$

where $\mathbf{a}_m$ is the vector of the m-th lattice site, G^3 is the number of unit cells, and the summation is over the principal region.

If we confine ourselves only to electric dipole transitions, then the Hamiltonian (5) will be diagonal in the spin states of the electrons participating in the transition. Inasmuch as the total and angular momenta of the system are conserved, it is clear that as the electron goes from band v into band c, the resultant hole should have momentum and spin with signs opposite to those possessed by the electron.

Since we are considering only allowed dipole transitions, the term proportional to A^2 in (5) makes no contribution to the kinematics in question, for the corresponding transition is forbidden. Introducing operators for the creation and annihilation of an electron in band c and of a hole in band v, and taking into account the foregoing and formulas (5)—(7), we can write the following expression for the total Hamiltonian of the system ($\hbar = 1$)

$$H = \sum_{p\sigma}(\varepsilon_c(p)\,a^+_{p\sigma}a_{p\sigma} + \varepsilon_v(p)\,b^+_{p\sigma}b_{p\sigma}) + \sum_{k,\lambda=1,2}\omega_k c^+_{k\lambda}c_{k\lambda}$$
$$+\left(g\xi\sum_{k,\lambda=1,2;\ p,\sigma}\mathbf{e}_{k\lambda}\left(\frac{1}{\omega_k V}\right)^{1/2}a^+_{p\sigma}b^+_{-p-\sigma}c_{k\lambda} + \text{herm. conj.}\right), \tag{8}$$

where $g = (2\pi)^{1/2}m$, m is the mass of the atomic electron,

$$\xi = -\int_\Omega U^*_{c0}\nabla U_{v0}\,dV,$$

and Ω is the unit cell volume.

In writing down (8) we have assumed that by virtue of the fact that the transitions are allowed, the functions U depended little on the quasimomenta, so that they can be taken for $\mathbf{p} = 0$; in addition, we neglect the photon momentum. The allowance for the recoil of the electrons (holes) will be discussed briefly later.

It follows from (8) that, generally speaking, it is impossible to use the representation

$$H = \sum_i H_i, \tag{9}$$

where the summation is over the individual car-

riers. Such a breakdown is possible only when the photon density is large, so that the contribution made to it by the radiating system can be neglected and we can assume the operators $c^{+}_{k\lambda}$ and $c_{k\lambda}$ to be simply c-numbers. In the latter case the carrier motion can be considered independently of the radiation field.

3. SINGLE-PHOTON TRANSITION

Let us consider the absorption of one photon. Here and below the minus sign will denote quantum numbers that determine the electron state, and the plus sign the hole state. The initial state of the system, when we have an electron-hole vacuum and a photon ($\mathbf{k}$, λ), is defined by the vector

$$|i\rangle = |\mathbf{k}, \lambda; 0_-; 0_+\rangle,$$

while the final state is defined by

$$|f\rangle = |0; \mathbf{p}_-\sigma_-; \mathbf{p}_+\sigma_+\rangle.$$

The matrix element of the transition is of the form

$$\langle f|S^{(1)}(t)|i\rangle = -ig(\xi\mathbf{e}_{k\lambda})(\omega_k V)^{-1/2}[(1-n(p_-\sigma_-)) \times (1-n(p_+\sigma_+))]^{1/2} F_{p_-p_+k}(t)\,\delta_{\mathbf{p}_-,-\mathbf{p}_+}\delta_{\sigma_-,-\sigma_+}, \quad (10)$$

where

$$F_{p_-p_+k}(t) = \frac{\exp[i(\varepsilon_c(p_-)+\varepsilon_v(p_+)-\omega(k))t]-1}{i(\varepsilon_c(p_-)+\varepsilon_v(p_+)-\omega(k))}.$$

