Theory of two-electron transitions in semiconductors

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A theoretical consideration of the radiative two-electron transitions in semiconductors is given. The expressions for the matrix elements are derived by means of perturbation theory. Also, possible enhancement mechanisms of the two-electron transitions in semiconductors with direct band gaps are discussed.

In a series of experimental works on the luminescence of the highly excited indirect-gap semiconductors Si and Ge Betzler, Conradt, Weller, and Zeh[1-6] have observed a new luminescence line at frequencies $\omega \approx 2E_g$, where E_g is the band gap of the semiconductors. This line is the result of the recombination of two electron-hole pairs into a photon. In this note we consider some general properties of the matrix elements and of the luminescence spectra of the recombination of two electrons and two holes into a photon in semiconductors with both direct and indirect band gaps.

In Refs. 1 and 5 it was noted that in the framework of perturbation theory the recombination of two electron-hole pairs into a photon is a process of first order with respect to the interaction of the electromagnetic field with the charge carriers, and of first order with respect to their Coulomb interactions. However, the Coulomb interaction is a consequence of the exchange of the virtual scalar photons, but these photons are not the unique particles which mediate the interactions between the charge carriers; there may be other virtual particles: spin-1 photons, phonons, etc. We shall obtain the matrix elements of the radiative two-electron transition processes taking into account the electromagnetic interaction of electrons and holes in its general form, and also the electron-phonon interaction. We denote the energy bands, spin projections, momenta and energies of electrons by c_i, s_i^c, p_i, and E_i^c, where $i=1,2$ and those of the unoccupied electron states which are considered as the holes by v_j, s_j^v, q_j, and E_j^v. We note that due to the requirement of Fermi statistics the matrix element of any process with two electrons and two holes in the initial state is of the form

$$\begin{aligned} M_{s_i^c s_j^v}&(c_i p_i E_i^c; v_j q_j E_j^v) \\ &= T_{s_1^c s_2^c s_1^v s_2^v}(c_1 p_1 E_1^c, c_2 p_2 E_2^c; v_1 q_1 E_1^v, v_2 q_2 E_2^v) \\ &\quad - T_{s_2^c s_1^c s_1^v s_2^v}(c_2 p_2 E_2^c, c_1 p_1 E_1^c; v_1 q_1 E_1^v, v_2 q_2 E_2^v) \\ &\quad + T_{s_2^c s_1^c s_2^v s_1^v}(c_2 p_2 E_2^c, c_1 p_1 E_1^c; v_2 q_2 E_2^v, v_1 q_1 E_1^v) \\ &\quad - T_{s_1^c s_2^c s_2^v s_1^v}(c_1 p_1 E_1^c, c_2 p_2 E_2^c; v_2 q_2 E_2^v, v_1 q_1 E_1^v), \end{aligned} \tag{1}$$

where

$$T_{s_1^c s_2^c s_1^v s_2^v}(c_1 p_1 E_1^c, c_2 p_2 E_2^c; v_1 q_1 E_1^v, v_2 q_2 E_2^v) \tag{2}$$

is some function of the momenta p_i, q_j.

We shall consider the interaction of charge carriers with the quantized electromagnetic field and the electron-phonon interaction in the lowest order of perturbation theory. The corresponding Feynman diagrams are given in Fig. 1 (when only electromagnetic interaction is taken into account) and Fig. 2 (contributions of the electron-phonon interaction). In this order we have

$$\begin{aligned} T_{s_1^c s_2^c s_1^v s_2^v}&(c_1 p_1 E_1^c, c_2 p_2 E_2^c; v_1 q_1 E_1^v, v_2 q_2 E_2^v) \\ &= \xi_\alpha \left(e^3 \sum_{i=1}^{5} F_i^\alpha + e \sum_{i=6,7} F_i^\alpha \right), \end{aligned} \tag{3}$$

