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Configuration Interaction in Donor-Acceptor Pairs*

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The effect of configuration interaction on the electronic states of donor-acceptor pairs in semiconductors is reported. Both the radial and angular dependences of electron- and positive-hole effective-mass functions are varied to minimize the total energy, corresponding to mixing higher s and p states into the eigenstates. The orbits are delocalized and intercore electron and hole densities reduced as a consequence of pairing. A substantial improvement in agreement between theory and experiment is found on including configuration interaction in the calculation of the pair spectra of gallium phosphide. Also, the effect on radiative lifetimes is calculated. The Coulomb overlap, correlation, and anisotropy of the effective masses are also considered, as well as changes in the coupling with the lattice.

I. INTRODUCTION

The electronic states of donor-acceptor pairs in semiconductors have previously been considered rigorously only to first order (Heitler–London approximation)[1] or with a second-order van der Waals term added with an adjustable parameter.[2] The availability of extensive fine structure in the emission spectra of III-V semiconductors and the explanation of these spectra by Hopfield, Thomas, and Gershenzon[2] in terms of radiative recombination at specific pairs indicate a need for an improved theory. The usual theory accounts for the general features of these spectra; however, a substantial discrepancy between theory and experiment exists in the dependence of radiative transition energy on donor-acceptor distance for the nearer-neighbor pairs.

Distant donor-acceptor pair emission spectra are usually fitted with

$$E_{\mathrm{ph}}(R) = E_{\mathrm{gap}} - (E_D + E_A) + \frac{e^2}{K_s R} - \frac{e^2}{K_s}\left(\frac{b}{R}\right)^6 \qquad (1)$$

assuming no overlap of the electronic distributions. R is the donor-acceptor separation, K_s the static dielectric constant, E_D and E_A the isolated donor and acceptor electronic binding energies, and b an arbitrary parameter in the van der Waals term used to improve the fit to experimental data. In Equation (1), K_s is the proper dielectric constant for the condition $\tau_0 \gg \tau_l$, where τ_0 is the orbital period for electronic motion and τ_l is the period for lattice vibrations.

The van der Waals term is the electronic correlation energy term for large R and is only valid for $R \gg a_A,\ a_D$. Assuming 1s-type wave functions,

$$a_A = e^2/2K_s E_A \quad \text{and} \quad a_D = e^2/2K_s E_D \ , \qquad (2)$$

this term represents the interaction of a neutral occupied donor and acceptor, without overlap of electronic distributions. To obtain the best fit to the data, Hopfield *et al.* found b to be the same magnitude as a_A or a_D.

Williams's[1] equation contains the effect of overlap, and does have the right dependence on R to improve somewhat the agreement between the observed spectrum and the theoretical spectrum,

$$E_{\mathrm{ph}}(R) = E_{\mathrm{gap}} - (E_A + E_D) + \frac{e^2}{K_s R} - \frac{e^2}{K_s R}\, e^{-2\rho_0}\left(1 + \tfrac{5}{8}\rho_0 - \tfrac{3}{4}\rho_0^2 - \tfrac{1}{6}\rho_0^3\right) \ . \qquad (3)$$

Here $\rho_0 = R/a_0$, and it is assumed $a_0 = a_A = a_D$.

II. THEORETICAL ANALYSIS OF TRANSITION ENERGY

We have now obtained a significant improvement using methods previously applied to the hydrogen molecule. A variation of parameters of the one-electron wave functions in a configuration-interaction treatment of the hydrogen molecule can be applied with equal validity to the donor-acceptor pair system. Wang's[3] and Rosen's[4] treatment of the hydrogen molecule results in the wave function being localized and rendered nonspherical with electronic density piling up between the nuclei. Adapting this to the excited donor-acceptor pair results in the electron and hole effective-mass functions being delocalized and rendered nonspherical with the electronic density thinning out

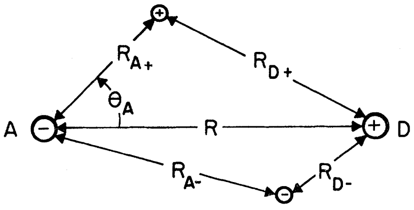

FIG. 1. Model of donor-acceptor pair.

between the nuclei.

