Excitonic Stark Shift: A Coupling to "Semivirtual" Biexcitons

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The optical Stark shift of the exciton is due to a coupling between the exciton and "semivirtual" biexcitonic states (bound and unbound). We show that at large detuning the excitonic shift is the same as the "dressed atom" blue shift. We predict that at small detuning the exciton-exciton interaction plays an important role and leads to an excitonic red shift at the two-photon absorption threshold when the molecular biexciton is stable.

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Two years ago, Hulin and co-workers discovered experimentally[1] the optical Stark effect in semiconductors: When a direct-gap material is irradiated by a pump laser beam in the transparency region, the exciton line undergoes a blue shift. The energy change depends on the pump laser characteristics (intensity and photon energy), but the most interesting property of the optical Stark effect is that the blue shift lasts only as long as the pump pulse, allowing optical gates as short as femtoseconds. This effect is crucially linked to the fact that the pump photons are in the transparency region where no real absorption occurs. In this Letter, (1) we present the origin of the optical Stark effect: The excitonic shift, as measured by a test beam, arises from the coupling between the exciton and all "semivirtual" biexcitonic states (bound or unbound); these virtual states are made from one real electron-hole (e-h) pair created by a test photon and one virtual e-h pair created by a pump photon. (2) We show why and when the optical Stark shift is different in atoms[2] and semiconductors: The difference comes from the Coulomb interaction and appears only when the detuning is small compared with the binding energy. (3) We predict a new effect: The excitonic blue shift observed at large detuning will become a red shift at small detuning, if the molecular biexciton is stable.[3]

First let us emphasize that the typical pump-laser intensity used in these experiments[1] can be treated as a small perturbation, since e-h bound states do exist. For a really intense pulse the excitons disappear.[4] As we are interested in the *excitonic* shift, this Letter deals with the low-laser-intensity limit, in which the shift can be viewed as the effect on the exciton energy of *one* additional virtual e-h pair created by the nonresonant pump beam.

Origin of the exciton Stark shift.— The various possible e-h pair eigenstates of the bare Hamiltonian H, without the pump beam, are the vacuum $|0\rangle$ with energy $E_0=0$, the excitons $|X_i\rangle$ with energy ω_{X_i}, the biexcitons $|XX_n\rangle$ with energy $2\omega_{XX_n}$, and so on. We loosely call both bound and unbound e-h pairs "excitons." Similarly we call all two e-h pair states, bound and unbound, "biexcitons." When the pump beam, with frequency ω_p, is turned on, it induces, in the rotating frame,[2] a perturbation $W=\lambda U+\lambda^* U^\dagger$ on H, where[5]

$$U^\dagger=\sum_k a_k^\dagger b_{-k}^\dagger=\sum_{ij}\phi_i^*(\mathbf{k})B_i^\dagger$$
$$=V^{1/2}\sum_i f_i^*(\mathbf{r}=0)B_i^\dagger, \tag{1}$$

and λ^2 is proportional to the laser intensity. V is the sample volume, $a_k^\dagger$ and $b_{-k}^\dagger$ are the e and h creation operators, and $B_i^\dagger$ creates an exciton $|X_i\rangle$ with wave function $\phi_i(\mathbf{k})$ [or $f_i(\mathbf{r})$].

In the rotating frame, the unperturbed exciton and biexciton energies are respectively $E_{X_i}=\omega_{X_i}-\omega_p$ and $E_{XX_n}=2(\omega_{XX_n}-\omega_p)$. In the presence of W, the vacuum energy becomes E_0' and the lowest exciton energy becomes E_{X_1}', so that the shift, $\delta\omega_{X_1}=(E_{X_1}'-E_0')-E_{X_1}$, is from perturbation theory[6] (valid for $\lambda\ll E_{X_1}$)

$$\delta\omega_{X_1}=\lambda^2\left(\sum_n\frac{|\langle XX_n|U^\dagger|X_1\rangle|^2}{E_{X_1}-E_{XX_n}}+\frac{|\langle 0|U|X_1\rangle|^2}{E_{X_1}}-\sum_i\frac{|\langle X_i|U^\dagger|0\rangle^2}{-E_{X_i}}\right). \tag{2}$$

