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Bound exciton recombination, and phonon replicas

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The recombination of a shallow exciton bound to the ionized donor is considered within the Hartree-Fock and the effective-mass approximations. The valence and conduction bands are assumed to be simple, i.e., nondegenerate except for spin. The exchange splitting and the longitudinal optical phonon replicas of the exciton recombination line are obtained from first principles.

I. INTRODUCTION

Excitons in semiconductors can form complexes bound at the crystal imperfections.[1] The crystal lattice vibrations influence the electronic optical spectra. Interaction with optical phonons gives replicas of the exciton recombination lines below the zero-phonon line.[1–3]

In this paper we consider the recombination of the exciton bound to an ionized donor in an ionic crystal. We take into account only the interaction between the exciton and longitudinal-optical (LO) phonons. Assuming the effective-mass approximation we describe the exciton by an envelope function.

First, starting from the many-electron model, we derive an equation for the exciton envelope function. We assume the Hartree-Fock individual-electron approximation and we neglect the spin-orbit interaction. Moreover, we make the following simplifying assumptions: (i) The valence and conduction bands are nondegenerate, therefore there is spin degeneracy only, and the form of the spin Bloch functions is $\psi_{\vec{k},\sigma}(r)=\psi_{\vec{k}}(\vec{r})\chi_\sigma(s)$. (ii) The maximum of the valence band and the minimum of the conduction band are at the Γ point in the Brillouin zone. (iii) The forbidden energy gap $E_g=E_c-E_v$ is large and the valence band is completely filled at low temperature.

It is not essential to assume the above form of the spin Bloch functions but it leads to a simple form for the expressions for the matrix elements to be calculated. For other types of the spin Bloch functions these expressions would be more complicated.

II. ENVELOPE FOR EXCITON BOUND TO IONIZED DONOR AND EXCHANGE SPLITTING

The Hamiltonian for valence electrons in a crystal with an ionized donor (at the origin of the coordinate system) is

$$\mathcal{H}_e=\sum_i\left(\frac{\vec{p}_i^{\,2}}{2m}+U(\vec{r}_i)-\frac{e^2}{|\vec{r}_i|}\right)+\sum_{i<j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,, \tag{1}$$

where $U(\vec{r})$ and $-e^2/|\vec{r}|$ are the potentials of the atomic cores and the ionized donor, respectively, $\vec{p}^{\,2}/2m$ is the electron kinetic energy, and $e^2/|\vec{r}_i-\vec{r}_j|$ is the Coulomb interaction energy of the electrons i, j. The number of unit cells in the crystal is N, so that the indices i, j label $2N$ valence electrons. Here we have assumed the static model of the crystal, where the ions are located at their equilibrium positions.

We describe the ground state of the valence electrons by the antisymmetrized product of the valence spin Bloch functions $\psi^{(v)}_{\vec{k},\sigma}(r)$ $[r\equiv(\vec{r},s)$ and $\sigma, s=\pm\frac{1}{2}]$

$$\Psi_0=[(2N)!]^{-1/2}\,P\psi^{(v)}_{\vec{k}_1,1/2}(r_1)\times\psi^{(v)}_{\vec{k}_1,-1/2}(r_2)\cdots\psi^{(v)}_{\vec{k}_N,1/2}(r_{2N-1})\psi^{(v)}_{\vec{k}_N,-1/2}(r_{2N})\,, \tag{2}$$

where P is the antisymmetrization operator. We assume Ψ_0 to be the eigenfunction of $\mathcal{H}_e$ in the zeroth-order approximation (unperturbed by the impurity potential).