The two-particle wave function for the donor-acceptor pair is

$$\Psi(+,\,-) = \psi_A(+)\psi_D(-) \quad , \tag{4}$$

where following Rosen's formulation

$$\psi_A(+) = \psi_A^0(+) + \sigma\psi_A^1(+) \quad , \tag{5}$$

$$\psi_A^0(+) = (\alpha_A^3/\pi)^{1/2} e^{-\alpha_A R_{A+}} \quad , \tag{6}$$

$$\psi_A^1(+) = -(\alpha_A^5/\pi)^{1/2} e^{-\alpha_A R_{A+}} R_{A+} \cos\theta_A \quad , \tag{7}$$

R_{A+} is the distance between the acceptor and its electronic particle, and θ_A is the angle between the radius vector $\vec{R}_{A+}$ and the line joining the donor and acceptor ions, as shown in Fig. 1. A similar equation applies for $\psi_D(-)$. In this analysis $\alpha_A = \alpha_D = \alpha_0$, and following Wang's formulation $\alpha_0 = Z/a_0$, where Z is the effective charge. The effective Hamiltonian for the donor-acceptor pair is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_-^2 + \nabla_+^2) + \frac{e^2}{K_s}\left(-\frac{1}{R} - \frac{1}{R_{+-}} - \frac{1}{R_{D-}} - \frac{1}{R_{A+}} + \frac{1}{R_{D+}} + \frac{1}{R_{A-}}\right) , \tag{8}$$

and the total energy is found from

$$E_{\text{tot}} = \int \Psi(+,\,-)\hat{H}\Psi(+,\,-)\,d\tau_1 d\tau_2 \Big/ \int \Psi^2(+,\,-)\,d\tau_1 d\tau_2 \quad , \tag{9}$$

which is minimized by varying Z and σ. The ionization energy

$$E_I = E_{\text{tot}} + e^2/K_s R \tag{10}$$

is easily found and can be used to determine the pair emission spectrum

$$E_{\text{ph}}(R) = E_{\text{gap}} - E_I \quad . \tag{11}$$

The variational parameters σ and Z necessary for minimizing E_I can be evaluated as a function of ρ_0. One can express E_I as

$$E_I = \frac{e^2}{K_s R}\left(-Z\rho + 1 + \frac{A + B\sigma + C\sigma^2 + D\sigma^3 + E\sigma^4}{1 + 2\sigma^2 + \sigma^4}\right) , \tag{12}$$

where

$$A = 2(Z-1)\rho + e^{-2\rho}\left(\tfrac{1}{6}\rho^3 + \tfrac{3}{4}\rho^2 - \tfrac{5}{8}\rho - 1\right) ,$$

$$B = -4e^{-2\rho}\left(\tfrac{1}{12}\rho^4 + \tfrac{11}{24}\rho^3 + \tfrac{11}{48}\rho^2\right) ,$$

$$C = 4(Z-1)\rho + \rho + 8/\rho^2 + e^{-2\rho}\left(\tfrac{7}{30}\rho^5 + \tfrac{89}{60}\rho^4 + \tfrac{369}{120}\rho^3 + \tfrac{37}{6}\rho^2 + \tfrac{109}{12}\rho + 14 + 16/\rho + 8/\rho^2\right) ,$$

$$D = 36/\rho^3 - 4e^{-2\rho}\left(\tfrac{1}{60}\rho^6 + \tfrac{7}{60}\rho^5 + \tfrac{113}{240}\rho^4 + \tfrac{697}{480}\rho^3 + \tfrac{2617}{960}\rho^2 + 6\rho + 12 + 18/\rho + 18/\rho^2 + 9/\rho^3\right) ,$$

$$E = 2(Z-1) + 54/\rho^4 + e^{-2\rho}\left(\tfrac{1}{140}\rho^7 + \tfrac{141}{2520}\rho^6 + \tfrac{19}{70}\rho^5 + \tfrac{893}{840}\rho^4 + \tfrac{10\,369}{6720}\rho^3 + \tfrac{2571}{640}\rho^2 + \tfrac{16\,651}{1280}\rho + 35 + 72/\rho + 108/\rho^2 + 108/\rho^3 + 54/\rho^4\right) ,$$

$$\rho = Z\rho_0 = ZR/a_0 \quad .$$

III. APPLICATION TO EXPERIMENTAL SPECTRA

The experimental pair emission spectrum of GaP doped with Zn and S which Hopfield, Thomas, and Gershenzon[2] measured is fitted with calculated values from Eqs. (1) (with and without van der Waals term), (3), and (11) in Fig. 2.

Curve D in Fig. 2 which includes configuration interaction has improved R dependence for the entire range of observed data, including the values at 10 and 11 Å usually omitted. To obtain a better fit with the data, the configuration-interaction curve was lowered 0.0046 eV to match the experimental values at large R. (*Note added in proof.* The over-all fit to all points is taken into account, as well as giving emphasis to the points at large R.) This correction of the value $E_{\text{gap}} - E_A - E_D$ is small so that our choice of the value of a_0 need not be revised for self-consistency. The van der Waals term is not included in curve D because it clearly is not valid at small R (see curve B), is negligible at large R (compare curves A and B), and is a doubtful approximation to the effects of correlation at intermediate R. The effects of Coulomb overlap are included in both curves C and D. To minimize the number of variational parameters and to simplify the calculations, the configuration interaction, and also the Coulomb overlap, are determined for $a_A = a_D$. In other words, a reduced a_0 of 9.1 Å is used.

