Signature of electromagnetic quantum fluctuations in exciton physics

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Abstract – Quantum fluctuations of the electromagnetic field are known to produce the atomic Lamb shift. We here reveal their iconic signature in semiconductor physics, through the blue-shift they produce to optically bright excitons, thus lifting the energy of these excitons above their dark counterparts. The electromagnetic field here acts in its full complexity: in addition to its longitudinal part via interband virtual Coulomb processes, the transverse part—which has been missed up to now—also acts via resonant and nonresonant virtual photons. These two parts beautifully combine to produce a bright exciton blue-shift independent of the exciton wave vector direction. Our work readily leads to a striking prediction: long-lived excitons must have a small bright-dark splitting. Although the analogy between exciton and hydrogen atom could lead us to see the bright exciton shift as a Lamb shift, this is not fully so: the Lamb shift comes entirely from virtual photons, whereas the Coulomb interaction also contributes to the exciton shift through the so-called “electron-hole exchange”.

Introduction. – Semiconductor excitons [1–3] are electron-hole pairs correlated by Coulomb attraction. Due to their internal degrees of freedom, excitons couple differently to light. Since photons have no spin, optically bright excitons are in a spin-singlet state \( S = 0; S_z = 0 \). Importantly, these excitons coexist with optically dark excitons in spin-triplet states \( S = 1; S_z = \pm 1 \) produced by carrier exchange between two bright excitons [3–5].

The coexistence of optically bright and dark excitons has numerous consequences on fundamental and applied physics. The seminal experiments on GaAs bulk [6] and quantum well [7–9] samples established that dark excitons have a lower energy than bright excitons, despite the fact that electrons and holes are spin-degenerate. As a result, all collective effects that rely on the lowest energy states, like Bose-Einstein condensation [10–13], are inevitably driven by dark excitons. In the emerging field of Excitonics [14], low energy and poor coupling to photons make dark excitons quite attractive: in quantum dots, dark states with long lifetime have recently allowed one to demonstrate photonic cluster states [15]. Still, dark states can play a detrimental role when bright excitons are used for processing optical information in semiconductor devices; the buildup of dark states out of bright states limits the device fidelity and optical efficiency [16,17].

So far, the bright-dark exciton splitting has been ascribed to the so-called “electron-hole exchange” through “short-range” and “long-range” Coulomb processes [18–21]. This understanding based on the Coulomb interaction only must miss part of the physics because the splitting it produces cancels in some directions of the exciton wave vector (see eq. (5)), a physically odd result that has never been questioned. The missed physics stems from the virtual photons that bright excitons can emit and reabsorb, as in the atomic Lamb shift [22–24], thereby inducing a similar blue-shift. This puzzling fact urges the physics behind the bright-dark exciton splitting to be reconsidered from scratch, as a first step toward controlling and manipulating these two types of excitons in novel experiments and semiconductor devices.

In this letter, we establish the microscopic origin of the splitting between dark and bright excitons and we relate this splitting to the quantum fluctuations of the longitudinal and transverse electromagnetic fields.

We show that the bright exciton blue-shift comes not only from the Coulomb interaction through virtual interband processes, commonly called “electron-hole exchange”, but also from processes involving virtual...
photons. Since dark excitons suffer neither of these processes, their energy stays unchanged; so, the bright-dark exciton splitting is equal to the bright exciton energy shift. As the Coulomb interaction follows from the longitudinal part of the electromagnetic field, while photons are associated with the transverse part, the bright-dark exciton splitting constitutes an iconic signature, in semiconductor physics, of quantum fluctuations in the theory of radiation, as, mutatis mutandis, does the Lamb shift in atomic physics.