The exciton, i.e., an excitation of one electron from the valence to the conduction band, can be described by the function[4]

$$\Psi_1=\sum_{\vec{k}_e,\vec{k}_h}\sum_{\sigma_e,\sigma_h}A(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h)\Phi(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h), \tag{3}$$

where

$$\Phi(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h)=[(2N)!]^{-1/2}\,P\,\psi^{(v)}_{\vec{k}_1,1/2}(r_1)\psi^{(v)}_{\vec{k}_1,-1/2}(r_2)\cdots\psi^{(v)}_{\vec{k}_h,\sigma_h}(r_{2i-1})\psi^{(c)}_{\vec{k}_e,\sigma_e}(r_{2i})\cdots\psi^{(v)}_{\vec{k}_N,1/2}(r_{2N-1})\psi^{(v)}_{\vec{k}_N,-1/2}(r_{2N}), \tag{4}$$

and the index c refers to the conduction band. We assume the direct excitation of an electron, so that the factors $A(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h)$ are nonvanishing for small $\vec{k}_e$, $\vec{k}_h$ only, and the summation over $\vec{k}_e$, $\vec{k}_h$ in Eq. (3) is around the Γ point in the Brillouin zone.

Ψ_1 is assumed to satisfy the equation

$$(\mathcal{H}_e-E)\Psi_1=0. \tag{5}$$

Now we introduce the exciton envelope function F with the Fourier transform

$$A(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h)=\frac{1}{\Omega}\iint d\vec{r}_e\,d\vec{r}_h\,F_{\sigma_e,\sigma_h}(\vec{r}_e,\vec{r}_h)\times\exp(-i\vec{k}_e\cdot\vec{r}_e+i\vec{k}_h\cdot\vec{r}_h), \tag{6}$$

where Ω is the volume of the crystal.

In order to derive the equation for F we use the effective-mass approximation, i. e., we assume the electron energy to be $E_v-\hbar^2\vec{k}^2/2m_h^*$ in the valence band and $E_c+\hbar^2\vec{k}^2/2m_e^*$ in the conduction band and we consider the following matrix element:

$$\langle\Phi(\vec{k}_e,\sigma_e;\vec{k}_h,\sigma_h)|\mathcal{H}_e-E|\Psi_1\rangle=0, \tag{7}$$

where $\langle\ |\ \rangle$ stands for

$$\sum_{s_1}\int d\vec{r}_1\cdots\sum_{s_{2N}}\int d\vec{r}_{2N}.$$

As a consequence we get the equation

$$\sum_{\beta}(H^{\mathrm{exc}}_{\alpha\beta}-E\delta_{\alpha\beta})F_\beta(\vec{r}_e,\vec{r}_h)=0, \tag{8}$$

where for simplicity we use the single index α (β) to characterize the relative spin orientations: $\alpha=1,2,3,4$ for $(\sigma_e,\sigma_h)=(\frac{1}{2},\frac{1}{2})$, $(-\frac{1}{2},-\frac{1}{2})$, $(\frac{1}{2},-\frac{1}{2})$, $(-\frac{1}{2},\frac{1}{2})$, respectively.

The nonvanishing elements $H^{\mathrm{exc}}_{\alpha\beta}$ are

$$\begin{aligned}H^{\mathrm{exc}}_{11}&=H^{\mathrm{exc}}_{22}=H,\\ H^{\mathrm{exc}}_{33}&=H^{\mathrm{exc}}_{44}=H+W\Omega_0\delta(\vec{r}_e-\vec{r}_h),\\ H^{\mathrm{exc}}_{34}&=H^{\mathrm{exc}}_{43}=-W\Omega_0\delta(\vec{r}_e-\vec{r}_h),\end{aligned} \tag{9}$$

with

$$H=E_0+E_g-\frac{\hbar^2}{2m_e^*}\Delta_e-\frac{\hbar^2}{2m_h^*}\Delta_h-\frac{e^2}{\epsilon_0|\vec{r}_e|}+\frac{e^2}{\epsilon_0|\vec{r}_h|}-\frac{e^2}{\epsilon_0|\vec{r}_e-\vec{r}_h|}, \tag{10}$$

where $E_0=\langle\Psi_0|\mathcal{H}_e|\Psi_0\rangle$ is the ground-state energy of the valence electrons. The exchange energy term is

$$W=\iint_{\Omega_0\Omega_0}d\vec{r}_1\,d\vec{r}_2\,u_0^{(v)*}(\vec{r}_1)u_0^{(c)*}(\vec{r}_2)\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\times u_0^{(c)}(\vec{r}_1)u_0^{(v)}(\vec{r}_2). \tag{11}$$