The remaining small discrepancy between the data and theoretical curve D for $R < 15$ Å can be accounted for by electronic correlation only if the correlation effect in donor-acceptor pairs is double that in H_2. Other effects which may contribute to the remaining discrepancy are anisotropy of both the effective masses and differences in radii of electron and positive-hole distributions. These affect the interactions through the overlap. We have calculated the overlap for $a_D = 6.8$ Å and $a_A = 13.6$ Å, which correspond through Eq. (2) to the experimental E_D and E_A, and find the overlap reduced about 10% but retaining the same R dependence. In other words, we have slightly over-included Coulomb overlap by taking $a_A = a_D$; the configuration interaction is believed less affected because we reduced the variational parameters from four to two.

An additional possible contribution to the remaining small discrepancy is related to the correct choice of dielectric constant K to use for various pairs. The static dielectric constant K_s applies for the delocalized electronic configurations occurring for small R, i.e., $\tau_0 > \tau_l$, but for more distant pairs K may depend on R and decrease below the value K_s. The period for orbital electron motion may become comparable with the lattice relaxation time for distant pairs. If the configuration curve is lowered by more than 0.0046 eV to obtain a better fit at small R, the fit for large R will deteriorate. This can be compensated for by the use of a dielectric constant $K(R) < K_s$ and would result in a better over-all fit with the experimental data.

Note added in proof. Our most recent calculations show that correlation is great enough to account for the discrepancy [see Proceedings of the Leningrad Luminescence Conference in J. Luminescence (to be published)].

IV. THEORY OF RADIATIVE LIFETIMES

These calculations of configuration interaction show that spherical delocalization of the Heitler–London wave functions occurs for $\rho_0 < 1.2$ which corresponds to $R < 11$ Å for the system considered. The major effect for $R \geq 11$ Å is the departure from spherical symmetry of the Heitler–London wave functions which reduces electronic overlap. Compared to values calculated with the Heitler–London wave functions the lifetime τ of the excited state will be larger and emission intensity I smaller for each pair.

Following the analysis of Shaffer and Williams[5] from the radiative dipole matrix element

$$d_{if} = e \int \psi_D(\vec{r})\psi_A(\vec{r} - \vec{R})\, d\vec{r} \int u_{v0}(\vec{r}_0)\vec{r}_0 u_{c0}(\vec{r}_0)\, d\vec{r}_0 \quad , \tag{13}$$

where u_{v0} and u_{c0} are periodic parts of Bloch functions, the effective-mass-function integral

$$\int \psi_D(\vec{r})\psi_A(\vec{r} - \vec{R})\, d\vec{r} \tag{14}$$

provides the relation between the Heitler–London and configuration-interaction physical parameters. Therefore the ratios of lifetimes and intensities are

$$\frac{\tau_{\mathrm{HL}}}{\tau} = \frac{I}{I_{\mathrm{HL}}}$$

$$= \left| \int [\psi_A^0(\vec{r} - \vec{R}) + \sigma\psi_A^1(\vec{r} - \vec{R})][\psi_D^0(\vec{r}) + \sigma\psi_D^1(\vec{r})]\, d\vec{r} \right/$$