What sets the exciton apart from the hydrogen atom is that the electromagnetic field acts in two totally different ways: the longitudinal field acts through interband Coulomb processes, while the transverse field acts through “resonant” and “nonresonant” interband processes, that is, photon absorption along with exciton creation and recombinaiton. The nonresonant coupling, commonly dropped for physics driven by real photons, must be kept for processes involving virtual photons: as a mathematical proof, the longitudinal and transverse electromagnetic fields produce contributions that respectively depend on the longitudinal and transverse components of the exciton wave vector \( \mathbf{K} \), which is physically reasonable. These contributions nicely combine to produce an energy shift that is free from these components, hence supporting that bright excitons do feel electromagnetic field fluctuations in their full complexity.

We moreover predict that the energy splitting \( \Delta_{BD} \) between bright and dark excitons must scale as

\[
\Delta_{BD} \propto \frac{|\Omega_{ph-X}|^2}{E_{gap}},
\]

where the energy-like parameter \( \Omega_{ph-X} \) is the Rabi coupling between exciton and photon, and \( E_{gap} \) is the band gap. As a direct consequence, the bright-dark splitting varies as the inverse of the exciton radiative lifetime. Although here derived for cubic crystals, this relation stays valid whatever the material structure and shape\(^1\), as supported by a strong dimensional argument: the physics of the shift involves two exciton-photon couplings; to end with an energy-like shift, they must be divided by an energy, which can only be the energy that creates the exciton, that is, the band gap. This amazingly simple result provides a useful tool for characterizing optically inactive excitons in new materials.

**Couplings to the electromagnetic field.**

- The Coulomb interaction comes from the longitudinal part of the electromagnetic field. There are two types of Coulomb processes.

  i) **Intraband** processes (fig. 1) correlate electron-hole pair into exciton. Since the Coulomb interaction does not act on the spin, each carrier keeps its spin. Moreover, the hole keeps its spatial index \( \mu \) due to spatial symmetry [3].

  ii) **Interband** processes (fig. 2) correspond to the recombinaiton of an electron-hole pair and the excitation of another pair. The fact that the Coulomb interaction conserves the spin imposes the electron-hole pairs that suffer interband processes to be in a spin-singlet state [3]. The interband Coulomb vertex can be shown (see the Supplementary Material SupplementaryMaterial.pdf (SM)) to depend on the center-of-mass wave vector \( \mathbf{K} \) of the pairs as

\[
\frac{2|\Lambda|^2}{E_{gap}^2} \left( \frac{\mathbf{K}}{\mathbf{R}} \cdot e_\mu_1 \right) \left( \frac{\mathbf{K}}{\mathbf{R}} \cdot e_\mu_2 \right),
\]

for pairs made of hole in a threefold spatial state \( \mu \). The unit vector \( e_\mu \) with \( \mu = (x, y, z) \) is along a cubic crystal axis, while the \( \Lambda \) parameter is defined in eq. (4). In contrast to intraband scatterings, the hole indices \( (\mu_1, \mu_2) \)

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\(^1\)The conduction band splitting of transition metal dichalcogenides, induced by the spin-orbit interaction, also produces a bright-dark splitting. This splitting is usually small compared to the splitting induced by electromagnetic quantum fluctuations.

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of the “in” and “out” pairs are not related for interband processes (fig. 2(c)).

- Photons associated with the transverse field also lead to interband processes. The emission of a photon with wave vector \( Q \) goes along with the recombin- nation of an electron-hole pair with center-of-mass wave vector \( -Q \). Photons are represented by dotted wavy lines. The associated vertices are given in eq. (3).

\[
\Lambda = \frac{\hbar}{\sqrt{\hbar^2 Q}} \langle e_{\lambda, Q} \cdot e_\mu \rangle, \tag{3}
\]

for resonant processes, \( \Lambda \) being replaced by \( \Lambda^* \) for nonresonant processes.

