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Charged excitons in direct-gap semiconductors

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The charged excitons are moving bound states of an exciton and an electron or a hole in semiconductors. The theory of these charged quasiparticles is given for direct-gap materials in the framework of the effective-mass approximation, taking into account the spin-orbit coupling and the electron-hole exchange interaction as a perturbation. The special cases of CuCl and CuBr are studied more extensively because they correspond to the most important binding energies. As a result charged excitons are stable enough to be observed in CuCl and CuBr. Arguments are given in favor of the interpretation of some lines as due to transitions between positive or negative charged excitons and free holes or electrons.

I. INTRODUCTION

Recently, much interest has been displayed in the electronic excited states of semiconductors. These states may be conveniently described in terms of different kinds of electron-hole quasiparticles. The existence of neutral complex excitations as the exciton or the excitonic molecule is now well established, but the question of the existence of charged quasiparticles remains open. The simplest ones may result from the binding of an exciton X with an electron (e) or a hole (h) leading to the excitonic ion X^- or the excitonic molecule ion $X_2{}^+$. These two kinds of charged excitons are quite analog to the hydrogen ion H^- and to the hydrogen molecule ion $H_2{}^+$.[1] But there exist some essential differences between them because the mass ratio of the two-component particles of opposite charges is not so small as in the atomic case, and because of the surrounding crystal electrons and ions. Up until now, there is no strong experimental evidence of the existence of charged excitons in spite of a recent controversy[2-4] about the possible occurrence of X^- as bound to an isoelectronic N impurity in GaP. Nevertheless they may, if observed, display some very interesting properties due to their fermion behavior at low densities. Furthermore, the charged excitons may play an important role as intermediate states in the formation of biexcitons and also of an electron-hole plasma by lowering the threshold of the Mott transition from the insulating excitonic phase to the metallic electron-hole plasma.[5] They might be observed at high excitation intensities and also as classical optical transitions. Indeed they are expected to have giant oscillators strengths in connection with relatively low binding energies.

The stability of both charged excitons against dissociation into an exciton and a free electron or hole has been investigated recently by different authors[6-10] and is well established[6-8] by means of very accurate variational calculations for all values of the effective-mass ratio σ. Furthermore, if $\sigma = m_e^*/m_h^*$ is smaller than unity the binding energy of the $X_2{}^+$ molecule ion is larger than that of the X^- ion. The computed energies appear to be the most important in the case of copper halides because the mass ratio σ is very small in these materials. Further, the effective dielectric constant ϵ^* which takes into account the electronic and the ionic polarization effects appears to be smaller than the usual static dielectric constant ϵ_0. Nevertheless it must be stressed that the values obtained for X^- are not much higher than the free-exciton exchange energy. So it is of importance to compare the electron-hole exchange energy of charged excitons with the previously obtained binding energies.[6-8]

The aim of the present paper is to investigate the stability of charged excitons under the electron-hole exchange interaction. We restrict ourselves to the case of the most favorable materials which are the copper halides CuCl and CuBr which are polar direct-gap materials. In a preliminary paper[11] we have shown that the short-range exchange interaction does not destroy the stability of charged excitons in CuCl and CuBr. In the present work we give the theory of charged excitons including short- and long-range exchange interactions. In Sec. II, we define three-particle excited states of the crystal which are eigenstates of an effective electron-hole Hamiltonian taking into account the spin and spin-orbit band degeneracies and generalizing that obtained by Haken.[12] The electron-hole exchange interaction is treated in Sec. III as a perturbation. We show that it separates into a short-range and a long-range contribution. In Sec. IV, we particularize to the special cases of CuCl and CuBr. As a result the long-range contribution vanishes in CuCl for both charged excitons whereas in CuBr further splitting arises due to that contribution. Finally, in Sec. V we compare our results with the experimental situation and discuss the interpretation of some lines as due to charged excitons.

II. THREE-PARTICLE EXCITED STATES OF A SEMICONDUCTOR

We consider semiconductors with a direct gap at the point $\Gamma(\vec{k}=0)$. At this point the degenerate valence and conduction Bloch functions $v_\beta(\xi)$ and $c_\alpha(\xi)$ belong to the irreducible representations Γ_i of the complete point group of the crystal. We have $\xi=[r,\zeta]$, where $\vec{r}$ and $\zeta=\pm\frac{1}{2}$ are spatial and spin coordinates. α and β are row indices for each representation. A Bloch function of wave vector $\vec{k}$ transforms under the action of the symmetry operations of the point group into a linear combination of Bloch functions with wave vectors $\vec{k}'$ obtained from the wave vector $\vec{k}$ by means of these symmetry operations performed on the reciprocal lattice. So at any point $\vec{k}$ of the first Brillouin zone the wave functions of the electrons in each band separately are linear combinations of Bloch functions corresponding to the different vectors $\vec{k}'$. However at symmetry point Γ the linear combinations reduce to one sole Bloch function. We can restrict our linear combinations to one Bloch function as for the point Γ and approximate its periodic part by the corresponding one at $\vec{k}=0$. Indeed the band states with small momentum play the principal role in the formation of excitonic complexes, if the electrons and holes are created by direct optical absorption. Thus the conduction- and valence-electron Bloch functions read approximately

