PHYSICAL REVIEW B VOLUME 28, NUMBER 10 15 NOVEMBER 1983

Radiative decay of the bound exciton in direct-gap semiconductors: The correlation effect

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(Received 31 May 1983)

We present a theory of the radiative decay of excitons bound to neutral donors and acceptors in direct-gap semiconductors within the spherical-effective-mass approximation. The calculation is carried out using a three-particle wave function which incorporates Pauli exchange and important interparticle correlation effects over the entire range of electron- to hole-mass ratios. Thus donor- and acceptor-bound excitons are treated within the same framework. Radiative lifetimes are studied and are found to be particularly sensitive to the interparticle distance between electron and hole for all mass ratios of physical interest. Calculations are carried out for the radiative decay rates of bound excitons in a number of materials and comparison is made with the measured radiative lifetimes of both donor- and acceptor-bound excitons in GaAs, InP, and CdS.

I. INTRODUCTION

Excitons in the solid are of importance in determining the optical properties of semiconductors. Studies of the free exciton (FE) can be found in the literature, and the theory of exciton absorption has been worked out by Elliott.[1] The formation of excitons usually appears as narrow peaks in the absorption edge of direct-gap materials. The free exciton can become bound to neutral shallow impurities to form the bound exciton (BE). The impurity acts as a site where electron-hole recombination can occur at an enhanced rate. In direct-gap materials the principal mechanism of recombination is radiative recombination in which an electron-hole pair recombine accompanied by emission of a photon. Auger recombination in which the energy of recombination promotes the third carrier into the band continuum is usually negligible in direct-gap semiconductors. The existence of the BE was first proposed by Lampert,[2] and absorption lines due to radiative recombination of electron-hole pairs in the BE were subsequently identified by Haynes.[3].

The intensity of these absorption lines is related to the radiative lifetime of the electron-hole pairs, and these lifetimes for acceptor- and donor-bound excitons have been studied in the spherical effective-mass approximation. In this model the nature of the BE is determined by the ratio between the effective mass of the impurity carrier and the effective mass of the carrier of opposite charge. This dimensionless mass ratio is denoted σ. In the limiting case where σ is small compared to unity, the impurity and the exciton combine to form a system which is the analog of an H_2 molecule. Where σ is large compared to unity one obtains the analog of the H^- ion. Since the electron effective mass is generally smaller than the hole effective mass in semiconductors, the acceptor and donor BE's are characterized by small and large values of σ, respectively.

Rashba and Gurgenishvili[4] developed a simple theory of the BE radiative lifetime which explained the enhancement of the BE oscillator strength over the free-exciton value. In their model they showed that the ratio of oscillator strengths of the BE to free-exciton values was proportional to the ratio of the volume of the center-of-mass wave function $\phi_v(R)$ to the volume of the primitive cell, i.e.,

$$\frac{f_{\mathrm{BE}}}{f_{\mathrm{FE}}}=\frac{1}{v_{\mathrm{vol}}}\left[\int \phi_v(r)d^3r\right]^2 ,$$

where $\phi_v(r)$ was determined from an effective-mass equation in which the interaction between the exciton and neutral impurity is taken to be a delta-function potential whose strength is adjusted to give the correct binding energy of the BE. This delta-function potential is qualitatively appropriate to the case of acceptor-bound excitons (A^0X), but is not adequate for the treatment of donor-bound excitons (D^0X), where the center-of-mass motion of the exciton is described qualitatively by the Morse potential. They found that for typical BE's f_{BE} would be on the order of 10^4 times larger than f_{ex}, i.e., $f_{\mathrm{BE}} \sim 10^2$. This simple model was rederived by Henry and Nassau and has been used in the analysis of experimental data by a number of authors[5-8] for both donor- and acceptor-bound excitons, despite the qualitative shortcomings in the donor-bound exciton case.

In the case of acceptor-bound excitons (A^0X), a theory of the radiative lifetime was worked out by Osbourn and Smith.[9] They presented calculations for GaAs and the HgCdTe alloy system and considered the dependence of the transition rates on the energy gap and on the acceptor binding energy. For HgCdTe, whose band gap varies as a function of composition, they found that radiative recombination dominates Auger recombination except in small-band-gap samples.

These recombination lifetime calculations suffer from a number of shortcomings. In the theory of Rashba and Gurgenesvili,[4] for example, the oscillator strength is due entirely to recombination between the electron-hole pair in the exciton while contributions due to recombination of the electron with the acceptor hole are ignored. Furthermore, as mentioned above, the center-of-mass wave function $\phi_v(r)$ is only qualitatively correct for the case of acceptor-bound excitons. The theory of Osbourn and Smith[9] ignores correlations between the particles entirely by using single-particle product wave functions. They argue that correlation will have little effect on the calculated oscillator strengths. In the acceptor BE regime, this seems reasonable since the distance between the core particles and the outer electron in acceptor BE's is approximately the distance of the outer electron from the acceptor. Our results confirm this is the case for $\sigma \gtrsim 100$ but not for $\sigma \lesssim 10$, which is typical for acceptor-bound excitons in real semiconductors.

Ungier *et al.*[10] have reported calculations on radiative recombination rates for bound excitons. They used a variational wave function which is capable of stabilizing the bound-exciton system for all mass ratios. However, their wave function gave an oscillator strength which is an order of magnitude too large in the H_2-molecule limit. Furthermore, their oscillator strength is a monotonic decreasing function of the mass ratio, which is in qualitative disagreement with the results obtained using an adiabatic approximation as will be demonstrated later. This is because the form of their variational function does not describe the vibrational behavior of a H_2 molecule adequately.

To improve upon these theories it is necessary to take correlation effects into account by using wave functions which depend on interparticle separations and in which Pauli exchange is included. Furthermore, the form of the wave function should be appropriate for both the H_2 molecule and the H^- ion (the two limiting cases of the bound-exciton system). This is necessary if one wishes to develop a theory for radiative recombination rates which is valid over a wide range of σ values and in particular for the intermediate case $\sigma \sim 1$.

In this paper we present such a calculation of radiative lifetimes for bound-exciton systems in the spherical-effective-mass approximation for direct-gap materials. The wave function we use is appropriate for the entire range of σ values, and it is shown that the resulting transition rates are sensitive to correlation effects. Our results are compared with experimental measurements of radiative rates.

