Optical Stark effect of the exciton. II. Polarization effects and exciton splitting

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We show that a laser beam, tuned in the transparency region of a direct-gap semiconductor, not only shifts but also splits the exciton levels. This splitting originates from the degeneracy of the valence band as the (σ_+,σ_-) parts of the light are not similarly coupled to the various exciton components. In the case of a fourfold-degenerate valence band, we find that, at large detuning, the shifts of the (2×4) eightfold exciton are exactly the shifts of a $(2+4)$ six-level atom. This is just the generalization of the simple band-structure case with one electron and one hole band in which the large detuning excitonic shift has the same value as that of the two-level (dressed) atom. We give the selection rules to observe the various shifted lines for typical pump-probe experiments. We also discuss the experimental conditions necessary to see an exciton red shift at the two-photon absorption threshold, when the molecular biexciton is stable.

I. INTRODUCTION

A new field[1] of fundamental interest was opened three years ago by the observation,[2] in semiconductors, of optical changes induced by below-gap laser excitation. Until that time, experiments were done with resonant or above-band-gap pumping, creating real electron-hole pairs. The observed effects are then caused partly by the laser excitation, and partly by the created electronic system, which evolves with time. The use of below-gap excitation separates these two effects and allows the study of purely laser-induced variations of the semiconductor properties. The original experiment[2] consisted of the observation of a blue shift of the exciton line. Such a blue shift had been previously observed with above-threshold excitation[3] and was interpreted in terms of a screening of the Coulomb interaction by the created electron-hole system. In this new experiment, the laser beam alone produces such a blue shift. The physical origin here is similar to that of light shifts in atomic physics. These atomic shifts were explained using the dressed-atom model[4] and are found to be proportional to the laser intensity.

In previous work,[1,5] we have shown that, although the problem is much more complicated in semiconductor than in atomic physics, due to the great number of interacting excitons, the exciton optical Stark shift reduces to the two-level dressed atom one at large detuning. The reason is that, at detuning large compared to the exciton binding energy, the Coulomb interaction can be neglected, and the valence- to conduction-band transition induced by the electron-photon coupling is similar to the two-level (dressed-atom) problem. At smaller detuning, however, the shift is modified. We have shown that the exciton optical Stark effect comes, in fact, from interactions between the two electrons and the two holes forming the biexcitonic (bound and unbound) states. At small detuning the Coulomb interaction dominates, while at large detuning the shift results from Pauli exclusion.

Besides the great number of interacting excitons, the problem is also more complicated in semiconductor than in physics due to the complexity of the band structure. This complexity usually leads only to more tedious calculations without introducing any new physical effect. It turns out, however, that in the exciton optical Stark problem, band structure induces quite a nice fundamental effect. As the photon corresponds to a kinetic momentum $J=1, M=\pm1$, the various conduction and valence states are not affected similarly by the electron-photon coupling, the conduction band being s like while the valence-band results from a p-like state with spin-orbit coupling. Consequently the exciton, which is a degenerate state when built from the bare conduction and valence bands, not only shifts but also splits[6] under below-gap laser excitation, due to different changes in the various conduction and valence levels. One finds, in particular, that the eightfold exciton line of bulk GaAs can split into up to five lines depending on the pump and probe beams. This result appeared, at first, in contradiction with the experimental observation of a unique broad shifted exciton line. However, this theoretical prediction has been verified recently,[7] using differential absorption spectra and a precise analysis of the underlying components of the exciton line. The experimental difficulties in observing the various "bumps" in the exciton line predicted by the theory come from the fact that the original exciton linewidth is larger than the laser-induced shifts and does not allow direct observation of a split line.

This paper is organized as follows. In Sec. II, we establish, from first principles, the electron-photon coupling including the kinetic momentum symmetries of the electronic system and the photon. Since this coupling is the key part of this work, it is crucial to write it precisely.

Even though its overall form is well known, the relative signs of the various terms of Eq. (5) are not. They are of importance in linear polarization cross effects. We also give the form of the electron-photon coupling appropriate to the optical Stark effect problem [Eqs. (8) and (13)].

In Sec. III, we give the notations for the electron system and define the exciton state basis appropriate to the optical Stark effect problem.

In Sec. IV, we derive the expression of the shifts for a degenerate exciton level, closely following our previous work[1,5] on the exciton optical Stark effect. As usual, band-structure effects lead to much more tedious calculations, one term of our previous work now being replaced by a matrix. We find that the exciton shifts appear as the eigenvalues of an 8×8, or 4×4, matrix, depending on whether the upper valence band is fourfold or twofold degenerate. In order to get this matrix in its simplest form, an appropriate basis for the exciton state is, indeed, of importance. This is the reason for the introduction of a particular hole basis [Eqs. (9) and (11)] in Sec. II, associated with the appropriate exciton basis defined in Sec. III.

In Sec. V, we calculate the shifts at large detuning. We show that (2×4) eightfold exciton (2 for the electron and 4 for the hole) splits into five levels, their shifts being exactly those of a $(2+4)$ six-level atom. This result is nothing but the generalization of our previous results for simple band structure with one electron state and one hole state: at large detuning, the exciton shift had the same value as the one for a two-level dressed atom. This result is also quite nice as it allows us to recover very easily the structural symmetry of the polarization effects, avoiding the exact treatment of exciton-biexciton coupling and many-body effects. It also explains why the exciton basis chosen previously is indeed the appropriate one.

In Sec. VI, we calculate the detuning dependence of the shifts and show that, up to very small detuning, the symmetries of the shifted exciton levels are not affected by the detuning. We find that the shifts are simply the large detuning ones multiplied by $(1+\alpha/2+\beta/2)$, α and β being exactly the coefficients we introduced in the simple band-structure case.[1,5] This result is again the (nonobvious) generalization of our previous one: the large detuning shift $2\lambda^2/\Omega_1$ becomes[5] $(2+\alpha+\beta-\gamma)\lambda^2/\Omega_1$ when the detuning decreases. The part in γ, however, cannot be so easily extended, since in its expression, the true biexcitonic structure that is not 8×8 degenerate appears. In relation to this problem, we calculate the effect of a molecular biexciton on the excitonic shift, and give the symmetry of the exciton component which red-shifts at the exciton-biexciton resonance.

In Sec. VII, we give the various selection rules for pump-probe experiments. They can be summarized by saying that the best condition in which to see all the shifted exciton lines on the same spectrum is to use circularly polarized beams, propagating in perpendicular directions. We also give the precise conditions necessary to see the red-shifted line in pump-probe experiments.

In Sec. VIII, we treat the case of GaAs multiple quantum wells separately and we explain the experimental results obtained for linear polarized pump and probe beams. This case clearly illustrates the analogy between semiconductor and atomic physics: We found that, for simple band structure, the large detuning exciton shift is that of a two-level dressed atom. These two levels must be understood to be valence and conduction bands, *not* vacuum and exciton. Doing this, the results of all this work on polarization effects are very easily recovered. On the other hand, if one speaks in terms of vacuum and exciton, one has to include the biexcitonic states, and all the interactions coming from them.

In Sec. IX we give a summary of the main results of this work.

The appendixes contain some more technical developments.

II. ELECTRON-PHOTON COUPLING

We first derive the electron-photon coupling when the valence- and conduction-band symmetries are taken into account. Since these symmetries are the key part of this work, the precise expression of this coupling is of importance. It is why we have found it useful to establish it from the very beginning.

A. General form

In the presence of a field vector potential $\mathbf{A}$, the electronic Hamiltonian becomes

$$H=(1/2m)(\mathbf{P}+e\,\mathbf{A}/c)^2+V_{\text{Coul}}+V_{\text{lattice}}\ . \tag{1}$$

Writing H as $H_0+\hat{W}$, one deduces that the electron-photon coupling, to lowest order in $\mathbf{A}$, is

$$\hat{W}=(e/2mc)(\mathbf{P}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{P})=(e/mc)\,\mathbf{A}\cdot\mathbf{P}\ , \tag{2}$$

if we choose the gauge such that $\nabla\cdot\mathbf{A}=0$. We then write the electronic part of the electron-photon coupling in second quantification while treating the electromagnetic field classically. This is appropriate if one is only interested in laser intensities such that the classical limit for the photon field is valid. The standard procedure for this transformation gives

$$P_x=\langle\phi_c|P_x|\phi_v\rangle b_c^\dagger b_v+\text{H.c.}\ , \tag{3}$$

if one keeps only the terms associated with transition between conduction and valence bands; $b_c^\dagger$ and $b_v^\dagger$ are the corresponding creation operators. Since the conduction and valence bands are, respectively, S- and P-like, symmetry arguments imply that P_x couples the conduction band only to a valence state with an x symmetry and that the associated matrix element, P, is the same for x, y, and z. This leads us to write, if $b_x^\dagger$ creates an x valence state,

$$\mathbf{A}\cdot\mathbf{P}=Pb_c^\dagger(A_xb_x+A_yb_y+A_zb_z)+\text{H.c.}\ , \tag{4}$$

$A_{x,y,z}$ being the vector-potential components. We will choose them to be real. The conduction and valence operators $b_c^\dagger$ and $b_{x,y,z}$ have the same spin value, as the operator $\mathbf{A}\cdot\mathbf{P}$ acts only on the orbital space. One then proceeds to a set of transformations from the conduction- and valence-band basis to the total electron-hole pair kinetic momentum basis. This is done in detail in Appen-

dix A. One finally obtains for the e-photon coupling

$$\begin{aligned}
&\hat{W}=W+W^{\dagger}\ ,\\
&W^{\dagger}=\sum_{\mathbf{k}}[W_B^{\dagger}(\mathbf{k})+W_C^{\dagger}(\mathbf{k})]\ ,\\
&W_B^{\dagger}(\mathbf{k})=(\tfrac{4}{3})^{1/2}[\lambda_+\mathbf{B}_1^{\dagger}(\mathbf{k})-\lambda_-\mathbf{B}_{-1}^{\dagger}(\mathbf{k})-\lambda_0\mathbf{B}_0^{\dagger}(\mathbf{k})]\ ,\\
&W_C^{\dagger}(\mathbf{k})=-(\tfrac{2}{3})^{1/2}[\lambda_+\mathbf{C}_1^{\dagger}(\mathbf{k})-\lambda_-\mathbf{C}_{-1}^{\dagger}(\mathbf{k})-\lambda_0\mathbf{C}_0^{\dagger}(\mathbf{k})]\ .
\end{aligned}\tag{5}$$

$\mathbf{B}_M^{\dagger}(\mathbf{k})$ creates an e-h pair $(\mathbf{k},-\mathbf{k})$ with total kinetic momentum $J=1,M$, built from a $J=\frac{3}{2}$ hole state, while $\mathbf{C}_M^{\dagger}(\mathbf{k})$ creates an e-h pair with the same kinetic momentum $J=1,M$, but built from a $J=\frac{1}{2}$ hole state. The factors $\lambda_{\pm,0}=(e/mc)PA_{\pm,0}$ are related to the usual coefficient $A_0=A_z$ and

$$A_{\pm}=2^{-1/2}(A_x\mp iA_y)\ .\tag{6}$$

Besides the factor $2^{1/2}$ between the two valence subbands, and the signs which may, at first, appear strange, the expression (5) has an expected form. Indeed, if one takes a circularly polarized beam, one knows that a σ_+ photon corresponds to a kinetic momentum $J=1,M=1$. The absorption of such a photon should produce an e-h pair with the same kinetic momentum. Since the absorption is ruled by the term $e^{-i\omega t}$ in the e-photon coupling, one notes that for a σ_+ photon, only λ_+ contains such a term (as, for $A_x=a\cos\omega t$, $A_y=a\sin\omega t$, $A_z=0$, one finds $A_{\pm}\sim e^{\mp i\omega t}$). Since the coefficient λ_+ in Eq. (5) is in front of $\mathbf{B}_1^{\dagger}$ and $\mathbf{C}_1^{\dagger}$, one concludes that a σ_+ photon indeed produces an e-h pair with kinetic momentum $J=1$, $M=1$. Regarding the signs in Eq. (5), we can verify that they have to be written that way for the sake of coherence, in the particular case of a linear laser beam (see Appendix B). These signs are of importance in the case of linear polarization cross effects.

In Eq. (5), the quantification axis for the kinetic momentum of the created e-h pair is *a priori* arbitrary. An appropriate choice may be along the photon momentum. In this case, $\lambda_0=0$, and the e-photon coupling, W_B or W_C, reduces to two terms. However, in problems dealing with pump-probe experiments, such a reduction is not *a priori* possible for both photons, except when the two laser beams are collinear. As we will see later, the use of noncollinear beams allows us to obtain a wider absorption spectrum for the optical Stark effect.

We wish to note that one often chooses the quantification axis along the $\mathbf{k}$ direction. This is, in fact, the appropriate choice if one speaks of heavy- and light-hole eigenstates as these states correspond simply in this case to a valence kinetic momentum $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$. However, for problems dealing with excitons, the $\mathbf{k}$-momentum direction is unimportant. Moreover, this choice could not have been used for the electron-photon coupling as the created e-h pair has an arbitrary $\mathbf{k}$. In relation with a quantification axis along $\mathbf{k}$, we show in Appendix C how one recovers from Eq. (5) the well-known fact[8] that the heavy-hole creation is anisotropic, with a $\sin^2\theta$ dependence, θ being the angle between the hole momentum $\mathbf{k}$ and the (linear) photon field $\mathbf{A}$.

B. Appropriate form for the excitonic Stark shift

In this paper we want to calculate the shift of the exciton line induced by a pump beam tuned in the transparency region. For the sake of simplicity, we will choose the quantification axis along the pump-photon direction so that the electron–pump-photon coupling equation (5) reduces to two terms (this will lead us to keep possibly three terms for the electron–test-photon coupling if the pump and test beams are not collinear). As the photon absorption is ruled by terms in $e^{-i\omega t}$ in the coupling Hamiltonian, the above choice of quantification axis implies that the coefficients $\lambda_{\pm}$ are, in the case of usual polarizations,

$$\begin{aligned}
&\lambda_+\neq 0,\quad \lambda_-=0\quad(\sigma_+\text{ beam})\ ,\\
&\lambda_+=0,\quad \lambda_-\neq 0\quad(\sigma_-\text{ beam})\ ,\\
&\lambda_+=\lambda_-,\quad(\text{linear }x)\ ,\\
&\lambda_+=-\lambda_-,\quad(\text{linear }y)\ ,
\end{aligned}\tag{7}$$

the coefficient λ_0 always being zero.