$$\begin{aligned}\phi_{c\vec{k}\alpha}(\xi)&=c_\alpha(\xi)\exp(i\vec{k}\cdot\vec{r}),\\ \phi_{v\vec{k}\beta}(\xi)&=v_\beta(\xi)\exp(i\vec{k}\cdot\vec{r}),\end{aligned}\tag{2.1}$$

and correspond to the energies $E_c(\vec{k})$ and $E_v(\vec{k})$. Because the effective one-electron Hartree-Fock Hamiltonian includes spin-orbit interaction, it does not commute with K_0, the complex conjugation operator, but with K the time reversal operator. So we conventionally define the hole Bloch functions by $\phi_h(\xi)=K\phi_v(\xi)$.

Now we define the states of the charged excitons. The cases of X^- and $X_2{}^+$ are analogous under permutation of the electrons and the holes. Therefore we treat only the case of X^- explicitly. We denote by $|\Phi_0\rangle$ the Hartree-Fock ground state of the crystal. Let us define crystal states of three particles of the following kind:

$$a^\dagger_{\vec{k}_1\alpha_1}a^\dagger_{\vec{k}_2\alpha_2}d^\dagger_{\vec{k}_3\beta_3}|\Phi_0\rangle\,,\tag{2.2}$$

where $a^\dagger_{\vec{k}\alpha}$ and $d_{\vec{k}\beta}$ are creation and annihilation operators of an electron and a hole in the Bloch states of the conduction band and the valence band, respectively. For small $\vec{k}$ values the above states constitute approximately a basis for a representation of the point group of the crystal. This representation is reducible because the direct product $\Gamma_c\times\Gamma_c$ is always reducible at least into a symmetric and an antisymmetric part. We denote by

$$\Phi^{r\nu,i}_{eeh}(\vec{k}_1,\vec{k}_2,\vec{k}_3)\rangle\rangle=\frac{1}{\sqrt{2}}\sum_{\alpha_1\alpha_2\beta}\gamma^{r\nu,i}_{\alpha_1\alpha_2\beta}a^\dagger_{\vec{k}_1\alpha_1}a^\dagger_{\vec{k}_2\alpha_2}d^\dagger_{\vec{k}_3\beta_3}|\Phi_0\rangle\tag{2.3}$$

a crystal state belonging to the ith row of the irreducible representation $\Gamma_{r,\nu}$. ν is a symmetry label which is (+) or (−) according to whether Γ_r is symmetric or antisymmetric with respect to the two electrons, whereas the $\gamma^{r\nu,i}_{\alpha_1\alpha_2\beta}$ are numerical coupling coefficients corresponding to a unitary transformation. In order to obtain eigenstates of the crystal Hamiltonian, we take linear combinations of the above crystal states:

$$|\Phi^{r\nu,i}_{X^-}\rangle=\sum_{\vec{k}_1\vec{k}_2\vec{k}_3}c^{\bar{\nu}}_{\vec{k}_1\vec{k}_2\vec{k}_3}|\Phi^{r\nu,i}_{eeh}(\vec{k}_1,\vec{k}_2,\vec{k}_3)\rangle\rangle\,.\tag{2.4}$$

Here $c^{\bar{\nu}}_{\vec{k}_1\vec{k}_2\vec{k}_3}$ denotes the envelope function in $\vec{k}$ space. We anticipate that for the ground state it belongs to the identity representation of the point group. $\bar{\nu}$ is the opposite symmetry label of ν. In some cases the electron-hole exchange interaction may mix the states (2.3) belonging to the irreducible representations of the point group. This point will be discussed in Sec. IV.

The wave function F_{X^-} of the charged exciton in ξ space reads

$$F^{r,i}_{X^-}(\xi_1,\xi_2,\xi_3)=\sum_{\vec{k}_1\vec{k}_2\vec{k}_3}c^{\bar{\nu}}_{\vec{k}_1\vec{k}_2\vec{k}_3}\sum_{\alpha_1\alpha_2\beta_3}\gamma^{r\nu,i}_{\alpha_1\alpha_2\beta_3}\phi_{e\vec{k}_1\alpha_1}(\xi_1)\phi_{e\vec{k}_2\alpha_2}(\xi_2)\phi_{h\vec{k}_3\beta_3}(\xi_3)\,.\tag{2.5}$$

For charged excitons of large orbits the wave function F_{X^-} separates into a product of a crystalline function f_{X^-} and an envelope function ϕ_{X^-}:

$$F_{X^-}^{r,i}(\xi_1, \xi_2, \xi_3) = \Omega^{3/2} \phi_{X^-}^{\bar{\nu}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) f_{X^-}^{r\nu,i}(\xi_1, \xi_2, \xi_3), \tag{2.6}$$

where

$$\phi_{X^-}^{\bar{\nu}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \Omega^{-3/2} \sum_{\vec{k}_1\vec{k}_2\vec{k}_2} c_{\vec{k}_1\vec{k}_2\vec{k}_3}^{\bar{\nu}} \exp(i\vec{k}_1 \cdot \vec{r}_1 + i\vec{k}_2 \cdot \vec{r}_2 - i\vec{k}_3 \cdot \vec{r}_3), \tag{2.7}$$

whereas

$$f_{X^-}^{r\nu,i}(\xi_1, \xi_2, \xi_3) = \sum_{\alpha_1\alpha_2\beta_3} \gamma_{\alpha_1\alpha_2\beta_3}^{r\nu,i} c_{\alpha_1}(\xi_1) c_{\alpha_2}(\xi_2) K v_{\beta_3}(\xi_3). \tag{2.8}$$

$\Omega = N\Omega_0$ denotes the volume of the crystal containing N elementary cells of volume Ω_0.