This is just the excitonic Stark shift. In particular, if the Coulomb interaction is neglected, the sums in Eq. (2) (easily performed since the eigenfunctions are plane waves) give $\delta\omega_{X_1}=2\lambda^2/E_{X_1}$, which is exactly the low-intensity, or large-detuning, value of the optical Stark shift for two-level atoms. Similarly, if the detuning E_{X_1} is very large, all the denominators in Eq. (2) are effectively equal to E_{X_1}. The sums over the exciton and biexciton states are performed through closure relations and one again finds $\delta\omega_{X_1}=2\lambda^2/E_{X_1}$.

There is practical difficulty with Eq. (2), standard in many-body perturbation theory: All three terms separately diverge with the volume of the sample V. It is physically obvious, however, that the excitonic shift should not depend on V. Because the last two terms, which describe the vacuum-exciton coupling, are exactly proportional[7] to V, they must

disappear completely from the shift, canceled by similar terms in the first sum of Eq. (2), i.e., the exciton-biexciton coupling. The cancellation of diverging terms corresponds to the elimination of disconnected diagrams in a diagrammatic calculation of the shift.

This observation leads to a very simple understanding of the excitonic Stark shift: It results entirely from the coupling between the exciton and all the *biexcitonic* states. We now proceed to calculate the shift and demonstrate that it is independent of the sample volume V.

Calculation of the shift.—As the exact biexcitonic states are unknown, there is no hope to perform the first sum of Eq. (2) for all detuning. One gets rid of this problem by using the Brillouin-Wigner form of the perturbation theory. Equation (2) is strictly equivalent to

$$\delta\omega_{X_1}=\lambda^2[\langle X_1|U(E_{X_1}-H)^{-1}U^\dagger|X_1\rangle+\langle X_1|U^\dagger(E_{X_1}-H)^{-1}U|X_1\rangle+\langle 0|UH^{-1}U^\dagger|0\rangle]. \tag{3}$$

When we note that U couples $|X_1\rangle$ only to $|0\rangle$, and that $|X_1\rangle=B_1^\dagger|0\rangle$, it is easy to check that Eq. (3) becomes

$$\delta\omega_{X_1}=\frac{\lambda^2}{E_{X_1}}\left(\langle X_1|[B_1^\dagger,[U,U^\dagger]]|0\rangle+\langle X_1|U\frac{H-2E_{X_1}}{H-E_{X_1}}U^\dagger|X_1\rangle-\langle 0|U\frac{H-E_{X_1}}{H}U^\dagger|0\rangle\right). \tag{4}$$

The first term of Eq. (4) gives exactly $2\lambda^2/E_{X_1}$ which is just the large-detuning behavior, as $[U,U^\dagger]=\sum_k(1-a_k^\dagger a_k-b_k^\dagger b_k)$. Physically, this limit results from the fermionic aspect of the particles.

Let us now calculate the corrections to the large-detuning behavior [namely the last two terms of Eq. (4)] and identify their physical origin. In this aim, we find it convenient to introduce the operator $C_1^\dagger$, defined by $[H,B_1^\dagger]=E_{X_1}(B_1^\dagger+C_1^\dagger)$, which describes the Coulomb interaction between excitons, as will be seen below [Eqs. (9) and (11)]. The excitonic shift can then be written

$$\delta\omega_{X_1}=(2+\alpha+\beta-\gamma)\lambda^2/E_{X_1}. \tag{5}$$

α, defined from Eq. (6), comes from Pauli exclusion among the e-h pairs forming the excitons. β and γ, defined in Eqs. (8) and (10), come from the Coulomb interaction between excitons. All three corrections are strictly zero for noninteracting electrons and holes.

