Frenkel versus charge-transfer exciton dispersion in molecular crystals

Pierluigi Cudazzo,1,2 Matteo Gatti,3 Angel Rubio,4 and Francesco Sottile4

1Nano-Bio Spectroscopy group, Dpto. Fysica de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain
2European Theoretical Spectroscopy Facility (ETSF)
3Laboratoire des Solides Irradiés, École Polytechnique, CNRS-CEA/DSM, F-91128 Palaiseau, France
4Fritz-Haber-Institut der Max-Planck-Gesellschaft, Theory Department, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

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Excitons are neutral electronic excitations that dominate the low-energy part of the optical spectra in insulators and semiconductors. They consist of bound electron-hole (e-h) pairs that can be excited in several ways: by absorption of light or by relaxation of free electrons and holes after optical or electrical pumping. They play an essential role in many semiconductor applications (e.g. for light-emitting diodes, lasers and photovoltaic cells) and give rise to the rich field of Bose-Einstein condensate. In all these cases it is fundamental to understand the decay rate and the propagation of the excitons. The latter is directly related to their energy dispersion as a function of momentum transfer. Recent advances in loss spectroscopies make it possible to map out the full momentum-energy exciton dispersion. On the other hand, the interpretation of these experimental spectra requires first-principles theoretical approaches able to describe and analyse excitons at finite momentum transfer. The Bethe-Salpeter equation (BSE) from many-body perturbation theory has become the most accurate framework to describe excitonic effects in the optical spectra of many materials. However optical spectroscopy probes the zero momentum-transfer limit only. Therefore the first-principles analysis of the exciton dispersion is still an important goal to reach.

Molecular crystals represent a textbook case that clearly illustrates the need of advanced theoretical tools to understand the exciton dispersion. Typically, the lowest-energy excited states in these materials are strongly localized Frenkel (FR) excitons, where the interacting e-h pairs are localized on the same molecular unit. Charge-transfer excitons (CT), in which e-h pairs are delocalized on different units, usually appear at higher energy in the spectra. However, when the molecular units are large enough, the effective interactions for e-h pairs localized on the same site or on two different sites become comparable and a competition between CT and FR excitons can occur. Under these conditions many-body effects become crucial to set the character of the excitons and an ab-initio treatment of the e-h interactions is thus required.

In the present work we solve the Bethe-Salpeter equation at finite momentum transfer to investigate two prototypical isoelectronic molecular crystals: picene and pentacene. By switching on the different e-h interactions step by step and analysing their effects, we are able to draw a general picture of the exciton dispersion. We show that while the dispersion of FR excitons is set by the exchange e-h interaction, the dispersion of CT states is mainly related to the electronic band structure. Our conclusions have a general validity that holds in all the systems in which the electron wavefunctions are strongly correlated.

The BSE excitonic hamiltonian in a basis of wavefunctions on the molecular units can be written as:

$$\hat{H}_{ex} = \sum_{R_i, R_j} h^e_{R_i, S_j} a_{R_i, S_j}^\dagger a_{R_j, S_j} - \sum_{R_i, S_j} h^h_{R_i, S_j} b_{R_i, S_j}^\dagger b_{R_j, S_j} + \sum_{R_i, S_j, P, Q, m} (2 i \epsilon_{Q_m, R_i} - W_{Q_m, R_i}) a_{R_i, S_j}^\dagger b_{R_j, S_j} b_{P, Q_m} a_{P, Q_m}. $$

(1)

Here and $a^\dagger$ (a) and $b^\dagger$ (b) are creation (annihilation) operators for electrons and holes, and the bold and thin letters indicate the lattice vectors and the molecular unit in the primitive cell, respectively. $h^e$ and $h^h$ are the one-particle hamiltonians for the motion of free electrons and holes, which are described by the band structure calculated in the GW approximation. The BSE kernel is given by the sum of $2\nu$, which includes only the $G \neq 0$ reciprocal-space components of the bare Coulomb interaction $\nu$, and the statically screened Coulomb interaction $W$. The matrix elements of $\tilde{v}$ and $W$ enter the BSE kernel as exchange and direct e-h interactions, respectively.