Averaging $|\langle f|S^{(1)}|i\rangle|^2$ over the electron motion, we obtain

$$W_{if} = \frac{g^2\overline{\xi^2}}{3}\frac{(1-n_-(p\sigma))(1-n_+(p\sigma))}{\omega_k V}2\pi\delta(\varepsilon_c(p)+\varepsilon_v(p)-\omega(k))t;$$

$$\frac{1}{3}\overline{\xi^2} = \frac{1}{4\pi}\int|\xi\mathbf{e}_{k\lambda}|^2\,do. \quad (11)$$

We have used above the well-known representation

$$\delta(x) = \lim_{t\to\infty}\frac{1}{\pi}\frac{\sin^2 xt}{x^2 t},$$

which holds true in the integral limit, when the time t is larger than $1/\Delta\omega$, where $\Delta\omega$ is the interval of "smearing" of the electron and hole distribution functions.

However, even in the case when we cannot introduce δ-functions, the time dependence of the transitions remains unchanged, and only the numerical coefficients change. This pertains both to single-photon and multiphoton transitions.

We assume, introducing effective masses, the usual dispersion law

$$\varepsilon_c(p) = \Delta + \frac{p^2}{2m_n}, \qquad \varepsilon_v(p) = \frac{p^2}{2m_p}, \quad (12)$$

where Δ is the width of the forbidden band.

Summing (11) over all final states with account of (12), we obtain the probability for absorption of a photon with a frequency in the interval ω, $\omega + d\omega$:

$$dW^{v}(\dot{\omega}) = \frac{2}{3\pi^3}\frac{g^2\overline{\xi^2}}{\hbar^2c^3}\frac{\mu}{\hbar}\left(\frac{2\mu}{\hbar}(\omega-\Delta)\right)^{1/2}\omega V t\,d\omega \quad (13)$$

(the constant $\hbar$ was introduced into the final result).

Introducing with the aid of the equation

$$\overline{\xi^2} = \hbar m\Delta f_{cv}/2$$

the oscillator strength $f_{c,v}$, we can rewrite (13) in the form

$$dW^{v}(\omega) = \frac{2e^2\Delta^2 f_{cv}}{3\pi^2\hbar c^3}\frac{\mu}{m}\left(\frac{2\mu}{\hbar}(\omega-\Delta)\right)^{1/2} V t\,d\omega. \quad (13')$$

By definition, the absorption coefficient for a unit interval of the frequency ω is equal to

$$\alpha(\omega) = \frac{N(\omega)}{c}w_0^{v}(\omega), \quad (14)$$

where $N(\omega)$ is the refractive index, c the velocity of light in vacuum, and $w_0^{\gamma}(\omega)$ the probability of absorbing a photon with frequency ω per unit time and per unit volume.

Substituting (13) or (13′) in (14), we arrive at an expression with the same dependence on the photon energy and on the reduced mass as the equation obtained in [4].

In that case when "single-photon" recombination is considered, it is necessary to introduce in formulas (13) and (13′) the "unit step" function

$$\theta = \begin{cases} 1, & \mathbf{p} \leqslant \{p_c^F, p_v^F\}_{min} \\ 0, & \mathbf{p} > \{p_c^F, p_v^F\}_{min} \end{cases}.$$

Allowance for the recoil of the carriers upon absorption (emission) of photons leads to rather trivial results. The recoil is largest for carriers with minimal effective mass. In the absorption (emission) of a photon the process begins with a photon energy equal to

$$\omega_{pr} = \Delta + \hbar k^2/2m,$$

where m is the mass of the carrier experiencing the recoil. In addition, an account of the recoil leads to the "cutoff" of the distribution functions at a quasimomentum equal to the photon momentum. In this case the density of the carriers which are "forbidden" to participate in the direct transition turns out to be quite large (at $k \sim 3\times10^4$ cm^{-1} we have $n \sim 10^{12}$ cm^{-3}). Thus, the calculations made are valid for sufficiently large occupation numbers of the bands and energies of the photons.

The analysis of the carrier recombination processes near the bottoms of the bands should be car-

ried out both with account of the interaction with the phonons, and with account of the possible exciton and polaron states.