(α) Writing U in terms of the B_i's and using

$$\langle 0|B_mB_nB_p^\dagger B_q^\dagger|0\rangle=\delta_{mp}\delta_{nq}+\delta_{mq}\delta_{np}-2\sum\phi_m^*(k)\phi_n^*(k)\phi_p(k)\phi_q(k),$$

one finds

$$\alpha=\langle 0|U(1-B_1B_1^\dagger)[(E_{X_1}-H)/H]U^\dagger|0\rangle=\sum_i(E_{X_1}-E_{X_i})a_i/E_{X_i}, \tag{6}$$

$$a_i=2\sum_{kk'}\phi_i^*(k')\phi_i(k)|\phi_1(k)|^2 \tag{7}$$

(for noninteracting particles, the ϕ's are plane waves and $\alpha=0$). As the detuning E_{X_1} increases from 0 to ∞, α decreases from $\alpha_1-2=5$ (in 3D)[8] to 0. More precisely, for E_{X_1} much larger than the exciton binding energy $\epsilon_{X_1}=E_g-\omega_{X_1}$, the high-energy unbound states contribute dominantly to α, and one finds $\alpha\cong 4(\epsilon_{X_1}/E_{X_1})^{1/2}$. At large detuning, this is the leading correction to the two-level atom shift $2\lambda^2/E_{X_1}$.

(β) Employing the explicit form[8] of the interaction operator $C_1^\dagger$, one finds[9]

$$\beta=\langle 0|U(E_{X_1}/H)B_1C_1^\dagger(E_{X_1}/H)U^\dagger|0\rangle=E_{X_1}\sum_{ij}\beta_{ij}/E_{X_i}E_{X_j}, \tag{8}$$

$$\beta_{ij}=2f_j(0)f_i^*(0)\int V^{-1}d^3r\,d^3r'\,d^3\rho\,d^3\rho' f_j^*(\mathbf{r}'-\rho)f_1^*(\mathbf{r}-\rho')f_1(\mathbf{r}-\rho)f_i(\mathbf{r}'-\rho')$$
$$\times[v(\mathbf{r}-\rho')+v(\mathbf{r}'-\rho)-v(\mathbf{r}-\mathbf{r}')-v(\rho-\rho')], \tag{9}$$

where $v(\mathbf{r})$ is the Coulomb interaction. As in the case of α, only the excitonic wave functions are needed to calculate β. Since dimensionally $\beta_{11}\sim\epsilon_{X_1}$, one might expect β to behave as ϵ_{X_1}/E_{X_1}. This is indeed what is found for small detuning E_{X_1}, and so in this regime β dominates α. However, at large detuning, $\beta\sim(\epsilon_{X_1}/E_{X_1})^2$ as $C_1^\dagger U^\dagger|0\rangle=0$, and α dominates β.

(γ) In γ, one has to deal with the Hamiltonian H operating on two e-h pairs. Using the closure relation for biexcitons, one finds[9]

$$\gamma=\langle 0|U(E_{X_1}/H)C_1[E_{X_1}/(H-E_{X_1})]C_1^\dagger(E_{X_1}/H)U^\dagger|0\rangle=\sum_n[E_{X_1}/(E_{XX_n}-E_{X_1})]\,|\sum_i\gamma_{ni}/E_{X_i}|^2, \tag{10}$$

$$\gamma_{ni}=f_i^*(0)\int V^{-1}d^3r\,d^3r'\,d^3\rho\,d^3\rho' f_1(\mathbf{r}-\rho)f_i(\mathbf{r}'-\rho')V^{1/2}F_n(\mathbf{r},\mathbf{r}',\rho,\rho')$$
$$\times[v(\mathbf{r}-\rho')+v(\mathbf{r}'-\rho)-v(\mathbf{r}-r')-v(\rho-\rho')], \tag{11}$$

where F_n is the biexciton wave function. At large E_{X_1}, γ decreases as (ϵ_{X_1}/E_{X_1}),[4] since $C_1^\dagger U^\dagger|0\rangle=0$, and is negligible compared to α. At small detuning, if the molecular biexciton is stable,[3] the denominator $E_{XX_1}-E_{X_1}$ in γ gives rise to a *new resonance* at $E_{X_1}=2(\omega_{X_1}-\omega_{XX_1})$ which lies below the excitonic one $E_{X_1}=0$. At this resonance, $\omega_p+\omega_{X_1}=2\omega_{XX_1}$: A real biexciton is made from one pump photon ω_p and one test photon ω_{X_1}. Very close to this pump absorption threshold, perturbation theory in the degenerate subspace made of the exciton and the molecular biexciton gives

$$\delta\omega_{X_1}=-\lambda|\langle XX_1|U^\dagger|X_1\rangle|. \quad (12)$$

The exciton line undergoes a *red shift* as should be seen in materials having well-bound biexcitons. This red shift is already apparent in Eq. (2) if one considers the $(E_{X_1}-E_{XX_1})^{-1}$ pole.