- As salient features of these couplings:
  i) the interband Coulomb interaction and the interband electron-photon interaction both act on spin-singlet pairs only, these pairs being bright;
  ii) although the Coulomb interaction and the electron-photon interaction follow \[3\] from different physics, (i) the interband Coulomb interaction and the interband resonant processes.

\[
\Delta^{(\mu, \mu)} \equiv \left( X_{K, \nu_0; \mu', S=0} | \hat{V}_{Coul}^{(\mu)} | X_{K, \nu_0; \mu, S=0} \right), \tag{6}
\]

i) For resonant processes, photon emission goes along with exciton recombination. So, the intermediate state \(| f \rangle \) is just the virtual photon \( K \), as shown in fig. 4(b).

\[
\Delta^{(\mu, \mu)} \equiv \frac{2|\Lambda_{\nu_0}|^2}{E_{\text{Coul}}^2 - \hbar^2 \omega^2 K} \sum_{\lambda, \nu} (e_{\lambda, K} \cdot e_{\mu})(e_{\lambda, K} \cdot e_{\mu}), \tag{7}
\]

with \( \omega_K \ll E_{K, \nu_0} \approx E_{\text{gap}} \), since \(| K | \approx 0 \) for photon.

- The exciton energy change induced by the interband Coulomb interaction follows from eq. (2). The matrix elements of this interaction in the \( \mu \)-degenerate ground-state \((\nu_0)\) exciton subspace read (see the Supplementary Material Supplementarymaterial.pdf)

\[
\Delta^{(\mu, \mu)} \equiv \left( X_{K, \nu_0; \mu', S=0} | \hat{V}_{Coul}^{(\mu)} | X_{K, \nu_0; \mu, S=0} \right), \tag{5}
\]
From eqs. (5), (7), we see that for $\mathbf{K} \parallel \mathbf{e}_\mu$, the contribution from virtual photons cancels, while the one from interband Coulomb interaction is maximum; this is the opposite for $\mathbf{K} \perp \mathbf{e}_\mu$, as is reasonable because the Coulomb interaction comes from the longitudinal field, while the photons are associated with the transverse field. Actually, these contributions nicely combine: as $(\mathbf{e}_X, \mathbf{e}_Y, \mathbf{K})$ and $\mathbf{e}_{Z,K} = \mathbf{K}/K$ form an orthonormal set,

$$\begin{align*}
\delta_{\mu', \mu} &= \mathbf{e}_\mu \cdot \mathbf{e}_{\mu'} \\
&= \sum_{\lambda'=\{X,Y,Z\}} (\mathbf{e}_\mu \cdot \mathbf{e}_{\lambda', \mathbf{K}}) \mathbf{e}_{\lambda', \mathbf{K}} \cdot \sum_{\lambda=\{X,Y,Z\}} (\mathbf{e}_{\mu} \cdot \mathbf{e}_{\lambda, \mathbf{K}}) \mathbf{e}_{\lambda, \mathbf{K}} \\
&= \sum_{\lambda=\{X,Y,Z\}} (\mathbf{e}_{\mu} \cdot \mathbf{e}_{\lambda, \mathbf{K}}) (\mathbf{e}_{\mu} \cdot \mathbf{e}_{\lambda, \mathbf{K}}),
\end{align*}$$

(8)

which proves that the sum of the longitudinal and transverse shifts does not depend on the $\mathbf{K}$ direction

$$\Delta(\mu', \mu) = \Delta(\mu', \mu) + \Delta(\mu', \mu) \approx \delta_{\mu', \mu} \frac{2|\Lambda_{\mu_0}|^2}{E_{gap}}. \quad (9)$$

The above bright exciton shift corresponds to the splitting between bright and dark excitons given in eq. (1): i) Dark excitons are not coupled to the electromagnetic field. So, their energy does not change. ii) According to eq. (3), the Rabi coupling for photons that creates a ground exciton, $\hbar \omega_{\mathbf{K}} \approx E_{gap}$, scales as

$$\Omega_{ph,X} \approx \frac{\Lambda_{\mu_0}}{\sqrt{E_{gap}}}. \quad (10)$$

iii) Since the exciton shift does not depend on the hole index $\mu$, the spin-orbit interaction, which enforces specific linear combinations of hole states, can only change the numerical prefactor of eq. (9), but not its form.