The crystal states (2.3) are eigenstates of the following effective electron-hole Hamiltonian:

$$H = H_0 + H_c\,, \tag{2.9}$$

where

$$H_0 = E_0 + \sum_{\vec{k}\alpha} E_c(\vec{k}) a_{\vec{k}\alpha}^\dagger a_{\vec{k}\alpha}^\dagger - \sum_{\vec{k}\beta} E_v(\vec{k}) d_{\vec{k}\beta}^\dagger d_{\vec{k}\beta}^\dagger \tag{2.10}$$

is the Hartree-Fock Hamiltonian in which E_0 is the energy of the full valence band. The correlation Hamiltonian reads

$$\begin{aligned} H_c = &- \sum_{\substack{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4 \\ \alpha_1\beta_2\beta_3\alpha_4}} a_{\vec{k}_1\alpha_1}^\dagger a_{\vec{k}_4\alpha_4} d_{\vec{k}_3\beta_3}^\dagger d_{\vec{k}_2\beta_2} \biggl(\int d^3\xi\, d^3\xi'\, \phi_{e\vec{k}_1\alpha_1}^*(\xi) \phi_{h\vec{k}_3\beta_3}^*(\xi') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{h\vec{k}_2\beta_2}(\xi') \phi_{e\vec{k}_4\alpha_4}(\xi) \\ &\qquad - \int d^3\xi\, d^3\xi'\, \phi_{e\vec{k}_1\alpha_1}^*(\xi') \phi_{h\vec{k}_3\beta_3}^*(\xi') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{h\vec{k}_2\beta_2}(\xi) \phi_{e\vec{k}_4\alpha_4}(\xi) \biggr) \\ &+ \frac{1}{2} \sum_{\substack{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4 \\ \alpha_1\alpha_2\alpha_3\alpha_4}} a_{\vec{k}_1\alpha_1}^\dagger a_{\vec{k}_2\alpha_2}^\dagger a_{\vec{k}_3\alpha_3} a_{\vec{k}_4\alpha_4} \int d^3\xi\, d^3\xi'\, \phi_{e\vec{k}_1\alpha_1}^*(\xi) \phi_{e\vec{k}_2\alpha_2}(\xi') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{e\vec{k}_3\alpha_3}(\xi') \phi_{e\vec{k}_4\alpha_4}(\xi) \\ &+ \frac{1}{2} \sum_{\substack{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4 \\ \beta_1\beta_2\beta_3\beta_4}} d_{\vec{k}_1\beta_1}^\dagger d_{\vec{k}_2\beta_2}^\dagger d_{\vec{k}_3\beta_3} d_{\vec{k}_4\beta_4} \int d^3\xi\, d^3\xi'\, \phi_{h\vec{k}_1\beta_1}^*(\xi) \phi_{h\vec{k}_2\beta_2}(\xi') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{h\vec{k}_3\beta_3}(\xi') \phi_{h\vec{k}_4\beta_4}(\xi). \end{aligned} \tag{2.11}$$

The two first terms describe the electron-hole direct and exchange interaction, respectively, whereas the two remaining terms correspond to the electron and hole interactions, respectively. The intraband exchange interaction has already been taken into account in the Hartree-Fock approximation.

Anticipating that the spatial extension of charged excitons is large, and neglecting in a first step the electron-hole exchange interaction, it may be shown that the Schrödinger equation separates into an equation for the crystalline function and another equation for the envelope function which reads

$$\left[-\frac{\hbar^2}{2m_e^*} \nabla_1^2 - \frac{\hbar^2}{2m_e^*} \nabla_2^2 - \frac{\hbar^2}{2m_h^*} \nabla_3^2 + \frac{e^2}{\epsilon} \left(\frac{1}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{23}} \right) - E_{X^-}^{\bar{\nu}} \right] \phi_{X^-}^{\bar{\nu}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = 0\,. \tag{2.12}$$

