Optical Stark effect of the exciton: Biexcitonic origin of the shift

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(Received 6 March 1989)

When a direct-gap semiconductor is irradiated in the transparency region, the exciton line blue shifts. This so-called optical Stark effect of the exciton is due to a coupling between the exciton and all biexcitonic states (bound or unbound). More precisely we show that the exciton shift results only from interactions between excitons (Coulomb interaction and Pauli exclusion). At large detuning, Pauli exclusion dominates, and the excitonic shift is the same as the dressed-atom blue shift. In material having a bound biexcitonic molecule, the excitonic blue shift, observed at large detuning, becomes a red shift at small detuning close to the exciton-biexciton resonance.

I. INTRODUCTION

The recent experimental observation,[1] by the ENSTA group, of the optical Stark effect of the exciton has raised considerable interest.[2–13] It was well known[14,15] in atomic physics that the energy levels of an atom are changed by a photon field. The so-called dressed-atom theory predicts for weak coupling a blue shift $2\lambda^2/\Omega$ of the transition frequency between two atomic levels. λ is the coupling matrix element, proportional to the square root of the number of photons, and Ω is the detuning, i.e., the energy difference between the atomic levels separation and the photon energy. In other words Ω is the departure from the resonance condition. Although excitons are commonly thought to be like hydrogen atoms, the shift of the exciton level has not been predicted theoretically, but first observed experimentally: when a direct-gap semiconductor is irradiated with a laser beam in the transparency region, the exciton line blue shifts. The energy change varies linearly with the laser intensity and very naturally this exciton Stark effect has been interpreted in terms of the dressed-atom theory, which was the only existing theory at that time.

One very remarkable feature of the optical Stark shift of the exciton is that the shift lasts only as long as the pump pulse, allowing optical gates as fast as femtoseconds. This property is crucially linked to the fact that photons in the transparency region are not absorbed by the semiconductor sample and only transient reactive effects are possible.

Besides its technological interest, the optical Stark effect of the exciton is quite interesting from a fundamental point of view as excitons are in fact not really atoms. A new theory, appropriate for semiconductors, i.e., starting with bare electrons and holes, was needed. One goal of this theory is to see if the simple dressed-atom picture is indeed valid and to understand why.

Our theory[5] is based on a perturbative approach, the electron-photon coupling W being treated to lowest order in perturbation. From it, one can see very clearly that the excitonic shift results only from a coupling between the exciton and all biexcitonic states, bound or unbound. One also immediately shows that the excitonic shift has the dressed-atom value at large detuning (large compared with the exciton binding energy). The reason is very simple: in this limit, the Coulomb energy is negligible. Therefore the momentum-conserving electron-photon interaction couples one valence state to one conduction state which are not mixed up with others by $V_{\rm Coul}$; the problem is then totally equivalent to the one of a two-level (dressed) atom. Finally as biexcitonic states appear to play an important role, one has to be careful in treating them correctly. In particular, one should cautiously keep the exact Coulomb interaction. This forces us to treat the electron-photon interaction only as a perturbation. We want to stress that W can be included exactly, i.e., to all orders, if the Coulomb interaction is simplified. This happens of course if the Coulomb interaction is totally neglected (free-electron limit) but also if the Coulomb interaction is treated within the Hartree-Fock approximation. In both cases, one expects to obtain a correct excitonic shift only in a regime where the Coulomb interaction is unimportant, i.e., at large detuning. In order to obtain the correct excitonic shift at all detunings, one has to keep the exact Coulomb interaction.

This paper is organized as follows. In Sec. II we set up the notations, write the Hamiltonian and the electron-photon coupling. In Sec. III we give the expression of the exciton shift and calculate it in two simple cases: (i) at large detuning and (ii) at all detunings when $V_{\rm Coul}$ is neglected. We also explain physically why the dressed-atom result is expected at large detuning. In Sec. IV, we discuss the biexcitonic origin of the shift. The shift is calculated in Sec. V for all detunings, $V_{\rm Coul}$ being treated exactly. We also discuss there the effect of a bound biexcitonic molecule on the shift of the lowest excitonic level. Section VI deals with the expression of the shift at resonance and the problems linked to it. Up to that point, the theory of the optical Stark shift of the exciton is presented simply, in terms of perturbation theory. In Sec. VII, we show how the problem can be formulated using a diagrammatic approach. This approach shows very clearly the importance, in the optical Stark effect, of Coulomb interaction between excitons. In most problems dealing with excitons this interaction is usually neglected.

Section VIII gives a rapid view of the state of the art, both experimentally and theoretically. We have put in the Appendix some more technical developments such as the effect of a finite photon momentum and the calculation of the coefficients α and β.

This work deals with the change induced on the excitonic level by a *continuous* excitation. However the experiments are actually done using ultrafast laser pulses; so that the connection between the experimental results and the steady-state theory has to be questioned. Indeed in some cases, the ultrashort pulse time dramatically modifies the observed spectra. It is, however, clear that a proper study of the simplest steady-state situation is of fundamental interest. The complexity of time-dependent effects has been recently investigated[8–13] both experimentally and theoretically as well as the regime in which agreement with steady-state results is expected.[9]

This paper is planned to be followed by a subsequent publication on polarization effects and exciton splitting (where we also consider only the effect of a continuous laser excitation). These polarization effects are linked to the symmetries of the valence and conduction bands. Although basically similar to the one presented here, the theory becomes much more cumbersome: the excitonic states being 2×4=eightfold degenerate, in the case of $J=\frac{3}{2}$ upper valence band, one term of the simple theory has to be replaced by an 8×8 matrix. . . . Although rather complicated, this theory turns out to give a simple and nice result:[6] it predicts that, beneath the observed blue-shifted exciton line, an excitonic splitting is hidden. Due to differences in the coupling constants between different valence and conduction states, the various degenerate exciton levels are not shifted similarly by the laser beam. Exciton splittings are usually induced by stress or magnetic field. It is the first case where one sees light inducing such an effect. This exciton splitting has been recently observed[2] both in bulk GaAs and in quantum wells. In this subsequent paper we will also discuss the effect of a bound biexcitonic molecule and describe in more detail how the associated red shift can be precisely observed. In a third publication, we will study the change induced by a laser beam on the absorption strength.

II. HAMILTONIAN AND COUPLING

The Hamiltonian H of an e-h system in a semiconductor is composed of a free-particle part H_0 and a Coulomb interaction V_{Coul} which contains e-e, h-h, and e-h contributions. The eigenstates of H corresponding to one e-h pair have the well-known hydrogenoïd form. Let us call $|X_i\rangle$ the excitonic state with wave function $\phi_{i\mathbf{k}}$ or $\phi_i(\mathbf{r})$ and energy $\omega_i=E_g-\varepsilon_i$, E_g being the band gap. ε_i is positive for bound states and negative for diffusion states. The eigenstates of H corresponding to two e-h pairs are not known exactly. One can, however, classify them into unbound e-h pair states, two-exciton-like states, and possibly molecular states in materials having a stable biexciton such as CuCl. We will call $|XX_n\rangle$ any of those biexcitonic states, $2\omega_n'=2(E_g-\varepsilon_n')$ their energy.

In the presence of a laser beam the conduction and valence bands are coupled. The corresponding (momentum-conserving) electron-photon interaction reads, in the rotating frame,[14] $W=U+U^\dagger$ with

$$U^\dagger=\sum_{\mathbf{k}}\lambda b^\dagger_{\mathbf{k}+\mathbf{q}/2}c^\dagger_{-\mathbf{k}+\mathbf{q}/2}\ , \tag{1}$$

where $\mathbf{q}$ is the photon momentum and λ which we take to be real (this is always possible) is the coupling matrix element, proportional to the square-root of the laser intensity and essentially wave-vector independent; $b^\dagger_{\mathbf{k}}$ and $c^\dagger_{\mathbf{k}}$ are the electron and hole creation operators. In the rotating frame, the interaction with a laser beam having a frequency ω_p is time independent; this implies in the electronic system an energy shift ω_p per e-h pair: namely, the bare excitonic energy becomes

$$\Omega_i=\omega_i-\omega_p \tag{2}$$

and the bare biexcitonic energy is

$$2\Omega_n'=2(\omega_n'-\omega_p)\ . \tag{3}$$

Ω_i is nothing but the so-called detuning with respect to the ith exciton level.

It is convenient to rewrite the free e-h pair creation operator $B^\dagger_{\mathbf{kq}}$ in terms of excitonic creation operators $B^\dagger_{i\mathbf{q}}$ as

$$B^\dagger_{\mathbf{kq}}\equiv b^\dagger_{\mathbf{k}+\mathbf{q}/2}c^\dagger_{-\mathbf{k}+\mathbf{q}/2}=\sum_i\phi^*_{i\mathbf{k}}B^\dagger_{i\mathbf{q}}\ , \tag{4}$$

where $B^\dagger_{i\mathbf{q}}$ creates an exciton $|X_{i\mathbf{q}}\rangle$ with translational momentum $\mathbf{q}$ and energy

$$\Omega_{i\mathbf{q}}=\Omega_i+\hbar^2q^2/2M \tag{5}$$

M being the total exciton mass.

This leads to rewrite the interaction $U^\dagger$, given in Eq. (1), as

$$U^\dagger=\sum_i\lambda_i^*B^\dagger_{i\mathbf{q}}\ , \tag{6}$$

$$\lambda_i^*=\lambda\sum_{\mathbf{k}}\phi^*_{i\mathbf{k}}=\lambda V^{1/2}\phi_i(\mathbf{r}=0)\ , \tag{7}$$

V being the sample volume. It turns out that the nonzero value of the photon momentum $\mathbf{q}$ does not play any role in the final result for the excitonic shift. So from now on, we will neglect it for simplicity. Nevertheless we will discuss that point in more detail in Appendix A.

III. EXPRESSION OF THE EXCITON SHIFT

In the absence of external excitation, the semiconductor absorption spectrum results from transitions between the vacuum $|0\rangle$ and the excitonic states $|X_j\rangle$. For simplicity, we will restrict ourselves here to the fundamental exciton, $j=1$. The generalization of the theory to excited excitonic states is easily obtained by changing the index "1" into "j" in the following equations.