When the molecular state is not stable, one should obtain in the same way a finite shift when $E_{X_1}\to 0$, but its precise value is much harder to obtain. As $0\cong E_{X_1}\cong E_{XX_1}\cong E_{XXX_1}\cong\cdots$ one should do degenerate perturbation theory in an infinite subspace made of the vacuum, the exciton, biexciton, triexciton, and so on, properly taking into account the Coulomb interaction. One again expects a limiting shift linear in λ, with a prefactor depending on the exciton-exciton interaction (the analog of the low-detuning shift 2λ of "dressed atoms").

Physical interpretation.—The blue shift is easy to understand at large detuning, as one can neglect the Coulomb interaction V_{Coul}. One free-electron level of the valence band is then coupled to only one free-electron level of the conduction band by the momentum-conserving laser interaction [Fig. 1(a)]. Thus the shift should be the same as for two-level atoms.[2] Since it mixes the conduction- and valence-band states, V_{Coul} is easiest to introduce if one speaks in terms of e-h pairs. Very naively, one can say that the vacuum is coupled to N exciton states while an exciton is only coupled to $N-1$ biexciton states, because of Pauli exclusion [Fig. 1(b)]. The two missing states (one for the electron and one for the hole) give the factor 2 in the blue shift $2\lambda^2/E_{X_1}$. This simple argument ignores the detailed structure of the exciton which adds the correction α. The Coulomb coupling between excitons pushes down the exciton energy, and if there is a level below the others, such as the molecular biexciton, its contribution will dominate at low detuning, inducing finally a *red shift* [Fig. 1(c)].

The importance of exciton-exciton interaction is illustrated in Figs. 1(d)–1(g). Without the pump beam, a test photon creates an e-h pair which interacts through V_{Coul} and recombines giving back a test photon: This is the bubble of Fig. 1(d). One way this process is affected by a pump beam is shown in Fig. 1(e): The pump photon creates a second e-h pair and these two pairs recombine in a crossed way. This class of diagrams summed to all orders in λ, for $V_{\text{Coul}}=0$, gives the "dressed atom" exact result. V_{Coul} also couples the two disconnected bubbles of diagram 1(f). This diagram, which corresponds to Coulomb interaction between excitons, does not appear in usual exciton problems, as the second e-h pair would also be created by a test photon, making the contribution of order λ_T^4 and so negligible. In the optical Stark effect, however, diagrams 1(e) and 1(f) [or 1(g)] are of the same order, i.e., $\lambda_T^2\lambda_P^2$, so that the Coulomb interaction between excitons cannot be neglected. Since only diagrams 1(f) and 1(g), which describe the effect of the biexcitonic states on the exciton, enter the exciton shift, the diagrammatic analysis confirms the origin of the shift explained above.