We have found that the e-photon coupling contains two parts $\hat{W}=\hat{W}_B+\hat{W}_C$. However, for a detuning small compared to the valence-band splitting, only one of the two couplings, $\hat{W}_B$ or $\hat{W}_C$, will play a role in the exciton shift. For materials such as GaAs, in which the upper valence band is fourfold degenerate, we will have to consider only $\hat{W}_B$, while for materials such as CuCl, we will keep only $\hat{W}_C$, the upper valence band being twofold degenerate.

Let us now consider the specific form of the electron-photon coupling. Even if W_B appears particularly simple in terms of the total e-h pair kinetic momentum operator $\mathbf{B}_M$, it turns out that it is not the appropriate form to calculate the optical Stark shift for excitons made from a $j=\frac{3}{2}$ valence band. As we will see later, the shifts appear as eigenvalues in a $[(2\times4)=8]$-fold subspace (2 for the electron, 4 for the hole). The corresponding 8×8 matrix, written in the $|J,M\rangle$ basis, with $J=1$ and 2, contains essentially no zero. So its analytical diagonalization is hopeless. Instead, the calculation of the excitonic shift appears particularly simple if one introduces a set of canonical hole operators $B_m(\mathbf{k})$, such that $B_{\pm3/2}(\mathbf{k})$ are the precise combinations of hole states which are coupled to the electron states $b_{\mp1/2}^{\dagger}(\mathbf{k})$. Namely, these hole operators are defined such that the coupling W_B reads

$$\begin{aligned}
W_B^{\dagger}(\mathbf{k})=&\ \Delta_+b_{-1/2}^{\dagger}(\mathbf{k})B_{3/2}^{\dagger}(-\mathbf{k})\\
&+\Delta_-b_{1/2}^{\dagger}(\mathbf{k})B_{-3/2}^{\dagger}(-\mathbf{k})\ .
\end{aligned}\tag{8}$$

From Eqs. (5) and (A9), one can identify these operators $B_{\pm3/2}$ to be

$$B_{\pm3/2}^{\dagger}=[\lambda_{\pm}c_{3/2,\pm3/2}^{\dagger}-(\tfrac{1}{3})^{1/2}\lambda_{\mp}c_{3/2,\mp1/2}^{\dagger}]/\Delta_{\pm}\ .\tag{9}$$

The bare hole operator $c_{j,m}$ corresponds to a hole state having a kinetic momentum (j,m). The normalizing coefficients $\Delta_{\pm}$ are

$$\Delta_{\pm}^2=\lambda_{\pm}^2+\tfrac{1}{3}\lambda_{\mp}^2\ .\tag{10}$$

The two other hole states necessary to form, with the

$B_{\pm 3/2}$, an orthogonal basis for the $J=\frac{3}{2}$ fourfold-hole subspace, are easily found to be

$$B^{\dagger}_{\pm 1/2}=[(\tfrac{1}{3})^{1/2}\lambda_{\mp}c^{\dagger}_{3/2,\pm 3/2}+\lambda_{\pm}c^{\dagger}_{3/2,\mp 1/2}]/\Delta_{\pm} \ . \quad (11)$$

One can check that the set of canonical hole operators $B_m(\mathbf{k})$ defined above are such that

$$[B_m(\mathbf{k}),B^{+}_{m'}(\mathbf{k}')]_{+}=\delta_{mm'}\delta_{\mathbf{k}\mathbf{k}'} \ . \quad (12)$$

We want to stress that the two hole states $B_{\pm 3/2}$ coupled to the conduction band depend on the laser characteristics via the coefficients $\lambda_{\pm}$. In the particular case of a σ_+ beam, they reduce to the bare $c_{3/2,3/2}$ and $c_{3/2,1/2}$ hole states, as expected: These are the only states forming with the $b_{-1/2}$ and $b_{1/2}$ electron states, an *e-h* pair with total kinetic momentum equal to that of a σ_+ photon, i.e., $J=1$, $M=1$.

In order to have a similar form for the operator W_C, coupling the conduction band to the $j=\frac{1}{2}$ hole subband, one can rewrite Eq. (5) as

$$W^{\dagger}_C(\mathbf{k})=\Delta'_{+}b^{\dagger}_{1/2}(\mathbf{k})C^{\dagger}_{1/2}(-\mathbf{k})+\Delta'_{-}b^{\dagger}_{-1/2}(\mathbf{k})C^{\dagger}_{-1/2}(-\mathbf{k}) \ , \quad (13)$$

where the operators $C_{\pm 1/2}$ are simply the bare hole operators $c_{1/2,\pm 1/2}$ and the coefficients $\Delta'_{\pm}$ are

$$\Delta'_{\pm}=\mp(\tfrac{2}{3})^{1/2}\lambda_{\pm} \ . \quad (14)$$

III. ELECTRONIC SYSTEM

The Hamiltonian H of the electronic system is composed of a kinetic part and a Coulomb interaction V_{Coul}. The kinetic part of a semiconductor valence band is somewhat complicated. It results from the $\mathbf{k}\cdot\mathbf{p}$ theory and is given by the Kohn and Luttinger 6×6 matrix. It can be separated into $j=\frac{1}{2}$ and $j=\frac{3}{2}$ states, the latter having the heavy- and light-holes as eigenstates. As said before, these eigenstates correspond exactly to $m=\pm\frac{3}{2},\pm\frac{1}{2}$ when the kinetic momentum quantification axis is along the hole momentum $\mathbf{k}$ (and so changes with $\mathbf{k}$).

The eigenstates of H can be classified as follows: the vacuum $|0\rangle$; the one *e-h* pair, bound or unbound states $|X\rangle$ that we call an "exciton." They form a subspace having a $(2\times 6)=12$ dimension; the two *e-h* pair, bound or unbound, states $|XX\rangle$ that we call a "biexciton." They form a subspace having a 12×12 dimension; and so on.

Due to the presence of the Kohn-Luttinger valence part in the Hamiltonian H, the *e-h* eigenstates are much more complex than in the simplest case of one nondegenerate hole band. Besides the degeneracy of the corresponding subspace, the precise eigenvalues and eigenfunctions are also much more difficult to obtain. However, Baldereschi and Lipari[9] have shown that, in the case of the lowest exciton level, it is a good approximation to replace the Kohn and Luttinger matrix by an average hole mass [its particular value in terms of the heavy- and light-hole masses being $m_h=2(1/m_H+1/m_L)^{-1}$]. This is quite nice since, within this approximation, the one-*e*-*h*-pair eigenstates of the Hamiltonian H appear simply as hydrogenlike levels, associated with an unique reduced mass $(1/m_e+1/m_h)^{-1}$. The 12D exciton subspace then spreads into an eight-fold-degenerate subspace separated from a fourfold one by a valence-band splitting Δ. The physical idea behind this approximation is that bound excitons are built from various hole states $\mathbf{k}$, leading to some kind of averaging over the hole masses. This approximation, which has been justified for the lowest exciton level, is *a priori* not valid for the high-energy diffusive states as, for these states; excitons appear rather like free electrons and holes, and the holes are either heavy or light. However, as the *e*-photon coupling creates *e-h* pairs $(\mathbf{k},-\mathbf{k})$ with every possible value of the momentum $\mathbf{k}$, it also induces some averaging over the hole masses. This may justify the use of, in problems dealing with *e-h* pairs created by photons, one averaged hole mass for all exciton levels.

Consequently, and also for the sake of simplicity in an already complex calculation, we will assume in this paper that the valence band can be replaced by an average hole mass. We will, however, keep the eightfold and fourfold degeneracies of the original hole subspace and their kinetic momentum symmetries as they are the key part of the polarization effects we want to derive.

The excitonic levels being eightfold or fourfold degenerate (if one neglects electron-hole exchange),[10] one can *a priori* use for the excitonic states any $8D$, or $4D$ basis. Since we are interested in the optical Stark effect, we choose the basis appropriate to the *e*-photon coupling defined in Sec. II B: more precisely, (i) in the case of eightfold excitons built from $j=\frac{3}{2}$ hole states, the expression (8) for W_B leads us to write the excitonic states as

$$|X_{sm}(i)\rangle=\mathbf{B}^{\dagger}_{sm}(i)|0\rangle \ , \quad (15)$$

with $s=\pm\frac{1}{2}$ and $m=\pm\frac{3}{2},\pm\frac{1}{2}$. The exciton creation operator $\mathbf{B}^{\dagger}_{sm}(i)$ are expressed in terms of free *e* and *h* operators as

$$\mathbf{B}^{\dagger}_{sm}(i)=\sum_{k}\phi_i(\mathbf{k})\mathbf{B}^{\dagger}_{sm}(\mathbf{k}) \ ,$$
$$\mathbf{B}^{\dagger}_{sm}(\mathbf{k})=b^{\dagger}_{s}(\mathbf{k})B^{\dagger}_{m}(-\mathbf{k}) \ , \quad (16)$$

where the hole operators B_m are the appropriate combinations defined in Eqs. (9) and (11). $\phi_i(\mathbf{k})$ is the usual exciton hydrogenlike wave function. The associated energy, in the rotating frame in which the electron–pump-photon coupling is time independent, is in fact, the detuning

$$\Omega_i=\omega_i-\omega_p=(E_g-\varepsilon_i)-\omega_p \ , \quad (17)$$

where E_g is the band gap and ω_p the photon frequency.

(ii) In the case of fourfold excitons, Eq. (13) for W_C leads us to write the excitonic states as

$$|X_{ss'}(i)\rangle=\mathbf{C}_{ss'}(i)|0\rangle \ , \quad (18)$$

where $s=\pm\frac{1}{2}$ and $s'=\pm\frac{1}{2}$. The exciton creation operator

$C^{\dagger}_{ss'}(i)$ is expressed again in terms of free e and h operators as

$$C^{\dagger}_{ss'}(i)=\sum_{k}\phi_i(\mathbf{k})C^{\dagger}_{ss'}(\mathbf{k}) ,$$
$$C^{\dagger}_{ss'}(\mathbf{k})=b^{\dagger}_{s}(\mathbf{k})C^{\dagger}_{s'}(-\mathbf{k}) , \tag{19}$$

where $\phi_i(\mathbf{k})$ is the same excitonic wave function as in Eq. (16), but the associated energy is now shifted by the valence-band splitting Δ:

$$\bar{\Omega}_i=(E_g+\Delta-\varepsilon_i)-\omega_p=\Omega_i+\Delta . \tag{20}$$

If we now turn to biexcitonic states, their exact expressions are basically unknown as in the simplest case of one nondegenerate hole band. We have, however, shown in Ref. 5 that one can avoid using them in the calculation of the exciton Stark shift, almost everywhere, by using the Brillouin-Wigner form of the perturbation theory. They appear, however, at small detuning, since the dominant contribution to the Stark shift includes their exact forms. We will come back to this problem in Sec. VI.

IV. EXPRESSION OF THE EXCITON SHIFT

The problem is calculating the energy change of the exciton states $|X_{sm}(i)\rangle$ or $|X_{ss'}(i)\rangle$ defined in Eq. (15) or (18), induced by the electron-photon coupling $\hat{W}=W_B^{+}+W_C^{+}+\text{H.c.}$, W_B^{+} and W_C^{+} being given in Eqs. (8) and (13). In this paper, we will only consider laser beams with low intensity, tuned in the transparency region, far from resonance, such that the coupling $\hat{W}$ can be treated within perturbation theory.

The calculation basically follows that of Ref. 5. It is, however, more complex as one has to include the exciton degeneracy. For the sake of simplicity, we will calculate the shift of the lowest exciton level. The case of an arbitrary level i can be easily obtained changing 1 into i.

The Stark shift of the exciton ($i=1$) results from the difference between the change of the exciton energy Ω_1' and vacuum energy E_0' induced by the e-photon coupling $\hat{W}$. As in Ref. 5, we will use the Brillouin-Wigner form of the perturbation theory. In Appendix D, we derive its expression for nondegenerate and degenerate states. This leads us to write the change of the vacuum state energy, to lowest order in $\hat{W}$, as

$$E_0'-E_0=\langle 0|\hat{W}(E_0-H)^{-1}\hat{W}^{\dagger}|0\rangle . \tag{21}$$

In the case of degenerate states, a similar procedure gives, for the eigenstates $|X'(1)\rangle$ of the perturbed exciton, a set of equations valid for any (s',m') (see Appendix D),

$$0=\sum_{s,m}[(\Omega_1'-\Omega_1)\delta_{ss'}\delta_{mm'} +\langle X_{s'm'}(1)|\hat{W}(H-\Omega_1)^{-1}\hat{W}|X_{s,m}(1)\rangle] \times\langle X_{s,m}(1)|X'(1)\rangle , \tag{22}$$

$\delta_{ss'}$ being the Kronecker function, $\delta_{ss'}=1$, if $s=s'$, and zero otherwise.

Equation (22) just means that the perturbed excitons $|X'(1)\rangle$ are the eigenstates of the operator $\hat{W}(H-\Omega_1)^{-1}\hat{W}$, restricted to the degenerate exciton subspace $|X_{s,m}(1)\rangle$; the perturbed energy being the associated eigenvalues.

If we now speak in terms of the exciton shift

$$\delta\omega_1=(\Omega_1'-E_0')-(\Omega_1-E_0) , \tag{23}$$

one deduces from Eqs. (21) and (22) that the Stark shifts $\delta\omega_1$ are the eigenvalues of the S operator defined as

$$S=\hat{W}(\Omega_1-H)^{-1}\hat{W}+\langle 0|\hat{W}H^{-1}\hat{W}|0\rangle I , \tag{24}$$

restricted to the degenerate exciton subspace, I being the identity (we have set $E_0=0$).