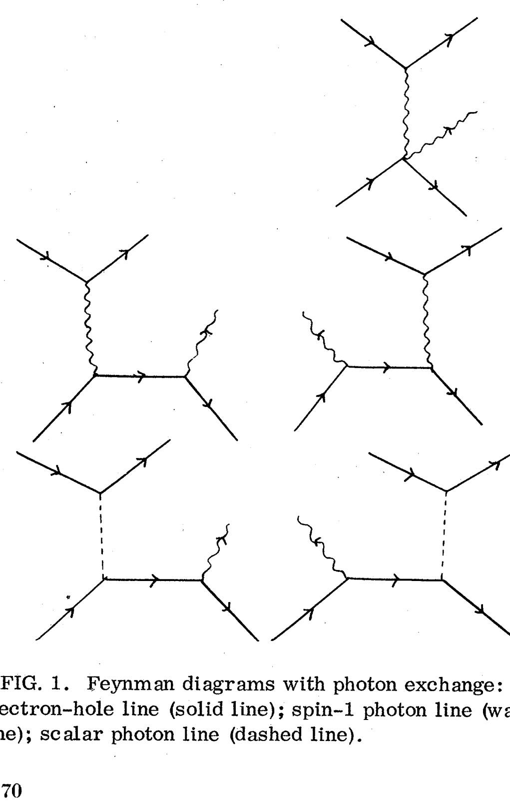

FIG. 1. Feynman diagrams with photon exchange: electron-hole line (solid line); spin-1 photon line (wavey line); scalar photon line (dashed line).

where

$$F_1^\alpha = -\frac{1}{m} \frac{(v_1 s_1^v q_1 | c_1 s_1^c p_1)(v_2 s_2^c q_2 | \Gamma^\alpha | c_2 s_2^c p_2)}{\epsilon [E_2^c(p_2) - E_2^v(q_2)]^2 - (p_2 - q_2)^2}, \tag{4a}$$

$$F_2^\alpha = \frac{(v_2 s_2^v q_2 | \Gamma^\beta | c_2 s_2^c p_2)}{\epsilon [E_2^c(p_2) - E_2^v(q_2)]^2 - (p_2 - q_2)^2} \sum_{n,s} \frac{(v_1 s_1^v q_1 | \Gamma^\beta | nsp_1)(nsp_1 | \Gamma^\alpha | c_1 s_1^c p_1)}{E^n(p_1) - E_1^c(p_1) + \omega}, \tag{4b}$$

$$F_3^\alpha = \frac{(v_2 s_2^v q_2 | \Gamma^\beta | c_2 s_2^c p_2)}{\epsilon [E_2^c(p_2) - E_2^v(q_2)]^2 - (p_2 - q_2)^2} \sum_{n,s} \frac{(v_1 s_1^v q_1 | \Gamma^\alpha | nsq_1)(nsq_1 | \Gamma^\beta | c_1 s_1^c p_1)}{E^n(q_1) - E_1^v(q_1) - \omega}, \tag{4c}$$

$$F_4^\alpha = -\frac{1}{\epsilon} \frac{(v_2 s_2^v q_2 | c_2 s_2^c p_2)}{\epsilon [E_2^c(p_2) - E_2^v(q_2)]^2 - (p_2 - q_2)^2} \sum_{n,s} \frac{(v_1 s_1^v q_1 | \Gamma^\alpha | nsq_1)(nsq_1 | c_1 s_1^c p_1)}{E^n(q_1) - E_1^v(q_1) - \omega}, \tag{4d}$$

$$F_5^\alpha = -\frac{1}{\epsilon} \frac{(v_2 s_2^v q_2 | c_2 s_2^c p_2)}{\epsilon [E_2^c(p_2) - E_2^v(q_2)]^2 - (p_2 - q_2)^2} \sum_{n,s} \frac{(v_1 s_1^v q_1 | nsp_1)(nsp_1 | \Gamma^\alpha | c_1 s_1^c p_1)}{E^n(p_1) - E_1^c(p_1) + \omega}, \tag{4e}$$