Further the effective masses of electrons and holes are assumed for simplicity to be isotropic in the terms corresponding to kinetic energy. Up to now we have not taken into account the polarization effects which are important in ionic materials such as copper halides. Therefore we introduce an effective dielectric constant ϵ in Eq. (2.12). The total three particle binding energy $E_{X^-}^{\bar{\nu}}$ is connected with the crystal excitation energy by the relation

$$E_{\text{crystal}} = 2E_c(0) - E_v(0) + E_{X^-}^{\bar{\nu}}\,. \tag{2.13}$$

Owing to the translational invariance of Eq. (2.2), we can separate the center-of-mass motion from the relative motion. We define the wave function associated to the envelope of the relative motion $\Psi_{X^-}^{\bar{\nu}}$ and corresponding to the three particle relative energy $E_{X^-,\text{rel.}}^{\bar{\nu}}$:

$$\begin{aligned} \phi_{X^-}^{\bar{\nu}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) &\equiv \phi_{X^-}^{\bar{\nu}}(\vec{r}, \vec{R}, \vec{R}_0) \\ &= \Omega^{-1/2} \exp(i\vec{K}_0 \cdot \vec{R}_0) \Psi_{X^-}^{\bar{\nu}}(\vec{r}, \vec{R}), \\ E_X^{\bar{\nu}} &= E_{X^-,\text{rel.}}^{\bar{\nu}} + \hbar^2 K_0^2 / 2M_0\,. \end{aligned} \tag{2.14}$$

Here $\vec{R}_0$, $\vec{K}_0$, and $M_0 = 2m_e^* + m_h^*$ stand for the center-of-mass coordinates, momentum, and mass. $\vec{R}$ and $\vec{r}$ are related to the coordinates of the three particle by

$$\vec{R} = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2) - \vec{r}_3, \quad \vec{r} = \vec{r}_2 - \vec{r}_1\,. \tag{2.15}$$

Equation (2.12) has been previously solved for the ground state in the cases of X^- and of X_2^+ for all values of the effective mass ratio $\sigma = m_e^*/m_h^*$. The main conclusion was that charged excitons are stable with respect to the dissociation into an exciton and a free electron or hole, but without taking into account the electron-hole exchange interaction, which will be treated in Sec. III.

III. ELECTRON-HOLE EXCHANGE INTERACTION IN CHARGED EXCITONS

The electron-hole exchange Hamiltonian reads

$$H_{\text{exch}}^{e-h} = \sum_{\substack{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4 \\ \alpha_1\beta_2\beta_3\alpha_4}} a^{\dagger}_{\vec{k}_1\alpha_1} a_{\vec{k}_4\alpha_4} d^{\dagger}_{\vec{k}_3\beta_3} d_{\vec{k}_2\beta_2} \times \int d^3\xi\, d^3\xi'\, \phi^*_{e\vec{k}_1\alpha_1}(\xi')\phi^*_{h\vec{k}_3\beta_3}(\xi') \times \frac{e^2}{|\vec{r}-\vec{r}\,'|}\, \phi_{h\vec{k}_2\beta_2}(\xi)\phi_{e\vec{k}_4\alpha_4}(\xi) . \tag{3.1}$$

For charged excitons of large orbits, we get a good approximation in first-order perturbation theory. The nonperturbed states $|\Phi_{X^-}^{ri}\rangle$ are assumed to be eigenfunctions of the Hamiltonian (2.11) neglecting the exchange terms. The exchange corrections ΔE are the eigenvalues of the following secular equation:

$$|H_{X^-}^{rs,ij}(\vec{K}_0) - \Delta E(\vec{K}_0)\delta_{rs}\delta_{ij}| = 0 , \tag{3.2}$$

with the orthogonality condition

$$\langle \Phi_{X^-}^{ri} | \Phi_{X^-}^{ij} \rangle = \delta_{rs}\,\delta_{ij} . \tag{3.3}$$

The exchange matrix elements between states belonging to the ith and jth rows of the representations Γ_r and Γ_s read:

$$H_{X^-}^{rs,ij}(\vec{K}_0) = \langle \Phi_{X^-}^{ri}(\vec{K}_0) | H_{\text{exch}}^{e-h} | \Phi_{X^-}^{sj}(\vec{K}_0) \rangle . \tag{3.4}$$

Owing to translational invariance, states with different $\vec{K}_0$ vectors are not mixed. Further, we neglect a possible hybridization of the envelope states due to the exchange interaction. Using (2.4), we may write the matrix elements (3.4):

$$H_{X^-}^{rs,ij}(\vec{K}_0) = 2 \int d^3\xi_1\, d^3\xi_2\, d^3\xi_3\, F_{X^-}^{ri}(\xi_1, \xi_2, \xi_1)^* \times \frac{e^2}{|\vec{r}_1 - \vec{r}_3|} F_{X^-}^{sj}(\xi_3, \xi_2, \xi_3) . \tag{3.5}$$

The factor 2 is a direct consequence of the Pauli exclusion principle. The electron-hole exchange takes place only with one of the two electrons, at the same time. The wave function F_{X^-} has to be normalized to unity

$$\int d^3\xi_1\, d^3\xi_2\, d^3\xi_3 F_{X^-}^{ri}(\xi_1, \xi_2, \xi_3)^* \times F_{X^-}^{sj}(\xi_1\xi_2\xi_3) = \delta_{rs}\,\delta_{ij} . \tag{3.6}$$