In the presence of the pump beam, tuned in the transparency region, no real e-h pairs are created; the electronic system is however modified via virtual excitations. The vacuum and the exciton state are both modified as well as their energy difference. This change is nothing but the shift of the exciton energy which can be, for ex-

ample, tested using a weak probe pulse. The changes in the electronic system result from the fact that the electron-photon interaction W creates or destroys one e-h pair. Treating W in the perturbation theory, one finds to lowest order in W that $|0\rangle$ is coupled to all electronic states $|X_i\rangle$ bound or unbound, while $|X_1\rangle$ is coupled to all biexcitonic states $|XX_n\rangle$ as well as to $|0\rangle$. These couplings lead to a shift in the exciton energy which is from second-order perturbation theory:

$$\delta\Omega_1=\sum_n \frac{|\langle XX_n|U^\dagger|X_1\rangle|^2}{\Omega_1-2\Omega'_n}+\frac{|\langle 0|U|X_1\rangle|^2}{\Omega_1} -\sum_i \frac{|\langle X_i|U^\dagger|0\rangle|^2}{-\Omega_i}\ , \tag{8}$$

the first-order term in W being zero. The first two terms correspond to the change of the excitonic level while the last one is the change of the vacuum energy.

The exact biexcitonic states being unknown; there is a problem in calculating the exciton shift as it appears in Eq. (8). This is however possible in two limiting cases.

A. Exciton at large detuning

When the detuning is large compared with the binding energies, all the denominators of Eq. (8) are essentially equal[16] to $\Omega_1\approx E_g-\omega_p\equiv\Omega$. They can be taken out of the sums which then appear as closure relations. Equation (8) becomes in this limit

$$\delta\Omega_1=\Omega^{-1}(-\langle X_1|UU^\dagger|X_1\rangle +|\langle 0|U|X_1\rangle|^2+\langle 0|UU^\dagger|0\rangle) \tag{9}$$

As from Eq. (1),

$$U^\dagger=\lambda\sum_{\mathbf{k}} B^\dagger_{\mathbf{k}}\ , \tag{10}$$

where $B^\dagger_{\mathbf{k}}$ creates an e-h pair $(\mathbf{k},-\mathbf{k})$, the last matrix element of Eq. (9) is just the number N of $\mathbf{k}$ states in the sample volume. Noting that $|X_1\rangle=B^\dagger_1|0\rangle$ and using the expression (6) for $U^\dagger$, one finds for the first term of Eq. (9)

$$\langle X_1|UU^\dagger|X_1\rangle=\sum_{i,j}\lambda_i\lambda_j^*\langle 0|B_1B_iB_j^\dagger B_1^\dagger|0\rangle\ .$$

From the definition of $B_{\mathbf{k}}$, it is easy to calculate the commutator

$$[B_{\mathbf{k}},B^\dagger_{\mathbf{k}'}]=\delta_{\mathbf{k}\mathbf{k}'}(1-b^\dagger_{\mathbf{k}}b_{\mathbf{k}}-c^\dagger_{-\mathbf{k}}c_{-\mathbf{k}})\ . \tag{11}$$

Using Eq. (11) and the expression of $B_i^\dagger$ in terms of $B^\dagger_{\mathbf{k}}$ deduced from Eq. (4),

$$B_i^\dagger=\sum_{\mathbf{k}}\phi_{i\mathbf{k}}B^\dagger_{\mathbf{k}} \tag{12}$$

one can calculate the commutator $[B_i,B_j^\dagger]$ and deduce the value of the matrix element

$$\langle 0|B_iB_jB_l^\dagger B_m^\dagger|0\rangle=\delta_{il}\delta_{jm}+\delta_{im}\delta_{jl}-2\sum_{\mathbf{k}}\phi^*_{i\mathbf{k}}\phi^*_{j\mathbf{k}}\phi_{l\mathbf{k}}\phi_{m\mathbf{k}}\ . \tag{13}$$

The last term of Eq. (13) clearly shows that excitons are not real bosons. Using Eqs. (7) and (13), this gives for the matrix element (10)

$$\langle X_1|UU^\dagger|X_1\rangle=\lambda^2\sum_{\mathbf{k}_1,\mathbf{k}_2}\phi_{1\mathbf{k}_1}\phi^*_{1\mathbf{k}_2}+\lambda^2\sum_i\sum_{\mathbf{k}_1,\mathbf{k}_2}\phi^*_{i\mathbf{k}_1}\phi_{i\mathbf{k}_2} -2\lambda^2\sum_{i,j}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}}\phi_{i\mathbf{k}_1}\phi^*_{j\mathbf{k}_2}\phi^*_{i\mathbf{k}}\phi_{j\mathbf{k}}|\phi_{1\mathbf{k}}|^2\ . \tag{14}$$

The first term of Eq. (14) is nothing but $|\lambda_1|^2$. It will drop out with $|\langle 0|U|X_1\rangle|^2$ in the expression (9) of the shift. The sum over i in the second term of Eq. (14) gives $\delta_{\mathbf{k}_1,\mathbf{k}_2}$ so that this second term equals the number N of sites and will drop with $\langle 0|UU^\dagger|0\rangle$ in Eq. (9). In the last term of Eq. (14), the sum over i and j gives $\delta_{\mathbf{k}_1\mathbf{k}}\delta_{\mathbf{k}_2\mathbf{k}}$ so that this term reduces to $\sum_{\mathbf{k}}|\phi_1(\mathbf{k})|^2$ which is nothing but 1. Going back to Eq. (9), one finally gets[17] for the lowest exciton shift at large detuning

$$\delta\Omega_1=2\lambda^2/\Omega\ . \tag{15}$$

This very simple result is nothing but the shift of a two-level dressed atom.

B. Free electron-hole pair at all detunings

Expression (8) for the shift can be calculated for all detunings if one neglects the Coulomb interaction and considers only free e-h pairs. In this case the one-pair eigenstates of the Hamiltonian H_0 are simply plane waves $B_{\mathbf{k}}|0\rangle$ with energy $\mathbf{k}^2/2m=\Omega_{\mathbf{k}}$ and the two-pair eigenstates are plane-waves product $B^\dagger_{\mathbf{k}}B^\dagger_{\mathbf{k}'}|0\rangle$ with energy $\Omega_{\mathbf{k}}+\Omega_{\mathbf{k}'}$. The "biexcitonic" states being now known, the shift of the one-pair states $B^\dagger_{\mathbf{k}_1}|0\rangle$ obtained from Eq. (8) is

$$\delta\Omega_{\mathbf{k}_1}=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}\frac{|\langle 0|B_{\mathbf{k}}B_{\mathbf{k}'}U^\dagger B^\dagger_{\mathbf{k}_1}|0\rangle|^2}{\Omega_{\mathbf{k}_1}-\Omega_{\mathbf{k}}-\Omega_{\mathbf{k}'}}+\frac{|\langle 0|UB^\dagger_{\mathbf{k}_1}|0\rangle|^2}{\Omega_{\mathbf{k}_1}} -\sum_{\mathbf{k}}\frac{|\langle 0|B_kU^\dagger|0\rangle|^2}{-\Omega_{\mathbf{k}}} \tag{16}$$

[the factor $\frac{1}{2}$ corrects double counting of the $(\mathbf{k},\mathbf{k}')$ pair state]. Using expression (10) for $U^\dagger$ and the commutator (11), one easily gets

$$\delta\Omega_{\mathbf{k}_1}=\sum_{\mathbf{k}\neq\mathbf{k}_1}\frac{\lambda^2}{-\Omega_{\mathbf{k}}}+\frac{\lambda^2}{\Omega_{\mathbf{k}_1}}+\sum_{\mathbf{k}}\frac{\lambda^2}{\Omega_{\mathbf{k}}}=\frac{2\lambda^2}{\Omega_{\mathbf{k}_1}} \tag{17}$$

which is again the two-level dressed-atom shift.

C. Physical origin of the dressed-atom limit

We found that at large detuning the exciton shift has the dressed-atom value. If one analyses precisely where the coefficient 2 of Eq. (15) or (17) comes from, one finds that it results from Pauli exclusion between the two e-h pairs forming the biexciton. Let us visualize very simply why one obtains this large detuning result (see Fig. 1).

If the detuning is large, compared with the exciton

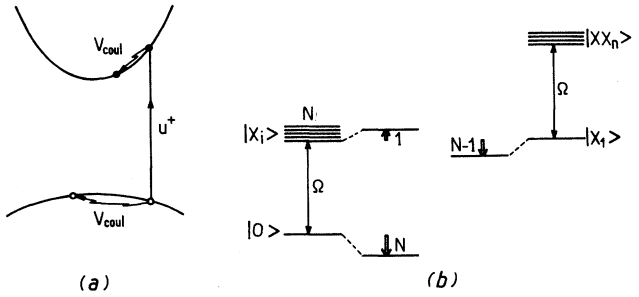

FIG. 1. (a) Coupling between valence-band states and conduction-band states induced by the electron-photon interaction $U^\dagger$, and further coupling between valence-band states and conduction-band states due to Coulomb interaction. (b) Shift of the vacuum and the one-pair states due to the electron-photon interaction.

binding energy which is a characteristic value of the Coulomb interaction, this means that V_{Coul} is a small perturbation which can even be neglected compared to the electron-photon interaction. The laser-induced coupling between valence and conduction bands conserves momentum, so it couples one valence state to only one conduction state. In the large detuning limit, i.e., where V_{Coul} can be neglected, the Coulomb interaction does not mix up those states and the problem reduces simply to a two-level system as for a dressed atom [see Fig. 1(a)].

It is then easy to see why the value of the shift comes only from Pauli exclusion at large detuning. In this limit, Coulomb interaction can be neglected and one can as well speak in terms of free e-h pairs. Coupling between the vacuum and any one-pair state pushes apart these two states by an amount λ^2/Ω [see Fig. 1(b)]. If all the one-pair states have more or less the same energy (i.e., if the detuning Ω is large) the coupling between $|0\rangle$ and all the N one-pair states pushes down the vacuum by $N\lambda^2/\Omega$. If we consider now a particular one-pair state $B^\dagger_{\mathbf{k}_1}|0\rangle$, it is pushed up by λ^2/Ω due to its coupling with $|0\rangle$ and pushed down by λ^2/Ω due to its coupling with any two-pair states (which have all the same energy 2Ω). Due to Pauli exclusion, $B^\dagger_{\mathbf{k}_1}|0\rangle$ is coupled to only $N-1$ two-pair states since $(\mathbf{k}_1,-\mathbf{k}_1)$ is already occupied in the initial one-pair state. This finally gives for the shift of the one-pair state $\{[1-(N-1)]-(-N)\}\lambda^2/\Omega=2\lambda^2/\Omega$, i.e., the dressed-atom value. (The link between the factor 2 and Pauli exclusion is actually clearer if the photon momentum is taken into account, see Appendix A.)