4. TWO-PHOTON TRANSITION

Assume that in the initial state the electrons and holes occupy levels up to p_c^F and p_v^F, respectively; there are no photons. In the final state there are photons of two sorts ($\mathbf{k}$, λ) and there are no pairs ($\mathbf{p}'_-\sigma'_-$; $\mathbf{p}'_+$, σ'_+) and ($\mathbf{p}''_-$, σ''_-; $\mathbf{p}''_+$, σ''_+).

Disregarding for the time being, as before, the "reabsorption" processes, that is, the kinetics of the two-photon state itself, we select from (4) only the very first term with k = 0. Leaving out the sign of the T-product we have for $S^{(2)}$ the matrix element

$$\langle f|S^{(2)}|i\rangle=(-i)^2\frac{\sqrt{2}}{2}\frac{g^2}{\omega_k V}(\mathbf{e}_{k\lambda}\xi)^2[n(p_-'\sigma_-')\times n(p_-''\sigma_-'')n(p_+'\sigma_+')n(p_+''\sigma_+'')]^{1/2}F_{p_-'p_+'k}(t)F_{p_-''p_+''k}(t)\times\delta_{\mathbf{p}_-',-\mathbf{p}_+'}\delta_{\mathbf{p}_-'',-\mathbf{p}_+''}\delta_{\sigma_-',-\sigma_+'}\delta_{\sigma_-'',-\sigma_+''}. \quad (15)$$

Expression (15) must be understood as a direct transition with simultaneous emission of two photons, whereby each pair of carriers recombines "independently" and the energy conservation law is satisfied in both cases. But at the same time the recombining pairs are bound in the sense that the following equation is satisfied:

$$dW^{2\nu}\neq dW^{\nu}dW^{\nu}. \quad (16)$$

Indeed, taking the square of the modulus of (15) and carrying out all the summations, we obtain for the probability of two-photon recombination with emission of two coherent photons (we have introduced $\hbar$)

$$dW^{2\nu}(\omega)=\frac{4}{25\pi^4}\frac{g^4\overline{\xi^4}}{\hbar^4c^3}\left(\frac{\mu}{\hbar}\right)^3(\omega-\Delta)V\theta t^2d\omega. \quad (17)$$

Comparing (17) and (13) we see that condition (16) is indeed satisfied. Introducing the oscillator strength with the aid of the equation

$$\overline{\xi^4}=\hbar^2m^2\Delta^2f_{cv}^2/4$$

we can rewrite (17) in the form

$$dW^{2\nu}(\omega)=\frac{1}{25\pi^4}\frac{g^4m^2\Delta^2}{\hbar^2c^3}f_{cv}^2\left(\frac{\mu}{\hbar}\right)^3(\omega-\Delta)V\theta t^2d\omega. \quad (17')$$

In the case when there are two photons of different types, ($\mathbf{k}$, λ) and ($\mathbf{k}'$, λ') in the final state, that is, radiation of incoherent photons takes place, the averaging over the electronic motion is of the form

$$\overline{|\xi\mathbf{e}_{k\lambda}|^2|\xi\mathbf{e}_{k'\lambda'}|^2}=\frac{1}{9}(\overline{\xi^2})^2.$$

Carrying out independent integrations over the final state of the photons, we arrive at the formula

$$dW^{\nu,\nu}=dW^{\nu}dW^{\nu}, \quad (18)$$

which does not depend on the wavelength. Thus, there is no spontaneous coherence in the semiconductor.

A description of the foregoing system in the time-linear (single-photon) approximation is valid only in the case when the following inequality holds:

$$dW^{2\nu}/dW^{\nu}\ll 1. \quad (19)$$

Assuming for an estimate $(\omega-\Delta)\sim 10^{14}$ sec^{-1}, $\mu\sim 10^{28}$ g, and $f_{cv}\sim 1$, we get

$$dW^{2\nu}/dW^{\nu}\sim 2\cdot 10^{13}t;$$

the numerical factor here has the dimension of frequency.

The dependence of (19) on the concentration is not strong; it is porportional to $(\omega^F-\Delta)^{1/2}$. The observations concerning the allowance for recoil are the same here as before.

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