Here for wave vectors $\vec{k}$ around the Γ point we approximated the Bloch functions $\psi_{\vec{k}}$ by their periodic parts $u_{\vec{k}}$ (normalized to unity in the volume of unit cell $\Omega_0=\Omega/N$) with $\vec{k}=0$ (cf. lecture notes of Elliott[5]). In the formula for H we have introduced a factor ϵ_0 which had been suggested by Roth[6] and Haken[7] to be the static dielectric constant for the shallow exciton.

There are four solutions of Eq. (8):

$$F^{(1)}_\alpha=f\delta_{1,\alpha},\quad F^{(2)}_\alpha=f\delta_{2,\alpha},\quad F^{(3)}_\alpha=f\tfrac{1}{2}\sqrt{2}\,(\delta_{3,\alpha}+\delta_{4,\alpha}),$$

and (12)

$$F^{(4)}_\alpha=g\tfrac{1}{2}\sqrt{2}\,(\delta_{3,\alpha}-\delta_{4,\alpha}),$$

where the functions f and g satisfy the equations

$$(H-E_1)f(\vec{r}_e,\vec{r}_h)=0 \tag{13}$$

and

$$[H+2W\Omega_0\delta(\vec{r}_e-\vec{r}_h)-E_2]g(\vec{r}_e,\vec{r}_h)=0. \tag{14}$$

As in the unbound exciton problem[4] the first three solutions of Eq. (8), $F^{(1)}$, $F^{(2)}$, and $F^{(3)}$ are the exciton envelope functions for the triplet states with eigenvalue $E=E_1$, while $F^{(4)}$ represents the singlet state with eigenvalue $E=E_2$.

Because of the smallness of the exchange energy term W we can approximate the function g by the known function f (considered, for example, in Refs. 8–10). Replacing g by f in Eq. (14) we obtain

$$E_2=E_1+2W\Omega_0(f|\delta(\vec{r}_e-\vec{r}_h)|f), \tag{15}$$

where $(\ |\ )$ stands for $\iint d\vec{r}_e\,d\vec{r}_h$, and $(f|f)=(g|g)=1$ because of the normalization $\langle\Psi_1|\Psi_1\rangle=1$.

The formula for the exchange splitting E_2-E_1 in Eq. (15) is entirely analogous to the corresponding result for an unbound exciton. For an unbound exciton the shift of the singlet state is also equal to $2W$ times the square of the envelope function taken at $\vec{r}_e=\vec{r}_h$.[4,11]

III. ELECTRIC DIPOLE TRANSITION PROBABILITY

Let Q denote a set of nuclear normal coordinates. In the Born-Oppenheimer approximation the vibrational states of the crystal $X_{0m}(Q)$ and $X_{1n}(Q)$ are, respectively, associated with the electronic states $\Psi_0(Q)$ and $\Psi_1(Q)$ which depend on electronic and nuclear coordinates. However, we will neglect the dependence of $\Psi_0(Q)$ and $\Psi_1(Q)$ on Q and we will use, respectively, the functions Ψ_0 and Ψ_1 defined by Eqs. (2) and (3). Ψ_0 and Ψ_1 are assumed to be the eigenfunctions of the electronic Hamiltonian $\mathcal{H}_e$ so that we will treat them as the functions unperturbed by the interaction $\mathcal{H}_{\mathrm{int}}$ [see Eq. (26)].

We will need to calculate the transition electric dipole moment matrix element, $\vec{M}_{01}(Q)$, between the initial and final electronic states $\Psi_1(Q)$ and $\Psi_0(Q)$. However, we will use the Condon approximation[12] in which this matrix element is independent of nuclear coordinates and we will calculate $\vec{M}_{01}$, between the states Ψ_1 and Ψ_0.

In this paper we are interested in the radiative emission transition 1 → 0, which corresponds to the transition from the excited (Ψ_1) to the ground (Ψ_0) electronic state.