Discussion. –

Through eq. (1), the bright-dark exciton splitting is related to two fundamental quantities: the band gap $E_{gap}$ and the exciton-photon Rabi coupling that depends on the bulk exciton Bohr radius $a_\chi$ and the momentum operator between valence and conduction states, $P_{c,v}$. Using eq. (4) and the ground-exciton wave function $e^{-r/a_\chi} / \sqrt{\pi a_\chi}$, we get

$$\Lambda_{\mu_0} = \Lambda L^{3/2} \langle \mathbf{r} = 0 \rangle |\langle 0 \rangle \rangle = \Lambda \sqrt{L^3 / \pi a_\chi^3} = 2 \frac{e^2 P_{c,v}}{m_0 a_\chi \sqrt{\epsilon_{sc}}} \sqrt{\epsilon_{sc}}. \quad (11)$$

By working with spin and linear polarizations, instead of spin-orbit eigenstates and circular polarizations, the interplay between $\mathbf{e}_\mu$ and $\mathbf{K}$ in terms of “longitudinal” and “transverse” contributions is easy to pin down. The splitting prefactors for spin-orbit eigenstates can then be obtained by writing these states in terms of $(\mu, s)$ hole states.

We have here derived the Coulomb and electron-photon vertices in vacuum. Yet, semiconductors have a dielectric constant $\epsilon_{sc}$ that comes from dressing the Coulomb interaction through interband Coulomb processes. It can be included by replacing $e^2$ with $e^2/\epsilon_{sc}$ in the $\Lambda$ parameter of eq. (4).

eq. (9) then gives the bright-dark splitting as

$$\Delta_{BD} = 2 \frac{|\Lambda_{\mu_0}|^2}{E_{gap}} = 8 \frac{E_{Kane}}{E_{gap}} \frac{e^2/\epsilon_{sc} a_\chi}{E_{gap}} \frac{\hbar^2}{2m_0 a_\chi^2}. \quad (12)$$

with the “Kane energy” $E_{Kane} = 2|P_{c,v}|^2 / m_0$.

For bulk GaAs ($E_{gap} \approx 1.5$ eV, $E_{Kane} \approx 23$ eV, $\epsilon_{sc} \approx 13$ and $a_\chi \approx 15$ nm [25]), the above equation gives $\Delta_{BD} \approx 100 \mu$eV splitting, which is somewhat larger than the reported value 20 $\mu$eV [6]. The very first reason for this disagreement can come from the approach used in ref. [6] to experimentally extract the bright-dark energy splitting. Indeed, this value was inferred by comparing computed and measured magneto-photoluminescence spectra. The deduced $\Delta_{BD}$ then relies on an effective treatment of the exchange interaction between excitons—that we here treat in an exact way. In addition, the values of $E_{Kane}$ and $a_\chi^3$ for bulk GaAs are not known with a high precision. These two parameters are crucial to derive the bright-dark splitting because along our work, this splitting is proportional to $E_{Kane}/a_\chi^3$. So, by increasing $a_\chi$ from 15 to 20 nm, the deduced $\Delta_{BD}$ increases from 100 to around 40 $\mu$eV and thus essentially agrees with ref. [6].

Although derived for bulk crystals, the transparent physics expressed in eq. (1) leads us to embrace its validity for reduced dimensions. We first note that $a_\chi^3$ in eq. (12) comes from the exciton volume, $4 \pi a_\chi^3 / 3$, over which the Coulomb or photon-exciton interaction occurs. In the quantum well, this volume is $w \pi a_\chi^2$, where the well width $w$ by construction is smaller than $a_\chi$. The in-plane Bohr radius $a_\chi(w)$ is also smaller because it decreases from $a_\chi$ to $a_\chi/2$ when $w$ decreases from infinity to zero. Thus, the resulting exciton volume is smaller for the quantum well than for the bulk, making the bright-dark splitting larger, as seen from their ratio for bulk and quantum well, estimated through

$$\left( \frac{4 \pi}{3} a_\chi^3 \right) \Delta_{BD} \sim (w \pi a_\chi^2(w)) \Delta_{BD}^{(QW)}. \quad (13)$$