$$F_6^\alpha = g_{c_2 v_2} \frac{\lambda(c_2 s_2^c p_2, v_2 s_2^v q_2)}{[E_2^c(p_2) - E_2^v(q_2)]^2 - \Omega(p_2 - q_2)^2} \sum_{n,s} g_{nv_1} \frac{\lambda(nsp_1, v_1 s_1^v q_1)(nsp_1 | \Gamma^\alpha | c_1 s_1^c p_1)}{E^n(p_1) - E_1^c(p_1) + \omega}, \tag{4f}$$

$$F_7^\alpha = g_{c_2 v_2} \frac{\lambda(c_2 s_2^c p_2, v_2 s_2^v q_2)}{[E_2^c(p_2) - E_2^v(q_2)]^2 - \Omega(p_2 - q_2)^2} \sum_{n,s} g_{c_1 n} \frac{\lambda(c_1 s_1^c p_1, nsq_1)(v_1 s_1^v q_1 | \Gamma^\alpha | nsq_1)}{E^n(q_1) - E_1^v(q_1) - \omega}, \tag{4g}$$

where $\alpha = 1, 2, 3$ is the vector index, ξ_α is the unit vector describing the photon polarization, e is the electronic charge, ω is the photon angular frequency, ϵ is the static dielectric constant of the semiconductor, $E^n(p)$ denotes the energy of the electron with momentum p in the energy band n, m is the electron mass, $(vs^v q | cs^c p)$ and $(vs^v q | \Gamma^\alpha | cs^c p)$ denote the integrals on the elementary cell V_0, where

$$(vs^v q | cs^c p) = \frac{1}{V_0} \int_{V_0} \mathfrak{u}_{vs^v q}(r)^* \mathfrak{u}_{cs^c p}(r) \, d^3 r,$$

$$(vs^v q | \Gamma^\alpha | cs^c p) = \frac{1}{V_0} \int_{V_0} \mathfrak{u}_{vs^v q}(r)^* \left(\frac{p+q}{2} - i \nabla \right)^\alpha \mathfrak{u}_{cs^c p}(r) \, d^3 r, \tag{5}$$

the $\mathfrak{u}_{nsp}(r)$ are the periodic factors of the Bloch wave functions of electrons, $\Omega(k)$ is the energy of the phonon with momentum k, the $g_{nn'}$ are the electron-phonon interaction constants with the initial and final electrons belonging to the energy band n and n', and $\lambda(nsp, n's'p')$ are the corresponding vertex functions. Here we use the unit system with $\hbar = c = 1$. The interband electron-phonon interaction constants $g_{nn'}, n \neq n'$, are usually smaller than the intraband ones, g_{nn}. Their values as well as the vertex functions depend essentially on the crystal structure and on the mechanism of the electron-lattice interaction (see Refs. 7 and 8).

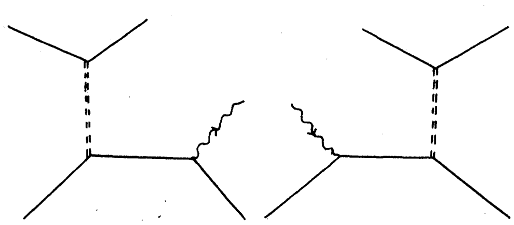

FIG. 2. Feynman diagrams with phonon exchange: electron-hole line (solid line); spin-1 photon line (wavey line); phonon line (double-dashed line).

Note that if we omit the amplitudes F_1, F_2, F_3, F_6, F_7, and approximate the scalar photon propagator

$$\frac{1}{\epsilon [E^n(p) - E^{n'}(p')]^2 - (p - p')^2}$$

by

$$-\frac{1}{(p - p')^2},$$

neglecting the retardation effect in the propagation of the interaction, we obtain the same matrix elements as those for the case when only the Coulomb interaction between the charge carriers is taken into account together with their interaction with the light.