Following Refs. 1 and 5, we express the exciton Stark shift as an expansion in binding energy divided by detuning. In order to do that, we extract formally the large-detuning behavior (obtained by replacing H in front of n-pair states by $n\Omega_1$) by adding and subtracting it from Eq. (24). This leads us to write, in the last matrix element of Eq. (24),

$$\langle 0|WH^{-1}W^{\dagger}|0\rangle\equiv\Omega_1^{-1}(\langle 0|[W,W^{\dagger}]|0\rangle +\langle 0|W(\Omega_1-H)H^{-1}W^{\dagger}|0\rangle) . \tag{25}$$

One indeed notes that the first matrix element of Eq. (25) does not depend on the detuning, while the second one goes to zero when the photon energy decreases.

Similarly the first operator of Eq. (24) can be identically written as

$$\hat{W}(\Omega_1-H)^{-1}\hat{W}\equiv\Omega_1^{-1}\{-[W,W^{\dagger}]+W^{\dagger}H(\Omega_1-H)^{-1}W +W(2\Omega_1-H)(\Omega_1-H)^{-1}W^{\dagger}\} . \tag{26}$$

Here again, the first term of Eq. (26) does not depend on the detuning, the second one gives exactly zero when restricted to the exciton subspace (as $HW|X\rangle\sim H|0\rangle=0$ if $E_0=0$), while the last term goes to zero when the photon energy decreases (as $W^{\dagger}|X\rangle\sim|XX\rangle$).

Using Eqs. (25) and (26) into Eq. (24), the restriction of the operator S to the exciton subspace reads

$$S=\Omega_1^{-1}(T+T') , \tag{27}$$
$$T=-[W,W^{\dagger}]+\langle 0|[W,W^{\dagger}]|0\rangle I , \tag{28}$$
$$T'=W(2\Omega_1-H)(\Omega_1-H)^{-1}W^{\dagger} +\langle 0|W(\Omega_1-H)H^{-1}W^{\dagger}|0\rangle I . \tag{29}$$

The T operator does not depend on the detuning, while T', restricted to excitons $|X_{sm}(1)\rangle$, goes to zero when the detuning increases. As T contains the commutator $[W,W^{\dagger}]$, which differs from zero due to Pauli exclusion, this shows that the large detuning limit of the exciton shift comes from Fermi statistics. This is exactly what we have found in our original work without exciton degeneracy. In this work, we also found that the corrections to the large-detuning limit cancel exactly if the Coulomb interaction is neglected. We will show that,

similarly, T' gives exactly zero for $V_{\text{Coul}}=0$.

In the next paragraph, we will study the large-detuning limit of the shift, i.e., the eigenvalues of T, and in the following one, we calculate its detuning dependence, i.e., the contribution of T'. At this stage, it is useful to not that, for detuning small compared to the valence-band splitting Δ, one can only keep one of the two couplings W_B or W_C in the calculation of the eight-fold or four-fold exciton shift, within terms of the order of Ω_1/Δ.

V. EXCITONIC SHIFT AT LARGE DETUNING

We have shown in Sec. IV that the excitonic shifts $\delta\omega_1$ at large detuning are given by the eigenvalues of the operator $\Omega_1^{-1}T$ restricted to the degenerate exciton subspace. We will consider separately the case of fourfold and eightfold excitons.

A. Fourfold exciton

The matrix elements of the operator T restricted to the exciton subspace $|X_{ss'}(1)\rangle$ read, when one keeps only W_C in the e-photon coupling,

$$\begin{aligned}T_{ss',rr'}&=\langle X_{ss'}(1)|T|X_{rr'}(1)\rangle\\&=\langle 0|\mathbf{C}_{ss'}(1)[W_C,W_C^\dagger]\mathbf{C}_{rr'}^\dagger(1)|0\rangle\\&\quad+\langle 0|[W_C,W_C^\dagger]|0\rangle\delta_{sr}\delta_{s'r'}\ ,\end{aligned}\tag{30}$$

with $s,s',r,r'=\pm\frac{1}{2}$. Noting that $\delta_{sr}\delta_{s'r'}=\langle 0|\mathbf{C}_{ss'}\mathbf{C}_{rr'}^\dagger|0\rangle$, one can rewrite Eq. (30) as

$$T_{ss',rr'}=\langle 0|\mathbf{C}_{ss'}(1)[\mathbf{C}_{rr'}^\dagger(1),[W_C,W_C^\dagger]]|0\rangle\ .\tag{31}$$

Using Eq. (19), it is easy to show that

$$T_{ss',rr'}=\sum_{\mathbf{k}}|\phi_1(\mathbf{k})|^2U_{ss',rr'}(\mathbf{k})=U_{ss',rr'}\tag{32}$$

as the matrix elements $U_{ss'rr'}$,

$$U_{ss'rr'}(\mathbf{k})=\langle 0|\mathbf{C}_{ss'}(\mathbf{k})[\mathbf{C}_{rr'}^\dagger(\mathbf{k}),[W_C(k),W_C^\dagger(\mathbf{k})]]|0\rangle\ ,\tag{33}$$

do not depend on $\mathbf{k}$. Its precise calculation using Eq. (13) for the coupling $W_C(\mathbf{k})$ gives

$$U_{ss'rr'}=\delta_{sr}\delta_{s'r'}\sum_{\pm}\Delta_{\pm}'^2(\delta_{s,\pm1/2}+\delta_{s',\pm1/2})\ ,\tag{34}$$

with $\Delta_{\pm}'$ given in Eq. (14). Equation (34) shows that the U matrix appears, on the $|X_{ss'}\rangle$ basis, in a diagonal form, its matrix elements being $2\Delta_+'^2$, $2\Delta_-'^2$, and $\Delta_+'^2+\Delta_-'^2$, twice.

Since the excitonic shifts are the eigenvalues of the operators $\Omega_1^{-1}T=\Omega_1^{-1}U$, it is straightforward to conclude that, at large detuning, the fourfold exciton splits into three shifted lines which correspond to

$$\begin{aligned}&2\Delta_+'^2/\Omega_1,\ \text{for}\ |X_{1/2,1/2}\rangle\ ,\\&2\Delta_-'^2/\Omega_1,\ \text{for}\ |X_{-1/2,-1/2}\rangle\ ,\\&(\Delta_+'^2+\Delta_-'^2)/\Omega_1,\ \text{for}\ |X_{+1/2,-1/2}\rangle\ \text{and}\ |X_{-1/2,+1/2}\rangle\ .\end{aligned}\tag{35}$$

The two first states correspond to a total e-h kinetic momentum $M=+1$ and -1 so they can be seen with a probe beam collinear to the pump and having σ_+ and σ_- components, respectively. However, the last shifted lines, which correspond to e-h states with $M=0$, can be seen only with a probe beam not collinear to the pump.

It is interesting to note that a similar calculation for the exciton $|X_{ss'}(i)\rangle$ would give the same shifts, so that, as for the simple case (i.e., without band degeneracy), one finds that the large-detuning value of the exciton shift does not depend on the specific excitonic level considered.

B. Eightfold exciton

We now perform a similar calculation for the eightfold exciton, the coupling W_B being given in Eq. (8) and the excitonic basis $|X_{sm}(1)\rangle$ in Eq. (16). The matrix elements of the corresponding operator T read

$$\begin{aligned}&T_{sm,s'm'}=\langle 0|\mathbf{B}_{sm}(1)[\mathbf{B}_{s'm'}^\dagger(1),[W_B,W_B^\dagger]]|0\rangle=\sum_{k}|\phi_1(\mathbf{k})|^2U_{sm,s'm'}(\mathbf{k})\ ,\\&U_{sm,s'm'}(\mathbf{k})=\langle 0|\mathbf{B}_{sm}(\mathbf{k})[\mathbf{B}_{s'm'}^\dagger(\mathbf{k}),[W_B(\mathbf{k}),W_B^\dagger(\mathbf{k})]]|0\rangle\ .\end{aligned}\tag{36}$$

As the hole operators $B_m(\mathbf{k})$, defined in Eqs. (9) and (11), also form an orthogonal set [see Eq. (12)], it is easy to find,

$$T_{sm,s'm'}=\delta_{ss'}\delta_{mm'}\sum_{\pm}\Delta_{\pm}^2(\delta_{s,\mp1/2}+\delta_{m,\pm3/2})\ .\tag{37}$$

We see that the T matrix 8×8 appears immediately in a diagonal form, thanks to the use of the hole operators B_m which are indeed the appropriate ones in this problem. We wish to note that unappropriate hole operators could lead to an 8×8 matrix without any zero, its eigenvalues being then quite uneasy to obtain.

From Eq. (37), one deduces that the eightfold exciton splits, under laser irradiation, into five shifted lines which correspond to

$$\begin{aligned}&2\Delta_+^2/\Omega_1\ \text{for}\ |X_{-1/2,3/2}\rangle\ ,\\&2\Delta_-^2/\Omega_1\ \text{for}\ |X_{1/2,-3/2}\rangle\ ,\\&(\Delta_+^2+\Delta_-^2)/\Omega_1\ \text{for}\ |X_{1/2,3/2}\rangle\ \text{and}\ |X_{-1/2,-3/2}\rangle\ ,\\&\Delta_+^2/\Omega_1\ \text{for}\ |X_{-1/2,1/2}\rangle\ \text{and}\ |X_{-1/2,-1/2}\rangle\ ,\\&\Delta_-^2/\Omega_1\ \text{for}\ |X_{1/2,1/2}\rangle\ \text{and}\ |X_{1/2,-1/2}\rangle\ ,\end{aligned}\tag{38}$$

$\Delta_\pm$ being given in Eq. (10). In the particular case of a σ_+ beam (i.e., $\lambda_+=\lambda$, $\lambda_-=0$) these shifts are respectively,

$2\lambda^2/\Omega_1$, $\frac{2}{3}\lambda^2/\Omega_1$, $\frac{4}{3}\lambda^2/\Omega_1$, λ^2/Ω_1, $\frac{1}{3}\lambda^2/\Omega_1$, while for a linear beam (i.e., $\lambda_+=\lambda_-$) these five shifts collapse into two different ones $2\lambda^2/\Omega_1$ and λ^2/Ω_1.

Excitons $|X_{sm}\rangle=b_s^\dagger B_m^\dagger|0\rangle$ are built from the hole combinations B_m defined in Eqs. (9) and (11). Going back to the hole operators $c_{j,m}$, quantified along the pump-photon momentum, we note that the states $|X_{-1/2,3/2}\rangle$, $|X_{1/2,-3/2}\rangle$, $|X_{-1/2,1/2}\rangle$, and $|X_{1/2,-1/2}\rangle$ correspond to *e-h* momentum $M=\pm1$ so it is possible to see these four shifted lines with a probe beam collinear to the pump and having σ_+ and σ_- components. However, the four other exciton states correspond to $M=2$ or 0 and so cannot be created with a probe photon collinear to the pump. Consequently, such a probe cannot see the shifted line $(\Delta_+^2+\Delta_-^2)/\Omega_1$. We will come back to this problem in Sec. VII and give the weights of the various absorption lines for typical pump-probe experiments.

Here again one can note that the excitonic shifts do not depend on the specific exciton level *i*, as in Ref. 5.

In our original work (Ref. 5) on the optical Stark shift, without conduction- and valence-state degeneracies, we also had an important conclusion for the exciton shift at large detuning, namely, the value of the shift is the same as that for the two-level atom, $2\lambda^2/\Omega_1$. We gave a physical interpretation for this result: at detuning large compared with the exciton binding energy, the Coulomb interaction can be neglected; one valence state is then coupled to one conduction state as for a two-level system, so one gets the same shift. This physical interpretation should also be valid when the valence and conduction band are degenerate. The corresponding result in the case of four valence states and two conduction states should be that the five shifts of the eightfold exciton, given in Eq. (38), are nothing but the ones of a [(2+4)=6]-level atom. We will show it below.

C. Six-level atom

One can, at first, note that the above shifts are different from the simple two-level value $2\lambda^2/\Omega_1$, λ being the coupling factor between these two levels. This comes from the fact that the two electron states are not coupled similarly to the various hole states. If all the couplings were λ, the above calculation would have given the same shift $2\lambda^2/\Omega_1$ for any exciton. In order to find the shifts [Eqs. (35) and (38)], one has to take into account the exact electron-photon coupling.

In order to speak in terms of valence and conduction states, we first have to rewrite the *e*-photon coupling W_B, given in Eq. (8) in terms of hole operators $B_{\pm3/2}$, in terms of valence-band operators. Using Eq. (A7), one finds that Eq. (8) becomes

$$W_B^\dagger(\mathbf{k})=\Delta_+ b_{-1/2}^\dagger \mathbf{A}_{-3/2}-\Delta_- b_{1/2}^\dagger \mathbf{A}_{3/2}\ , \tag{39}$$

where the valence-band operators $A_{\pm3/2}$ are

$$\mathbf{A}_{\pm3/2}=[\lambda_\pm b_{3/2,\mp3/2}-(\tfrac{1}{3})^{1/2}\lambda_\mp b_{3/2,\pm1/2}]/\Delta_\pm\ , \tag{40}$$

$b_{j,m}$ being the electron valence-band state, with kinetic momentum (j,m). It is then easy to conclude that at small laser intensity the conduction states $b_{-1/2}$ and valence state $A_{-3/2}$, being coupled by W_B, are pushed apart by a quantity Δ_+^2/Ω_1, while the conduction and valence states $b_{1/2}$ and $A_{3/2}$ are pushed apart by Δ_-^2/Ω_1 (see Fig. 1). The valence states $A_{\pm1/2}$ are not coupled to the conduction band so they are not affected by the laser beam. One then deduced the following shifts for the various valence to conduction-band transitions:

$2\Delta_+^2/\Omega_1$ for $A_{-3/2}\rightarrow b_{-1/2}$, i.e., $|X_{-1/2,3/2}\rangle$,

$2\Delta_-^2/\Omega_1$ for $A_{3/2}\rightarrow b_{1/2}$, i.e., $|X_{1/2,-3/2}\rangle$,

$(\Delta_+^2+\Delta_-^2)/\Omega_1$ for $A_{3/2}\rightarrow b_{-1/2}$, i.e., $|X_{-1/2,-3/2}\rangle$,

and $A_{-3/2}\rightarrow b_{1/2}$, i.e., $|X_{1/2,3/2}\rangle$,

Δ_+^2/Ω_1 for $A_{\pm1/2}\rightarrow b_{-1/2}$, i.e., $|X_{-1/2,\pm1/2}\rangle$,

Δ_-^2/Ω_1 for $A_{\pm1/2}\rightarrow b_{1/2}$, i.e., $|X_{1/2,\pm1/2}\rangle$. (41)

One verifies that these shifts are just those of Eq. (38).