This condition separates into two orthogonality conditions for the envelope and the crystalline functions, respectively, using the decompositions (2.6) together with (2.14). Because of the periodicity of the crystalline function and its rapid variation with respect to the envelope function, it is easy to see that the condition (3.6) is satisfied if

$$\int_{\Omega^2} d^3r\, d^3R\, |\Psi_{X^-}^{\bar{\nu}}(\vec{r}, \vec{R})|^2 = 1$$

and

$$\int_{\Omega^3} d^3\xi_1\, d^3\xi_2\, d^3\xi_3\, f_{X^-}^{r\nu i}(\xi_1, \xi_2, \xi_3)^* \times f_{X^-}^{s\nu i}(\xi_1, \xi_2, \xi_3) = \delta_{rs}\,\delta_{ij} . \tag{3.7}$$

Taking into account the above separation, we may write the matrix elements (3.5) as follows:

$$H_{X^-}^{rs,ij}(\vec{K}_0) = 2\Omega^2 \int_{\Omega^3} d^3\xi_1\, d^3\xi_2\, d^3\xi_3 \left[\exp\left(-i\vec{K}_0 \cdot \frac{m_e^* + m_h^*}{M_0} (\vec{r}_1 - \vec{r}_3)\right) \tilde{\Psi}_{X^-}^{\bar{\nu}}(\vec{r}_2 - \vec{r}_1)^* \tilde{\Psi}_{X^-}^{\bar{\nu}}(\vec{r}_2 - \vec{r}_3)\right] \times \left(f_{X^-}^{r\nu i}(\xi_1, \xi_2, \xi_3)^* \frac{e^2}{|\vec{r}_1 - \vec{r}_3|} f_{X^-}^{s\nu j}(\xi_3, \xi_2, \xi_3)\right), \tag{3.8}$$

where we have defined $\tilde{\Psi}_{X^-}(\vec{r}) \equiv \Psi_{X^-}(\vec{r}, \frac{1}{2}\vec{r})$. Owing to the periodicity of the crystalline function and to the slow variation of the envelope function, we obtain in a first step

$$H_{X^-}^{rs,ij}(\vec{K}_0) = 2\Omega^2 \sum_{l'l''l'''} \tilde{\Psi}_{X^-}^{\bar{\nu}}(\vec{R}_{l''} - \vec{R}_{l'})^* \Psi_{X^-}^{\bar{\nu}}(\vec{R}_{l''} - \vec{R}_{l'''}) \exp\left(-i\vec{K}_0 \cdot \frac{m_e^* + m_h^*}{M_0} (\vec{R}_{l'} - \vec{R}_{l'''})\right) \times \int_{\Omega_0^3} d^3\xi_1\, d^3\xi_2\, d^3\xi_3\, f_{X^-}^{r\nu i}(\xi_1, \xi_2, \xi_1)^* \frac{e^2}{|\vec{r}_1 - \vec{r}_3 + \vec{R}_{l'} - \vec{R}_{l'''}|} f_{X^-}^{r\nu j}(\xi_3, \xi_2, \xi_3) , \tag{3.9}$$

where the sum runs over the lattice points $\vec{R}_l$. At this stage, it is convenient to separate this sum into two terms: a short-range (SR) contribution, and a long-range (LR) contribution.

The short-range part corresponds to $\vec{R}_{l'}=\vec{R}_{l'''}$ and reads after transforming the lattice sum into an integral, and using the symmetry properties of the function f:

$$H^{rs,ij}_{X^-,\mathrm{SR}}=2\Omega_0 I^{\bar{\nu}}_{X^-}J^{r_\nu,ij}_{X^-,\mathrm{SR}}\delta_{rs}\,, \tag{3.10}$$

where the envelope exchange integral

$$I^{\bar{\nu}}_{X^-}=\int_{\Omega}d^3r\,|\Psi^{\bar{\nu}}_{X^-}(\vec{r},\tfrac{1}{2}\vec{r})|^2 \tag{3.11}$$

is the sum of the squares of the probability amplitudes that an electron and a hole are located at the same point. The short-range crystalline exchange integral reads

$$J^{r_\nu,ij}_{X^-,\mathrm{SR}}=N^3\int_{\Omega_0^3}d^3\xi_1\,d^3\xi_2\,d^3\xi_3\,f^{r_\nu i}_{X^-}(\xi_1,\xi_2,\xi_1)^*\times\frac{e^2}{\epsilon_{\mathrm{SR}}|\vec{r}_1-\vec{r}_3|}f^{r_\nu j}_{X^-}(\xi_3,\xi_2,\xi_3)\,, \tag{3.12}$$

where we have introduced a phenomenological short-range dielectric constant, which is different from that of the effective envelope.