II. THEORY

The bound-exciton state is expanded in terms of linear combinations of the products of the single-particle Bloch states associated with the unperturbed solid. In the effective-mass approximation it can be written as

$$|\psi\rangle = \sum_{\mu_1,\mu_2,\mu_3} C(J,M;\mu_1,\mu_2,\mu_3)F(\vec{r}_1,\vec{r}_2,\vec{r}_3) \times |\mu_1\rangle |\mu_2\rangle |\mu_3\rangle \ , \tag{1}$$

where $C(J,M;\mu_1,\mu_2,\mu_3)$ are spin angular-momentum addition coefficients and $|\mu\rangle$ denotes the periodic part of a Bloch state at the band extremum with spin component μ. For the conduction band $\mu=-\frac{1}{2},\frac{1}{2}$ and for the valence band $\mu=-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}$ in the limit of strong spin-orbit interaction. $F(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ is the envelope function, which is the eigenstate of the effective-mass Hamiltonian

$$H = H_1(\vec{r}_1)+H(\vec{r}_2)+H_3(\vec{r}_3)+v(1,2)-v(1,3)-v(2,3),$$

where $H_i(\vec{r}_i)$ is the single-particle effective-mass Hamiltonian for particle i and $v(i,j)$ is the mutual Coulomb interaction between particle i and j. In a spherical model in which the angular dependence of the effective-mass tensor is neglected and in which the fourfold degenerate valence band is approximated by a single band, the three-body effective-mass Hamiltonian is given in effective atomic units (in which energy is measured by $e^4m^*/2\epsilon_0^2\hbar^2$, where ϵ_0 is the dielectric constant, m^* is the effective mass of particle 1, and distance is measured by $\epsilon_0\hbar^2/m^*e^2$) by

$$H = -\nabla_1^2-\nabla_2^2-\sigma\nabla_3^2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{2}{r_3}+\frac{2}{r_{12}} -\frac{2}{r_{13}}-\frac{2}{r_{23}} \ , \tag{2}$$

where subscripts 1 and 2 refer to the electrons (holes) in donor (acceptor) systems, and 3 refers to the hole (electron). The mass ratio σ is the ratio between the effective masses of particles 1 and 3. We refer to particles 1 and 2 as the core particles and to 3 as the outer particle.

Three interesting special cases are contained in the Hamiltonian which are worth mentioning briefly. In the limit of large σ the mass of the outer particle becomes vanishingly small so that the kinetic energy term dominates over the other terms involving the outer particle. Thus in the ground state the outer-particle wave function becomes spread out over an infinite volume and essentially disappears from the system leaving behind an analog of the H^- ion. In this case it is quite easy to obtain an estimate of the outer-particle wave function by the approximation $r_{13}=r_{23}=r_3$. Then the wave function is separable and is given by the eigenstate of $H_3 \equiv -\sigma\nabla_3^2-2/r_3$. This corresponds to a hydrogen atom with a ground-state Bohr radius $a=\sigma$.

In the opposite extreme of vanishing σ, the outer particle becomes very heavy and the kinetic energy term becomes small. We are thus left with the analog of the H_2 molecule. The special case $\sigma=1$ corresponds to positronium hydride (PsH) whose wave function has been studied by a number of authors.[11-14]

To study the relative importance of correlation in the radiative decay of bound-exciton systems, we performed three calculations with different degrees of sophistication. In the first calculation the correlation effects are completely neglected. In the second calculation the dominating effects of electron-electron correlation are included, and in the final calculation dominating effects of both electron-electron and electron-hole correlation are included.

To obtain an envelope wave function without correlation effects, we chose a variational wave function of the following simple-product form:

$$F_1(\vec{r}_1,\vec{r}_2,\vec{r}_3)=Ne^{-\alpha r_1}e^{-\alpha r_2}e^{-\gamma r_3} \ , \tag{3}$$

in which the particles are in 1*s* Slater orbitals. The coefficients α and γ are obtained by the Ritz variational method of minimizing the expectation value of the Hamiltonian. N is the normalization constant. This is essentially the wave function used by Osbourn and Smith in their calculation of radiative transition rates.[9]

One expects this wave function to be adequate to describe recombination in the large-σ limit where the outer-particle wave function is approximately a Slater orbital. The next level of sophistication, which is more adequate in the large-σ limit, consists of improving the wave function to get a better description of the H^--ion core. This is accomplished by allowing the identical particles 1 and 2 to occupy independent 1*s* orbitals in a ground-state singlet orbital. Thus an improved variational wave function of the following form was considered

$$F_2(\vec{r}_1,\vec{r}_2,\vec{r}_3)=N(e^{-\alpha_1 r_1}e^{-\alpha_2 r_2}+e^{-\alpha_1 r_1}e^{-\alpha_2 r_1})e^{-\gamma r_3} . \quad (4)$$

Again, N is the normalization constant. This wave function takes the radial correlation of particles 1 and 2 into account. In what follows we will refer to F_1 and F_2 as the restricted and unrestricted variational wave functions, respectively.

In the third calculation electron-hole correlation effects are taken into account by including the electron-hole relative coordinate in the wave function in an explicit way. The wave function is written as

$$F_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)=N[\phi_D(\vec{r}_1)\phi_C(\vec{R}_{23})\phi_X(\vec{r}_{23})+(1\leftrightarrow 2)] , \quad (5)$$

where ϕ_D and ϕ_X are Slater 1*s* orbitals describing the donor and exciton, respectively, N is the normalization constant, and ϕ_C is a wave function describing the center-of-mass motion of the exciton. $\vec{R}_{23}=[\sigma/(1+\sigma)]\vec{r}_2+[1/(1+\sigma)]\vec{r}_3$ is the center-of-mass coordinate for the exciton, and $\vec{r}_{23}=\vec{r}_2-\vec{r}_3$ is the relative coordinate of the electron and hole in the exciton. The symbol $(1\leftrightarrow 2)$ in Eq. (5) represents the exchange term, in which the roles of particles 1 and 2 are interchanged.