(i) This result is physically very important. The fact that the five shifts of the eightfold exciton are exactly the ones of a six-level atom is indeed a very fundamental proof of the idea that excitons appear like dressed-atoms at large detuning.

(ii) This result is also very useful as it allows us to obtain extremely easily the eightfold exciton shifts and the corresponding correct polarization effects in pump-probe experiments. It is all the more useful as the first corrections to the large-detuning behavior of the shifts have the same symmetries, as will be shown later.

(iii) This result is also useful as it allows us to understand why the hole operators B_m, which may have appeared complicated at first, are indeed the appropriate ones for the exciton Stark effect. As soon as one remarks that the exciton shifts have to be those of a multilevel atom, it is clear that the appropriate basis for this problem is the one in which valence to conduction-band transitions appear in their simplest form and not the one in which the exciton-photon coupling is simple. It is why the total kinetic momentum exciton basis, $|X_{JM}\rangle$ with $J=2$ and 1, which at first may have appeared a good choice for the eightfold exciton, in view of Eq. (5) for the electron-photon coupling, turns out to be a rather poor choice for the expression of the matrix T.

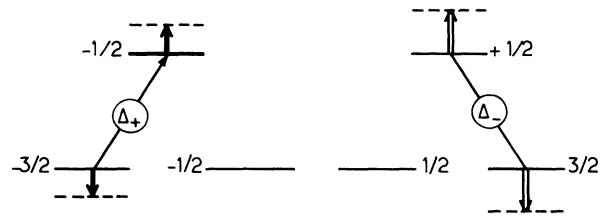

FIG. 1. Shifts of the conduction and valence states b_s and A_m (with $s=\pm\frac{1}{2}$ and $m=\pm\frac{3}{2},\pm\frac{1}{2}$), defined in Eq. (40) induced by the electron-photon coupling. $\Delta_\pm$ are defined in Eq. (10) in terms of the $\sigma_\pm$ components of the light.

For the sake of completeness, we have calculated in Appendix E the exact six-level atom eigenstates for any laser intensity.

VI. DETUNING DEPENDENCE OF THE EXCITONIC SHIFT

The problem now is to calculate the terms coming from the part T' in the excitonic shift [Eq. (29)] restricted to the degenerate exciton subspace. More precisely, in the case of the eightfold exciton we have to calculate

$$T'_{sm,s'm'}=\langle 0|W_B\{\mathbf{B}_{sM}(1)(H-2\Omega_1)(H-\Omega_1)^{-1}\mathbf{B}^{\dagger}_{s'm'}(1) -\delta_{ss'}\delta_{mm'}(H-\Omega_1)H^{-1}\}W_B^{\dagger}|0\rangle \ . \quad (42)$$

As in Ref. 5, we write these matrix elements as an expansion in binding energy divided by detuning. This is performed by introducing the operator $V^{\dagger}_{sm}(1)$ defined as

$$[H,\mathbf{B}^{\dagger}_{sm}(1)]=\Omega_1[\mathbf{B}^{\dagger}_{sm}(1)+\mathbf{V}^{\dagger}_{sm}(1)] \ . \quad (43)$$

The explicit calculation of $\mathbf{V}_{sm}(1)$ is done in Appendix F. The operator $\mathbf{V}^{\dagger}_{sm}(1)$ which creates one e-h pair has the same structure as the operator $C^{\dagger}(1)$ introduced in Ref. 5. It basically corresponds to Coulomb interaction between excitons, as seen later. Noting that

$$(H-2\Omega_1)(H-\Omega_1)^{-1}\mathbf{B}^{\dagger}_{s'm'}(1)=\mathbf{B}^{\dagger}_{s'm'}(1)(H-\Omega_1)H^{-1}+\Omega_1(H-\Omega_1)^{-1}\mathbf{V}^{\dagger}_{s'm'}(1)\Omega_1H^{-1} \ , \quad (44)$$

the T' matrix can be written, in the spirit of Ref. 5, as

$$T'=\hat{\alpha}+\hat{\beta}-\hat{\gamma} \ , \quad (45)$$

where the $\hat{\alpha},\hat{\beta},\hat{\gamma}$ matrices are defined by

$$\alpha_{sm,s'm'}=\langle 0|W_B\{\mathbf{B}_{sm}(1)\mathbf{B}^{\dagger}_{s'm'}(1)-\delta_{ss'}\delta_{mm'}\}(H-\Omega_1)H^{-1}W_B^{\dagger}|0\rangle \ , \quad (46)$$

$$\beta_{sm,s'm'}=\langle 0|W_B\Omega_1H^{-1}\mathbf{B}_{sm}(1)\mathbf{V}^{\dagger}_{s'm'}(1)\Omega_1H^{-1}W_B^{\dagger}|0\rangle \ , \quad (47)$$

$$\gamma_{sm,s'm'}=\langle 0|W_B\Omega_1H^{-1}\mathbf{V}_{sm}(1)\Omega_1(H-\Omega_1)^{-1}\mathbf{V}^{\dagger}_{s'm'}\Omega_1H^{-1}W_B^{\dagger}|0\rangle \ . \quad (48)$$

In the first two terms, $\hat{\alpha}$ and $\hat{\beta}$, the Hamiltonian H acts only on one-e-h-pair states, allowing their exact calculation. We will show that they can, in fact, be expressed extremely simply in terms of the T matrix. In the last term $\hat{\gamma}$, H acts on two-pair states so the exact biexcitonic wave functions are needed to calculate it explicitly.

We have said in the last paragraph that T' gives exactly zero if the Coulomb interaction is neglected. It is already obvious that $\hat{\beta}$ and $\hat{\gamma}$ give zero if $\mathbf{V}_{sm}=0$. We will show that $\hat{\alpha}$ gives zero also.

A. Calculation of $\hat{\alpha}$

Using Eq. (16), one can write the coupling $W_B(\mathbf{k})$, given in Eq. (8), in terms of the exciton operators $\mathbf{B}_{sm}(i)$,

$$W_B^{\dagger}(\mathbf{k})=\sum_i \phi_i^*(\mathbf{k})W_B^{\dagger}(i) \ ,$$
$$W_B^{\dagger}(i)=\Delta_+B^{\dagger}_{-1/2,3/2}(i)+\Delta_-B^{\dagger}_{1/2,-3/2}(i) \ . \quad (49)$$

This expression W_B leads to

$$(H-\Omega_1)H^{-1}W_B^{\dagger}|0\rangle=\sum_i\sum_{\mathbf{k}}\phi_i(\mathbf{k})(\Omega_i-\Omega_1)\Omega_i^{-1}W_B^{\dagger}(i)|0\rangle \ . \quad (50)$$

Using Eqs. (49) and (50) in Eq. (46), one finds

$$\alpha_{sm,s'm'}=\sum_i\sum_{\mathbf{k}}\phi_i(\mathbf{k})\sum_{\mathbf{k}'}\phi_i^*(\mathbf{k}')(\Omega_i-\Omega_1)\Omega_i^{-1}\langle 0|\mathbf{B}_{sm}(1)[[W_B(\mathbf{k}'),W_B^{\dagger}(\mathbf{k}')],\mathbf{B}^{\dagger}_{s'm'}(1)]|0\rangle \ . \quad (51)$$

Writing $\mathbf{B}_{sm}(1)$ in terms of $\mathbf{B}_{sm}(\mathbf{k})$, one shows that this last matrix element is proportional to $U_{sm,s'm'}(\mathbf{k})$, given in Eq. (34). It is then easy to conclude that the $\hat{\alpha}$ and T matrices are proportional. More precisely,

$$\alpha_{sm,s'm'}=(\alpha/2)T_{sm,s'm'} \ ,$$
$$a=2\sum_i(\Omega_1-\Omega_i)\Omega_i^{-1}\sum_{\mathbf{k},\mathbf{k}'}\phi_i^*(\mathbf{k}')\phi_i(\mathbf{k})|\phi_1(\mathbf{k})|^2 \ . \quad (52)$$

It is nice to find that α is the same coefficient as the one defined in the simple case, without valence- and conduction-band degeneracy (Ref. 5). We recall[5] that the physical origin of this term is that the two excitons "feel" each other because they are not real bosons; in three dimensions, the variation of α with detuning goes from $4(\varepsilon_1/\Omega_1)^{1/2}$ at large detuning to 5 at small detuning; if the Coulomb interaction is neglected, the ϕ's are plane waves and $\alpha=0$.

In the case of a fourfold exciton one finds the same result, namely

$$\alpha_{ss',rr'}=(\alpha/2)T_{ss',rr'} \ . \quad (53)$$

B. Calculation of $\hat{\beta}$

It is somewhat less easy to show (see Appendix G) that one finds for $\hat{\beta}$ a result as simple as the one for $\hat{\alpha}$, namely

$$\beta_{sm,s'm'}=(\beta/2)T_{sm,s'm'} , \tag{54}$$

β being the same coefficient as the one found in the simple case (Ref. 5) (see Appendix G). We recall[5] that, at large detuning, β goes to zero faster than α (which is then the leading large-detuning correction), while, at small detuning, β diverges as β_{11}/Ω_1, (with $\beta_{11}=\frac{52}{3}\varepsilon_1$ in three dimensions) and so dominates.

Up to that stage, we find that the excitonic shifts, which are the eigenvalues of

$$\Omega_1^{-1}(T+\hat{\alpha}+\hat{\beta})=\Omega_1^{-1}(1+\alpha/2+\beta/2)T , \tag{55}$$

are simply the large-detuning ones, multiplied by $1+\alpha/2+\beta/2$. This result is just the nonobvious generalization of our previous one, with a simple band structure, namely the large-detuning shift $2\lambda^2/\Omega_1$ transforms into $(2+\alpha+\beta)\lambda^2/\Omega_1$ when the detuning decreases. This result is also quite nice as, the eigenstates being, of course, the same as those for T, the selection rules for pump-probe experiments are not affected by the first two detuning-dependent terms. They are still simply the ones for a six-level atom.

C. Calculation of $\hat{\gamma}$

Unfortunately, this nice result does not apply to $\hat{\gamma}$: the matrix $\hat{\gamma}$ is not proportional to T. The main reason is that $\hat{\alpha}$ and $\hat{\beta}$ contain only the excitonic eigenstates which are eightfold degenerate, while $\hat{\gamma}$ deals with the true biexcitonic eigenstates, which are not 8×8 degenerate. The internal structure of biexcitonic states appear there.

As explained in our previous work, γ along with β are the dominant contributions to the excitonic shift at small detuning. However, β gives a positive contribution to the shift while γ gives a negative one; so it is not clear whether the exciton red-shifts or still blue-shifts at resonance. The small-detuning behavior is, in fact, clear only when the biexcitonic molecule is well bound. γ is then the only dominant term at the two-photon biexcitonic resonance and the exciton line clearly red-shifts.

We now consider this problem and concentrate on materials, such as CuCl, having a stable biexcitonic molecule. Such materials have a $J=\frac{1}{2}$ upper valence band so that their excitons are initially fourfold degenerate. We have already shown that, at large detuning, the fourfold exciton splits into three blue-shifted lines [see Eq. (35)]. As shown in Appendix H, only one particular combination of the fourfold states is affected by the existence of a stable biexcitonic molecule and red-shifts at the biexcitonic resonance, namely

$$|X_R\rangle=\Delta'_+|X_{-1/2,-1/2}\rangle+\Delta'_-|X_{1/2,1/2}\rangle . \tag{56}$$

The corresponding shift is

$$-\tfrac{2}{3}\lambda^2\gamma^2(\Omega_1-\varepsilon_m)^{-1} , \tag{57}$$

ε_m being the molecular binding energy.

The three other exciton states $|X_{1/2,-1/2}\rangle$, $|X_{-1/2,1/2}\rangle$, and

$$\Delta'_+|X_{1/2,1/2}\rangle+\Delta'_-|X_{-1/2,-1/2}\rangle \tag{58}$$

are not affected by the existence of a stable molecule. So only one of the four exciton lines red-shifts at the two-photon resonance, $\Omega_1=2\Omega_{xx}=2(\omega_{xx}-\omega_p)=2\Omega_1-\varepsilon_m$. By continuity, one expects that the exciton line which red-shifts has the smallest blue shift at large detuning. This can be easily checked in the simple case of a σ_+ beam; from Eq. (56), one sees that $|X_{-1/2,-1/2}\rangle$ is the only state which red-shifts while from Eq. (35), it is the only one which does not blue-shift at large detuning.

At resonance, $2\Omega_{xx}=\Omega_1$, the molecular biexciton is degenerate with the four exciton states. Perturbation theory done in this degenerate subspace easily shows that the excitonic red-shift saturates to

$$\delta\Omega_1=-|\langle XX|W_C^\dagger|X_{1/2,1/2}\rangle|^2 + |\langle XX|W_C^\dagger|X_{-1/2,-1/2}\rangle|^2=-\gamma\lambda , \tag{59}$$

with a linear dependence in λ, i.e., a dependence in the square root of the laser intensity, as expected for a resonance.

VII. SELECTION RULES FOR PUMP-PROBE EXPERIMENTS

In the preceding sections of this work we have found that, under laser excitation, the degenerate exciton line splits into various shifted lines. Let us now derive how these lines can be seen with pump-probe experiments.

The absorption spectrum of a probe beam results from the Fermi golden rule. The weights of the various shifted lines are given by

$$U_n=|\langle X'_n|W_t^\dagger|0\rangle|^2 , \tag{60}$$

$|X'_n\rangle$ being the eigenstates of the electronic system in presence of a pump beam. Their expressions, on the excitonic basis $|X_{sm}(1)\rangle$, are given in Eq. (35), for fourfold excitons, and in Eq. (38) for eightfold excitons. We have shown that the shifts corresponding to $|X'_n\rangle$ are up to the $\hat{\gamma}$ contribution, the large-detuning ones, multiplied by $1+\alpha/2+\beta/2$, i.e., up to very small detuning, the symmetries of the eigenstates are unaffected by the detuning dependence; only the shifts vary.