If the Condon approximation is made, the total emission probability per unit time is[12]

$$P_{01}=\frac{n^3}{\epsilon_\infty}\frac{64\pi^4}{3hc^3}|\vec{M}_{01}|^2\int\nu^3G_{01}(\nu)\,d(h\nu), \tag{16}$$

where n^3/ϵ_∞ indicates the presence of crystal medium, n being the refractive index, while ϵ_∞ is the high-frequency dielectric constant. The function characterizing the spectrum is

$$G_{01}(\nu) = \mathrm{av}_n \sum_m \left| \int X^*_{0m}(Q) X_{1n}(Q)\, dQ \right|^2 \times \delta(E_{1n} - E_{0m} - h\nu), \tag{17}$$

where E_{1n} and E_{0m} are the eigenenergies of the vibrational states X_{1n} and X_{0m} [see Eq. (28)] and ν is the frequency of the emitted photon. The average av_n is understood to be an average over the initial vibrational states weighting each with the customary Boltzmann factor $\exp(-E_{1n}/kT)$. The eigenfunctions X_{0m} and X_{1n} belong to two different Hamiltonians [defined by Eq. (27)] and are not orthogonal with respect to each other.

IV. ELECTRIC DIPOLE MOMENT

The electric dipole moment matrix element depends on envelope function

$$\begin{aligned}\vec{\mathrm{M}}_{01} &= \langle \Psi_0 | e \sum_i \vec{\mathrm{r}}_i | \Psi_1 \rangle \\ &= \Omega_0 \sum_\sigma \mathrm{sgn}\,\sigma \int_\Omega d\vec{\mathrm{r}}\, F_{-\sigma,\sigma}(\vec{\mathrm{r}}, \vec{\mathrm{r}}) \\ &\qquad \times u_0^{(v)*}(\vec{\mathrm{r}}) e \vec{\mathrm{r}}\, u_0^{(c)}(\vec{\mathrm{r}}),\end{aligned} \tag{18}$$

where $\mathrm{sgn}\,\sigma = \sigma/|\sigma|$. We see that only one solution of Eq. (8), $F^{(4)}$, gives rise to a nonvanishing electric dipole matrix element (18). Thus (as in the case of unbound exciton[4]) only the singlet state $\Psi_1^{(4)}$ corresponding to the envelope function $F^{(4)}$ is the state of the bound exciton which can recombine radiatively.

If we approximate the function g by the function f, the matrix element (18), between $\Psi_1^{(4)}$ and Ψ_0 can be written

$$\vec{\mathrm{M}}_{01}^{(4)} = -\sqrt{2}\Omega_0 \int_\Omega d\vec{\mathrm{r}} f(\vec{\mathrm{r}}, \vec{\mathrm{r}}) u_0^{(v)*}(\vec{\mathrm{r}}) e \vec{\mathrm{r}}\, u_0^{(c)}(\vec{\mathrm{r}}). \tag{19}$$

Taking into account the slow variation of f with its arguments in Eq. (19) we get

$$\vec{\mathrm{M}}_{01}^{(4)} = -\sqrt{2} \int_\Omega d\vec{\mathrm{r}} f(\vec{\mathrm{r}}, \vec{\mathrm{r}}) \int_{\Omega_0} d\vec{\mathrm{r}}_1\, u_0^{(v)*}(\vec{\mathrm{r}}_1) e \vec{\mathrm{r}}_1\, u_0^{(c)}(\vec{\mathrm{r}}_1). \tag{20}$$

We have estimated the electric quadrupole moment matrix element. If the energy of the emitted photon is 5 eV and the lattice constant is 5 Å, the electric quadrupole moment is of the order of 1% of $|\vec{\mathrm{M}}_{01}^{(4)}|$.