Now, we determine the lattice sum corresponding to the long-range part of the matrix elements (3.9), by expanding the Coulomb potential energy in terms of multipolar momenta.[13,14] Using the orthogonality relations between Bloch functions, we obtain in a straightforward way successively

$$\begin{aligned}H^{rs,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)=2\Omega^2\sum_{\substack{l'l''l'''\\ l'\neq l'''}}&\tilde{\Psi}^{\bar{\nu}}_{X^-}(\vec{R}_{l''}-\vec{R}_{l'})^*\tilde{\Psi}^{\bar{\nu}}_{X^-}(\vec{R}_{l''}-\vec{R}_{l'''})\exp\left(-i\vec{K}_0\frac{m_e^*+m_h^*}{M_0}(\vec{R}_{l'}-\vec{R}_{l'''})\right)\\ &\times\int_{\Omega_0^3}d^3\xi_1\,d^3\xi_2\,d^3\xi_3\,f^{r_\nu i}_{X^-}(\xi_1,\xi_2,\xi_1)^*\frac{e^2}{|\vec{R}_{l'}-\vec{R}_{l'''}|^5}\\ &\times\{(\vec{r}_1\cdot\vec{r}_3)(\vec{R}_{l'''}-\vec{R}_{l'})^2-3[\vec{r}_1\cdot(\vec{R}_{l'''}-\vec{R}_{l'})][\vec{r}_3\cdot(\vec{R}_{l'''}-\vec{R}_{l'})]\}f^{s_\nu j}_{X^-}(\xi_3,\xi_2,\xi_3)\end{aligned} \tag{3.13}$$

and

$$\begin{aligned}H^{rs,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)=\frac{2\Omega^2}{N^3}\sum_{\substack{l'l'''\\ l'\neq l'''}}&\exp\left(-i\vec{K}_0\frac{m_e^*+m_h^*}{M_0}(\vec{R}_{l'}-\vec{R}_{l'''})\right)\frac{1}{|\vec{R}_{l'}-\vec{R}_{l'''}|^5}\\ &\times\left[\left(\sum_{\alpha}\vec{D}^{r_\nu i}_{X^-}(\alpha)^*\cdot\vec{D}^{s_\nu j}_{X^-}(\alpha)\right)(\vec{R}_{l'}-\vec{R}_{l'''})^2\right.\\ &\left.\quad-3\sum_{\alpha}[\vec{D}^{r_\nu i}_{X^-}(\alpha)^*\cdot(\vec{R}_{l'}-\vec{R}_{l'''})][\vec{D}^{s_\nu j}_{X^-}(\alpha)\cdot(\vec{R}_{l'}-\vec{R}_{l'''})]\right]\\ &\times\sum_{l''}\tilde{\Psi}^{\bar{\nu}}_{X^-}(\vec{R}_{l''}-\vec{R}_{l'})^*\tilde{\Psi}^{\bar{\nu}}_{X^-}(\vec{R}_{l''}-\vec{R}_{l'''})\,,\end{aligned} \tag{3.14}$$

where we have introduced the effective electric dipole vector related to band-to-band transitions:

$$\vec{D}^{r_\nu i}_{X^-}(\alpha)=\sum_{\alpha'\beta}\gamma^{r_\nu i}_{\alpha'\alpha\beta}\int_{\Omega}d^3\xi\,c_{\alpha'}(\xi)e\vec{r}kv_{\beta}(\xi)\,. \tag{3.15}$$

It must be stressed that there are many dipole vectors, each corresponding to a possible state of the third particle, whereas in the case of the exciton, there is one sole dipole vector. We remark that the main contribution to the sum (3.14) arises from terms corresponding to slow $\vec{R}_l$ vectors. Further, taking into account the smooth variation of the envelope function in $\vec{r}$ space, we separate the long-range contribution into a product of crystalline and envelope parts. It appears that the last one is the same as for the short-range contribution:

$$H^{rs,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)=2\Omega_0 I^{\bar{\nu}}_{X^-}J^{r_\nu s_\nu,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)\,, \tag{3.16}$$

where the long-range crystalline exchange integrals read

$$\begin{aligned}J^{r_\nu s_\nu,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)=\sum_{l\neq 0}&\exp\left(-i\vec{K}_0\frac{m_e^*+m_h^*}{M_0}\cdot\vec{R}_l\right)\frac{1}{\epsilon_{\mathrm{LR}}|\vec{R}_l|^5}\\ &\times\left[\left(\sum_{\alpha}\vec{D}^{r_\nu i}_{X^-}(\alpha)^*\cdot\vec{D}^{s_\nu j}_{X^-}(\alpha)\right)\vec{R}_l^2\right.\\ &\left.\quad-3\sum_{\alpha}[\vec{D}^{r_\nu i}_{X^-}(\alpha)^*\cdot\vec{R}_l][\vec{D}^{s_\nu j}_{X^-}(\alpha)\cdot\vec{R}_l]\right].\end{aligned} \tag{3.17}$$

Here we have also introduced a phenomenological long-range effective dielectric constant ϵ_{LR}, which may be identified[15,16] with the high-frequency dielectric constant ϵ_∞. As a result, we obtain the following expression for the exchange matrix elements:

$$H^{r_\nu s_\nu,ij}_{X^-}(\vec{K}_0)=2\Omega_0 I^{\bar{\nu}}_{X^-}[J^{r_\nu,ij}_{X^-,\mathrm{SR}}\delta_{rs}+J^{r_\nu s_\nu,ij}_{X^-,\mathrm{LR}}(\vec{K}_0)]\,. \tag{3.18}$$