The operator $W_t^\dagger$ is the electron–probe-photon coupling. It has the same form as the electron–pump-photon coupling equation (5), with three nonzero coefficients μ_+,μ_-,μ_0 if the probe beam is not collinear with the pump.

We will consider separately the cases of fourfold and eightfold excitons, and give in a third subsection the conditions necessary to observe the redshift induced by an excitonic molecule. General expressions will be given for the weights of the various shifted lines including the three components μ_+, μ_-, and μ_0 of the probe. We will give in Figs. 2–4 specific results for typical pump-probe experiments with a probe collinear or perpendicular to the pump, both having either circular or linear polarizations.

A. Fourfold exciton

Using Eqs. (A10) and (5), one finds

$$W_t^\dagger|0\rangle=\mu_+|X_{1/2,1/2}\rangle-\mu_-|X_{-1/2,-1/2}\rangle -2^{-1/2}\mu_0(|X_{1/2,-1/2}\rangle+|X_{-1/2,1/2}\rangle)\ . \quad (61)$$

From the eigenstates of the split exciton, given in Eq. (35), one deduces the following weights for the three shifted exciton lines:

$$\mu_+^2 \text{ for } 2\Delta_+'^2/\Omega_1\ ,$$
$$\mu_-^2 \text{ for } 2\Delta_-'^2/\Omega_1\ , \quad (62)$$
$$\mu_0^2 \text{ for } (\Delta_+'^2+\Delta_-'^2)/\Omega_1\ .$$

Let us consider these results in some particular cases.

1. σ_+ pump beam

For a σ_+ pump beam (see Fig. 2), $\Delta'_-=0$ so that the shifts are, respectively, $2\Delta'^2/\Omega_1$, 0, and Δ'^2/Ω_1, with $\Delta'=\frac{2}{3}\lambda$.

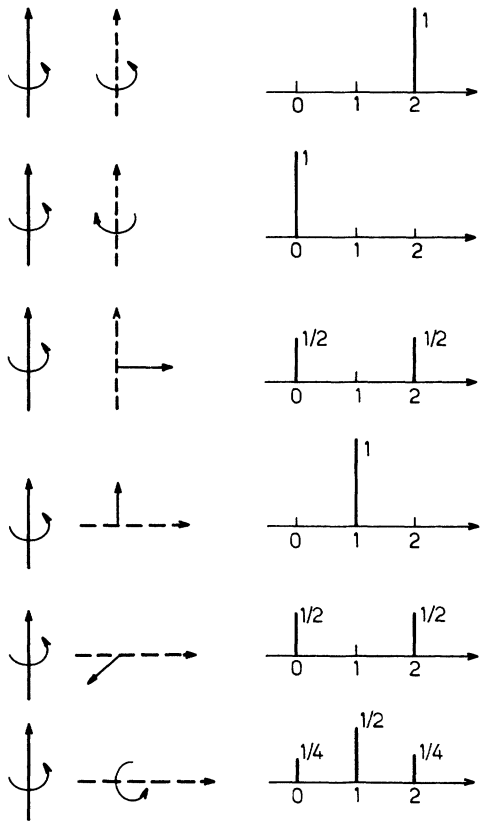

FIG. 2. Possible spectra for pump-probe experiments in the case of a fourfold exciton made from a $J=\frac{1}{2}$ valence band. The shifts are in units of Δ'^2/Ω_1. The pump has a circular polarization. The pump- and probe-photon momenta are either parallel or perpendicular. The probe polarization is either circular or linear. All three shifted exciton lines are seen only on the last spectrum, when the two laser beams are circularly polarized and propagate in perpendicular directions.

(i) A σ_+ probe beam, collinear to the pump, corresponds to $\mu_-=\mu_0=0$. With it, one can see only the line $2\Delta'^2/\Omega_1$. Similarly a σ_- probe sees only the unshifted line.

(ii) A linear probe beam, parallel to the pump, corresponds to $\mu_+=\pm\mu_-$, $\mu_0=0$. With it, one sees the two lines $2\Delta'^2/\Omega_1$ and 0, with the same weight.

(iii) The third line, Δ'^2/Ω_1, can be seen only with a probe beam not collinear to the pump. If the probe beam has a linear polarization parallel to the pump-photon momentum, one only sees that third line ($\mu_+=\mu_-=0$, $\mu_0\neq0$). If the polarization is perpendicular to the pump-photon momentum, one sees only the two other lines.

The best experiment to see the three shifted lines on the same spectrum is to use a circularly polarized beam, propagating perpendicularly to the pump (in this case $\mu_+=\mu_-=2^{-1/2}\mu_0$).

2. Linear pump beam

For a linear pump beam, $\Delta'_+=\pm\Delta'_-$, the three exciton lines are equally shifted and the pump photons do not split the exciton degeneracy. This unique unsplit shifted line can, of course, be seen with any probe beam.

B. Eightfold exciton

Using Eqs. (A9) and (5), one finds that

$$W_t^\dagger|0\rangle=(3^{1/2}/2)(\mu_+|x_{-1/2,3/2}\rangle+\mu_-|x_{1/2,-3/2}\rangle) -\tfrac{1}{2}(\mu_+|x_{1/2,1/2}\rangle+\mu_-|x_{-1/2,-1/2}\rangle) +2^{-1/2}\mu_0(|x_{1/2,-1/2}\rangle-|x_{-1/2,1/2}\rangle)\ , \quad (63)$$

where

$$|x_{sm}\rangle=b_s^\dagger c_{3/2,m}^\dagger|0\rangle\ . \quad (64)$$

It is useful to note that these $|x_{sm}\rangle$ states differ from the exciton basis $|X_{sm}\rangle$ used previously, the states $|X_{sm}\rangle$ being expressed from the appropriate combination B_m of hole operators $c_{3/2,m}$, defined in Eqs. (9) and (11). Keeping this in mind, one easily deduces the following weights of the five shifted lines, obtained in Eq. (38):

$$\frac{(3\lambda_+\mu_++\lambda_-\mu_-)^2}{12\Delta_+^2} \text{ for } 2\Delta_+^2/\Omega_1\ ,$$
$$\frac{(3\lambda_-\mu_-+\lambda_+\mu_+)^2}{12\Delta_-^2} \text{ for } 2\Delta_-^2/\Omega_1\ ,$$
$$\frac{\mu_0^2}{6}\left[\frac{\lambda_-^2}{\Delta_+^2}+\frac{\lambda_+^2}{\Delta_-^2}\right] \text{ for } \frac{\Delta_+^2+\Delta_-^2}{\Omega_1}\ , \quad (65)$$
$$\frac{(\lambda_-\mu_+-\lambda_+\mu_-)^2}{4\Delta_+^2}+\frac{\lambda_-^2\mu_0^2}{2\Delta_-^2} \text{ for } \frac{\Delta_+^2}{\Omega_1}\ ,$$
$$\frac{(\lambda_-\mu_+-\lambda_+\mu_-)^2}{4\Delta_-^2}+\frac{\lambda_+^2\mu_0^2}{2\Delta_+^2} \text{ for } \frac{\Delta_-^2}{\Omega_1}\ .$$

One can check that the sum of these five weights gives $\mu_+^2+\mu_-^2+\mu_0^2$, as expected. One also notices that one of the lines, $(\Delta_+^2+\Delta_-^2)/\Omega_1$, can be seen only if the probe and the pump are not collinear (as $\mu_0\neq0$). Let us now consider some particular cases.

1. σ_+ pump beam

For a σ_+ pump beam (see Fig. 3), $\lambda_+=\lambda$, $\lambda_-=0$, i.e., $\Delta_+^2=\lambda^2$, $\Delta_-^2=\lambda^2/3$, the above results give

$$\begin{aligned} &3\mu_+^2/4 \text{ for } 2\lambda^2/\Omega_1 ,\\ &\mu_+^2/4 \text{ for } 2\lambda^2/3\Omega_1 ,\\ &\mu_0^2/2 \text{ for } 4\lambda^2/3\Omega_1 ,\\ &\mu_-^2/4 \text{ for } \lambda^2/\Omega_1 ,\\ &3\mu_-^2/4+\mu_0^2/2 \text{ for } \lambda^2/3\Omega_1 . \end{aligned} \tag{66}$$

a. Pump and probe collinear. A σ_+ probe, $\mu_-=\mu_0=0$, "sees" only the two first lines, with relative weights $\frac{3}{4}$ and $\frac{1}{4}$.

A σ_- probe, $\mu_+=0$, "sees" the last two ones with relative weights $\frac{1}{4}$ and $\frac{3}{4}$.

A linear probe, $\mu_+=\pm\mu_-$, $\mu_0=0$, "sees" four of the five lines with relative weights $\frac{3}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, and $\frac{3}{8}$.

b. Pump and probe perpendicular. A linear probe, with a polarization parallel to the pump-photon momentum ($\mu_0\neq0$, $\mu_x=\mu_y=0$) "sees" the two lines $4\lambda^2/3\Omega_1$ and $\lambda^2/3\Omega_1$ with the same weights.

Here, again, the five lines can be seen with a circularly polarized probe, perpendicular to the pump ($\mu_+^2=\mu_-^2=\mu_x^2/2=\mu_0^2/2$); the relative weights are $\frac{3}{16}$, $\frac{1}{16}$, $\frac{1}{4}$, $\frac{1}{16}$, and $\frac{7}{16}$.

2. Linear pump beam

For a linear pump beam (see Fig. 4), $\lambda_+=\lambda_-$, i.e., $\Delta_+^2=\Delta_-^2=2\lambda^2/3$, the five exciton lines collapse into two lines. From Eq. (65), one finds

$$\begin{aligned} &(5\mu_+^2+5\mu_-^2+6\mu_+\mu_-)/8+\mu_0^2/4 \text{ for } 4\lambda^2/3\Omega_1 ,\\ &3(\mu_+-\mu_-)^2/8+3\mu_0^2/4 \text{ for } 2\lambda^2/3\Omega_1 . \end{aligned} \tag{67}$$

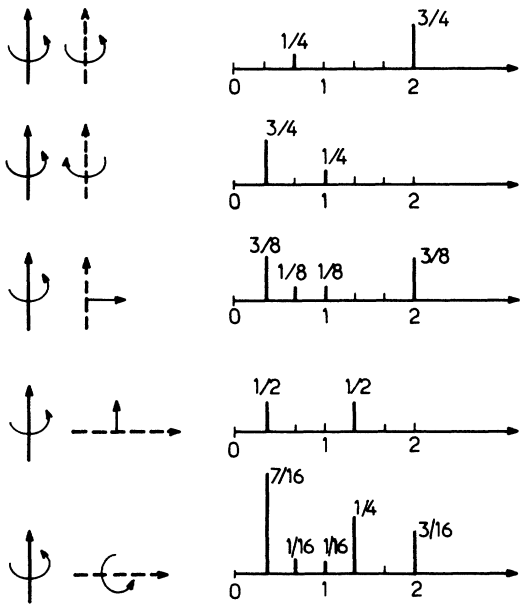

FIG. 3. Same as Fig. 2 in the case of eightfold exciton made from a $J=\frac{3}{2}$ valence band. The shifts are in units of λ^2/Ω_1. All five shifted exciton lines are seen when the two laser beams are circularly polarized and propagate in perpendicular directions.

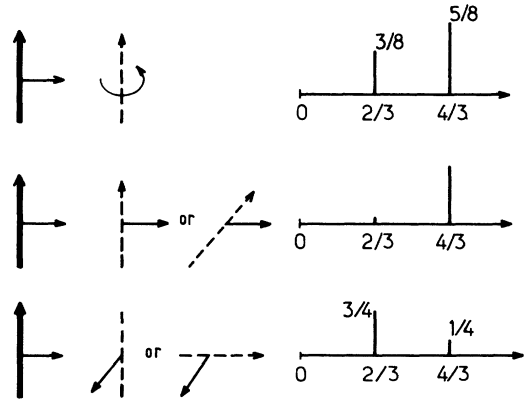

FIG. 4. Same as Fig. 3 for a linearly polarized pump beam.

a. Pump and probe collinear. A circular probe "sees" the two lines with relative weights $\frac{5}{8}$ and $\frac{3}{8}$.

A linear probe, parallel to the pump ($\mu_+=\mu_-$), "sees" only the first line.

A linear probe, perpendicular to the pump ($\mu_+=-\mu_-$), "sees" both lines, with relative weights $\frac{1}{4}$ and $\frac{3}{4}$.

b. Pump and probe perpendicular. A linear probe with polarization parallel or perpendicular to the pump polarization "sees" the same results as above (as expected).

A circular probe also "sees" the two lines, but with relative weights $\frac{5}{8}$ and $\frac{3}{8}$.

C. Excitonic red shift

We have found previously that, in material having a stable biexcitonic molecule, such as CuCl, one component of the fourfold exciton red-shifts for $\Omega_1=2\Omega_{xx}$, i.e., $\omega_x+\omega_p=2\omega_{xx}$. This resonance corresponds to the creation of a biexcitonic molecule from a pump photon ω_p and a probe photon creating the exciton. As the molecule has a symmetric orbital part, one expects this resonance to be observable if, from the probe and pump photons, one can produce an antisymmetric spin part. In particular, we do not expect to see the red-shifted line from pump-probe experiments where both beams have a σ_+ polarization. Let us show it in more detail.

The exciton eigenstate which red-shifts at the biexcitonic resonance, is given in Eq. (65). Since the weight of the probe-photon absorption line is

$$U_R=|\langle X_R|W_t^\dagger|0\rangle|^2/\langle X_R|X_R\rangle , \tag{68}$$

where $W_t^\dagger|0\rangle$ is given in Eq. (61), one finds

$$U_R=(\lambda_+\mu_-+\lambda_-\mu_+)^2/(\lambda_+^2+\lambda_-^2) . \tag{69}$$

One concludes that the red-shifted line can be observed (i.e., $U_R\neq0$) using a σ_+ pump and a σ_- or linear probe. In the case of a linearly polarized pump beam ($\lambda_+=\lambda_-$),

the red shift is seen with a circular probe or with a linear probe having the same polarization as the pump one ($\mu_+ = \mu_-$).