This very simple understanding of the large detuning behavior of the exciton shift will appear very useful in more complicated situations, such as the one encountered for the exciton-shift dependence on light polarization.[6]

IV. BIEXCITONIC ORIGIN OF THE EXCITON SHIFT

In the last paragraph we have been able to calculate the exciton shift in the large detuning limit and we have shown that the value of the shift originates from Pauli exclusion between the two e and the two h forming the biexcitonic states. More generally we will now show that the value of the exciton shift can only come from biexcitonic terms. For this purpose let us return to Eq. (8). Using Eqs. (6) and (7) it is easy to notice that the last two terms of the shift (8) are exactly proportional to the sample volume. These last terms both correspond to the coupling between excitons and vacuum. As it is physically obvious that the final expression of the exciton shift should not depend on the sample volume, those terms have to disappear with similar terms included in the first sum of Eq. (8). (In other words, the perturbation W shifts each level by a V infinite amount, but the energy difference between various levels stays finite.) This just means that the shift $\delta\Omega_1$ comes only from the (volume-finite) part of this first sum which is simply the coupling between the exciton and all biexcitonic states, bound or unbound. The elimination of the vacuum-coupled terms corresponds to the elimination of disconnected diagrams in a diagrammatic calculation of the shift (see Sec. VII).

The terms proportional to V have to cancel exactly from Eq. (8). As the exact biexcitonic eigenstates are unknown, if V_{Coul} is not neglected, the exact disappearance of the volume for any value of the detuning can only be obtained formally. One finds this result by keeping in mind that these terms disappear for free particles, i.e., when $V_{\text{Coul}}=0$. In this aim, we note that Eq. (8) is strictly equivalent to

$$\delta\Omega_1=\left\langle X_1\left|U\frac{1}{\Omega_1-H}U^\dagger\right|X_1\right\rangle+\left\langle X_1\left|U^\dagger\frac{1}{\Omega_1}U\right|X_1\right\rangle+\left\langle 0\left|U\frac{1}{H}U^\dagger\right|0\right\rangle \tag{18}$$

[insertion of closure relations in the terms of Eq. (18) gives back Eq. (8)]. We now manipulate Eq. (18) in order to rewrite it as a large detuning leading term plus a correction. One can easily check that Eq. (18) can be rewritten as

$$\delta\Omega_1=\frac{1}{\Omega_1}\left[\langle X_1|[U^\dagger,U]|X_1\rangle+\langle 0|UU^\dagger|0\rangle+\left\langle X_1\left|U\frac{2\Omega_1-H}{\Omega_1-H}U^\dagger\right|X_1\right\rangle+\left\langle 0\left|U\frac{\Omega_1-H}{H}U^\dagger\right|0\right\rangle\right]. \tag{19}$$

The first two terms do not depend on the detuning while the last two ones go to zero when the detuning increases (their numerators do not depend on ω_p while their denominators do). Using the commutator Eq. (11), it is straightforward to show that the first two terms of Eq. (19), which are equal to $\langle 0|B_1[U^\dagger,U]B_1^\dagger-[U^\dagger,U]|0\rangle$, give simply $2\lambda^2$. This factor 2, which originates from Pauli exclusion on the two-pair states, is just the one found in the large detuning limit of the last paragraph.

V. CALCULATION OF THE EXCITONIC SHIFT: DETUNING DEPENDENCE

Let us now calculate the corrections to the large detuning value $2\lambda^2/\Omega_1$, namely, the last two terms of Eq. (19).

We do not know how H acts on two-pair states but we know how H acts on one-pair states. In order to make use of this information as much as possible, we will commute $(H-\Omega_1)^{-1}$ and $B_1^\dagger$. For that we first calculate

$$[H,B_1^\dagger]=\Omega_1(B_1^\dagger+C_1^\dagger)\ . \tag{20}$$

This is a defining equation for $C_1^\dagger$. The operator $C_1^\dagger$ corresponds to Coulomb interaction between excitons: without it, the excitons would evolve as independent particles. Using the exact expression of $V_{\rm Coul}$ and expressing $B_1^\dagger$ in terms of $B_{\mathbf{k}}^\dagger$, it is easy to find (see Appendix B) that $C_1^\dagger$ is given by

$$\Omega_1 C_1^\dagger=\sum_{\mathbf{kq}} V_{\mathbf{q}}(\phi_{1\mathbf{k}}^*-\phi_{1\mathbf{k}+\mathbf{q}}^*)b_{\mathbf{k}+\mathbf{q}}^\dagger c_{-\mathbf{k}}^\dagger \times\sum_{\mathbf{k}'}(b_{\mathbf{k}'-\mathbf{q}}^\dagger b_{\mathbf{k}'}-c_{-\mathbf{k}'-\mathbf{q}}^\dagger c_{-\mathbf{k}'})\ , \tag{21}$$

where $V_{\mathbf{q}}$ is the Coulomb matrix element for momentum transfer $\mathbf{q}$. Equation (20) gives

$$\frac{1}{H-\Omega_1}B_1^\dagger=B_1^\dagger\frac{1}{H}-\frac{\Omega_1}{H-\Omega_1}C_1^\dagger\frac{1}{H}\ . \tag{22}$$

Noting that $|X_1\rangle=B_1^\dagger|0\rangle$, it is then easy to check that the shift Eq. (19) can be rewritten as

$$\delta\Omega_1=\frac{\lambda^2}{\Omega_1}(2+\alpha+\beta-\gamma)\ ; \tag{23}$$

α,β,γ are the corrections to the large detuning value. They are defined as

$$\lambda^2\alpha=\left\langle 0\left|U(B_1B_1^\dagger-1)\frac{H-\Omega_1}{H}U^\dagger\right|0\right\rangle\ , \tag{24}$$

$$\lambda^2\beta=\left\langle 0\left|U\frac{\Omega_1}{H}B_1C_1^\dagger\frac{\Omega_1}{H}U^\dagger\right|0\right\rangle\ , \tag{25}$$

$$\lambda^2\gamma=\left\langle 0\left|U\frac{\Omega_1}{H}C_1\frac{\Omega_1}{H-\Omega_1}C_1^\dagger\frac{\Omega_1}{H}U^\dagger\right|0\right\rangle\ . \tag{26}$$

α and β can be calculated exactly as, in these terms, H acts only on one-pair states. However, the intrinsic problem linked to our poor knowledge of the exact biexcitonic eigenstates cannot disappear completely from the calculation of the shift. It remains in γ, as H acts on two-pair states: it is not possible to find an exact value of γ. Nevertheless, it will be easy to find, in γ, the effect of a bound biexcitonic molecule.

We now calculate α, β, and γ and check what we already know about them, namely, they go to zero at large detuning, they are exactly zero if $V_{\rm Coul}$ is neglected (already obvious for β and γ as $C_1^\dagger=0$ if $V_{\rm Coul}$ is neglected) and, of course, they do not depend on the sample volume.

A. Calculation of α

As $B_i^\dagger|0\rangle$ is an eigenstate of H, α is easily calculated if one uses for $U^\dagger$ its expression in terms of $B_i^\dagger$ [Eq. (6)]. Using the matrix element (13) and the orthogonality relation $\sum_j\phi_{j\mathbf{k}}\phi_{j\mathbf{k}'}^*=\delta_{\mathbf{k}\mathbf{k}'}$, one can rewrite expression (24) for α as

$$\alpha=\sum_i\frac{\Omega_1-\Omega_i}{\Omega_i}\alpha_i\ , \tag{27}$$

$$\alpha_i=2\sum_{\mathbf{k}\mathbf{k}'}\phi_{i\mathbf{k}'}^*\phi_{i\mathbf{k}}|\phi_{1\mathbf{k}}|^2\ . \tag{28}$$

One can check that $\alpha\equiv0$ as expected if $V_{\rm Coul}=0$. In this case, the $\phi_i(\mathbf{r})$ are plane waves, the $\phi_{i\mathbf{k}}$ are δ functions, and $\alpha_i=0$ for $i\neq1$ which gives $\alpha=0$. For the exact Coulomb interaction, the coefficient α is calculated using the exact excitonic wave functions.

(i) At small detuning, $\Omega_1\to0$, α goes to α_1-2 as

$$\sum_i\alpha_i=2$$

due to orthogonality relations [in three dimensions (3D), one finds $\alpha_1=7$, see Appendix C]. This gives in the excitonic shift $\lambda^2(2+\alpha)/\Omega_1\approx\lambda^2\alpha_1/\Omega_1$. Note that this contribution to the shift is written only in terms of the lowest excitonic state.

(ii) At large detuning, i.e., large $\Omega=E_g-\omega_p$, Ω_i goes to infinity while $\Omega_1-\Omega_i$ does not change (this difference does not depend on the photon energy ω_p). So one expects α to go to zero. More precisely the dominant contributions to α come from the high-energy states. The contribution of these terms can be summed up analytically using the exact diffusive wave function (see Appendix C). We find[5] in 3D

$$\alpha(\Omega_1\to\infty)\approx4(\varepsilon_1/\Omega_1)^{1/2}\ . \tag{29}$$

Zimmermann[7] has performed a numerical calculation of α. It is interesting to note that this "large" detuning behavior Eq. (29), is quite good as, even for $\varepsilon_1/\Omega_1=1$, it gives the correct value within 10%.

In conclusion we have found that, at small detuning, α goes to 5 and at large detuning α goes to 0 as $4(\varepsilon_1/\Omega)^{1/2}$, this behavior coming from the high-energy diffusion states.