It is of interest to compare these matrix elements with those quite analogous which are obtained in the case of the excitonic ground state[15]

$$H_X^{rs,ij}(\vec{K}_0)=\Omega_0|\Psi_X(0)|^2[J_{X,\mathrm{SR}}^{r,ij}\delta_{rs}+J_{X,\mathrm{LR}}^{rs,ij}(\vec{K}_0)]. \tag{3.19}$$

Here $|\Psi_X(0)|^2=1/(\pi a_X)^3$, a_X being the $1s$ excitonic Bohr radius, whereas

$$J_{X,\mathrm{SR}}^{r,ij}=N^2\int_{\Omega_0^2}d^3\xi_1\,d^3\xi_2\,f_X^{r,i}(\xi_1,\xi_1)^*\times\frac{e^2}{\epsilon_{\mathrm{SR}}|\vec{r}_1-\vec{r}_2|}f_X^{r,j}(\xi_2,\xi_2), \tag{3.20}$$

$$J_{X,\mathrm{LR}}^{rs,ij}(\vec{K}_0)=\sum_{l\neq0}\exp(i\vec{K}_0\cdot\vec{R}_0)\frac{1}{\epsilon_{\mathrm{LR}}|\vec{R}_l|^5}\times[(\vec{D}_X^{r,i*}\cdot\vec{D}_X^{s,j})\vec{R}_l^2-3(\vec{D}_X^{r,i*}\cdot\vec{R}_l)(\vec{D}_X^{s,j}\cdot\vec{R}_l)]. \tag{3.21}$$

The exchange integrals J_{X^-}, $J_{X_2^+}$, and J_X related to the crystal structure will be determined in Sec. IV for CuCl and CuBr.

In order to compute integral (3.11), we have used the relative envelope wave function previously obtained[6] for the ground state of the negative charged exciton X^-. This function is symmetric with respect to the exchange of the two identical particles and reads

$$\Psi_{X^-}^+(\vec{r},\vec{R})\equiv\Psi_{X^-}^+(s,t,u)=\mathfrak{N}\sum_{mnp}c_{mnp}k^{m+n+p}\exp\left(-\frac{ks}{2}\right)s^mt^nu^p, \tag{3.22}$$

where the coordinates s,t,u are related to the three mutual distances r_{12}, r_{13}, and r_{23}:

$$\begin{aligned}&s=r_{13}+r_{23},\quad s\geq0,\\&t=r_{13}-r_{23},\quad -s\leq t\leq s,\\&u=r_{12},\quad |t|\leq u\leq s.\end{aligned} \tag{3.23}$$

The scaling factor k as well as the 34 linear parameters c_{mnp} corresponding to the conditions $m+n+p\leq5$ and n even, have been computed previously[6] by means of a variational method. The normalization constant $\mathfrak{N}$ reads further

$$\mathfrak{N}=\frac{k^3}{2\pi}\left(\sum_{\substack{mnp\\m'n'p'}}c_{mnp}c_{m'n'p'}\frac{(m+m'+n+n'+p+p'+5)![(p+p')+2(n+n')+6]}{(n+n'+1)(n+n'+3)(n+n'+p+p'+3)(n+n'+p+p'+5)}\right). \tag{3.24}$$

As a result, the envelope exchange integral reads

$$I_{X^-}^+=\frac{16\pi}{k^3}\mathfrak{N}^2\sum_{\substack{mnp\\m'n'p'}}c_{mnp}c_{m'n'p'}\times(m+m'+n+n'+p+p'+2)!. \tag{3.25}$$

In Fig. 1 we have reported the variations of $I_{X^-,X_2^+}^+/|\Psi_X(0)|^2$ vs σ. The values corresponding to the positive charged exciton X_2^+ have been deduced from those obtained for $\sigma\geq1$ for X^- by means of symmetry considerations, as reported previously.[7] We remark that the above ratio is always less than unity, corresponding to a more extended wave function in the case of charged excitons. Indeed the Coulomb repulsion between the two identical particles and the Pauli exclusion principle are lowering the probability of finding an electron and a hole at the same point. Further, for $\sigma\leq1$, we have $I_{X^-}^+\leq I_{X_2^+}^+$ which is consistent with higher binding energies in the case of the positive charged exciton.

IV. STRUCTURE OF CHARGED EXCITONS IN CuCl AND CuBr

CuCl and CuBr are polar direct gap materials whose band structure is well known.[17,18] Neglecting spin-orbit coupling, the band calculations lead to a lowest conduction band and an uppermost valence band, with corresponding Bloch functions belonging at $\vec{k}=0$ to the representations Γ_1 and Γ_5 of the point group T_d. The notations of Koster *et al.*[19] will be used throughout this paper. The

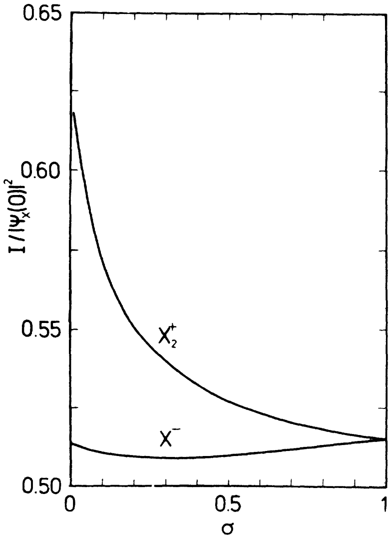

FIG. 1. Envelope exchange integrals of charged excitons as a function of $\sigma=m_e^*/m_h^*$.