The effective potential for the center-of-mass motion ϕ_C can be represented by the soluble potential[15]

$$V_C(R)=\frac{A}{R^2}-\frac{B}{R} , \quad (6)$$

where A and B are constants that depend on σ. Thus we are motivated to use the exact solution of this potential for the center-of-mass motion. We have

$$\phi_C(R)=\left[\frac{1}{4\pi\Gamma(\tau_0+1)}(2b_0)^{\tau_0+1}\right]^{1/2}R^{(\tau_0/2-1)}e^{-b_0 R} . \quad (7)$$

The parameters τ_0 and b_0 are related to A and B by

$$\tau_0=1+\sqrt{1+4A}$$

and

$$b_0=B/\tau_0 .$$

These parameters are determined variationally by minimizing the expectation value $\langle F_3 \mid H \mid F_3 \rangle$ of the total energy of the bound exciton. In the limit of large σ, the parameter τ_0 approaches 2 and the relative and center-of-mass coordinates can be approximated by $\vec{r}_{23}=\vec{r}_3$ and $\vec{R}_{23}=\vec{r}_2$. In this limit the wave function $F_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ is identical in form with $F_2(\vec{r}_1,\vec{r}_2,\vec{r}_3)$. In the above opposite limit in which σ approaches zero, our wave function $F_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ describes the H_2 molecule in the Heitler-London approximation.

By expanding the ϕ_D and ϕ_X Slater orbitals as a sum of 4 or 5 optimized Gaussian orbitals with exponents given by Huzenaga[16] and by expanding ϕ_C as a sum of four optimized Gaussian orbitals, it is possible to compute all the required matrix elements in closed form. These matrix elements are listed in Appendix A. In this calculation the donor and exciton wave-function exponents are fixed at their noninteracting values of 1 and $1/(1+\sigma)$, respectively.[17]

The wave functions we have chosen to study correlation effects have the advantage that they are easy to visualize and interpret in terms of the correlation effects which have been included. Furthermore, all of the matrix elements for these wave functions can be calculated in closed form. This greatly facilitates the computational task and makes the inclusion of band-structure effects in a future calculation tractable.

The radiative recombination rate of a bound exciton is given by[18]

$$\frac{1}{\tau_R}=\frac{2e^2\omega^2 n}{3c^3 m}f , \quad (8a)$$

where

$$f=\frac{2}{\hbar\omega m}\frac{1}{g_{\mathrm{BE}}}\sum_{\alpha,I,F}|\langle I \mid P_\alpha \mid F\rangle|^2 , \quad (8b)$$

$|I\rangle$ denotes the initial bound-exciton state given by (1), and $|F\rangle$ denotes the final impurity ground state given by

$$|F\rangle=\phi(\vec{r})\,|\mu_F\rangle , \quad (9)$$

where $\phi(\vec{r})$ is the envelope function for the neutral impurity, and $|\mu_F\rangle$ is the periodic part of the associated Bloch state at the band extremum with spin component μ_F. Here g_{BE} is the spin degeneracy of the bound exciton, n is the index of refraction, m is the mass of a free electron, and α denotes the three possible components of the momentum operator.

Let us first consider zinc-blende materials. For D^0X, $g_{\mathrm{BE}}=4$; for A^0X, $g_{\mathrm{BE}}=12$. For acceptor-bound excitons we have

$$\sum_{\alpha,I,F}|\langle I \mid P_\alpha \mid F\rangle|^2=12\,|\langle S \mid P_x \mid X\rangle|^2\,|\langle I \mid F\rangle|^2 , \quad (10)$$

and for donor-bound excitons,

$$\sum_{\alpha,I,F}|\langle I \mid P_\alpha \mid F\rangle|^2=4\,|\langle S \mid P_x \mid X\rangle|^2\,|\langle I \mid F\rangle|^2 . \quad (11)$$

Here $|\langle S \mid P_x \mid X\rangle|^2$ is the optical-matrix element between Bloch states at the conduction-band minimum and valence-band maximum, and the overlap integral $\langle I \mid F\rangle$ is defined by

$$\langle I\,|\,F\rangle \equiv \int F(\vec{r}_1,\vec{r}_2,\vec{r}_2)\phi(\vec{r}_1)d^2r_1d^3r_2 \ , \tag{12}$$

where $F(\vec{r}_1,\vec{r}_2,\vec{r}_2)$ is the envelope function of the bound exciton with $\vec{r}_3$ set equal to $\vec{r}_2$. Details of this derivation are given in Appendix B.

Thus we can see that the radiative decay rates for both donor- and acceptor-bound excitons in zinc-blende materials are given by

$$\frac{1}{\tau_R} = \left[\frac{2e^2\omega^2 n}{3c^3 m}\right]\left[\frac{P^2}{\hbar\omega}\right] |\langle I\,|\,F\rangle|^2 \ , \tag{13}$$

where $P^2 \equiv (2/m)\,|\langle S\,|P_x\,|X\rangle|^2$. A similar derivation shows that (13) holds for wurtzite materials as well (see Appendix B). It is a straightforward matter to calculate this overlap integral for the normalized envelope functions and the results are presented in the next section. In particular the overlap for our wave function F_3 is given by

$$\langle F_3\,|\,F\rangle = N\phi_X(0)\int \phi_C(\vec{R})d^3r + \cdots \ , \tag{14}$$

where N is the normalization constant for F_3, $\phi_X(0)$ is the exciton wave function evaluated at the origin, $\phi_C(R)$ is the center-of-mass wave function, and the ellipsis includes an exchange term. The exchange term is typically less than 10% of the leading term in Eq. (14) for all mass ratios.

While the wave function F_3 is qualitatively correct for all mass ratios, it systematically overestimates the radiative rate. This problem arises because the potential for the center-of-mass motion in the Heitler-London approximation is too shallow, giving rise to a center-of-mass wave function, which is too diffuse. This causes us to overestimate the center-of-mass volume integral in (14). In order to estimate the effects of the remaining correlations, we define a corrected wave function F_4 obtained from F_3 by scaling the parameter b_0 by a constant factor. This results in a more localized center-of-mass wave function. By choosing a single scaling factor it is possible to obtain the correct transition rates in the limiting cases $\sigma \rightarrow 0$ and $\sigma \rightarrow \infty$, as will be discussed in the next section.

III. RESULTS AND DISCUSSIONS

A. Energy spectra

The stability of the BE system within the spherical effective-mass approximation has been studied by a number of authors with the use of various approaches.[19–21] The most successful of these calculations performed to date was undertaken by Stebe and Munschy.[20] They used a variational wave function which included correlations between all the particles in the BE system and found that the BE system is bound for all values of σ. Furthermore, they succeeded in improving the variational binding energies obtained by other workers over the entire range of σ values.

Figure 1 shows the binding energy (E_B) in effective Rydbergs (Ry*) of the BE system as a function of the mass ratio σ for the three calculations we have performed as well as the results obtained by Stebe and Munschy.[20] Our results for the third wave function confirm the binding of the BE system for all values of σ. Our binding energies are lower than those of Stebe and Munschy which can be primarily attributed to the failure of our basis set to include the correlation effects completely. It is noted from this figure that for $\sigma \gtrsim 10$, the unrestricted variational calculation gives slightly larger binding energy than does the third calculation.