V. EXCITON-PHONON COUPLING AND CALCULATION OF $G_{01}(\nu)$

The total Hamiltonian for our problem is the sum of the electronic and vibrational Hamiltonians plus a term representing the interaction of electrons with only one branch of LO phonons:

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{\mathrm{vib}} + \mathcal{H}_{\mathrm{int}}, \tag{21}$$

where

$$\mathcal{H}_{\mathrm{vib}} = \frac{1}{2} \sum_{\vec{\mathrm{q}}} [P(\vec{\mathrm{q}}) P^*(\vec{\mathrm{q}}) + \omega_1^2 Q(\vec{\mathrm{q}}) Q^*(\vec{\mathrm{q}})] \tag{22}$$

and $\mathcal{H}_{\mathrm{int}}$ is the sum of one-electron terms $\mathcal{H}_{\mathrm{int}} = \sum_i \mathcal{V}(\vec{\mathrm{r}}_i)$ $(i = 1, \ldots, 2N)$, where $\mathcal{V}(\vec{\mathrm{r}})$ is the Fröhlich interaction

$$\mathcal{V}(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{q}}} \gamma_{\vec{\mathrm{q}}} Q(\vec{\mathrm{q}})\, e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}, \tag{23}$$

with

$$\gamma_{\vec{\mathrm{q}}} = -\frac{i\hbar\omega_1}{|\vec{\mathrm{q}}|} \left(\frac{2\omega_1}{m\hbar}\right)^{1/4} \left(\frac{4\pi\alpha}{\Omega}\right)^{1/2}. \tag{24}$$

Here $Q(\vec{\mathrm{q}})$ is the normal coordinate of the longitudinal mode with the wave vector $\vec{\mathrm{q}}$, ω_1 is the LO-phonon frequency assumed to be constant, i.e., independent of $\vec{\mathrm{q}}$, and the dimensionless Fröhlich coupling constant α is

$$\alpha = (e^2/\hbar)(\epsilon_\infty^{-1} - \epsilon_0^{-1})(m/2\hbar\omega_1)^{1/2}. \tag{25}$$

In the Born-Oppenheimer approximation the equations

$$(\mathcal{H}_e + \mathcal{H}_{\mathrm{int}}) \Psi_a(Q) = E_a(Q) \Psi_a(Q) \quad \text{for } a = 0, 1 \tag{26}$$

define the eigenvalues $E_a(Q)$ which are the additional potentials in the Hamiltonians

$$H_a = \mathcal{H}_{\mathrm{vib}} + E_a(Q) \tag{27}$$

determining the vibrational wave functions

$$H_a X_{am}(Q) = E_{am} X_{am}(Q). \tag{28}$$

We evaluate the eigenvalues $E_a(Q)$ in first-order perturbation theory, i.e., we use in Eq. (26) the "eigenfunctions" of $\mathcal{H}_e$, Ψ_a $(a = 0, 1)$, where for $a = 1$ we take the singlet state $\Psi_1^{(4)}$ which can recombine radiatively. For the interaction in (23) we find eigenvalues of Eqs. (26) of the form

$$\begin{aligned} E_0(Q) &= E_0 + \sum_{\vec{\mathrm{q}}} A_{\vec{\mathrm{q}}} Q(\vec{\mathrm{q}}), \\ E_1(Q) &= E_2 + \sum_{\vec{\mathrm{q}}} B_{\vec{\mathrm{q}}} Q(\vec{\mathrm{q}}). \end{aligned} \tag{29}$$

We will need only the difference $D_{\vec{\mathrm{q}}} = B_{\vec{\mathrm{q}}} - A_{\vec{\mathrm{q}}}$

$$\begin{aligned} D_{\vec{\mathrm{q}}} &= \gamma_{\vec{\mathrm{q}}} \Omega_0 \int_\Omega \int_\Omega d\vec{\mathrm{r}}_e\, d\vec{\mathrm{r}}_h \sum_{\sigma_e, \sigma_h} |F^{(4)}_{\sigma_e, \sigma_h}(\vec{\mathrm{r}}_e, \vec{\mathrm{r}}_h)|^2 \\ &\qquad \times [\,|u_0^{(c)}(\vec{\mathrm{r}}_e)|^2 e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_e} - |u_0^{(v)}(\vec{\mathrm{r}}_h)|^2 e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_h}\,]. \end{aligned} \tag{30}$$