For $w = 5$ nm and $a_\chi(w) \approx 0.7 a_\chi$ [25], this gives $\Delta_{BD}^{(QW)} / \Delta_{BD} \approx 7$, in agreement with experimental data for the GaAs bulk [6] and quantum well [7,8] samples.

Another bright-dark splitting of interest concerns the interlayer excitons in the coupled GaAs quantum well, which have been used to explore the Bose-Einstein condensation and related superfluidity [12,26–31]. We can estimate the bright-dark splitting by noting that it varies as the inverse of the exciton radiative lifetime. Starting from the splitting measured for intralayer excitons in a single GaAs quantum well [7,8], we can derive the interlayer splitting from the change in radiative lifetime. Experiments showed that the radiative lifetime for intralayer...
excitons is a few tens of picoseconds [32], while it is three orders of magnitude larger [29,33] for interlayer excitons. This gives the bright-dark splitting for coupled GaAs quantum well in the range of 200 neV. Interestingly, this value is comparable to the energy difference between excitons having the two lowest center-of-mass wave vectors 0 and $(2\pi/L)$, for an in-plane size $L$ of a few µm. The $\Delta_{BD}$ amplitude thus confirms the dominant role of optically dark states for the exciton Bose-Einstein condensation reported in coupled GaAs quantum wells [27,30,31].

– The physical understanding we provide for the bright exciton blue-shift has some connection with the Lamb shift [22] between the 2S$_{1/2}$ and 2P$_{1/2}$ levels of a hydrogen atom, which results from the emission and reabsorption of virtual photons [23,24]. Yet, although semiconductor excitons are commonly seen as the solid-state analog of hydrogen atoms, their couplings to the electromagnetic field are qualitatively different due to wave vector conservation because a valence hole is much lighter than a proton. Indeed, when a photon is emitted by the recombination of an exciton in a direct-gap semiconductor, the photon is given not only the energy but also the center-of-mass wave vector of the exciton [3]. By contrast, the photon emitted by an atom results from the electron transition between allowed states; this determines the emitted photon energy but not its wave vector due to the heavy-atom recoil [24].

– Finally, let us stress that the physics we here present heavily relies on the difference between exciton and polariton.

1) In the polariton regime, the exciton-photon coupling is “strong” and must be included exactly; strong actually means large compared with the inverse carrier coherence time (see footnote 4). For short coherence time, the exciton changes its wave vector much faster than the photon re-emission; the original photon is then lost, and the polariton mode cannot develop.

2) In the exciton regime, the exciton-photon coupling is “weak” and can be treated at lowest order, as done here. It produces the long-missed part of the bright exciton shift, as necessary to produce a bright-dark splitting that does not cancel in some exciton wave vector directions, which otherwise would be physically odd.

Conclusion. – We have analytically derived the energy splitting between optically bright and dark excitons in cubic semiconductor crystals, using the second quantization formalism for field and matter, as required when dealing with quantum fluctuations. We trace this splitting back to the Coulomb interaction through interband virtual processes, joined by the electron-photon interaction through interband resonant and nonresonant virtual processes, these two interactions being related to the longitudinal and transverse parts of the electromagnetic field. Their contributions increase the bright exciton energy, but do not affect dark excitons. As physically reasonable, the bright-dark splitting does not depend on the direction of the exciton wave vector, a point that would have been missed if only the Coulomb interaction through “electron-hole exchange” were considered, as previously done [18–21], or if only the virtual photon emission and absorption were taken into account, as in the case of the atomic Lamb shift [22–24]. Our key result, eq. (1), leads us to predict that long-lived excitons, weakly coupled to photons, must have a small bright-dark energy splitting, a valuable result in view of the difficulty in measuring quantities related to dark states.