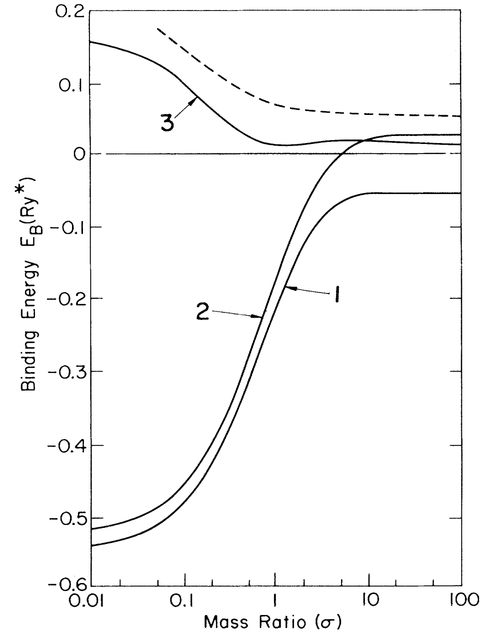

FIG. 1. Binding energies (E_B) of the bound exciton plotted as functions of the mass ratio (σ). Curves labeled 1, 2, and 3 are obtained using the trial wave functions F_1, F_2, and F_3, respectively. The results obtained by Stebe and Munschy (Ref. 20) (dashed curve) are included for comparison.

B. Wave functions

The variational wave functions F_1 and F_2 were found with the use of the Ritz variational principle. The variational parameters obtained by minimizing the variational energy E_v for different values of the electron- to hole-mass ratio σ are shown in Table I along with the computed binding energy (E_B).

As a function of σ, the inverse Bohr radius of the outer particle γ is seen to increase as expected, and in the limit of large σ, γ approaches the hydrogenic limit $\gamma_- = 1/\sigma$. In the large-σ limit the unrestricted variational wave function F_2 gives a reasonable approximation to the bound exciton, and stable binding is achieved. Both the variational wave functions F_1 and F_2 are poor approximations in the small-σ regime.

We now consider the third wave function F_3. The optimized values for τ_0 and b_0 as functions of the mass ratio σ are found to be well described by polynomial expansions in the quantity $X = (1/\sigma)^{1/4}$,

$$\tau_0 = 2.4X^2 - 1.4X + 2$$

and

TABLE I. Variational parameters and binding energies (E_B) of bound excitons in the restricted and unrestricted variational calculations. The negative value of E_B means that the system is unbound.

	Restricted			Unrestricted			
σ	α	γ	$E_B(\text{Ry}^*)$	α_1	α_2	γ	$E_B(\text{Ry}^*)$
0.02	0.847	0.526	−0.539	1.131	0.561	0.506	−0.515
0.05	0.843	0.513	−0.519	1.128	0.555	0.493	−0.494
0.10	0.836	0.494	−0.488	1.123	0.546	0.474	−0.462
0.15	0.829	0.477	−0.461	1.118	0.538	0.458	−0.434
0.20	0.823	0.462	−0.435	1.114	0.530	0.442	−0.408
0.30	0.813	0.435	−0.391	1.107	0.517	0.416	−0.362
0.40	0.804	0.412	−0.354	1.101	0.505	0.393	−0.323
0.50	0.796	0.392	−0.323	1.096	0.494	0.373	−0.290
0.60	0.789	0.375	−0.296	1.092	0.485	0.356	−0.262
0.70	0.783	0.359	−0.273	1.088	0.476	0.340	−0.237
0.80	0.777	0.345	−0.252	1.085	0.469	0.326	−0.216
0.90	0.772	0.333	−0.235	1.082	0.461	0.314	−0.197
1.00	0.767	0.321	−0.219	1.080	0.455	0.302	−0.180
1.50	0.749	0.275	−0.163	1.070	0.428	0.257	−0.119
2.00	0.737	0.242	−0.130	1.064	0.408	0.225	−0.081
3.00	0.721	0.197	−0.094	1.056	0.379	0.182	−0.038
4.00	0.709	0.162	−0.077	1.052	0.360	0.153	−0.016
5.00	0.705	0.145	−0.068	1.049	0.346	0.133	−.0031
6.00	0.701	0.128	−0.063	1.047	0.335	0.117	.0051
7.00	0.698	0.115	−0.060	1.046	0.327	0.105	0.011
10.0	0.693	0.087	−0.056	1.043	0.311	0.081	0.019
20.0	0.689	0.048	−0.054	1.040	0.292	0.046	0.026
30.0	0.688	0.033	−0.054	1.040	0.287	0.032	0.027
50.0	0.688	0.012	−0.054	1.039	0.284	0.020	0.027
100.0	0.688	0.010	−0.054	1.039	0.283	0.010	0.027

$$b_0=0.59X^2-0.32X+0.28\ .$$

The form of these expressions is chosen so that they give correct σ dependence for both large and small mass ratios. Figure 2 shows the normalized ground-state center-of-mass wave function as a function of the center-of-mass coordinate R for different values of σ. Examining this wave function we can see clearly the transition of the BE system from the H_2-molecule limit to the H^--ion limit. For small σ, the center-of-mass coordinate is simply the position of the heavy outer particle, and the center-of-mass wave function is a zero-point vibrational state centered at a distance corresponding to the internuclear distance of the diatomic H_2 molecule in the Heitler-London approximation. In the H^--ion regime the center-of-mass coordinate represents the position of the outer core particle. Thus the vibrational wave function is centered very close to the origin and spread out in coordinate space. While the wave function F_3 obtained by minimizing the total energy with respect to the variational parameters τ_0 and b_0 is qualitatively correct, it yields a wave function which overestimates the radiative rate by approximately a factor of 3. As mentioned previously, this problem arises because the exciton center-of-mass motion obtained in the present approximation is too diffuse. It is possible to correct this problem by scaling the parameter b_0 by a constant factor for all mass ratios. We chose $b_0=1.4$ so that