B. Calculation of β

Writing again $U^\dagger$ in terms of $B_i^\dagger$ one can rewrite expression (25) for β as

$$\beta=\Omega_1\sum_{ij}\frac{\beta_{ij}}{\Omega_i\Omega_j}\ , \tag{30}$$

$$\beta_{ij}=V\phi_j(0)\phi_i^*(0)\langle0|B_jB_1\Omega_1C_1^\dagger B_i^\dagger|0\rangle\ . \tag{31}$$

Using Eq. (21) for $C_1^\dagger$, it is easy to check that the matrix element appearing in β_{ij} is

$$\langle0|B_jB_1\Omega_1C_1^\dagger B_i^\dagger|0\rangle=2\sum_{\mathbf{k},\mathbf{k}'}V_{\mathbf{k}'-\mathbf{k}}(\phi_{1\mathbf{k}}-\phi_{1\mathbf{k}'})(\phi_{i\mathbf{k}}-\phi_{i\mathbf{k}'})\phi_{1\mathbf{k}}^*\phi_{j\mathbf{k}'}^*\ . \tag{32}$$

The physical meaning of the matrix element appears more clearly if one rewrites the wave functions in $\mathbf{r}$ space. Using

$$V_q=V^{-1}\int d^3r\,v(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}$$

with $v(\mathbf{r})=e^2/r$, one then finds that β_{ij} reads

$$\beta_{ij}=2\phi_j(0)\phi_i^*(0)\int \frac{1}{V}d^3r\,d^3r'\,d^3\rho\,d^3\rho'\,\phi_1(\mathbf{r}-\boldsymbol{\rho})\phi_i(\mathbf{r}'-\boldsymbol{\rho}') \times[v(\mathbf{r}'-\boldsymbol{\rho})+v(\mathbf{r}-\boldsymbol{\rho}') -v(\mathbf{r}-\mathbf{r}')-v(\boldsymbol{\rho}-\boldsymbol{\rho}')] \times\phi_1^*(\mathbf{r}-\boldsymbol{\rho}')\phi_j^*(\mathbf{r}'-\boldsymbol{\rho}) . \quad (33)$$

The factor $1/V$ cancels the translational invariance of the system so that β_{ij} is indeed volume independent as expected.

From Eq. (33), one sees that β_{ij} corresponds physically to all possible Coulomb interactions between any two carriers of two excitons, the e-h interaction being attractive while the e-e or h-h ones are repulsive.

(i) At small detuning, the dominant term in β comes from $i=j=1$, so that $\beta\approx\beta_{11}/\Omega_1$. Dimensional argument show that β_{11} is of the order of the exciton binding energy ε_1. A precise calculation gives, in 3D, $\beta_{11}=\frac{52}{3}\varepsilon_1$ (see Appendix D). So that at small detuning

$$\beta(\Omega_1\to 0)\approx\tfrac{52}{3}\varepsilon_1/\Omega_1 . \quad (34)$$

(ii) In order to find the large detuning behavior for β, we may set $H\approx\Omega_1$ in the definition Eq. (25) which leads to

$$\lambda^2\beta\approx\frac{1}{\Omega_1}\langle 0|UB_1(\Omega_1 C_1^\dagger)U^\dagger|0\rangle . \quad (35)$$

(Note that the same procedure applied to α leads to a divergent result. This is why the large detuning behavior of α is $\sim\Omega_1^{-1/2}$ and not $\sim 1/\Omega_1$). From Eqs. (1) and (21), one finds that $C_1^\dagger U^\dagger|0\rangle=0$. This is physically rather obvious: $U^\dagger$ creates an electron and a hole at the same place in space. Therefore the Coulomb interaction with an other exciton, which is precisely what $C_1^\dagger$ corresponds to, is clearly zero. Since in this $1/\Omega_1$ expansion, the coefficient of the $1/\Omega_1$ term vanishes, it is natural to conclude that $\beta\sim 1/(\Omega_1)^2$ at large detuning. However this assumes that there appears no divergence in the corresponding coefficient analogous to what is found in the calculation of α. More precisely $C_1^\dagger U^\dagger|0\rangle=0$ implies

$$\sum_i \beta_{ij}=0 .$$

This allows to rewrite β as

$$\beta=\sum_{i,j}\frac{(\Omega_1-\Omega_i)}{\Omega_i\Omega_j}\beta_{ij} . \quad (36)$$

If $\sum_{i,j}\Omega_i\beta_{ij}$ converges, β behaves as $1/\Omega^2$. If it diverges, the behavior will be between $1/\Omega^2$ and $1/\Omega$. But anyway it seems quite likely that, at large detuning, β is negligible compared to α. Note that at small detuning we had the opposite situation since β diverges while α goes to a finite value.

C. Calculation of γ

In γ, the Hamiltonian H acts on two e-h pair states so that, unlike for α and β, the true two-pair eigenstates must appear in γ. As these eigenstates are basically unknown, there is no hope to perform a precise calculation of γ. One can nevertheless extract some limiting behaviors. Closure relations for biexcitonic states included on both sides of $(H-\Omega_1)^{-1}$ in Eq. (26), leads to write γ as

$$\gamma=\sum_n\frac{\Omega_1}{2\Omega_n'-\Omega_1}|\gamma_n|^2 , \quad (37)$$

$$\gamma_n=\langle XX_n|(C_1^\dagger\Omega_1)U^\dagger|0\rangle=\sum_i\frac{\gamma_{ni}}{\Omega_i} , \quad (38)$$

$$\gamma_{ni}=\sqrt{V}\,\phi_i(0)\langle XX_n|(C_1^\dagger\Omega_1)B_i^\dagger|0\rangle . \quad (39)$$

Using expression (21) for $C_1^\dagger$ and going to $\mathbf{r}$ space, one finds

$$\gamma_{ni}=\phi_i^*(0)\int V^{-1}d^3r\,d^3r'\,d^3\rho\,d^3\rho'\,\phi_1(\mathbf{r}-\boldsymbol{\rho}) \times\phi_i(\mathbf{r}'-\boldsymbol{\rho}')V^{1/2}F_n(\mathbf{r}\mathbf{r}'\boldsymbol{\rho}\boldsymbol{\rho}') \times[v(\mathbf{r}-\boldsymbol{\rho}')+v(\mathbf{r}'-\boldsymbol{\rho})-v(\mathbf{r}-\mathbf{r}') -v(\boldsymbol{\rho}-\boldsymbol{\rho}')] , \quad (40)$$

F_n being the biexcitonic wave function. V^{-1} cancels the V factor coming from the translational invariance of the system while $V^{1/2}$ cancels the standard normalization factor of the biexcitonic wave function, so that γ is indeed volume independent as expected.

As for β_{ij}, one easily sees that γ_{ni} physically corresponds to all possible Coulomb interactions between any two carriers of a two-pair state. However in γ appear the true biexcitonic eigenstates F_n while β_{ij} contains only products of two excitonic eigenstates.

(i) At large detuning, γ goes to zero as expected: $\Omega_i\approx\Omega$ in this limit and $\sum_i\gamma_{ni}=0$ as $C_1^\dagger U^\dagger|0\rangle=0$. More precisely, noting that

$$\gamma_n=\sum_i\gamma_{ni}/\Omega_i\equiv\sum_i\gamma_{ni}(\Omega_1-\Omega_i)/\Omega_1\Omega_i ,$$

one finds, using similar arguments as for β, that γ goes to zero as $(\varepsilon_1/\Omega_1)^4$ or at the very least as $(\varepsilon_1/\Omega_1)^2$. Anyway, it is negligible compared to α.

(ii) At small detuning, the behavior of γ is controlled by the lowest biexcitonic levels. The problem is very simple if there is one stable molecular state well below the other biexcitonic energies. In this case its contribution is dominant for detunings small compared with the energy difference between the fundamental biexciton and the others states. γ then behaves as

$$\gamma\approx|\gamma_1|^2\Omega_1/(2\Omega_1'-\Omega_1)=|\gamma_1|^2\Omega_1/(\Omega_1-\varepsilon_1') , \quad (41)$$

where ε_1' is the binding energy of the molecular biexciton $(2\Omega_1'\equiv 2\Omega_1-\varepsilon_1')$. This molecular state induces a resonance at $\Omega_1=\varepsilon_1'$ which corresponds to $\omega_p=\omega_1-\varepsilon_1'$, i.e., below the exciton threshold $\omega_p=\omega_1$. Below this resonance, γ is positive so that the corresponding shift $\delta\Omega_1$, given in Eq. (23), is negative. This means that in materials having a stable molecular biexciton, the exciton line, which always blue shifts at large detuning, should red shift close to the biexciton resonance as there is only one contribution (in γ) to the $(\Omega_1-\varepsilon_1')$ pole. Physically this

red shift merely corresponds to the anticrossing of the exciton and the biexciton, coupled by the pump field. This red shift was obvious already in the first expression of $\delta\Omega_1$, Eq. (8). Indeed keeping only the $n=1$ term in the first sum, one finds $\delta\Omega_1=|\langle XX_1|U^\dagger|X_1\rangle|^2/(\Omega_1-2\Omega_1')$ which is negative.

If there is no well-bound molecular state, then the lowest biexcitonic energy is $2\Omega_1'\approx 2\Omega_1$, these energy levels being quasidegenerate. Let us label n_1 the corresponding states. Noting from Eq. (37) that

$$\gamma > \Omega_1^{-2}\sum_{n_1}|\gamma_{n_1,1}|^2 , \tag{42}$$

one concludes that, at small detuning, γ diverges as Ω_1^{-2}. More precisely, dimensional arguments lead in this regime to

$$\gamma(\Omega_1\to 0)\sim(\varepsilon_1/\Omega_1)^2 \tag{43}$$

so that γ dominates β.

D. Conclusions

We have found that at large detuning, the main correction to the dressed-atom blue shift $2\lambda^2/\Omega_1$ comes from α, which originates from Pauli exclusion between two e-h pairs. The nonanalytic behavior $\alpha\sim(\varepsilon_1/\Omega_1)^{1/2}$ results from the coupling between the lowest exciton and all the high-energy diffusive eigenstates of one additional e-h pair. On the opposite, at small detuning, the corrections come mainly from β and γ and originate from the Coulomb interaction between two $1-s$ excitons. We find that β diverges as ε_1/Ω_1 while γ diverges as $(\varepsilon_1/\Omega_1)^2$. They both dominate α which stays constant at small detuning.

The problem is now to know if γ, which is positive and therefore competes with β, produces really an observable red shift at resonance. We consider this question in the next paragraph.

VI. EXCITONIC SHIFT AT RESONANCE

In the preceding paragraph, we have obtained the detuning dependence of the exciton Stark shift. Its expression, Eq. (23), has a diverging behavior at resonance. This unphysical result comes of course from the unproper use of a perturbative treatment close to resonance. Nevertheless this approach makes us aware that there is one term, γ, which seems to force a red shift of the exciton at small detuning and that, in this term, the exact biexcitonic eigenstates play a crucial role. The question is now: does the exciton, which always blue shifts at large detuning, always red shifts at small detuning?