VIII. GaAs MULTIPLE QUANTUM WELL

We end this work by considering separately the case of GaAs multiple quantum wells. The first experiments on the excitonic optical Stark effect were done in this material using linearly polarized pump and probe beams. The experimental absorption spectra are found to be independent of the relative polarizations. It has been argued at first that these spectra should depend on polarizations, using the following naive argument: an x-pump photon is coupled only to an exciton having an x symmetry, so that only the x exciton should be shifted. An x-probe beam "sees" such a shifted exciton while a y-probe beam would see only an unshifted state.

We now explain why the experimental results are indeed the expected ones and why the above argument fails. In order to show it as simply as possible, we use the fact demonstrated above, that up to the very small detuning $\hat{\gamma}$ contribution, the symmetries of the various shifted exciton lines can be obtained from a multilevel atom, for which the correct electron-photon coupling symmetries are, however, included. The problem is similar to the one of bulk GaAs with a $j=\frac{3}{2}$ valence band. One has, however, to include the fact that the heavy- and light-hole degeneracy is lifted in multiple quantum wells. Using Eqs. (39) and (40), the electron-photon coupling reads, in terms of conduction and valence operators,

$$W_B^\dagger = -b_{1/2}^\dagger(\lambda_- b_{3/2,3/2} - \lambda_+ 3^{-1/2} b_{3/2,-1/2}) + b_{-1/2}^\dagger(\lambda_+ b_{3/2,-3/2} - \lambda_- 3^{-1/2} b_{3/2,1/2}) \,. \quad (70)$$

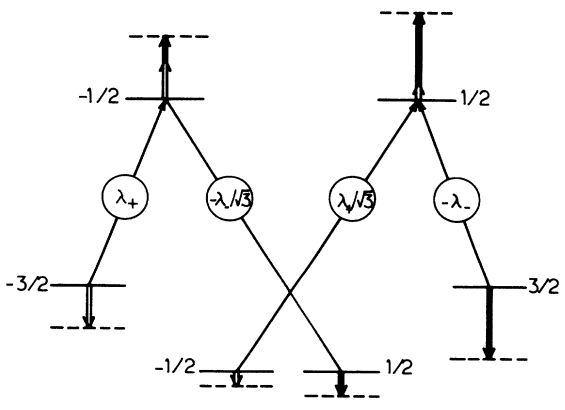

FIG. 5. In the case of GaAs multiple quantum well, the various valence and conduction states are coupled differently to the σ_+, σ_- components of the pump, inducing different shifts.

One deduces (see Fig. 5) that the shifts of the two conduction states ($\pm\frac{1}{2}$) are $(\lambda_\mp^2 + \lambda_\pm^2/3)/\Omega_1$, the shifts of the two valence states ($\pm\frac{3}{2}$) are $\lambda_\mp^2/\Omega_1$, and the shifts of the two valence states ($\pm\frac{1}{2}$) are $\lambda_\mp^2/3\Omega_1$. A linear pump beam, $\lambda_+ = \pm\lambda_-$, does not differentiate the two conduction or valence states, the above shifts being, respectively, $2\lambda^2/3\Omega_1$, $\lambda^2/2\Omega_1$, and $\lambda^2/6\Omega_1$. Consequently, a probe beam, which induces a valence to conduction-band transition, sees only one fourfold heavy-hole exciton line, with a $2\lambda^2/3\Omega_1 + \lambda^2/2\Omega_1 = 7\lambda^2/6\Omega_1$ shift and one fourfold light-hole exciton line with a $5\lambda^2/6\Omega_1$ shifts, whatever the probe polarization is. On the other hand, for a circular pump beam, the various valence and conduction levels are shifted differently, inducing a splitting of the fourfold exciton level. This induces different absorption spectra depending in the probe polarizations.

IX. ANALOGY WITH ATOMIC PHYSICS

The above example illustrates clearly how the analogy between semiconductor and atomic physics should be made. Due to the fact that in the absence of band-structure degeneracy the large-detuning exciton shift has the two-level dressed-atom value, one may think that these two levels are either the valence and the conduction bands, or the vacuum and the exciton. One might, however, expect some problems with a naive use of the second picture, as the e-photon coupling would imply not only transitions between exciton and vacuum, but also transitions between exciton and biexciton, so that the coupled system is not simply "two levels." On the other hand, if one keeps in mind the physical origin and the large-detuning value of the shift, $2\lambda^2/\Omega_1$, as being a free-particle limit, one can easily identify the correct "two levels" as being the valence and conduction bands. It is then straightforward to generalize the calculation of the excitonic shift to the case of a degenerate band structure: An exciton made from a twofold conduction band and a fourfold valence band, should have the shift of a (2+4)-level atom (as far as the internal structure of the true biexcitonic states does not play a role, i.e., not for very small detuning). We wish, however, to say that, even if the above analogy is of great help in simply understanding the dressed-exciton problem, it was not, *a priori*, entirely obvious. It is why the theory exposed in this work starts with exciton states and their couplings with vacuum and biexcitons.

X. CONCLUSION

In this work we have done the following.

(1) We have rederived from the start the electron-photon coupling taking into account the symmetries of the photon and of the electronic system.

(2) We have used it to calculate the optical Stark shift of the exciton, taking into account the band-structure degeneracy.

(3) We have shown that a laser beam, tuned in the transparency region of a semiconductor, not only shifts but also splits the exciton line. More precisely, a fourfold exciton, built from the $j=\frac{1}{2}$ valence band, can split into up to three lines, while the eightfold exciton, built from a

$j=\frac{3}{2}$ valence band, can split into up to five lines.

(4) We have given the conditions to observe these shifted lines in pump-probe experiments.

(5) We have discussed the observability of the exciton red shift caused by the existence of a stable biexitonic molecule.

(6) We have shown that up to very small detuning the exciton shifts can be easily understood in terms of the shifts of a multilevel atom, two levels for the conduction band and four (or two) levels for the valence band. As an illustration, we have explained the experimental result in GaAs multiple quantum wells, obtained with linear pump and probe beams.

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APPENDIX A: DERIVATION OF THE ELECTRON-PHOTON COUPLING EQUATION (5)

From the values of the $Y_{l,m}(\theta,\varphi)$ functions,

$$\begin{aligned} Y_{1,0}(\theta,\varphi)&=(\tfrac{3}{4}\pi)^{1/2}\cos\theta=[(\tfrac{3}{4}\pi)^{1/2}\rho^{-1}]z\ , \\ Y_{1,\pm1}(\theta,\varphi)&=(\tfrac{3}{8}\pi)^{1/2}(\mp\sin\theta\, e^{\pm i\varphi}) \\ &=[(\tfrac{3}{4}\pi)^{1/2}\rho^{-1}]2^{-1/2}(\mp x-iy)\ , \end{aligned} \tag{A1}$$

one deduces

$$\begin{aligned} |x\rangle&=2^{-1/2}(-|1\rangle+|-1\rangle)\ , \\ |y\rangle&=i2^{-1/2}(|1\rangle+|-1\rangle)\ , \\ |z\rangle&=|0\rangle\ . \end{aligned} \tag{A2}$$

This transforms Eq. (4) into[11]

$$\mathbf{A}\cdot\mathbf{P}=Pb_c^{\dagger}(A_+b_{-1}-A_-b_1+A_{-0}b_0)+\text{H.c.}\ , \tag{A3}$$

where $b_l^{\dagger}$ creates a valence electron in an orbital state $1,l=\pm1,0$ and $A_{\pm}$ have the usual definition [Eq. (6)].

The operator $\mathbf{A}\cdot\mathbf{P}$, acting only on the orbital space, couples conduction and valence states with the same spin value, so that if one adds the spin part, the electron-photon coupling in Eq. (2) reads

$$\begin{aligned} \hat{W}&=W+W^{\dagger}\ , \\ W^{\dagger}&=\sum_{s=\pm1/2}b_s^{\dagger}(\lambda_+b_{-1,s}-\lambda_-b_{1,s}+\lambda_0b_{0,s})\ , \end{aligned} \tag{A4}$$

where $\lambda_{\pm,0}=(e/mc)PA_{\pm,0}$. The operator $b_s^{\dagger}$ creates a conduction electron with spin s, while $b_{l,s}^{\dagger}$ creates a valence electron with spin s and orbital momentum $1,l=\pm1,0$. Note that $\lambda_{\pm,0}$ are associated with transitions having a kinetic momentum change $\pm1,0$.

The next step is to write the $|l;s\rangle$ valence states on the valence kinetic momentum basis, $|j=\frac{3}{2},m\rangle$ and $|j=\frac{1}{2},m\rangle$. From the usual relations for kinetic momentum summation,

$$\begin{aligned} |j=\tfrac{3}{2},\pm\tfrac{3}{2}\rangle&=|l=\pm1;s=\pm\tfrac{1}{2}\rangle\ , \\ |j=\tfrac{3}{2},\pm\tfrac{1}{2}\rangle&=(\tfrac{2}{3})^{1/2}|0;\pm\tfrac{1}{2}\rangle\mp(\tfrac{1}{3})^{1/2}|\pm1;\mp\tfrac{1}{2}\rangle\ , \\ |j=\tfrac{1}{2},\pm\tfrac{1}{2}\rangle&=\pm(\tfrac{2}{3})^{1/2}|\pm1;\mp\tfrac{1}{2}\rangle\mp(\tfrac{1}{3})^{1/2}|0\pm\tfrac{1}{2}\rangle\ , \end{aligned} \tag{A5}$$

one finds that, in $W^{\dagger}$, λ_+ is the prefactor of

$$\begin{aligned} \sum_{s=\pm1/2}b_s^{\dagger}b_{-1,s}&=b_{-1/2}^{\dagger}b_{3/2,-3/2} \\ &+b_{1/2}^{\dagger}[(\tfrac{1}{3})^{1/2}b_{3/2,-1/2} \\ &-(\tfrac{2}{3})^{1/2}b_{1/2,-1/2}]\ , \end{aligned} \tag{A6}$$

where $b_{j,m}^{\dagger}$ creates a valence state (j,m) with $j=\frac{3}{2},m=\pm\frac{3}{2},\pm\frac{1}{2}$ or $j=\frac{1}{2},m=\pm\frac{1}{2}$.

The last step is to transform electron-valence operators $b_{j,m}^{\dagger}$ into hole operators $c_{j,m}$ in order to obtain the electron-photon coupling in terms of electron-hole pair creation. The rule for this transformation is to change the electron momentum $\mathbf{k}$ into $-\mathbf{k}$ and the electron kinetic momentum m into $-m$. There is also an alternative sign change in the transformation. (This sign change is indeed necessary to recover the exact total e-h pair kinetic momentum states [Eq. (A9)].) One finds

$$\begin{aligned} c_{1/2,1/2}^{\dagger}(\mathbf{k})&=b_{1/2,-1/2}(-\mathbf{k})\ , \\ c_{1/2,-1/2}^{\dagger}(\mathbf{k})&=-b_{1/2,1/2}(-\mathbf{k})\ ; \\ c_{1,1}^{\dagger}(\mathbf{k})&=b_{1,-1}(-\mathbf{k})\ , \\ c_{1,0}^{\dagger}(\mathbf{k})&=-b_{1,0}(-\mathbf{k})\ , \\ c_{1,-1}^{\dagger}(\mathbf{k})&=b_{1,-1}(-\mathbf{k})\ ; \\ c_{3/2,3/2}^{\dagger}(\mathbf{k})&=b_{3/2,-3/2}(-\mathbf{k})\ , \\ c_{3/2,1/2}^{\dagger}(\mathbf{k})&=-b_{3/2,-1/2}(-\mathbf{k})\ , \\ c_{3/2,-1/2}^{\dagger}(\mathbf{k})&=b_{3/2,1/2}(-\mathbf{k})\ , \\ c_{3/2,-3/2}^{\dagger}(\mathbf{k})&=-b_{3/2,3/2}(-\mathbf{k})\ , \end{aligned} \tag{A7}$$

and so on. This leads us to rewrite Eq. (A6) as

$$\begin{aligned} \sum_s b_s^{\dagger}b_{-1,s}&=[-(\tfrac{1}{3})^{1/2}b_{1/2}^{\dagger}c_{3/2,1/2}^{\dagger}+b_{-1/2}^{\dagger}c_{3/2,3/2}^{\dagger}] \\ &-(\tfrac{2}{3})^{1/2}b_{1/2}^{\dagger}c_{1/2,1/2}^{\dagger}\ . \end{aligned} \tag{A8}$$

The term in the square bracket of Eq. (A8) can be identified with the cration of an e-h pair with total kinetic momentum $|J=1,M=-1\rangle$, made from $j=\frac{3}{2}$ and $s=\frac{1}{2}$ states. More precisely, using the total kinetic momentum summation

$$\begin{aligned} |J=1,M=\pm1\rangle&=\pm(\tfrac{3}{4})^{1/2}|m=\pm\tfrac{3}{2};s=\mp\tfrac{1}{2}\rangle+\tfrac{1}{2}|\pm\tfrac{1}{2};\pm\tfrac{1}{2}\rangle\ , \\ |J=1,M=0\rangle&=(\tfrac{1}{2})^{1/2}(|\tfrac{1}{2};-\tfrac{1}{2}\rangle-|-\tfrac{1}{2};+\tfrac{1}{2}\rangle) \end{aligned} \tag{A9}$$

for $\frac{3}{2}$ and $\frac{1}{2}$ momenta, and

$$|J=1, M=\pm 1\rangle = |m=\pm\tfrac{1}{2}; s=\pm\tfrac{1}{2}\rangle ,$$
$$|J=1, M=0\rangle = (\tfrac{1}{2})^{1/2}(|\tfrac{1}{2};-\tfrac{1}{2}\rangle + |-\tfrac{1}{2};\tfrac{1}{2}\rangle) \tag{A10}$$

for $\frac{1}{2}$ and $\frac{1}{2}$ momenta, one obtains for the factor of λ_+ in $W^\dagger$, Eq. (A8).

$$\lambda_+[(\tfrac{4}{3})^{1/2}\mathbf{B}_1^\dagger(\mathbf{k}) - (\tfrac{2}{3})^{1/2}\mathbf{C}_1^\dagger(\mathbf{k})] . \tag{A11}$$

Doing a similar procedure for the factors of λ_- and λ_0, it is then easy to deduce the electron-photon coupling given in Eq. (5).