Due to the strong localization of the electronic wavefunctions on the molecular units, it is possible to neglect...
In the absence of e-h interactions \( \bar{v} \), we see that along Fig. 1(b), i.e. to induce a Davydov splitting (DS). In particular, we see that along a more intense FR peak is located at lower energy than FR\(^+\) [11]. On the contrary, CT states do not feel the exchange e-h interaction [see Eq. (3)] and their energy remains unchanged [compare Fig. 1(a) and Fig. 1(b)]. If instead we take into account only the direct e-h interaction \( \bar{W} = 0 \), the CT exciton has a lower energy than the CT exciton [see Fig. 1(c)]. Moreover, the CT excitons are no longer degenerate: in fact the direct e-h interaction \( W \) depends on the e-h separation and thus different CT excitons are determined by different inter-site matrix elements \( W \). On the contrary, since \( \bar{v} = 0 \) the degeneracy between symmetric and antisymmetric states is preserved. Finally, we take into account both \( W \) and \( \bar{v} \) [see Fig. 1(d)]. The exchange e-h interaction \( \bar{v} \) is felt only by the FR exciton, hence the energy difference between FR and CT states is reduced. In pentacene the exchange e-h interaction is so strong that when \( \bar{v} \) is added to \( W \) both symmetric and antisymmetric FR excitons skip above the lowest CT exciton [compare Fig. 1(c) and Fig. 1(d)]. As a consequence, in pentacene the lowest-energy excited state in absence of hopping is a pure CT exciton. This for instance does not happen in picene where the exchange e-h interaction is not large enough to compensate the effect of the direct on-site \( W \) and the lowest excited state is a pure Frenkel exciton.

In the tight-binding picture the exciton dispersion is caused by the scattering of the e-h pair from site to site. In general, scattering processes are induced by the hopping through the interaction of an electron (or a hole) with the crystal field or through the effective e-h interaction. However, when the overlap between wavefunc-

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**Textual Content**

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**Diagram**

![Diagram](image-url)

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**Footnotes**

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\[ \sim \]
lar, for \( q \) the FR state has an exciton bandwidth of 
0.4 eV, which is \(~ 0.1 \text{ eV} \) for the FR\(^{-}\) state [see Fig. 2(a)]. This suggests that the exchange e-h processes involving equivalent and inequivalent molecules compensate each other in the antisyemtic state, having \( I(\mathbf{q}) \) and \( J(\mathbf{q}) \) opposite sign for FR\(^{-}\) excitons [see Eq. (2)]. On the other hand, for \( q \) along \( b^* \) [see Fig. 2(b)] the dispersion is negligible.

To investigate the effects of the hopping of free electrons and holes, we relax the constraint of flat bands and we solve the BSE including the full dispersion of the HOMO-LUMO bands. First of all, through its \( q \) dependence, the hopping induces a finite dispersion of CT states [which otherwise is 0, see Figs. 2(a)-(b)] and modifies the intrinsic dispersion of FR excitons given by \( I(\mathbf{q}) \) and \( J(\mathbf{q}) \) [see Eq. (2)]. Moreover, switching on the hopping induces a mixing of FR and CT states (the coupling term \( H_{CT-FR} \) is no longer zero): in a real material the excited states are always a mixture of the two excitonic solutions. The hopping hence removes the degeneracy between symmetric and antisymmetric CT states, giving rise to two mixed excitons with symmetric \((\text{CT}+\text{FR})^\pm \) and antisymmetric \((\text{CT}+\text{FR})^- \) character. The mixing between CT and FR excitons is stronger when the hopping is larger and when the energy difference between pure CT and FR states is smaller. The e-h exchange interaction, through the terms \( I(\mathbf{q}) \) and \( J(\mathbf{q}) \) in Eq. (2), changes the energy difference between pure FR and CT excitons as a function of \( q \). In turn, this variation of their separation modulates the mixing effect due to the hopping (which is larger when the excitons get closer in energy). We thus see that the exchange e-h interaction, through the hopping, has also an (indirect) effect on CT excitons.

Therefore, from this general analysis we can conclude that the exciton dispersion in molecular crystal arises from a delicate competition between hopping and exchange e-h interaction. The \textit{ab initio} BSE results confirm these conclusions. We find [see Fig. 2(c)-(d)] that the lowest exciton in pentacene, at 1.55 eV at \( q = 0 \), is a \((\text{CT}+\text{FR})^- \) state. It is related to the lowest CT exciton in Fig. 2(a) and (b). The corresponding symmetric \((\text{CT}+\text{FR})^+ \) state is at 1.76 eV at \( q = 0 \), giving a Davydov splitting of 0.2 eV. In between these two excitons, other combinations of FR and CT excitons appear. The width of the dispersion of these \((\text{CT}+\text{FR})^\pm \) states varies between 0.05 and 0.20 eV, which is rightly the order of magnitude of the HOMO-LUMO bandwidths. In particular the exciton dispersion is larger along the \( b^* \) axis [see Fig. 2(d)], where the first exciton has a bandwidth of 0.14 eV that is about twice as large as the dispersion along \( a^* \) [see Fig. 2(c)]. This difference is an indirect effect of the exchange e-h interaction. Because of it, along \( a^* \) FR excitons have an intrinsic finite dispersion, which is instead negligible along \( b^* \) [see Fig. 2(a)-(b)]. Therefore, as \( q \) increases, FR and CT get further apart along \( a^* \), reducing their coupling induced by the hopping, while this does not occur along \( b^* \).