A. Stable biexcitonic molecule

As already discussed above, the answer is obvious if there is a stable molecular biexciton as the pole at the exciton-biexciton resonance, $\Omega_1=\varepsilon_1'$, appears only in γ. In this case, it is also very simple to calculate the shift at resonance. It simply results from perturbation theory in the (twofold) degenerate subspace made of the exciton and the molecular biexciton. One finds a red shift at resonance.

$$\delta\Omega_1=-\lambda|\langle XX_1|U^\dagger|X_1\rangle| . \tag{44}$$

Note that far from resonance, the exciton shift varies as λ^2 while at resonance, it varies as λ, i.e., the square root of the laser intensity. This is similar to the two-level atom shift which goes from $2\lambda^2/\Omega_1$ to 2λ, the crossover region taking place for $\Omega_1\sim\lambda$.

The influence of a biexcitonic molecule on the exciton energy at small detuning has to be related to previous works[18] on the biexciton. Most of them were related to the two-photon absorption resonance: the corresponding anticrossing B induces a blue shift of the biexciton line (see Fig. 2). This shift depends on the laser intensity. In the exciton Stark effect, we deal with the anticrossing A which corresponds to $2\omega_1'=\omega_1+\omega$, i.e., $\Omega_1=\varepsilon_1'$. The biexciton line again blue shifts while the exciton line red shifts; these shifts also depend on the laser intensity. The third anticrossing C corresponds to the standard polariton effect,[19] and induces an excitonic blue shift.

We finally want to stress that a stable biexcitonic molecule can influence the exciton shift only if this molecule is indeed coupled to the exciton. In other words, one expects to see this red shift only if the molecule can be produced from a pump photon and a test photon (which produces the observed exciton). However, the correct study of this problem requires the consideration of polarization effects. Due to the exciton splitting associated to the optical Stark effect, the conditions of observation are somewhat restrictive[6] and will be discussed in a subsequent paper.

B. Without stable molecule

The preceding case had the advantage to isolate one particular two e-h pair state, the biexcitonic molecule, associated with a well-separated pole $\Omega_1=\varepsilon_1'$. If the molecule is not stable or barely stable, the pole $\Omega_1\approx 0$ corresponds to the resonance between the exciton and many two-pair states. But, worst, it also corresponds to the resonance with three-pair, four-pair, . . . , states as, for $\Omega_1'\approx\Omega_1\approx 0$, one also has $\Omega_1''\approx\Omega_1\approx 0$, $\Omega_1'''\approx\Omega_1\approx 0$, and so on. . . . Consequently, in order to obtain the excitonic

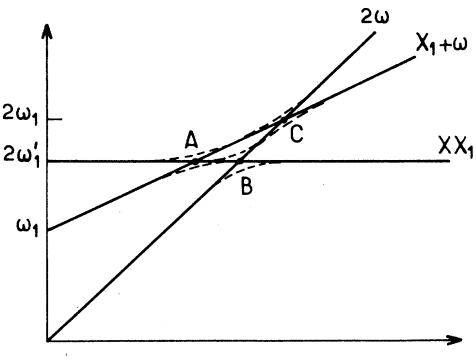

FIG. 2. Energy of the biexciton, of the exciton plus photon, and of two photons as a function of pump-photon energy.

shift at resonance, one should do degenerate perturbation theory in an infinite subspace made of the vacuum, the excitons, biexcitons, triexcitons, and so on. Moreover, we have learned from the calculation of the exciton shift out of resonance that it is necessary to treat the Coulomb interaction exactly. So that, at resonance, one should also include the exact Coulomb interaction. This is a formidable problem. Presently we can say that we expect a limiting shift linear in λ, with a prefactor depending on the exciton-exciton interaction. However, in the absence of precise calculation, we cannot tell the sign of this prefactor, i.e., if the exciton indeed red shifts at resonance. We think that, at resonance, the exciton line can in fact red shift or blue shift, depending on materials.

The experimental observation of a resonant optical Stark shift behavior, which varies as the square root of the laser intensity, will be most probably mixed up with the effect of real exciton creation as the excitonic linewidth is usually larger than the detuning necessary to observe this regime. However, the optical Stark shift might be separated from the real particle effects as the later one depends on the total number of created excitons and therefore increase during the pulse duration while the optical Stark shift should follow the pulse instantaneous intensity.

VII. DIAGRAMMATIC APPROACH

We now consider the exciton Stark shift within a diagrammatic approach. Even if finally it will appear that this is not the simplest way to calculate the shift, the diagrammatic approach has the advantage to show very simply and clearly that the couplings between two e-h pairs play the key role in the optical Stark effect.

Let us outline the standard procedure. We will follow the usual notations and rules for diagrams as found for example in Ref. 20. The absorption $A(\omega_T)$ of a test laser beam with photon energy ω_T is related to the imaginary part of the response function $S(\mathbf{q},\omega_T)$. More precisely, one has

$$A(\omega_T)=-2\,\mathrm{Im}S(0,\omega_T)\ . \tag{45}$$

(a) In the standard case of an e-h system in the absence of a pump laser beam, the function $S(\mathbf{0},\omega_T)$ is given by the usual sum of ladder diagrams shown in Fig. 3(a). One finds

$$S(\mathbf{0},\omega_T)=-2\lambda_T^2\left[\sum_{\mathbf{k}} G_0(\mathbf{k},\omega_T) + \sum_{\mathbf{kk'}} G_0(\mathbf{k},\omega_T)V_{\mathbf{k},\mathbf{k'}}G_0(\mathbf{k'},\omega_T)+\ldots\right], \tag{46}$$

where λ_T is the electron-test photon coupling constant and G_0 is defined in terms of the bare electron and hole propagators as

$$G_0(\mathbf{k},\omega_T)=-\int\frac{id\omega}{2\pi}G_{0h}(\mathbf{k},\omega)G_{0e}(\mathbf{k},\omega+\omega_T)\ , \tag{47}$$

where

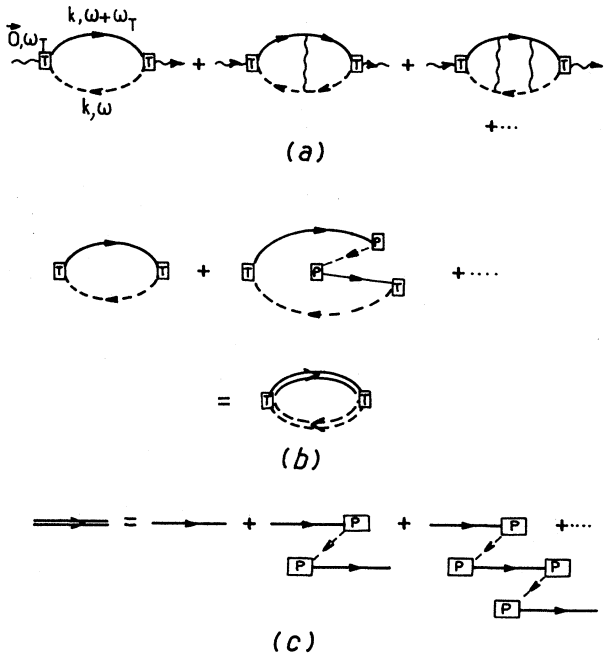

FIG. 3. (a) Ladder diagrams for the response function with Coulomb interaction and without pump photons. (b) Diagrams with pump photons, but without Coulomb interaction. (c) Dressed electron propagator in the presence of pump photons.

$$\begin{aligned} G_{0e}(\mathbf{k},\omega)&=(\omega-E_g-\mathbf{k}^2/2m_e+i\eta)^{-1}\ ,\\ G_{0h}(\mathbf{k},\omega)&=(\omega+\mathbf{k}^2/2m_h-i\eta)^{-1}\ . \end{aligned} \tag{48}$$

This gives for G_0

$$G_0(\mathbf{k},\omega_T)=(\omega_T-E_g-\mathbf{k}^2/2m+i\eta)^{-1}\ ,$$

where m is the reduced exciton mass. One then calculates the infinite sum appearing in Eq. (46) introducing

$$\begin{aligned} P_0(\mathbf{k},\omega_T)&=\Gamma_0(\mathbf{k},\omega_T)G_0(\mathbf{k},\omega_T)\ ,\\ \Gamma_0(\mathbf{k},\omega_T)&=1+\sum_{\mathbf{k'}}V_{\mathbf{kk'}}G_0(\mathbf{k'},\omega_T)\Gamma_0(\mathbf{k'},\omega_T)\ . \end{aligned} \tag{49}$$

Equation (46) then simply reads

$$S(\mathbf{0},\omega_T)=-2\lambda_T^2\sum_{\mathbf{k}}P_0(\mathbf{k},\omega_T)\ , \tag{50}$$

where $P_0(\mathbf{k},\omega_T)$ is solution of the integral equation

$$G_0^{-1}(\mathbf{k},\omega_T)P_0(\mathbf{k},\omega_T)=1+\sum_{\mathbf{kk'}}V_{\mathbf{kk'}}P_0(\mathbf{k'},\omega_T)\ . \tag{51}$$

This equation is easily solved using our knowledge of the exact one e-h pair eigenstates in the presence of the true Coulomb potential, i.e., the solutions of the corresponding Schrödinger equation (as seen later, we will stop at that stage the calculation of the optical Stark shift by lack of knowledge of the exact two e-h eigenstates). Expanding P_0 on the excitonic basis

$$P_0(\mathbf{k},\omega_T)=\sum_i C_i(\omega_T)\phi_i^*(\mathbf{r}=0)\phi_{i\mathbf{k}} \tag{52}$$

and using the properties of the ϕ_i's, namely,

$$(\omega_i-\mathbf{k}^2/2m)\phi_{i\mathbf{k}}=\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}\phi_{i\mathbf{k}'} , \tag{53}$$

Eq. (50) implies for the coefficients $C_i(\omega_T)$

$$C_i(\omega_T)=(\omega_i-\omega_T-i\eta)^{-1} \tag{54}$$

so that Eq. (45) gives for the absorption the usual result

$$A(\omega_T)=4\pi\lambda_T^2\sum_i|\phi_i(\mathbf{r}=0)|^2\delta(\omega_i-\omega_T) . \tag{55}$$

(b) We now consider the changes induced by a pump laser beam, i.e., we look for the new diagrams appearing in the calculation of the response function. A pump photon ω_p can be transformed into an e-h pair, or an e-h pair can recombine into a photon ω_p. This modifies the diagrams of Fig. 3(a) in the following way.