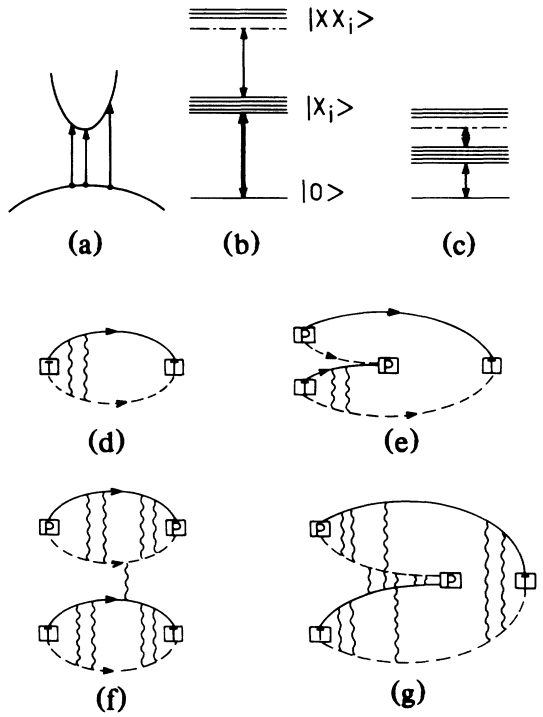

FIG. 1. Transition (a) from the valence to the conduction band or (b),(c) from the vacuum to exciton and biexciton states at (b) large and (c) small detuning. (d)–(g) Electron-hole (electron, solid line; hole, dashed line) pairs created by a test (T) or pump (P) photon. The wavy line is the Coulomb interaction.

State of the art.—Experimentally it has been shown[1,10] that at large detuning the excitonic shift is indeed proportional to λ^2/E_{X_1}. Because of uncertainty in the laser intensity, there is no precise determination of the numerical prefactor. Clean measurements of the saturation value of the shift for small E_{X_1} are difficult because the finite exciton linewidth produces real absorption. However, an excitonic *red shift*, induced by the exciton-exciton interaction, should be observable in materials having stable molecular biexcitons.

A theory of the exciton Stark shift has been previously

proposed by Schmitt-Rink and Chemla.[11] They attributed the effect to a Bose condensate of virtual excitons and insisted on the "quite different character" of the Stark shift in "dressed atoms" and semiconductors which they assigned to the fermionic aspect of the particles. We have shown that Bose condensation is not the origin of the shift nor Fermi statistics the reason for the difference. Their final result $2\lambda^2 f_1^2(0)/N_S E_{X_1}$ is nothing other than the small-E_{X_1} limit of our $(2+\alpha)\lambda^2/E_{X_1}$, which we have shown not to be the leading term. In effect they neglected the Coulomb interaction between excitons which is a good approximation in usual exciton problems but not in this one. The exciton Stark shift comes from the coupling between the exciton and all the biexcitonic states (bound or unbound).

If one neglects the Coulomb interaction V_{Coul}, one finds the "dressed atom" blue shift, which increases, from $2\lambda^2/E_{X_1}$ to 2λ, with decreasing detuning E_{X_1}.

When E_{X_1} is large compared with the exciton binding energy, V_{Coul} does not play any role and one again finds the "dressed atom" blue shift $2\lambda^2/E_{X_1}$, which can be understood as coming from Pauli exclusion among the e-h pairs making up the biexcitons.

For small E_{X_1}, V_{Coul} induces two effects: It produces a bound state, the exciton, which (because it is not a true boson) adds a term α to the blue shift. V_{Coul} also produces Coulomb interactions *between* excitons. This leads, in material having a stable molecular biexciton, to an excitonic red shift close to the two-photon absorption threshold $\omega_p + \omega_{X_1} = 2\omega_{XX_1}$.

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[2]C. Cohen-Tannoudji, Metrologia **13**, 161 (1977); C. Cohen-Tannoudji, and S. Reynaud, J. Phys. B **10**, 345 (1977).

[3]And if the pump and test beam polarizations are such that the molecular state can be made from them.

[4]As observed experimentally, D. Hulin, private communication.

[5]For simplicity we neglect here the (s,p) symmetry of the carriers. The very interesting polarization effects induced by it, as well as the details of the present work, will be presented elsewhere.

[6]Coupling to triexcitons is higher order in λ.

[7]Since $|X_i\rangle = B_i^\dagger|0\rangle$, $|\langle X_i|U^\dagger|0\rangle|^2 = V|f_i(0)|^2$.

[8]The exciton Stark shift exists in bulk materials as well as in quantum wells. The presented theory is basically unmodified in 2D.

[9]The V^{-1} appearing in Eqs. (9) and (11) cancels the translational invariance of the system. The $V^{1/2}$ in Eq. (11) cancels the standard normalization factor of the biexcitonic wave function.

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