Finally, in Fig. 2(a)-(b) we report the spectra of \( \epsilon_2 \) as a function of \( q \) for pentacene, solving the BSE for a converged set of bands (so we relax the last constraint about using only HOMO and LUMO bands). For the lowest-energy peaks we find the same results as those obtained by considering only the HOMO-LUMO bands [see Fig. 2(c)-(d)], confirming that the HOMO-LUMO bands give by far the most important contribution to these excitons. The lowest \((\text{CT}+\text{FR})^- \) state is visible for a polarization along the \( a^* \) axis, while its \((\text{CT}+\text{FR})^+ \) counterpart is visible only along the \( b^* \) axis. Both excitons remain visible up to \( \Gamma \) point of the second Brillouin zone, where their
oscillator strengths drop to zero and the spectral weight is transferred to higher energy \((\text{CT}+\text{FR})\) states. Interestingly, at large momentum transfer along the \(b^*\) axis a new peak appears at energy smaller than that of the \((\text{CT}+\text{FR})^+\) state that determines the onset at \(\mathbf{q} = 0\). This new peak corresponds to the lowest \((\text{CT}+\text{FR})^-\) exciton, which is dipole forbidden at small momentum transfer along the \(b^*\) axis, but becomes visible at larger \(\mathbf{q}\).

We can now compare pentacene with picene [see Fig. 3(c)-(d)], in which the lowest excited states are localized Frenkel excitons. In particular at \(\mathbf{q} = 0\) the symmetric and antisymmetric \(\text{FR}^+\) and \(\text{FR}^-\) states are visible along the \(b^*\) and \(a^*\) axis, respectively, with a Davydov splitting of about 0.02 eV, that is one order of magnitude smaller than in pentacene. These lowest excitons, in contrast to pentacene, involve the contributions of several bands besides the HOMO-LUMO transitions. The mixing of HOMO-LUMO transitions with higher energy excitations makes the contributions from the direct e-h interaction \(W\) larger, while it does not affect the kinetic term in Eq. (1). As a result, the exciton binding energy is also increased, giving rise to a strongly localized FR exciton, well separated in energy from the CT ones. As a consequence, the mixing with higher energy CT excitons is negligible in picene. The lowest excited state thus preserves its intrinsic FR character and its dispersion is set by the exchange e-h interaction only. In Fig. 3(c)-(d) we see that for small \(\mathbf{q}\) belonging to the first Brillouin zone, the FR\(^+\) exciton has a positive dispersion, while the FR\(^-\) state has a negative dispersion. For both excitons the bandwidth is about 0.02 eV, which is one order of magnitude smaller than in pentacene, suggesting that in the two systems the mechanism of the exciton dispersion is completely different. These findings are confirmed by recent electron energy-loss spectroscopy (EELS) experiments \[25, 26\]. While an exciton band structure with bandwidths of about 100 meV has been observed for pentacene, picene has not shown a measurable dispersion for \(\mathbf{q}\) belonging to the \(a^*b^*\) plane. The present work thus provides the tools for the interpretation also of these recent experimental results.

In conclusion, by combining \textit{ab initio} many-body BSE calculations for picene and pentacene with a simple model interpretation, we have drawn a general picture of the exciton dispersion in molecular crystals. We have shown that the exciton dispersion is the result of the interplay between two competing mechanisms: the electron and hole hopping and the electron-hole exchange interaction. The investigation of the exciton dispersion gives valuable insights about the nature of the excitons, allowing one to tell the difference between localized Frenkel excitons and delocalized charge-transfer excitons. This analysis is of general validity and can be exploited to describe other strongly correlated insulators with localized electronic wavefunctions.

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For picene and pentacene we have used the experimental crystal structures of Refs. [19, 20]. In both cases, converged BSE spectra have been obtained with a 6×6×4 grid of \( k \) point, 53 occupied and 29 empty bands. Ground-state and GW band-structure calculations have followed those in Refs. [16, 21, 22] and have been performed with the Abinit [23] code. For the BSE at finite \( q \) we have used the EXC code [24].