(i) If we first forget the Coulomb interaction, we start with only the first bubble in the diagrams [3(a)]. The effect of the pump laser corresponds to add an infinite number of diagrams to that bubble as shown in Fig. 3(b). They are easily summed up to all orders in the electron-pump photon coupling λ_p, if one introduces renormalized e and h propagators [see Fig. 3(c)]:

$$\begin{aligned} G_e(\mathbf{k},\omega)&=G_{0e}(\mathbf{k},\omega)+\lambda_p^2 G_{0e}(\mathbf{k},\omega)G_{0h}(\mathbf{k},\omega-\omega_p)\\ &\quad\times G_{0e}(\mathbf{k},\omega)+\cdots ,\\ &=[G_{0e}^{-1}(\mathbf{k},\omega)-\lambda_p^2 G_{0h}(\mathbf{k},\omega-\omega_p)]^{-1} ,\\ G_h(\mathbf{k},\omega)&=[G_{0h}^{-1}(\mathbf{k},\omega)-\lambda_p^2 G_{0e}(\mathbf{k},\omega+\omega_p)]^{-1} . \end{aligned} \tag{56}$$

This gives for the renormalized bubble

$$\begin{aligned} S(0,\omega_T)&=-2\lambda_T^2\sum_{\mathbf{k}} G(\mathbf{k},\omega_T)\\ G(\mathbf{k},\omega_T)&=-\int\frac{i}{2\pi}d\omega G_e(\mathbf{k},\omega+\omega_T)G_h(\mathbf{k},\omega) \end{aligned} \tag{57}$$

and from a simple calculation, one gets

$$\mathrm{Im}G(\mathbf{k},\omega_T)=\frac{\pi}{4}\delta(\Omega-Y_{\mathbf{k}})\left[\frac{E_{\mathbf{k}}+\Omega}{\Omega}\right]^2 , \tag{58}$$

where $\Omega=\omega_T-\omega_p$, $E_{\mathbf{k}}=\mathbf{k}^2/2m+E_g-\omega_p$, and $Y_{\mathbf{k}}^2=E_{\mathbf{k}}^2+4\lambda_p^2$. Going back to the absorption definition (45), one finds that, in the absence of Coulomb interaction, the test laser absorption in the presence of a pump laser beam is

$$\begin{aligned} A(\omega_T)&=|\lambda_T|^2\frac{(2m)^{3/2}}{4\pi}[(\Omega^2-4\lambda_p^2)^{1/2}+\omega_p-E_g]^{1/2}\\ &\quad\times\frac{[\Omega+(\Omega^2-4\lambda_p^2)^{1/2}]^2}{\Omega(\Omega^2-4\lambda_p^2)^{1/2}} \end{aligned} \tag{59}$$

for ω_T larger than a threshold ω_{T0} given by

$$\omega_{T0}=\omega_p+[(E_g-\omega_p)^2+4\lambda_p^2]^{1/2} . \tag{60}$$

This threshold insures that the bracket appearing in Eq. (59) is positive. Equation (59) gives the absorption to all order in λ_p, i.e., in the pump intensity. It corresponds to the free e-h case discussed above: when the Coulomb interaction is neglected, the problem reduces to a two-level system as one hole state ($-\mathbf{k}$) is only coupled to one electron state $\mathbf{k}$. In this case the e-pump photon coupling can be treated exactly (i.e., to all orders).

(ii) The problem becomes much more complicated if the exact Coulomb interaction is introduced. One may think of retaining only certain classes of diagrams (these are usually the ones we can sum up...). For example, one can keep renormalized ladder diagrams, using renormalized propagators and renormalized e-pump photon interaction as shown on Fig. 4. These diagrams can be nicely summed up to all orders in λ_p. Unfortunately it is completely inconsistent to keep only those diagrams. This is simply seen by considering the change induced by the pump beam at lowest order. It corresponds to processes having two λ_p interactions. One class of diagrams of the order of λ_p^2 is shown in Fig. 5(a). It belongs to the class shown in Fig. 4. However diagrams like the ones of Fig. 5(b) are also second order in the pump and are not included. Moreover, one should also consider at the same order, diagrams such as Fig. 5(c) which are completely different. They are made of two loops, which were disconnected in the absence of Coulomb interaction. The simplest version of these diagrams, shown on Fig. 5(d), corresponds to Coulomb interaction between excitons. It is a very usual approximation to neglect them in problems on excitons. This is indeed usually correct as the second e-h pair (or exciton), necessary for such an exciton interaction to take place, would be created by another test photon leading to terms in λ_T^4, negligible for a weak test. On the opposite, in the optical Stark effect, diagrams like 5(d) are exactly of the same order, namely, $\lambda_T^2\lambda_p^2$, as the other diagrams producing an exciton shift.

From the above discussion, we conclude that Coulomb interaction between excitons enters crucially in the response to a test beam. We also conclude that the effect of the pump beam, to lowest order, comes from processes where two e-h pairs interact so that true biexcitonic states play a key role in the exciton shift. As the correct treatment of Coulomb interaction between two e-h pairs is obviously linked to the knowledge of biexcitonic eigen-

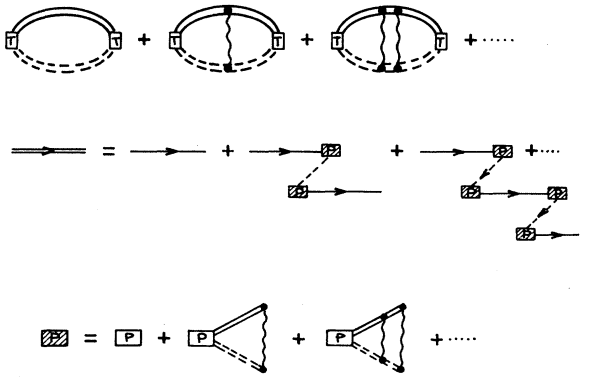

FIG. 4. Skeleton diagrams for the response function in the presence of Coulomb interaction and pump photon, with dressed propagators and pump vertex corrections.

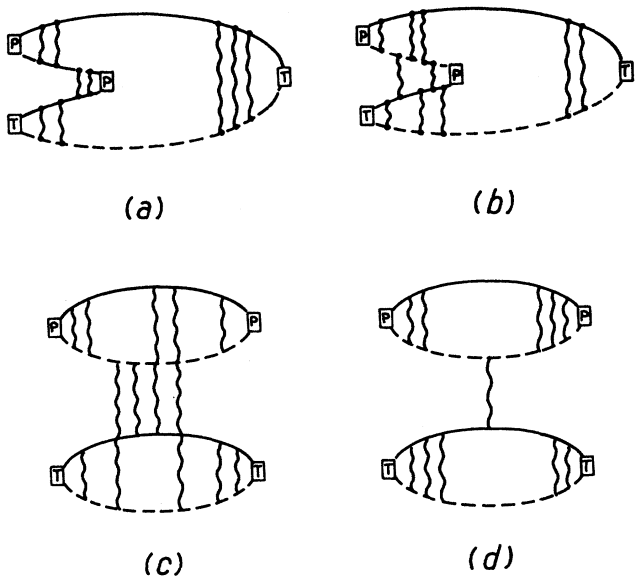

FIG. 5. (a) Typical diagram of the class represented in Fig. 4 to lowest order in pump intensity. (b) Analogous diagram not included in this class. (c) Typical diagram with two interacting excitons not included in this class. (d) Simplest diagram with two interacting excitons.

states, (i.e., the solution of the hydrogen molecule like Hamiltonian with its bound and unbound states), clearly the diagrammatic approach is of no help for that. As for the bare exciton absorption, where diagrams are not really useful, the diagrammatic approach is not the simplest way to calculate the excitonic shift in the optical Stark effect. It is better to assume that biexcitonic states are known and perform a simple perturbation theory as done above. Note, however, that one advantage of the diagrammatic approach is to immediately get rid of the volume infinite terms by retaining only connected diagrams.

VIII. STATE OF THE ART

The optical Stark effect of the exciton has first been observed experimentally. At that time, there was no appropriate theory for semiconductors and the observed blue shift of the exciton has been interpreted in terms of the dressed-atom picture, well known in atomic physics. As developed above, this picture is in fact totally valid at large detuning, as in this limit the Coulomb interaction plays no role. It has been found experimentally that at constant detuning, the excitonic shift varies linearly with the laser intensity although this is no longer valid for the highest experimental intensities where the variations appear sublinear. It has also been shown that the shift variation is consistent with an Ω_1^{-1} behavior. However the experiments are not yet precise enough to allow the observation of a detuning variation such as the one appearing in our prefactor $(2+\alpha+\beta-\gamma)$. Although obtained from experiments done under femtosecond laser excitations, the above results appear consistent with theoretical results based on a steady-state approach. Finally the red shift induced at the biexcitonic resonance has not yet been observed for technical reasons which hopefully will be overcome.

We now turn to a comparison of our work with other theoretical approaches. Leaving apart all those dealing with the ultrashort pulse aspect of the problem, one mainly has to compare our work with the Schmitt-Rink and Chemla (SRC) theory[4] and the various improved extensions.[7,11–13] They are all based on an Hartree-Fock treatment of the Coulomb interaction from the start. This approximation has the advantage to produce a Hamiltonian having only bilinear products of electron and hole operators. One can then, in principle, treat the electron-photon coupling exactly (i.e., not only as a perturbation) but the corresponding calculation is actually not carried out. Instead SRC's final result corresponds only to a shift to lowest order in the pump intensity. Such a result could have been obtained much more simply using perturbation theory from the start. Moreover, as we have shown above, the use of perturbation theory for the electron-photon coupling allows to treat Coulomb interaction *exactly* and not only in Hartree Fock. This is quite important, as once Coulomb interaction is treated within the Hartree-Fock approximation, there is no hope to get any bound biexcitonic molecule and no possibility of red shift induced by it. More precisely one cannot find our term γ, at all. Let us stress again that γ is essential not only when the biexciton is bound but also when it is unbound as it is, together with β, the dominant term at small detuning.