The expression (4a)–(4g) of the amplitudes F_i^α are valid for semiconductors with both direct and indirect band gaps, if we consider only the lowest order of perturbation theory. In the case of direct-band-gap semiconductors the denominator of the photon propagator vanishes at the values of the momenta satisfying the condition

$$\epsilon [E^c(p) - E^v(q)]^2 = (p - q)^2, \tag{6}$$

and the integrals in the expressions of the transition rates will be divergent if we use Eqs. (4a)–(4g) for F_i^α. To avoid this difficulty we must also take into account the higher-order terms of the perturbation series.

In semiconductors with direct band gaps the top of the valence band and the bottom of the conduction band are located at the same point in the Brillouin zone. The momenta p_2 and q_2 in the matrix element

$(v_2 s_2^v q_2 | c_2 s_2^c p_2)$

of Eqs. (4c) and (4d) are almost equal, and this matrix element (with $p_2 \approx q_2$) vanishes, being the scalar product of two wave functions of electrons in two different stationary states. Therefore in semiconductors with direct band gaps and with allowed electrical dipole transitions only Feynman diagrams with the exchange of a spin-1 photon contribute to the matrix element,

$$F_4^\alpha = F_5^\alpha = 0 .$$

When the higher-order corrections are taken into account we have the following expression for the propagator of the spin-1 photon:

$$\frac{\delta_{\alpha\beta}}{\epsilon[E^c(p) - E^v(q)]^2 - (p-q)^2 + i\gamma} .$$

Here the imaginary part γ of the denominator is proportional to e^2 and determines the absorption rate for a photon with momentum $k = p - q$, the electron momenta p and q satisfying condition (6). Instead of the above-mentioned divergence we actually have the resonance effect owing to the possibility of the emission of a real photon in the recombination of one pair and the subsequent anti-Stokes Raman scattering of this photon by another pair. The resonance region in which the denominator of the photon propagator is very small will give the main contributions to the transition rates. After integration over p_i and q_i in this resonance region there arises a new factor γ^{-1} in the expressions of the total probabilities. Since γ is proportional to e^2 the transition rates will be proportional to $e^{6-2} = e^4$, but not to e^6, although the amplitudes contain e^3. This means that when the semiconductors with direct band gaps are highly excited there exists a new enhancement mechanism due to the resonance connected with the possibility of the exchange of a real photon by two electron-hole pairs in the transitions of these charge carriers.

It is important to remark that if instead of the electromagnetic interaction between the charge carriers considered in the framework of quantum field theory we consider only their Coulomb interaction, i.e., if we take into account only the two amplitudes F_4^α and F_5^α and omit the energy difference in the denominator of the scalar photon propagator,

$$\frac{1}{\epsilon[E^c(p) - E^v(q)]^2 - (p-q)^2} \to - \frac{1}{(p-q)^2} ,$$

we shall lose the resonance effect.

For semiconductors with indirect band gaps the energy difference in the denominator of the photon propagator is negligible in comparison with the momentum difference

$$\epsilon[E^c(p) - E^v(q)]^2 \ll (p-q)^2 .$$

There will be no resonance in the corresponding transition amplitudes.

Finally we note that in the matrix elements of the Feynmen diagrams with phonon exchange there may also be the enhancement mechanism due to the presence of the phonon propagator.

[1]K. Betzler and T. Weller, Phys. Rev. Lett. 26, 640 (1971).

[2]K. Betzler and R. Conradt, Solid State Commun. 10, 79 (1972).

[3]K. Betzler and R. Conradt, Phys. Rev. Lett. 28, 1562 (1972).

[4]W. Zeh, K. Betzler, and R. Conradt, Solid State Commun. 14, 967 (1973).

[5]K. Betzler, T. Weller, and R. Conradt, Phys. Rev. B 6, 1394 (1972).

[6]K. Betzler and R. Conradt, Solid State Commun. 17, 823 (1975).

[7]R. Ludon, Proc. R. Soc. Lond. A 275, 218 (1963).

[8]P. M. Platzman and N. Tzoar, Phys. Rev. 182, 510 (1969).