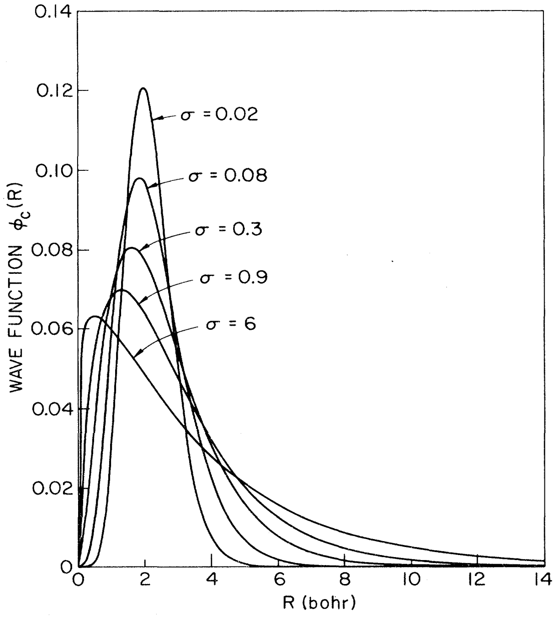

FIG. 2. Wave functions $\phi_C(R)$ of the center-of-mass motion of the exciton bound to a neutral impurity for a number of mass ratios plotted as functions of the radial distance R.

the resulting wave function F_4 gave correct decay rates in both the H_2-molecule limit ($\sigma \to 0$) and the H^--ion limit ($\sigma \to \infty$). For small mass ratios ($\sigma < 0.1$), accurate description for the center-of-mass motion wave function $\phi_C(R)$ can be obtained by adopting the adiabatic approximation. The effective potential for the center-of-mass motion in this approximation is given by the Morse potential, which can be approximated by the expression (6) with $A=1.4$ and $B=2.0$ for R near the minimum point R_0. Thus $\tau_0 = 2.4\sqrt{1/\sigma}$ and $b_0 = 0.83\sqrt{1/\sigma}$ for $\sigma < 0.1$. For large mass ratios ($\sigma > 100$) the bound-exciton wave function can be described by the product of a single-hole wave function ($e^{-r/\sigma}$) and a H^- core wave function. The H^- core wave function can be approximately represented by Chandrasekhar's variational form[22]

$$\phi_{H^-}(\vec{r}_1,\vec{r}_2) = (e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} + e^{-\alpha_1 r_2} e^{-\alpha_2 r_1})(1 + c r_{12})$$

with $\alpha_1 = 1.075$, $\alpha_2 = 0.478$, and $c = 0.312$. With this approximation, the bound-exciton radiative decay rates can be calculated analytically.

The suitability of the BE wave function for transition-rate calculations near $\sigma = 1$ was tested by calculating the two-photon annihilation rate for PsH. In atomic units, the annihilation rate is shown by Navin *et al.*[11] to be given by the integral

$$P = 100.94 \langle I \mid \delta(\vec{r}_{13}) \mid I \rangle ,$$

in units of ns^{-1}. Using our wave functions F_3 and F_4, we obtain annihilation rates of 1.84 and 2.35 ns^{-1}, which are in good agreement with the 2.22 ns^{-1} obtained by Navin *et al.*[11] This again represents a substantial improvement over 0.372 and 0.378 ns^{-1}, respectively, obtained by using our restricted and unrestricted variational wave functions F_1 and F_2.

C. Transition rates

The $| \langle I \mid F \rangle |^2$ overlap between the initial and final states which is proportional to the oscillator strength and radiative decay rate is plotted in Fig. 3 as a function of σ for the wave functions considered. The results obtained by the adiabatic approximation for $\sigma < 0.1$ and by using Chandrasekhar's wave function for $\sigma > 100$ are also included for comparison. It is seen that our results using F_4 agree well with the two limiting-case calculations. As expected, correlation between the core particles and the outer particle causes an enhancement in the radiative transition rate. The calculated radiative decay rate is seen to be very sensitive to correlation effects, most notably in the intermediate limit $\sigma \sim 1$, where the use of the final wave function gives rise to an oscillator strength about a factor of 20 larger than that obtained by use of an uncorrelated wave function.

The general shape of the curve as a function of σ can be understood qualitatively from (12). In the limit of large σ, $\phi_C(R)$ becomes a constant function describing the motion of one of the core particles in the analog of the H^- ion, and hence the behavior of $| \langle F_4 \mid F \rangle |^2$ as a function of σ is dominated by the behavior of $\phi_X(0)$. Thus for large σ

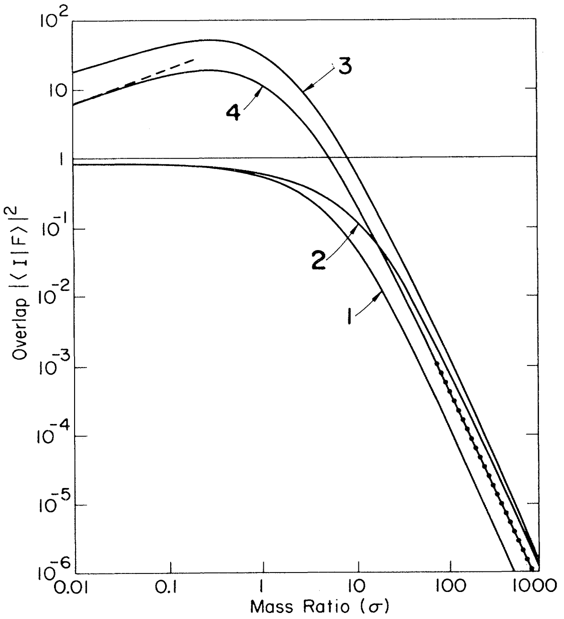

FIG. 3. Overlap integrals $| \langle I \mid F \rangle |^2$ for the radiative decay of the bound exciton plotted as functions of the mass ratio (σ). Curves 1—4 are obtained using the trial wave functions F_1, F_2, and F_3 and the corrected wave function F_4, respectively. The dashed curve denotes the results obtained by adopting an adiabatic approximation for mass ratios (σ) less than 0.1. The dotted curve denotes the results obtained by using the H^- wave function of Chandrasekhar (Ref. 22).

$$| \langle F_4 \mid F \rangle |^2 \sim \left[\frac{1}{\sigma} \right]^3 .$$

In the case of small σ, $\phi_X(0)$ is approximately constant and the behavior of $| \langle F_4 \mid F \rangle |^2$ is then determined by the volume integral of the center-of-mass wave function. Hence

$$| \langle F_4 \mid F \rangle |^2 \sim \left| \int 4\pi R^2 \phi_C(R) dR \right|^2 = \frac{4\pi (2)^{\tau_0+1}}{\Gamma(\tau_0+1)} \frac{\{\Gamma[(\tau_0/2)+2]\}^2}{b_0^3}$$

as a function of σ, this integral increases as the center-of-mass wave function becomes broader. Hence the peak in the curve is due to a competition between the increase in the volume of the center-of-mass motion and the spreading of the exciton wave function with increasing mass ratio.