The final result of SRC corresponds only to our term $2+\alpha$ taken in the *small* detuning limit. First this result is claimed to explain experimental data taken at *large* detuning. Moreover, even at small detuning the leading terms in the shift do not come from α, but from β and γ. The term β which corresponds to Coulomb interaction between excitons has been dropped by SRC, probably on the ground that it is usually a good approximation to neglect this interaction for problems on excitons. We have extensively shown why this approximation cannot be valid for the optical Stark shift. Recently Zimmerman[11] has identified our term β at a formal stage, in the work of SRC [Eq. (51) in Ref. 4]. However in order to do that, he seems to have dropped the last term of Eq. (51) in

$$\lim_{q\to 0}\left[\mathbf{q}\cdot\frac{\partial\psi_{\mathbf{k}}}{\partial\mathbf{k}}\right]2V_q\left[\mathbf{q}\cdot\frac{\partial\psi^*_{\mathbf{k}'}}{\partial\mathbf{k}'}\right]\Big/(1-2n_{\mathbf{k}'})\ .$$

This strange term cancels only for $1S$ (or even-parity) excitons. We do not see its meaning in the general case, and our theory does not produce such a term.

As a physical interpretation, SRC have invoked a similarity with Bose condensation to explain the optical Stark effect of the exciton. We explain it instead in terms of a coupling between the exciton and all biexcitonic states. More precisely, we have shown that the excitonic shift can be understood as a measure of the interactions (statistical or Coulomb) between the two e-h pairs forming the biexcitonic states. We think that the idea of Bose condensation is somewhat misleading: in the optical Stark effect the coherence is trivial as it comes from the

pump-photon coherence. It is imposed externally in contrast with the usual spontaneous (thermal) Bose condensation.

Finally we find it quite important to stress that the dressed-atom picture is completely valid at large detuning, even if the first corrective term in $4(\varepsilon_1/\Omega_1)^{1/2}$, coming from α, is already sizeable for $\Omega_1=10\varepsilon_1$. The physical understanding of why the dressed-atom picture is valid, is in fact very instructive as it led us to easily predict the polarization effects. This large detuning limit, which was not shown in the original work of SRC, has been recovered by R. Zimmermann.

IX. CONCLUSIONS

In this paper we have shown the following.

(1) The optical Stark shift of the exciton is due to a coupling between the exciton and all biexcitonic states, bound and unbound.

(2) The shift can be understood as a measure of the interactions between excitons or better between the two e-h pairs forming the biexcitonic states.

(3) These interactions are of two kinds: Coulomb interaction which gives the leading terms at small detuning and statistical interaction (i.e., Pauli exclusion) which dominates at large detuning.

(4) At large detuning, the shift reduces to the (two-level) dressed-atom value, as in this limit the Coulomb interaction is negligible.

(5) In materials having a stable biexcitonic molecule, the exciton line, which blue shifts as in any material at large detuning, will red shift close to the two-photon (pump plus probe) absorption threshold.

ACKNOWLEDGMENTS

We wish to thank C. Benoit à la Guillaume, D. Hulin, and M. Joffre for very stimulating discussions.

APPENDIX A: PHOTON MOMENTUM NONZERO VALUE

We take into account here the nonzero value of the photon momentum. Even if the final expression of the excitonic shift does not depend on the precise value of the photon momentum, the form of the early stage of the calculation is modified if one includes a nonzero momentum value.

The exciton Stark effect is observed using pump-probe experiments. In such an experiment two different photons are present in the sample, with different energies and wave vectors. Probe photons produce transition between vacuum $|0\rangle$ and the lowest exciton states $|X_{1\mathbf{q}'}\rangle$, which have the same translational momentum $\mathbf{q}'$ as the probe photon. Pump photons modify both states, $|0\rangle$ and $|X_{1,\mathbf{q}'}\rangle$. The vacuum is coupled to the N excitonic states $|X_{i\mathbf{q}}\rangle$, $\mathbf{q}$ being the pump-photon momentum. However as $\mathbf{q}\neq\mathbf{q}'$, these pump photons do not couple the state $|X_{i\mathbf{q}'}\rangle$ back to the vacuum, as it appears in the second term of Eq. (8) for the shift. They only couple $|X_{1\mathbf{q}'}\rangle$ to the biexcitonic states $|XX_{n,\mathbf{q}'+\mathbf{q}}\rangle$.

In the simple large detuning limit, where one can think in terms of free e-h pairs, Pauli exclusion implies that there are only $N-2$ biexcitonic states entering in the coupling (instead of $N-1$ as for $\mathbf{q}=\mathbf{q}'=0$): indeed the e and h momenta $\mathbf{k}'+\mathbf{q}'/2, -\mathbf{k}'+\mathbf{q}'/2$ are already occupied in the original e-h pair created by the probe photon. The pump photon creates a second e-h pair $\mathbf{k}+\mathbf{q}/2$, $-\mathbf{k}+\mathbf{q}/2$. Pauli exclusion imposes $\mathbf{k}'+\mathbf{q}'/2\neq\mathbf{k}+\mathbf{q}/2$ and $-\mathbf{k}'+\mathbf{q}'/2\neq-\mathbf{k}+\mathbf{q}/2$. This excludes two values of $\mathbf{k}$ if $\mathbf{q}\neq\mathbf{q}'$ (and only one value if $\mathbf{q}=\mathbf{q}'=0$). Taking into account the vacuum and exciton changes, one finds for the excitonic shift at large detuning $[N-(N-2)]\lambda^2/\Omega_1=2\lambda^2/\Omega_1$, i.e., the usual dressed-atom limit. We recall that the coefficient 2 appears in a different way if $\mathbf{q}=\mathbf{q}'=0$: the exciton is coupled to the vacuum (1 state) and to $(N-1)$ biexcitonic states, as only one value of $\mathbf{k}$ is excluded for $\mathbf{q}=\mathbf{q}'$. The vacuum being still coupled to N excitonic states, one finds for the shift $[N+(1)-(N-1)]\lambda^2/\Omega_1$, i.e., again $2\lambda^2/\Omega_1$.

The above argument shows very simply that at large detuning the excitonic shift does not depend on the photon momentum, even if the intermediate calculations are somewhat different for $\mathbf{q}=\mathbf{q}'=0$ and $\mathbf{q}\neq\mathbf{q}'$. Let us outline how indeed one recovers for $\mathbf{q}\neq\mathbf{q}'$ the expression (23) for the excitonic shift as this expression has basically been obtained for $\mathbf{q}=\mathbf{q}'=0$.

In a pump-probe experiment, one measures the energy difference between the states $|0\rangle$ and $|X_{1\mathbf{q}'}\rangle$ induced by the e-pump photon coupling Eq. (6). As $X_{1\mathbf{q}'}$ is not coupled to the vacuum, the excitonic shift contains only two terms: Eq. (18) is replaced by

$$\delta\Omega_1=\left\langle X_{1\mathbf{q}'}\left|U\frac{1}{\Omega_1-H}U^\dagger\right|X_{1\mathbf{q}'}\right\rangle+\left\langle 0\left|U\frac{1}{H}U^\dagger\right|0\right\rangle . \quad \text{(A1)}$$

Equation (A1) is then transformed as Eq. (18). This leads to Eq. (A2) instead of Eq. (19):

$$\delta\Omega_1=\frac{1}{\Omega_1}\left[-\langle X_{1\mathbf{q}'}|UU^\dagger|X_{1\mathbf{q}'}\rangle+\langle 0|UU^\dagger|0\rangle+\left\langle X_{1\mathbf{q}'}\left|U\frac{2\Omega_1-H}{\Omega_1-H}U^\dagger\right|X_{1\mathbf{q}'}\right\rangle+\left\langle 0\left|U\frac{\Omega_1-H}{H}U^\dagger\right|0\right\rangle\right] . \quad \text{(A2)}$$

The first two terms of Eq. (A2) are detuning independent. They give also 2. This is seen by noting that $U|0\rangle=0$ and $U|X_{1\mathbf{q}'}\rangle$ is also zero, as U can only destroy an e-h pair with total momentum $\mathbf{q}$. This gives for the first two terms of Eq. (A2) the same expression as for Eq. (19), namely, $\langle 0|B_{1\mathbf{q}'}[U^\dagger,U]B^\dagger_{1\mathbf{q}'}-[U^\dagger,U]|0\rangle$. Using the same commutator Eq. (11), it is then easy to verify that this term is just 2.

The form of the last two terms of Eq. (A2) is exactly the one of Eq. (19). This detuning dependent part is calculated exactly in the same way. In particular this gives for α

$$\alpha=\sum_i \frac{\Omega_{1q'}-\Omega_{iq}}{\Omega_{iq}}\alpha_{i,q-q'} ,$$

$$\alpha_{i,q}=\sum_{k,k'}\phi^*_{ik'}(\phi_{ik+q/2}+\phi_{ik-q/2})|\phi_{1k}|^2 .$$

One checks that $\alpha_{i,q-q'}$ is exactly α_i for $q=q'$. As the photon momenta are much smaller than the electron characteristic momentum, the calculated value of α is essentially not affected by the nonzero value of q and q'. A similar conclusion is obtained for β and γ.