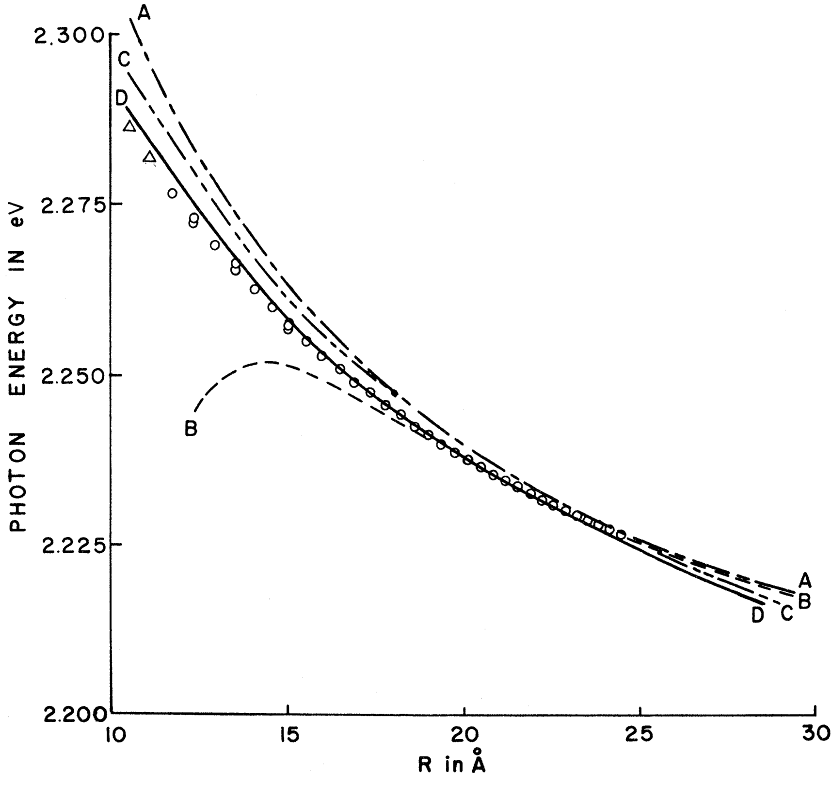

FIG. 2. Radiative transition energies of pairs vs donor-acceptor distances. Curve A, e^2/K_sR term only; curve B, $e^2/K_sR + (e^2/K_s)(b/R)^6$; curve C, e^2/K_sR + Coulomb overlap; and curve D, e^2/K_sR + Coulomb overlap + configuration interaction. Theoretical curves A and B and experimental points are from Ref. 2.

$$\int \psi_A^0(Z=1,\ \vec{r}-\vec{R})\psi_D^0(Z=1,\ \vec{r})d\vec{r}\,\Bigg|^2 , \qquad (15)$$

which become for $\rho \gtrsim 1.2\rho_0$:

$$\frac{\tau_{\rm HL}}{\tau} = \frac{I}{I_{\rm HL}}$$

$$= \left| 1 - \sigma\rho + \frac{\sigma^2}{5}\,\frac{\rho^4 + 2\rho^3 - 3\rho^2 - 15\rho - 15}{\rho^2 + \rho + 1} \right|^2 . \qquad (16)$$

The maximum value of σ obtained by the variation principle is 0.15 and this occurs for $\rho_0 = 1.5$ ($R = 13.6$ Å) and $Z = 1$. For this case the ratios given in Eq. (16) are 0.55 and approach unity for larger values of ρ_0.

V. CONCLUSIONS

Summarizing, we have included configuration interaction in the quantum mechanics of the electronic states of donor-acceptor pairs and thus substantially improved the agreement between theory and experiment of the dependence of the radiative transition energy on donor-acceptor distance. A small revision in the sum of the ionization energies of separated donor and acceptor is probable. The possible origins of the remaining slight discrepancy in the R dependence are considered. The effect of configuration interaction on radiative lifetimes of pairs is evaluated and the theoretical lifetimes are found to be increased by as much as a factor of 2.

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Magnetophonon Structure in the Longitudinal Magnetoresistance of Nonpolar Semiconductors

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The magnetophonon effect in nonpolar nondegenerate semiconductors is investigated by solving the Boltzmann equation exactly in the Ohmic limit for combined optical- and acoustic-phonon scattering of carriers in parallel electric and magnetic fields. The solution is used in computing the longitudinal magnetoresistance at several temperatures and ratios of acoustic- to optical-phonon scattering. As this ratio increases from zero at intermediate temperatures, the Gurevich–Firsov (GF) resonance maxima are found to broaden and shift toward higher magnetic field, with pronounced minima developing at the resonance fields before the magnetophonon structure vanishes at large acoustic-phonon scattering. As the temperature increases, additional (pseudoresonance) minima develop between the GF extrema, and are comparable in amplitude to the latter when kT approximates the optical-phonon energy. At these temperatures the GF extrema are minima, even in the absence of elastic scattering. The results are compared with displaced-Maxwellian computations. The various effects are explained by physical arguments, which suggest that the same effects should occur for polar materials also.

I. INTRODUCTION

The magnetophonon effect is an oscillatory behavior of various transport properties of nondegenerate semiconductors, as a function of applied magnetic field, and is due to resonant interactions between the longitudinal-optical (LO) phonons of the material and the cyclotron motion of the charge carriers. The resonance magnetic fields are defined by

$$N\omega_c = \omega_0 , \qquad (1)$$

where N is an integer, ω_0 is the angular frequency of the LO phonons at $k=0$, and ω_c is the cyclotron frequency, given by $\omega_c = eB/m^*$, where B is the magnetic field, and m^* is the carrier effective mass. These resonances will here be referred to as the Gurevich–Firsov (GF) resonances, after the first workers in the field.[1,2]

Measurements of Ohmic longitudinal magnetore-