We can use curve 4 of Fig. 3 and (13) to calculate radiative lifetimes for donor- and acceptor-bound excitons in various direct-gap materials. Results of these calculations are tabulated in Table II along with experimentally measured values for GaAs, InP, and CdS. The results seem to be in reasonable agreement with experiment for the case of acceptor-bound exciton data to within a factor of ~ 3. For the case of donor-bound excitons, our theoretical results are in disagreement with the experimental data by an order of magnitude.

The disagreement between theory and experiment may be explained as follows. The experimentally measured lifetime of the bound exciton is usually a combination of the time of formation and the actual radiative lifetime of the bound exciton.[5] The formation time for the acceptor-bound excitons in CdS has been measured by Henry and Nassau[5] to be between 0.65 and 1.3 ns. This formation time could account for the difference between the measured and calculated lifetimes. If we assume the formation time for the D^0X is of the same order of magnitude, then the measured lifetime in the case of D^0X reflects the formation time and not the much shorter radiative lifetime.

IV. SUMMARY AND CONCLUSIONS

We have developed a theory of the radiative lifetime of excitons bound to neutral donors and acceptors in direct-gap semiconductors within the spherical effective-mass approximation which incorporates Pauli exchange and important interparticle correlation effects. The wave functions incorporate correlation effects in their functional form, are easy to visualize in terms of the correlation effects which have been included, and allow calculation of the matrix elements in closed form. The final wave function gives a stable bound exciton for all values of the mass ratio σ and is sufficient for the calculation of radiative decay rates within the limitations of effective-mass theory. The dependence of the radiative rate on mass ratio σ is studied and is found to be sensitive to correlation effects. A principle feature of the dependence of the radiative rate on the mass ratio is an enhancement at intermediate values of σ, which is seen to be the result of correlation between electron and hole coordinates. This effect can account for an enhancement in the calculated radiative rate by a factor of 10 to 20 above the radiative rates calculated with wave functions in which correlation effects are ignored. The theoretical method used here can be extended to indirect semiconductors, where the band-structure effect is also important.[9] This application will be reported in a future publication.

ACKNOWLEDGMENTS

We acknowledge fruitful discussions with M. Klein. This work was supported by the U. S. Navy Office of Naval Research under Contract No. N00014-81-K-0430. We also acknowledge the use of the computing facility provided by the University of Illinois Materials Research Laboratory.

APPENDIX A: CALCULATION OF MATRIX ELEMENTS

The envelope wave function F_3 is written as

$$|F_3\rangle = \sum_n C_n |f_n\rangle , \tag{A1}$$

where

$$|f_n\rangle = |\phi_D(r_1) e^{-\alpha_n R_{23}^2} \phi_X(\rho_{23})\rangle + (1 \leftrightarrow 2) . \tag{A2}$$

The exchange term is obtained by interchanging particles 1 and 2, and the donor and exciton wave functions ϕ_D and ϕ_X are expanded as sums of Gaussians, e.g.,

$$\phi_D(r) = \frac{1}{(\pi a_0)^{1/2}} e^{-a_0 r} = \sum_l C_l e^{-\beta_l (a_0 r)^2} , \tag{A3}$$

where the exponents β_l and expansion coefficients C_l are

TABLE II. Radiative lifetimes of bound excitons. The available experimental data are included in parentheses.

Subst.	E_g (eV)	P^2 (eV)	m_e	m_h	n	σ	$\lvert\langle I \vert F\rangle\rvert_d^2$	$\lvert\langle I \vert F\rangle\rvert_a^2$	τ_d (ns)	τ_a (ns)
GaN	3.62[a]	20[b]	0.2[c]	0.8[c]	2.4[c]	0.25	18.78	1.87	0.021	0.21
GaAs	1.52[a]	25.7[a]	0.067[a]	0.5[c]	3.4[c]	0.13	16.66	0.54	0.031 (1.07)[d]	0.96 (1.6)[e]
GaSb	0.81[a]	22.4[a]	0.045[a]	0.39[c]	3.9[c]	0.12	15.93	0.39	0.062	2.5
InP	1.42[a]	20.4[a]	0.08[a]	0.40[c]	3.37[c]	0.2	18.27	1.23	0.038 (0.5)[f]	0.58 (1.5)[f]
InAs	0.42[a]	22.2[a]	0.023[a]	0.33[c]	3.42[c]	0.069	13.15	0.13	0.17	17.1
InSb	0.237[a]	23.1[a]	0.014[a]	0.18[c]	3.75[c]	0.078	13.69	0.18	0.25	18.9
ZnO	3.4[a]	20[b]	0.32[c]	0.27[c]	2.02[c]	1.19	10.73	13.49	0.047	0.038
CdS	2.56[a]	20[b]	0.20[c]	0.99[g]	2.5[c]	0.20	18.3	1.27	0.030 (0.5)[b]	0.42 (1.03)[h]
CdTe	1.6[a]	20.7[a]	0.096[a]	0.35[c]	2.75[c]	0.27	18.79	2.30	0.041	0.33
PbS	0.29[a]	20[b]	0.1[c]	0.1[c]	3.7[c]	1.0	11.89	11.89	0.27	0.27

[a] P. Lawaetz (Ref. 23).
[b] Rough estimation.
[c] J. I. Pankove (Ref. 24).
[d] Hwang and Dawson (Ref. 6).
[e] Hwang (Ref. 7).
[f] U. Heim (Ref. 8).
[g] J. J. Hopfield (Ref. 25).

defined by Huzenaga.[16] Thus $|f_n\rangle$ is given by the expansion

$$|f_n\rangle=\sum_{l,m}D_lX_m\,|g_{nlm}\rangle\ , \tag{A4}$$

where

$$|g_{nlm}\rangle=|e^{-\beta_l(a_Dr_1)^2}e^{-\alpha_nR_{23}^2}e^{-\beta_m(a_X\rho_{23})^2}\rangle+(1\leftrightarrow 2)\ . \tag{A5}$$

The D_l and X_m are expansion coefficients for the donor and exciton wave functions, respectively.