APPENDIX B: CALCULATION OF THE OPERATOR $C_1^\dagger$

The operator $C_1^\dagger$ is defined in Eq. (20). Its calculation relies on the calculation of the commutator $[H,B_1^\dagger]$. $B_1^\dagger$ is given in Eq. (12). The Hamiltonian H of the electronic system is composed of a kinetic part H_{kin} and a Coulomb interaction between two electrons V_{ee}, two holes V_{hh}, an electron and a hole V_{eh}. From

$$[b_k^\dagger b_k,B_{k'}^\dagger]=B_k^\dagger\delta_{kk'} \tag{B1}$$

one immediately deduces that

$$[H_{kin},B_1^\dagger]=\sum_k(\varepsilon_{ek}+\varepsilon_{hk})\phi_{1k}B_k^\dagger , \tag{B2}$$

where ε_{ek} and ε_{hk} are the free e and h energies. From

$$[b_{k+q}^\dagger b_{k'-q}^\dagger b_{k'}b_k,B_1^\dagger]=2\phi_{1k}b_{k+q}^\dagger b_{k'-q}^\dagger b_{k'}c_{-k}^\dagger \tag{B3}$$

it is easy to find that

$$[V_{ee},B_1^\dagger]=\sum_{k,k',q}V_q\phi_{1k}b_{k+q}^\dagger c_{-k}^\dagger b_{k'-q}^\dagger b_{k'} \tag{B4}$$

the commutator $[V_{hh},B_1^\dagger]$ being quite similar. In the last commutator, $[V_{eh},B_1^\dagger]$, appears a different term as V_{eh} is basically the interaction producing the exciton. One precisely finds

$$\begin{aligned}[V_{eh},B_1^\dagger]=&\sum_{k,q}V_q\phi_{1,k+q}B_k^\dagger\\&+\sum_{k,k',q}V_q\phi_{1k}b_{k+q}^\dagger c_{-k}^\dagger c_{-k'-q}^\dagger c_{-k'}\\&+\sum_{k,k',q}V_q\phi_{1k+q}b_{k+q}^\dagger c_{-k}^\dagger b_{k'-q}^\dagger b_{k'} .\end{aligned} \tag{B5}$$

Going back to the commutator $[H,B_1^\dagger]$, one finds that the first term of Eq. (B5) added to the commutator (B2) produces exactly $\Omega_1 B_1^\dagger$. This is easily seen as

$$\sum_k\left[(\varepsilon_{ek}+\varepsilon_{hk})\phi_{1k}-\sum_q V_q\phi_{1,k+q}\right]B_k^\dagger=\sum_k\Omega_1\phi_{1k}B_k^\dagger=\Omega_1B_1^\dagger \tag{B6}$$

due to the property of ϕ_{1k}, solution of the exciton Schrödinger equation. It is then straightforward to get, from the remaining terms of $[H,B_1^\dagger]$, the value of $C_1^\dagger$ obtained in Eq. (21).

APPENDIX C: CALCULATION OF α

The first correction, α, to the large detuning shift is given by Eq. (27). Let us first calculate α_i defined in Eq. (28). Introducing the excitonic wave functions in r space, Eq. (28) reads

$$\alpha_n=2\phi_n^*(0)\int d^3r_1\,d^3r_2\,\phi_n(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\phi_1(\mathbf{r}_1-\mathbf{r}_2) . \tag{C1}$$

The integration over $\mathbf{r}_2$ is easily performed using $\phi_1(r)=(\pi a_0^3)^{-1/2}e^{-r/a_0}$ and bipolar variables, r_2 and $r_2'=|\mathbf{r}_1-\mathbf{r}_2|$. One finds

$$\begin{aligned}&\int d^3r_2\,\phi_1(\mathbf{r}_2)\phi_1(\mathbf{r}_1-\mathbf{r}_2)\\&\quad=\frac{1}{\pi a_0^3}\frac{2\pi}{r_1}\int_0^\infty r_2\,dr_2\,e^{-r_2/a_0}\int_{|r_1-r_2|}^{r_1+r_2}r_2'\,dr_2'e^{-r_2'/a_0} ,\\&\quad=e^{-r_1/a_0}\left[\frac{1}{3}\frac{r_1^2}{a_0^2}+\frac{r_1}{a_0}+1\right] .\end{aligned} \tag{C2}$$

α_i then becomes a first-order integral

$$\alpha_n=8\pi a_0^3\phi_n^*(0)\int_0^\infty\rho^2\left[\frac{\rho^2}{3}+\rho+1\right]e^{-\rho}\phi_n(a_0\rho)d\rho . \tag{C3}$$

One notes that $\alpha_n\neq0$ for $\phi_n^*(0)\neq0$, i.e., only for excitonic states with S symmetry. The exact excitonic wave function is given in terms of the degenerate hypergeometric function[21]

$$\phi_n(r)=(4\pi)^{-1/2}C_n e^{-r/na_0}F(-n+1,2,2r/na_0) \tag{C4}$$

n being an integer for bound states while $n=-i/ka_0$ for diffusion states. C_n is a normalization factor. The wave function $\phi_n(r)$ can be written as well[21] using an integral representation for the degenerate hypergeometric function:

$$\begin{aligned}\phi_n(r)=&(4\pi)^{-1/2}C_n\frac{na_0}{4i\pi r}\\&\times\int_C dt\,e^{2rt/na_0}(t+\tfrac{1}{2})^{-n-1}(t-\tfrac{1}{2})^{n-1} ,\end{aligned} \tag{C5}$$

where the contour C goes counterclockwise around the cut between $t=-\frac{1}{2}$ and $t=\frac{1}{2}$.

One can then calculate α_n by integrating over ρ in Eq. (C3). Making use of the integral representation Eq. (C5), this leads to

$$\alpha_n=\frac{8\pi a_0^3}{(4\pi)^{1/2}}\phi_n^*(0)C_n\frac{n}{2}\frac{1}{2i\pi}\int_C dt(t+\tfrac{1}{2})^{-n-1}(t-\tfrac{1}{2})^{n-1}\left[\frac{1}{(1-2t/n)^2}+\frac{2}{(1-2t/n)^3}+\frac{2}{(1-2t/n)^4}\right] . \tag{C6}$$

The calculation is completed by extending the contour to infinity and taking into account the contribution of the pole at $t=n/2$ (this implies $n\neq1$). The first term in the large parentheses gives zero, while the two others give, respectively,

$-4n^3(n-1)^{n-2}/(n+1)^{n+2}$ and $-\frac{16}{3}n^5(n-1)^{n-3}/(n+1)^{n+3}$.

Alternatively, the integral

$$\int_0^\infty e^{-\lambda z} z^\nu F(\alpha,\gamma,qz)=\Gamma(\nu+1)\lambda^{-\nu-1}(1-q/\lambda)^{-\alpha}F(\alpha,\gamma-\nu-1,\gamma,q/(q-\lambda)) \tag{C7}$$

obtained from Ref. (21), allows to calculate α_n for $n\neq 1$. One finds, since $\phi_n(0)=(4\pi)^{-1/2}C_n$:

$$\alpha_n=4a_0^3C_n^2\left[\frac{n-1}{n+1}\right]^{n-1}\left[\frac{n}{n+1}\right]^5\left[4F\left[-n+1,-3,2,\frac{2}{1-n}\right]+\left[\frac{n+1}{n}\right]F\left[-n+1,-2,2,\frac{2}{1-n}\right]+\left[\frac{n+1}{n}\right]^2F\left[-n+1,-1,2,\frac{2}{1-n}\right]\right] \tag{C8}$$

From the expansion of the hypergeometric function $F(\alpha,\beta,\gamma,z)$, one easily checks that the three F entering in α_n are finite polynomials, β being a negative integer. More precisely the first F is $-n(n+1)/3(1-n)^2$. The second one is $(1+n)/3(1-n)$ while the third one is zero.

Finally we obtain for α_n, the compact expression

$$\alpha_n=4a_0^3C_n^2\frac{(n-1)^{n-3}}{(n+1)^{n+3}}n^4(1-\tfrac{7}{3}n^2),\quad n\neq 1\ . \tag{C9}$$

(1) *For bound states,* n is an integer and $C_n=2/(a_0n)^{3/2}$ so that

$$\alpha_n^{(\text{bound})}=16n\frac{(n-1)^{n-3}}{(n+1)^{n+3}}(1-\tfrac{7}{3}n^2),\quad n\neq 1\ . \tag{C10}$$

This gives for the $\alpha_n^{(\text{bound})}$ a rapidly converging series since $\alpha_2=-800/9^3$, $\alpha_3=-15/4^3$, while α_1 is easily calculated directly from Eq. (C3). One finds $\alpha_1=7$.

(2) *For diffusion states,* $n=-i/ka_0=-i/K$ and $C_k=2[K/(1-e^{-2\pi/K})a_0^3]^{1/2}$. This gives

$$\alpha_k^{(\text{unbound})}=-16\frac{K}{1-e^{-2\pi/K}}\frac{K^2+\frac{7}{3}}{(K^2+1)^3}e^{-2\arctan K/K} \tag{C11}$$

since $[(i-K)/(i+K)]^{i/K}=\exp(-2\arctan K/K)$. For large K, one finds $\alpha_K\approx -8/\pi K^2$. Using this value of α_K, one can deduce the large detuning behavior of α, which comes from the large K diffusion states. From the definition (27) of α, one finds, as $\Omega_K=\hbar^2\mathbf{k}^2/2m=K^2\varepsilon_1$,

$$\alpha^{(\text{large})}\approx\sum_{\text{large } k}\frac{\Omega_1-\Omega_k}{\Omega_k}\alpha_k=\int^\infty dK\frac{-K^2}{K^2+\Omega/\varepsilon_1}\frac{-8}{\pi K^2}$$
$$\approx 4(\varepsilon_1/\Omega)^{1/2}\ . \tag{C12}$$

APPENDIX D: CALCULATION OF β_{11}

From the definition Eq. (33) of β_{11} and the explicit value of $\phi_1(\mathbf{r})$ given in Appendix C one can write β_{11} as

$$\beta_{11}=(8/\pi^3)\varepsilon_1(I_1-I_2)\ , \tag{D1}$$

where the two quantities to be calculated, I_1 and I_2, are

$$I_1=\int d^3r\,d^3r'\,d^3\rho\,r^{-1}e^{-|\mathbf{r}-\boldsymbol{\rho}|-|\mathbf{r}'-\boldsymbol{\rho}'|-r-r'}\ , \tag{D2}$$

$$I_2=\int d^3r\,d^3\rho\,d^3\rho'\,r^{-1}e^{-|\mathbf{r}-\boldsymbol{\rho}|-|\mathbf{r}-\boldsymbol{\rho}'|-\rho-\rho'}\ . \tag{D3}$$

We first consider I_1. The integration over $\mathbf{r}$ and $\mathbf{r}'$ are easily performed using bipolar variables, as in Appendix C. One finds, respectively, $\pi e^{-\rho}(\rho+1)$ and $\pi e^{-\rho}(\rho^2/3+\rho+1)$. Performing similarly the integration over $\mathbf{r}$ and $\mathbf{r}'$ in I_2, one obtains for the difference I_1-I_2

$$I_1-I_2=4\pi^3\int_0^\infty r(r^2/3+r+1)(2r^2/3-1)e^{-2r}dr\ . \tag{D4}$$

This last integral, easily calculated, gives finally $I_1-I_2=13\pi^3/6$, leading to $\beta_{11}=\frac{52}{3}\varepsilon_1$.

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