Now we calculate the function $G_{01}(\nu)$ by the method used by Gummel and Lax.[12,13] We write the function $G_{01}(\nu)$ with the Fourier transform[12]

$$G_{01}(\nu) = h^{-1} \int_{-\infty}^{+\infty} e^{-2\pi i\nu t}\, G_{01}(t)\, dt \tag{31}$$

of

$$G_{01}(t) = \mathrm{tr}(e^{-itH_0/\hbar}\, e^{itH_1/\hbar}\, e^{-\beta H_1})/\mathrm{tr}(e^{-\beta H_1}), \qquad (32)$$

where $\beta = 1/kT$. If we express the Hamiltonians H_a for $a = 0, 1$ in real, normal vibrational coordinates,[14] the trace (32) can be evaluated by use of the density matrix for the harmonic oscillator.[13,15]

For low temperatures, i.e., for $kT \ll \hbar\omega_1$, the result for $G_{01}(\nu)$ can be expressed in the form

$$G_{01}(\nu) = \sum_{n=0}^{n_1} G_{01}^{(n)}(\nu), \qquad (33)$$

where $G_{01}^{(n)}(\nu)$ describing the n-phonon process is

$$G_{01}^{(n)}(\nu) = h^{-1}\, e^{-C}(1/n!)C^n \delta(\nu_0 - \nu - n\nu_1). \qquad (34)$$

The summation over n in Eq. (33) extends up to $n_1 = E[\nu_0/\nu_1]$, where $E[x]$ stands for the integer just below x, $\nu_0 = (E_2 - E_0)/h$, $\nu_1 = \omega_1/2\pi$ and the distribution factor C is

$$C = (2\hbar\omega_1^3)^{-1} \sum_{\vec{q}} |D_{\vec{q}}|^2. \qquad (35)$$

Because the exciton envelope F is a slowly varying function of its arguments, we see from Eq. (30) that $D_{\vec{q}}$ is essentially nonvanishing only for small $\vec{q}$. For small $\vec{q}$ we can write

$$D_{\vec{q}} = \gamma_{\vec{q}} \int_\Omega \int_\Omega d\vec{r}_e\, d\vec{r}_h \,|\, f(\vec{r}_e, \vec{r}_h)\,|^2 \times (e^{i\vec{q}\cdot\vec{r}_e} - e_n^{i\vec{q}\cdot\vec{r}}) \;. \qquad (36)$$

If the number of LO-phonon branches is S and if we assume the same frequency constant ω_1 for each LO-phonon branch, the result appears in the same form as for one LO-phonon branch [Eq. (33)]. The difference is only in the distribution factor C which has to be replaced by $C' = SC$. Thus for S LO-phonon branches

$$G_{01}^{(n)}(\nu) = h^{-1}\, e^{-SC}(1/n!)(SC)^n \delta(\nu_0 - \nu - n\nu_1). \qquad (37)$$

VI. CONCLUSION

Starting from the Hartree-Fock and the effective-mass approximations we derive the equation for the envelope of the shallow exciton bound to an ionized donor. The exchange splitting and the electric dipole matrix element are expressed in terms of the envelope. The interaction of the exciton with LO phonons is considered and the distribution of the LO-phonon replicas of the bound exciton recombination line is calculated.

For the shallow exciton the envelope function varies slowly in configuration space. For this envelope the Fourier components with small wave vectors are essential and the exciton interaction with the LO phonons is well described by the Fröhlich coupling which favors small phonon wave vectors $\vec{q}$. In $D_{\vec{q}}$, Eq. (30), the factor $\gamma_{\vec{q}}$, Eq. (24), is inversely proportional to $|\vec{q}|$ and the integral also has the largest value for small $\vec{q}$. Thus $D_{\vec{q}}$ is essentially nonvanishing for small $\vec{q}$ only. Therefore in the distribution factor C, Eq. (35), only small phonon wave vectors are essential and the dependence of this factor on the exciton envelope becomes independent of the Bloch functions, which results in considerable simplification [see Eq. (36)].

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