Using the transformation from particle coordinates to center-of-mass and relative coordinates, i.e.,

$$\vec{\rho}_{23}=\vec{r}_2-\vec{r}_3$$

and

$$\vec{R}_{23}=(\sigma\vec{r}_2+\vec{r}_3)/(1+\sigma)\ ,$$

we see that $|g_{nlm}\rangle$ can be expressed as

$$|g_{nlm}\rangle=|e^{-a_1r_1^2}e^{-a_2r_2^2}e^{-a_3r_3^2}e^{-2a_4\vec{r}_2\cdot\vec{r}_3}\rangle+(1\leftrightarrow 2)\ , \tag{A6}$$

where we introduce transformed quantities as follows:

$$a_1=\beta_la_D^2\ , \tag{A7a}$$

$$a_2=\alpha_n\mu_1^2+\beta_ma_X^2\ , \tag{A7b}$$

$$a_3=\alpha_n\mu_2^2+\beta_ma_X^2\ , \tag{A7c}$$

$$a_4=\alpha_n\mu_1\mu_2-\beta_ma_X^2\ . \tag{A7d}$$

The general matrix elements in the basis of (A5) are expressed in the following standard form:

$$M_{nn'}=\langle f_n|M|f_{n'}\rangle=\sum_{\substack{l,l'\\m,m'}}D_lD_{l'}X_mX_{m'}M(n,n';l,l',m,m')\ , \tag{A8}$$

where $M(n,n';l,l',m,m')$ are matrix elements relative to the basis (A6), i.e.,

$$M(n,n';l,l'm,m')=\langle g_{nlm}|M|g_{n'l'm'}\rangle\ . \tag{A9}$$

The matrix elements (A9) are obtainable in closed form and can be worked out in a straightforward manner. The results are listed below.

Overlap:

$$\langle g_{nlm}|g_{n'l'm'}\rangle=B_1B_{23}+B_3B_{234}\ . \tag{A10}$$

Nuclear interaction for core particles:

$$\left\langle g_{nlm}\left|\frac{1}{r_1}\right|g_{n'l'm'}\right\rangle=\frac{2}{\sqrt{\pi}}B_1B_{23}\left[(S_1)^{1/2}+\left[\frac{\gamma_{23}}{S_3}\right]^{1/2}\right]+\frac{2}{\sqrt{\pi}}B_3B_{234}\left[\left[\frac{\gamma_{234}}{S_3(a_1'+a_2)-a_4^2}\right]^{1/2}+\left[\frac{\gamma_{234}}{S_3(a_1+a_2')-a_4'^2}\right]^{1/2}\right]\ . \tag{A11}$$

Nuclear interaction for outer particle:

$$\left\langle g_{nlm}\left|\frac{1}{r_3}\right|g_{n'l'm'}\right\rangle=\frac{4}{\sqrt{\pi}}B_1B_{23}\left[\frac{\gamma_{23}}{S_2}\right]^{1/2}+\frac{4}{\sqrt{\pi}}B_3B_{234}\left[\frac{\gamma_{234}}{(a_1'+a_2)(a_2'+a_1)}\right]^{1/2}\ . \tag{A12}$$

Mutual interaction between core particles:

$$\left\langle g_{nlm}\left|\frac{1}{r_{12}}\right|g_{n'l'm'}\right\rangle=\frac{4}{\sqrt{\pi}}B_1B_{23}\left[\frac{S_1\gamma_{23}}{S_1S_3+\gamma_{23}}\right]^{1/2}+\frac{4}{\sqrt{\pi}}B_3B_{234}\left[\frac{\gamma_{234}}{S_1S_3+\gamma_{23}}\right]^{1/2}\ . \tag{A13}$$

Mutual interaction between core and outer particle:

$$\left\langle g_{nlm}\left|\frac{1}{r_{13}}\right|g_{n'l'm'}\right\rangle=\frac{2}{\sqrt{\pi}}B_1B_{23}\left[\left[\frac{\gamma_{23}}{S_2+S_3+2S_4}\right]^{1/2}+\left[\frac{S_1\gamma_{23}}{S_2(S_1+S_3)-S_4^2}\right]^{1/2}\right]+\frac{2}{\sqrt{\pi}}B_3B_{234}\left[\left[\frac{\gamma_{234}(a_1+a_2')}{\gamma_{234}+(a_1'+a_2)(a_1+a_2'+a_4')^2}\right]^{1/2}+\left[\frac{\gamma_{234}(a_1'+a_2)}{\gamma_{234}+(a_1+a_2')(a_1'+a_2+a_4)^2}\right]^{1/2}\right]\ . \tag{A14}$$

Kinetic energy of core particles:

$$\langle g_{nlm} \,|\, -\nabla_1^2 \,|\, g_{n'l'm'} \rangle = 6B_1B_{23}\left[\Gamma_1 + \frac{\Gamma_2 S_2 S_3 + \Gamma_4 S_2 S_4 - S_4(a_2' a_4 + a_4' a_2)}{\gamma_{23}}\right]$$
$$+6B_3B_{234}\left[\frac{a_1' a_2[S_3(a_2' + a_1) - a_4'^2] - a_1' a_4^2(a_1 + a_2')}{\gamma_{234}}\right.$$
$$\left. + \frac{a_1 a_2'[S_3(a_1' + a_2) - a_4^2] - a_1 a_4'^2(a_2 + a_1')}{\gamma_{234}}\right] . \qquad \text{(A15)}$$

Kinetic energy for outer particle:

$$\langle g_{nlm} \,|\, -\nabla_3^2 \,|\, g_{n'l'm'} \rangle = 12B_1B_{23}\left[\frac{S_2 a_3 a_3' + S_3 a_4 a_4' - S_4(a_3' a_4 + a_4' a_3)}{S_2 S_3 - S_4^2}\right]$$
$$+12B_3B_{234}\left[\frac{[a_3(a_1' + a_2) - a_4^2][a_3'(a_1 + a_2') - a_4'^2]}{S_3(a_1' + a_2)(a_2' + a_1) - a_4^2(a_2' + a_1) - a_4'^2(a_1' + a_2)}\right] . \qquad \text{(A16)}$$

In Eqs. (A10)—(A16), we define the following quantities:

$$S_i = a_i + a_i' \ , \quad i = 1, \ldots, 4 \qquad \text{(A17)}$$

$$\gamma_{23} = S_2 S_3 - S_4^2 \ , \qquad \text{(A18)}$$

$$\gamma_{234} = S_3(a_1' + a_2)(a_2' + a_1) - a_4'^2(a_1' + a_2) - a_4^2(a_2' + a_1) \qquad \text{(A19)}$$

$$B_i = \left[\frac{\pi}{S_i}\right]^{3/2} , \quad i = 1, 3 \qquad \text{(A20)}$$

$$B_{23} = \left[\frac{\pi^2}{\gamma_{23}}\right]^{3/2} , \qquad \text{(A21)}$$

$$B_{234} = \left[\frac{\pi^2 S_3}{\gamma_{234}}\right]^{3/2} , \qquad \text{(A22)}$$

$$\Gamma_i = \left[\frac{a_i a_i'}{a_i + a_i'}\right] , \quad i = 1, \ldots, 4 \ . \qquad \text{(A23)}$$

The a's are defined by the transformation equation (A7).