APPENDIX B: SIGN COHERENCE IN EQ. (5)

Consider a linear beam with $A_x = A_y = 0$, $A_z = A$. The electron-photon coupling, Eq. (5), gives

$$-\lambda_0 \mathbf{B}_0^\dagger \sim -A\,\mathbf{B}_z^\dagger \tag{B1}$$

using Eq. (6) for the relation between the $(J=1,M)$ states and the (x,y,z) basis. If one now considers a new axis (x',y',z') such that x' is along z, the same linear beam corresponds to $A_{x'} = A$ and $A_{y'} = A_{z'} = 0$, i.e., $A'_+ = A'_- = 2^{-1/2}A$ and $A'_0 = 0$. Within this new basis, the e-photon coupling, Eq. (5), reads, using Eq. (A2),

$$\lambda'_+\mathbf{B}_1^\dagger - \lambda'_-\mathbf{B}_{-1}^\dagger \sim 2^{-1}A(-\mathbf{B}_{x'}^\dagger - i\mathbf{B}_{y'}^\dagger) - 2^{-1}A(\mathbf{B}_{x'}^\dagger - i\mathbf{B}_{y'}^\dagger)$$
$$= -A\,\mathbf{B}_{x'}^\dagger . \tag{B2}$$

As x' lies along z, this is nothing but $-A\,\mathbf{B}_z^\dagger$, i.e., the expression (B1) of the e-photon coupling found in the first basis (x,y,z). This shows that the signs in front of λ_+, λ_-, and λ_0 are indeed coherent.

APPENDIX C: ANISOTROPIC CREATION OF HEAVY AND LIGHT HOLES

From the Fermi golden rule, one finds that the probability to create a heavy hole is proportional to

$$\sum_{S=\pm 1/2} \sum_{M=\pm 3/2} |\langle SM|W^\dagger|0\rangle|^2 , \tag{C1}$$

$|0\rangle$ being the vacuum. Heavy holes indeed correspond to $M=\pm\frac{3}{2}$ if one chooses the quantification axis z' for S and M along the momentum $\mathbf{k}$ of the created hole. Let (x',y',z') be the associated basis. For a linearly polarized beam, the e-photon coupling reads $-\lambda_0\mathbf{B}_0^\dagger = -\lambda_0\mathbf{B}_z^\dagger$ with the z axis along the field potential $\mathbf{A}$. If (θ,φ) are the Euler angles of $\mathbf{A}$ in the (x',y',z') basis, the operator $\mathbf{B}_z$ reads in terms of $\mathbf{B}_{x',y',z'}$

$$\mathbf{B}_z^\dagger = \sin\theta\cos\varphi\,\mathbf{B}_{x'}^\dagger + \sin\theta\sin\varphi\,\mathbf{B}_{y'}^\dagger + \cos\theta\,\mathbf{B}_{z'}^\dagger \tag{C2}$$

One can then write $\mathbf{B}_{x',y',z'}$ in terms of $\mathbf{B}'_{\pm 1,0}$ using Eq. (A2). One finds

$$\mathbf{B}_z^\dagger = -2^{-1/2}\sin\theta\, e^{-i\varphi}\mathbf{B}_1'^\dagger + 2^{-1/2}\sin\theta\, e^{i\varphi}\mathbf{B}_{-1}'^\dagger + \cos\theta\,\mathbf{B}_0'^\dagger . \tag{C3}$$

Using the decomposition of $|J=1,M\rangle$ states on $|J=\frac{3}{2},M;S=\frac{1}{2},S\rangle$ states given in Eq. (A9) one finds that the part in $\mathbf{B}_z^\dagger$ corresponding to heavy holes (i.e., terms in $c_{\pm 3/2}^\dagger$) is

$$-(\tfrac{3}{8})^{1/2}[\sin\theta\, e^{-i\varphi}b_{-1/2}^\dagger c_{3/2}^\dagger + \sin\theta\, e^{i\varphi}b_{1/2}^\dagger c_{-3/2}^\dagger) + \cdots . \tag{C4}$$

It is then easy to conclude from Eq. (C1) that the probability to create a heavy hole is indeed proportional to $\sin^2\theta$, θ being the angle between z and z', i.e., the linear field $\mathbf{A}$ and the hole momentum $\mathbf{k}$.

APPENDIX D: BRILLOUIN-WIGNER FORM OF THE PERTURBATION THEORY FOR NONDEGENERATE AND DEGENERATE STATES

1. Nondegenerate state

In the case of a nondegenerate state, such as the vacuum $|0\rangle$, the closure relation

$$1 = |0\rangle\langle 0| + P_{0\perp} \tag{D1}$$

used in the definition of the perturbed vacuum $|0'\rangle$ gives

$$0 = (H+\hat{W}-E_0')|0'\rangle$$
$$= (E_0+\hat{W}-E_0')|0\rangle\langle 0|0'\rangle + (H+\hat{W}-E_0')P_{0\perp}|0'\rangle . \tag{D2}$$

Multiplying Eq. (D2) by $P_{0\perp}$, the projector orthogonal to $|0\rangle$, one obtains

$$0 = P_{0\perp}\hat{W}|0\rangle\langle 0|0'\rangle + P_{0\perp}(H+\hat{W}-E_0')P_{0\perp}|0'\rangle \tag{D3}$$

as $P_{0\perp}|0\rangle = 0$. We now invert the operator $(H+\hat{W}-E_0')$ restricted to the subspace orthogonal to $|0\rangle$. As $P_{0\perp}^2 = P_{0\perp}$, Eq. (D3) gives

$$P_{0\perp}|0'\rangle = -[P_{0\perp}(H+\hat{W}-E_0')P_{0\perp}]^{-1}P_{0\perp}\hat{W}|0\rangle\langle 0|0'\rangle . \tag{D4}$$

Going back to Eq. (D2), projected over $\langle 0|$ and using Eq. (D4) in the last term of Eq. (D2), one obtains the Brillouin-Wigner form for the perturbated energy

$$E_0' = E_0 + \langle 0|\hat{W}|0\rangle - \langle 0|\hat{W}P_{0\perp}[P_{0\perp}(H+\hat{W}-E_0')P_{0\perp}]^{-1}P_{0\perp}\hat{W}|0\rangle , \tag{D5}$$

as $\langle 0|(H-E_0')P_{0\perp} = 0$. Equation (D5) is an exact equation for E_0'. This equation, written to lowest order in $\hat{W}$, gives Eq. (21), the state $W^\dagger|0\rangle$ being unambiguously orthogonal to $|0\rangle$ as $\hat{W}$ creates or destroys one e-h pair.

2. Degenerate state

In the case of degenerate states $|X_{sm}(1)\rangle$, having all the same energy Ω_1, a similar procedure leads us to use the closure relation

$$1=\sum_{s,m}|X_{sm}(1)\rangle\langle X_{sm}(1)|+P_{1\perp} \tag{D6}$$

in front of the perturbed exciton $|X'(1)\rangle$, defined by

$$\begin{aligned}0&=(H+\hat{W}-\Omega_1')|X'(1)\rangle\\&=\sum_{s,m}(\Omega_1-\Omega_1'+\hat{W})|X_{sm}(1)\rangle\langle X_{sm}(1|X'(1)\rangle\\&\quad+(H+\hat{W}-\Omega_1')P_{1\perp}|X'(1)\rangle\ .\end{aligned} \tag{D7}$$

Noting that Eq. (D7) leads us

$$\begin{aligned}P_{1\perp}|X'(1)\rangle=-\sum_{s,m}&[P_{1\perp}(H+\hat{W}-\Omega_1')P_{1\perp}]^{-1}\\&\times P_{1\perp}\hat{W}|X_{sm}(1)\rangle\langle X_{sm}(1)|X'(1)\rangle\ ,\end{aligned} \tag{D8}$$

the projection of Eq. (D7) over any exciton state $\langle X_{s'm'}(1)|$ gives

$$\begin{aligned}(\Omega_1'-\Omega_1)\langle X_{s'm'}(1)|X'(1)\rangle&\\=\sum_{s,m}\{\langle X_{s'm'}(1)|\hat{W}|X_{s,m}(1)\rangle&-\langle X_{s'm'}|\hat{W}P_{1\perp}[P_{1\perp}(H+\hat{W}-\Omega_1')P_{1\perp}]^{-1}P_{1\perp}\hat{W}|X_{s,m}(1)\rangle\}\langle X_{s,m}(1)|X'(1)\rangle\ ,\end{aligned} \tag{D9}$$

which is, for a degenerate level, analogous to Eq. (D5). Equation (D9), written to lowest order in $\hat{W}$, gives Eq. (22).

Here again the states $\hat{W}|X_{s,m}(1)\rangle$, being either vacuum or two-pair states, are indeed orthogonal to the exciton subspace.

APPENDIX E: SIX-LEVEL ATOM SHIFTS

Without Coulomb interaction, it is easy to diagonalize exactly the total Hamiltonian $H_a'=H_a+W_B^\dagger+W_B$ where the bare Hamiltonian H_a is

$$H_a=(E_c+\Omega_1)\sum_{s=\pm1/2}b_s^\dagger b_s+E_v\sum_m A_m^\dagger A_m \tag{E1}$$

and $m=\pm\frac{3}{2},\pm\frac{1}{2}$. For simplicity we set the valence energy $E_v=0$. One finds

$$\begin{aligned}H_a'=&E_{+-}b_{1/2}'^\dagger b_{1/2}'+E_{++}b_{-1/2}'^\dagger b_{-1/2}'\\&+E_{--}A_{3/2}'^\dagger A_{3/2}+E_{-+}A_{-3/2}'^\dagger A_{-3/2}\ .\end{aligned} \tag{E2}$$

where the eigenvalues are given by

$$E_{nn'}=[\Omega_1+n(\Omega_1^2+4\Delta_{n'}^2)^{1/2}]/2\ , \tag{E3}$$

n and n' being either $+$ or $-$. The corresponding eigenstates are

$$\begin{aligned}b_{1/2}'^\dagger&=(E_{+-}b_{1/2}^\dagger+\Delta_-A_{3/2}^\dagger)/(E_{+-}^2+\Delta_-^2)^{1/2}\ ,\\A_{3/2}'^\dagger&=(E_{--}b_{1/2}^\dagger+\Delta_-A_{3/2}^\dagger)/(E_{--}^2+\Delta_-^2)^{1/2}\ ,\end{aligned} \tag{E4}$$

and similarly for $b_{-1/2}'$ and $A_{-3/2}'$. The states $A_{\pm1/2}$, not being coupled to the conduction band, are still not affected by the laser beam. It is then easy to check that the small $-\Delta_\pm$ limit of Eqs. (E3) and (E4) give back the low-laser-intensity results given in Eq. (41), while, at resonance, the shifts are linear in $\Delta_\pm$, i.e., proportional to the square root of the laser intensity, as expected.

APPENDIX F: CALCULATION OF THE OPERATOR $\mathbf{V}_{sm}(1)$ DEFINED IN EQ. (43)

The Hamiltonian H is composed of a kinetic part $H_{\rm kin}$ and a Coulomb interaction between two electrons, V_{ee}, two holes, V_{hh}, and one electron and one hole, V_{eh}. From

$$\begin{aligned}[b_{s'}^\dagger(\mathbf{k}+\mathbf{q})b_{s'}(\mathbf{k}),\mathbf{B}_{sm}^\dagger(1)]&\\=\sum_{\mathbf{k}'}\phi_i(\mathbf{k}')[b_{s'}^\dagger(\mathbf{k}+\mathbf{q})b_{s'}(\mathbf{k}),b_s^\dagger(\mathbf{k}')B_m^\dagger(-\mathbf{k}')]\ ,&\\=\delta_{ss'}\phi_1(\mathbf{k})b_{s'}^\dagger(\mathbf{k}+\mathbf{q})B_m^\dagger(-\mathbf{k})\ ,\end{aligned} \tag{F1}$$

one easily deduces that

$$[H_{\rm kin},\mathbf{B}_{s,m}^\dagger(1)]=\sum_{\mathbf{k}}(\varepsilon_{e\mathbf{k}}+\varepsilon_{h\mathbf{k}})\phi_1(\mathbf{k})\mathbf{B}_{s,m}^\dagger(\mathbf{k})\ , \tag{F2}$$

where $\varepsilon_{e\mathbf{k}}$ and $\varepsilon_{h\mathbf{k}}$ are the free e and h energies.