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Data availability statement: All data that support the findings of this study are included within the article (and any supplementary files).

REFERENCES

[1] Knox R. S., Theory of Excitons (Academic Press) 1963.
[2] Cho K., Excitons, Topics in Current Physics, Vol. 14, (Springer-Verlag) 1979.
[3] Combescot M. and Shimura S.-Y., Excitons and Cooper Pairs: Two Composite Bosons in Many-Body Physics (Oxford University Press) 2015.
[4] Combescot M., Betbeder-Matibet O. and Dubin F., Phys. Rep., 463 (2008) 215.
[5] Combescot M., Combescot R., Alloing M. and Dubin F., Phys. Rev. Lett., 114 (2015) 090401.
[6] Eckert W., Lösch K. and Bimberg D., Phys. Rev. B, 20 (1979) 3303.
[7] Blackwood E., Snelling M. J., Harley R. T., Andrews S. R. and Foxon C. T. B., Phys. Rev. B, 50 (1994) 14246.
[8] Amand T. et al., Phys. Rev. Lett., 78 (1997) 1355.
[9] Mashkov I. V. et al., Phys. Rev. B, 55 (1997) 13761.
[10] Combescot M., Betbeder-Matibet O. and Combescot R., Phys. Rev. Lett., 99 (2007) 176403.
[11] Combescot M. and Leuenberger M., Solid State Commun., 149 (2009) 13.
[12] Combescot M., Combescot R. and Dubin F., Rep. Prog. Phys., 80 (2017) 066401.
[13] Shimura S.-Y. and Combescot M., Phys. Rev. Lett., 123 (2019) 097401.
[14] Unuchek D., Ciarrocchi A., Avsar A., Sun Z., Watanabe K., Taniguchi T. and Kis A., Nat. Nanotechnol., 14 (2019) 1104.
[15] Schwarz I. et al., Science, 354 (2016) 434.
[16] Rivera P., Yu H., Seyler K. L., Wilson N. P., Yao W. and Xu X., Nat. Nanotechnol., 13 (2018) 1004.
[17] Robert C. et al., Nat. Commun., 11 (2020) 4037.
[18] Pikus G. E. and Bir G. L., Sov. Phys. JETP, 33 (1971) 108.
[19] Maialle M. Z., de Andrada e Silva E. A. and Sham L. J., Phys. Rev. B, 47 (1993) 15776.
[20] Fu H., Wang L.-W. and Zunger A., Phys. Rev. B, **59** (1999) 5568.
[21] Luo J.-W., Bester G. and Zunger A., New J. Phys., **11** (2009) 123024.
[22] Lamb W. E. and Retherford R. C., Phys. Rev., **72** (1947) 241.
[23] Bethe H. A., Phys. Rev., **72** (1947) 339.
[24] Cohen-Tannoudji C., Dupont Roc J. and Grynberg G., *Atom-Photon Interactions: Basic Processes and Applications* (Wiley-VCH) 1998.
[25] Bastard G., *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Editions de Physique) 1990.
[26] High A. A. et al., Nature, **483** (2012) 584.
[27] Alloing M. et al., EPL, **107** (2014) 10012.
[28] Shilo Y. et al., Nat. Commun., **4** (2013) 2335.
[29] Beian M. et al., EPL, **119** (2017) 37004.
[30] Anankine R. et al., Phys. Rev. Lett., **118** (2017) 127402.
[31] Dang S. et al., Phys. Rev. Lett., **122** (2019) 117402.
[32] Deveaud B., Clerot F., Roy N., Satzke K., Sermage B. and Katzer D. S., Phys. Rev. Lett., **67** (1991) 2355.
[33] Sivalertporn K., Mouchliadis L., Ivanov A. L., Philp R. and Muljarov E. A., Phys. Rev. B, **85** (2012) 045207.