APPENDIX B: CALCULATION OF OSCILLATOR STRENGTH

The oscillator strength f is given by

$$f = \frac{2}{\hbar\omega m}\left[\frac{1}{g_{\rm BE}}\right] \sum_{\alpha,I,F} |\langle I \,|\, P_\alpha \,|\, F \rangle|^2 \ , \qquad \text{(B1)}$$

where $\hbar\omega$ is the energy of the emitted photon, m is the electron mass, $g_{\rm BE}$ is the degeneracy of the initial bound-exciton state, and P_α is the momentum operator with component α. The summation sign in (B1) represents a sum over final states F, initial states I, and component α.

For donor-bound excitons the two electrons in the conduction band are coupled to form a spin singlet state of total spin zero. Thus the total angular momentum $J = \frac{3}{2}$, and the spin-Bloch part of the initial state defined in (1) is given by

$$|J,M\rangle = \sum_{\sigma_1,\sigma_2,\mu} C(0,0;\sigma_1,\sigma_2)\delta_{M\mu} \,|S,\sigma_1\rangle \,|S,\sigma_2\rangle \,|\mu\rangle \ , \qquad \text{(B2)}$$

where $|S,\sigma_1\rangle$ and $|S,\sigma_2\rangle$ denote the s-like conduction-band Bloch state for the two electrons with spin σ_1 and σ_2, respectively; $|\mu\rangle$ denote the four degenerate valence-band Bloch states. In (B2) the nonzero Clebsch-Gordan coefficients are $C(0,0;\frac{1}{2},-\frac{1}{2}) = -C(0,0;-\frac{1}{2},\frac{1}{2}) = 1/\sqrt{2}$. For zinc-blende materials,

$$|\mu\rangle = \sum_{\alpha',\sigma} C(\tfrac{3}{2},\mu;\alpha',\sigma) \,|\alpha'\rangle \,|\sigma\rangle \ , \qquad \text{(B3)}$$

where $|\sigma\rangle$ is the hole spinor, $|\alpha'\rangle$ denotes the three p-like Bloch states, and $C(\frac{3}{2},\mu;\alpha,\sigma)$ are Clebsch-Gordan coefficients. The spin-Bloch part of the final electron state is given by $|S,\sigma_f\rangle$. Using (B2) and (B3) we have

$$\sum_{M,\sigma_f,\alpha} |\langle J,M \,|\, P_\alpha \,|\, S,\sigma_f \rangle|^2 = 2 \sum_{M,\alpha,\sigma_f} \left| \frac{1}{\sqrt{2}} \sum_{\alpha',\sigma} C(\tfrac{3}{2},M;\alpha',\sigma) \langle -\sigma \,|\, \sigma_f \rangle \langle S \,|\, P_\alpha \,|\, \alpha' \rangle (-1)^{1/2+\sigma} \right| , \qquad \text{(B4)}$$

where we have converted the hole bra state $\langle\alpha'|\ \langle\sigma|$ into an electron ket state $(-1)^{1/2+\sigma}|\alpha'\rangle\ |-\sigma\rangle$ in the recombination process. A factor of 2 was introduced in (B4), because the hole can recombine with either of the two electrons. This procedure can be verified by field theory.[26] $\langle S \,|\, P_\alpha \,|\, \alpha' \rangle$ is the momentum matrix element, which equals $\langle S \,|\, P_x \,|\, X \rangle \delta_{\alpha\alpha'}$. Summing the Clebsch-Gordan coefficients, one obtains

$$\sum_{M,\sigma_f,\alpha} |\langle J,M \,|\, P_\alpha \,|\, S,\sigma_f \rangle|^2 = 4 \,|\langle S \,|\, P_x \,|\, X \rangle|^2 \ . \qquad \text{(B5)}$$

For wurtzite materials (e.g., CdS) a similar calculation yields

$$\sum_{M,\sigma_f,\alpha} |\langle J,M|P_\alpha|S,\sigma_f\rangle|^2 = 2|\langle S|P_x|X\rangle|^2 . \tag{B6}$$

The extra factor of 2 is compensated for in (11) by the fact that $g_{\rm BE}=2$ in these materials. The calculation for acceptor-bound excitons is similar. The total angular momentum (J) of the acceptor-bound exciton in zinc-blende materials can be $\frac{1}{2}$, $\frac{3}{2}$, or $\frac{5}{2}$. The initial state is given by

$$|J,M\rangle = \sum_{\mu_1\mu_2,\sigma_3} C(J,M;\mu_1,\mu_2,\sigma_3)\,|\mu_1\rangle\,|\mu_2\rangle\,|S,\sigma_3\rangle \tag{B7}$$

and the final hole state is given by $|\mu_F\rangle$. Thus for zinc-blende materials,

$$\sum_{J,M,\alpha,\mu_F} |\langle J,M|P_\alpha|\mu_F\rangle|^2 = 2\sum_{J,M,\alpha,\mu_F}\Bigg|\sum_{\mu_1,\mu_2,\sigma_3} C(J,M;\mu_1,\mu_2,\sigma_3)\sum_{\alpha_1,\sigma_1} C(\tfrac{3}{2},\mu_1;\alpha_1,\sigma_1) \times(-1)^{1/2+\sigma_1}\langle\mu_2|\mu_F\rangle\langle\sigma_1|\sigma_3\rangle\langle\alpha_1|P_\alpha|S\rangle\Bigg|^2 . \tag{B8}$$

As in the case for donor-bound excitons, (B8) can be converted into a sum over Clebsch-Gordan coefficients which can be evaluated explicitly to give

$$\sum_{\alpha,I,F} |\langle I|P_\alpha|F\rangle|^2 = 12|\langle S|P_x|X\rangle|^2\langle I|F\rangle|^2 . \tag{B9}$$

For wurtzite materials the case for acceptor-bound excitons is the same as for donor-bound excitons, since the hole has spin-$\frac{1}{2}$.

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