Using Eq. (F1), one also finds

$$\begin{aligned}[V_{ee},\mathbf{B}_{sm}^\dagger(1)]=\sum_{\mathbf{q}}V_{\mathbf{q}}\sum_{\mathbf{k}}&\phi_1(\mathbf{k})b_s^\dagger(\mathbf{k})B_m^\dagger(-\mathbf{k}-\mathbf{q})\\&\times\sum_{\mathbf{s}',\mathbf{k}'}b_{s'}^\dagger(\mathbf{k}'+\mathbf{q})b_{s'}(\mathbf{k}')\end{aligned} \tag{F3}$$

and a similar result for V_{hh}. Turning to V_{eh}, Eq. (F1) leads to

$$\begin{aligned}[V_{eh},\mathbf{B}_{sm}^\dagger(1)]=\sum_{\mathbf{q},\mathbf{k}}V_{\mathbf{q}}\phi_1(\mathbf{k}+\mathbf{q})\mathbf{B}_{sm}^\dagger(\mathbf{k})+\sum_{\mathbf{q},\mathbf{k}}V_{\mathbf{q}}b_s^\dagger(\mathbf{k}+\mathbf{q})B_m^\dagger(-\mathbf{k})&\\\times\left[\phi_1(\mathbf{k}+\mathbf{q})\sum_{\mathbf{S},\mathbf{k}}b_S^\dagger(\mathbf{k}-\mathbf{q})b_S(\mathbf{k})+\phi_1(\mathbf{k})\sum_{\mathbf{M},\mathbf{k}}B_M^\dagger(\mathbf{k}-\mathbf{q})B_M(\mathbf{k})\right]\ .\end{aligned} \tag{F4}$$

As $H=H_{\rm kin}+V_{ee}+V_{hh}-V_{eh}$, Eq. (F2) plus the first term of Eq. (F4) restores in the commutator $[H,\mathbf{B}^{\dagger}_{sm}(1)]$, Eq. (43), the exciton part $\Omega_1\mathbf{B}^{\dagger}_{sm}(1)$. It is then easy to check that the other terms lead to the following value of the operator $\mathbf{V}^{\dagger}_{sm}(1)$:

$$\Omega_1\mathbf{V}^{\dagger}_{sm}(1)=\sum_{\mathbf{q}\neq 0}V_q\sum_{\mathbf{k}}[\phi_1(\mathbf{k})-\phi_1(\mathbf{k}+\mathbf{q})]b^{\dagger}_s(\mathbf{k}+\mathbf{q})B^{\dagger}_m(-\mathbf{k})\left[\sum_{\mathbf{k}'s'}b^{\dagger}_{s'}(\mathbf{k}'-\mathbf{q})b_{s'}(\mathbf{k}')-\sum_{\mathbf{k}'m'}B^{\dagger}_{m'}(-\mathbf{k}'-\mathbf{q})B_{m'}(-\mathbf{k}')\right] . \quad \text{(F5)}$$

APPENDIX G: CALCULATION OF THE $\hat{\beta}$ MATRIX

We derive here Eq. (54). We first replace W_B in Eq. (47) by its expression (49) in terms of $W_B(i)$, so that H^{-1} gives Ω_i^{-1}. The $\hat{\beta}$ matrix then reads

$$\begin{aligned}&\hat{\beta}=\sum_{i,j}(\Omega_1/\Omega_i\Omega_j)\sum_{\mathbf{k}_1,\mathbf{k}_2}\phi_i(\mathbf{k}_1)\phi^{*}_j(\mathbf{k}_2)\hat{\beta}'(i,j) ,\\ &\beta'_{sm,s'm'}(i,j)=\langle 0|\mathbf{B}_{sm}(1)W_B(i)\Omega_1\mathbf{V}^{\dagger}_{s'm'}(1)W^{\dagger}_B(j)|0\rangle ,\end{aligned} \quad \text{(G1)}$$

where $W^{\dagger}_B(j)$ contains the exciton operators $\mathbf{B}^{\dagger}_{s_1m_1}(j)$. The next step is to show, using the expression (F5) for $\mathbf{V}^{\dagger}_{s'm'}(1)$ that

$$\begin{aligned}&\Omega_1\mathbf{V}^{\dagger}_{s'm'}(1)\mathbf{B}_{s_1m_1}(j)|0\rangle\\ &\quad=\sum_{\mathbf{q}\neq 0}V_q\sum_{\mathbf{k}}[(\phi_1(\mathbf{k}')-\phi_1(\mathbf{k}'+\mathbf{q})]\sum_{\mathbf{k}_1}[\phi_k(\mathbf{k}_1)-\phi_j(\mathbf{k}_1-\mathbf{q})]b^{\dagger}_s(\mathbf{k}'+\mathbf{q})B^{\dagger}_{m'}(-\mathbf{k}')b^{\dagger}_{s_1}(\mathbf{k}_1-\mathbf{q})B^{\dagger}_{m_1}(-\mathbf{k}_1)|0\rangle .\end{aligned} \quad \text{(G2)}$$

Using this expression in $\hat{\beta}'$ and writing $\mathbf{B}_{sm}(i)$ and $W_B(i)$ in terms of the $\mathbb{B}(k)$'s, there appear in $\hat{\beta}'$ matrix elements such as

$$\langle 0|B_m(-\mathbf{k})b_s(\mathbf{k})B_{m_2}(-\mathbf{k}_2)b_{s_2}(\mathbf{k}_2)b^{\dagger}_{s'}(\mathbf{k}'+\mathbf{q})B^{\dagger}_{m'}(-\mathbf{k}')b^{\dagger}_{s_1}(\mathbf{k}'-\mathbf{q})B^{\dagger}_{m_1}(-\mathbf{k}_1)|0\rangle , \quad \text{(G3)}$$

where (S,M) or (S',M') are only $(\pm\frac{1}{2},\pm\frac{3}{2})$. This matrix element differs from zero either if $\mathbf{k}=\mathbf{k}'+\mathbf{q}=\mathbf{k}_1=\mathbf{k}_2+\mathbf{q}$ and $s=s'$, $s_1=s_2$, $m=m_1$, $m'=m_2$, or if $\mathbf{k}=\mathbf{k}'=\mathbf{k}_1-\mathbf{q}=\mathbf{k}_2-\mathbf{q}$ and $m=m'$, $m_1=m_2$, $s=s_1$, $s_2=s'$. Due to the only possible values of (S,M) in W_B, $s=s'$ implies $m=m'$ so that $m_1=m_2$: This shows that the matrix $\hat{\beta}'$ appear diagonal also on the exciton basis $\mathbf{B}_{sm}$. More precisely, from Eq. (49) for W_B, one finds that the kinetic momentum part of $\beta'_{sm,s'm'}$ leads to

$$\delta_{ss'}\delta_{mm'}\sum_{\pm}\Delta^2_{\pm}(\delta_{s,\pm\frac{1}{2}}+\delta_{m,\pm\frac{3}{2}}) , \quad \text{(G4)}$$

which is exactly the matrix element of T. Following the $\mathbf{k}$ part of the matrix element (G5), one finds in front of it, for any (ss',mm'), a coefficient

$$\sum_{i,j}(\Omega_1/\Omega_i\Omega_j)V\phi_i(0)\phi^{*}_j(0)\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}'-\mathbf{k}}[\phi_1(\mathbf{k})-\phi_1(\mathbf{k}')]\phi^{*}_1(\mathbf{k})[\phi_j(\mathbf{k})-\phi_j(\mathbf{k}')]\phi^{*}_i(\mathbf{k}') , \quad \text{(G5)}$$

which is exactly the coefficient $\beta/2$ appearing in our previous work. If one writes it in $\mathbf{r}$ space, one finds

$$\beta=\Omega_1\sum_{i,j}\beta_{ij}/\Omega_i\Omega_j , \quad \text{(G6)}$$

$$\begin{aligned}\beta_{ij}=2\phi_j(0)\phi^{*}_i(0)\int V^{-1}d^3r\,d^3r'\,d^3\rho\,d^3\rho'\,\phi_1(\mathbf{r}-\rho)\phi_i(\mathbf{r}'-\rho')\\ \times[V(\mathbf{r}'-\rho)+V(\mathbf{r}-\rho')-V(\mathbf{r}-\mathbf{r}')-V(\rho-\rho')]\phi^{*}_1(\mathbf{r}-\rho')\phi^{*}_j(\mathbf{r}'-\rho) ,\end{aligned} \quad \text{(G7)}$$

where V is the sample volume which cancels the translational invariance of the system. From the terms in the square brackets of (G7), one sees that β corresponds to Coulomb interaction between electrons and holes of two-pair states.

APPENDIX H: EXCITONIC RED SHIFT

The simplest way to find the effect of a biexcitonic molecule on the exciton shift at small detuning is to come back to the original expression (24) for the shift and to look for the pole $(\Omega_1-2\Omega_{xx})^{-1}$, $2\Omega_{xx}$ being the biexciton energy in the rotating frame, $2\Omega_{xx}=2(\omega_{xx}-\omega_p)$. This pole appears only in the first term of S,

$$\begin{aligned}S_{ss',rr'}&\sim\langle X_{ss'}(1)|W_C|XX\rangle\langle XX|(\Omega_1-H)^{-1}|XX\rangle\\ &\quad\times\langle XX|W^{\dagger}_C|X_{rr'}(1)\rangle\\ &=(\Omega_1-2\Omega_{xx})^{-1}D^{*}_{ss'}D_{rr'} ,\end{aligned} \quad \text{(H1)}$$

$$D_{ss'}=\langle XX|W^{\dagger}_C|X_{ss'}(1)\rangle . \quad \text{(H2)}$$

The matrix elements $D_{ss'}$ are calculated noting that the

exciton operator can be expanded on creation operators in real space as

$$\mathbb{C}^{\dagger}_{ss'}(1)=\int d^3r\, d^3\rho\, \phi_1(\mathbf{r}-\rho)V^{-1/2}b^{\dagger}_s(r)C^{\dagger}_{s'}(\rho)\ . \tag{H3}$$

Similarly, the biexciton state reads

$$\begin{aligned}|XX\rangle=4^{-1}\int\ & d^3r_1 d^3r_2 d^3\rho_1 d^3\rho_2 F(r_1,r_2,\rho_1,\rho_2)\\ &\times b^{\dagger}_{1/2}(r_1)b^{\dagger}_{-1/2}(r_2)\\ &\times C^{\dagger}_{1/2}(\rho_1)C^{\dagger}_{-1/2}(\rho_2)|0\rangle\ .\end{aligned} \tag{H4}$$

In Eq. (H4), we have used the well-known fact that the orbital part F of the molecular wave function is symmetric so that the kinetic momentum part has to be antisymmetric with respect to the permutation (r_1,r_2) or (ρ_1,ρ_2). This implies that the two electrons and the two holes have different momentum.

Using Eqs. (H3), (13), and the analog of (49), one can write the coupling $W^{\dagger}_C$ as

$$\begin{aligned}\sum_k\sum_i \phi^*_i(\mathbf{k})\int\ & d^3r' d^3\rho' \phi_i(\mathbf{r}'-\rho')V^{-1/2}\\ &\times[\Delta'_+ b^{\dagger}_{1/2}(r')C^{\dagger}_{1/2}(\rho')\\ &+\Delta'_- b^{\dagger}_{-1/2}(r')C^{\dagger}_{-1/2}(\rho')]\ .\end{aligned} \tag{H5}$$

This finally gives, for the matrix element $D_{ss'}$, the following value:

$$D_{ss'}=\gamma(\Delta'_+\delta_{s,-1/2}\delta_{s',-1/2}+\Delta'_-\delta_{s,1/2}\delta_{s',1/2})\ , \tag{H6a}$$

$$\begin{aligned}\gamma=\sum_i \phi^*_i(\mathbf{r}=\mathbf{0})\int\ & V^{-1}d^3r\, d^3\rho\, d^3r'\, d^3\rho'\, \phi_1(\mathbf{r}-\rho)\\ &\times\phi_i(r'-\rho')V^{1/2}F^*(\mathbf{r},\mathbf{r}',\rho,\rho')\ .\end{aligned} \tag{H6b}$$

V^{-1} cancels the translational invariance of the problem, while $V^{1/2}$ is the usual normalization factor in the biexcitonic wave function so that γ is indeed volume independent.

We now show that the coefficient γ defined above is nothing but our coefficient $\gamma_{n=1}$, defined in our previous work, which contains explicitly the Coulomb interaction.

We could, as well, have calculated the contribution of a biexcitonic molecule from $\gamma_{ss',rr'}$ [Eq. (48)]. This would have led us to calculate

$$D'_{ss'}=\langle XX|\mathbf{V}^{\dagger}_{ss'}\Omega_1 H^{-1}W^{\dagger}_C|0\rangle\ , \tag{H7}$$

in which the Coulomb interaction appears explicitly via $\mathbf{V}^{\dagger}_{ss'}$. We now show that, close to resonance, $\Omega_{xx}\approx\Omega_1$, the two quantities $D_{ss'}$ and $D'_{ss'}$ are opposite.

Using the definition Eq. (F5) of $\mathbb{V}_{ss'}$, one can rewrite Eq. (H7) as

$$\begin{aligned}D'_{ss'}&=\langle XX|[(H-\Omega_1)\mathbf{B}^{\dagger}_{ss'}(1)-\mathbf{B}^{\dagger}_{ss'}(1)H]\\ &\quad\times H^{-1}W^{\dagger}_C|0\rangle\ ,\\ &=(\Omega_{xx}-\Omega_1)\langle XX|\mathbf{B}^{\dagger}_{ss'}(1)H^{-1}W^{\dagger}_C|0\rangle\\ &\quad-\langle XX|\mathbf{B}^{\dagger}_{ss'}(1)W^{\dagger}_c|0\rangle\ .\end{aligned} \tag{H8}$$

The first term of (H8) goes to zero at resonance, and so does not contribute to the pole, while the second one is just $-D_{ss'}$, as $\mathbf{B}^{\dagger}$ and $W^{\dagger}$ commute. A calculation, similar to the one done for $D_{ss'}$ leads to a coefficient γ having the form of Eq. (H6) with an extra factor which is exactly the (Coulomb) terms in square brackets appearing in β_{ij} [Eq. (G7)]. This shows that the coefficient γ in Eq. (H6), is nothing but the coefficient $-\gamma_{n=1}$ defined in our previous work.

Going back to the $(4\times4)S$ matrix, one deduces from Eqs. (H1) and (H6) that the divergent part of the biexcitonic resonance reads

$$\frac{\gamma^2}{\Omega_1-2\Omega_{xx}}\begin{vmatrix}\Delta'^2_- & \Delta'_+\Delta'_- & 0 & 0\\ \Delta'_+\Delta'_- & \Delta'^2_+ & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{vmatrix} \tag{H9}$$

the exciton basis being, respectively, $|X_{1/2,1/2}\rangle$, $|X_{-1/2,-1/2}\rangle$, $|X_{1/2,-1/2}\rangle$, and $|X_{-1/2,1/2}\rangle$.

As the excitonic shifts are the eigenvalues of the S matrix, one easily concludes that there is only one combination of the fourfold exciton which red-shifts at resonance $\Omega_1=2\Omega_{xx}$, the one given in Eq. (56). The three other exciton states are not affected by the $\Omega_1-2\Omega_{xx}$ pole. Noting that from Eq. (14), $\Delta'^2_+ +\Delta'^2_-=\frac{2}{3}(\lambda^2_+ +\lambda^2_-)=\frac{2}{3}\lambda^2$, λ^2 being proportional to the laser intensity, it is easy to check the value of the associated eigenstate [Eq. (57)].

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[11]Note that Eq. (A2) implies $b_y=-i2^{-1/2}(b_1+b_{-1})$.