Γ_1 conduction basis function $\phi(\vec{r})$ is s-like, whereas the Γ_5 valence basis functions $\{\Phi_{x_i}, x_i = x, y, z\}$ are p-like functions resulting from hybridization of the $3p$ orbitals (CuCl), or the $4p$ orbitals (CuBr) of the halogen and the $3d$ orbitals of the metal. This last contribution is very significative in the case of CuCl. Taking into account the spin-orbit coupling, the Γ_1 level becomes Γ_6, whereas the Γ_5 level splits into Γ_7 and Γ_8. In CuBr, the uppermost valence band is now Γ_8 while the situation is reversed in CuCl due to the important contribution of the $3d$ copper orbitals. The spin-orbit splitting $\lambda(\Gamma_7 - \Gamma_8)$ amounts to 549 and 1096 cm^{-1} in CuCl and CuBr, respectively.[20] These values are large in comparison with the experimental exciton exchange shifts ($\sim 50\ \text{cm}^{-1}$) in both substances. This fact justifies our perturbation method.

The electron conduction and valence band Bloch functions at $\vec{k} = 0$ in both substances then read

$$\begin{aligned}
\Gamma_6 &: \quad C_\alpha(\vec{r}, \zeta) = \phi(\vec{r})\langle \zeta \,|\, \alpha\rangle, \quad \alpha = \pm\tfrac{1}{2};\\
\Gamma_7 &: \quad V_\beta^7(\vec{r}, \zeta) = [\tfrac{1}{3}(\tfrac{3}{2} + \beta)]^{1/2}\psi_{\beta+1/2}(\vec{r})\langle \zeta \,|\, -\tfrac{1}{2}\rangle\\
&\qquad - [\tfrac{1}{3}(\tfrac{3}{2} - \beta)]^{1/2}\psi_{\beta-1/2}(\vec{r})\langle \zeta \,|\, \tfrac{1}{2}\rangle, \quad \beta = \pm\tfrac{1}{2};\\
\Gamma_8 &: \quad V_\beta^8(\vec{r}, \zeta) = [\tfrac{1}{3}(\tfrac{3}{2} + \beta)]^{1/2}\psi_{\beta-1/2}(\vec{r})\langle \zeta \,|\, \tfrac{1}{2}\rangle\\
&\qquad + [\tfrac{1}{3}(\tfrac{3}{2} - \beta)]^{1/2}\psi_{\beta+1/2}(\vec{r})\langle \zeta \,|\, -\tfrac{1}{2}\rangle,\\
&\qquad \beta = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}, \qquad (4.1)
\end{aligned}$$

where the p-like hybrid functions $\{\psi_i, i = \pm 1, 0\}$ are related to the Γ_5 basis functions Φ_{x_i}:

$$\psi_{\pm 1} = \mp(i/\sqrt{2})(\Phi_x, \pm i\Phi_y), \quad \psi_0 = i\Phi_z. \qquad (4.2)$$

The corresponding Γ_7 and Γ_8 valence hole functions $W_\beta(\vec{r},\zeta) = KV_\beta(\vec{r}, \zeta)$ are obtained using the following phase conventions[19]:

$$\begin{aligned}
&K\psi_i = (-1)^{l-i}\psi_{-i}, \quad l = 1;\\
&K\langle \zeta \,|\, \sigma\rangle = (-1)^{1/2-\sigma}\langle \zeta \,|\, -\sigma\rangle, \quad \sigma = \pm\tfrac{1}{2}; \qquad (4.3)
\end{aligned}$$

and read

$$\begin{aligned}
\Gamma_7 &: \quad W_\beta^7(\vec{r}, \zeta) = (-1)^{\beta+1/2}[\tfrac{1}{3}(\tfrac{3}{2} + \beta)]^{1/2}\psi_{-\beta-1/2}(\vec{r})\langle \zeta \,|\, \tfrac{1}{2}\rangle\\
&\qquad + (-1)^{\beta-1/2}[\tfrac{1}{3}(\tfrac{3}{2} - \beta)]^{1/2}\psi_{-\beta+1/2}(\vec{r})\langle \zeta \,|\, -\tfrac{1}{2}\rangle,\\
&\qquad \beta = \pm\tfrac{1}{2};\\
\Gamma_8 &: \quad W_\beta^8(\vec{r}, \zeta) = (-1)^{\beta-3/2}(\tfrac{3}{2} + \beta)]^{1/2}\psi_{-\beta+1/2}(\vec{r})\langle \zeta \,|\, -\tfrac{1}{2}\rangle\\
&\qquad + (-1)^{\beta+3/2}[\tfrac{1}{3}(\tfrac{3}{2} - \beta)]^{1/2}\psi_{-\beta-1/2}(\vec{r})\langle \zeta \,|\, \tfrac{1}{2}\rangle,\\
&\qquad \beta + \pm\tfrac{1}{2}, \pm\tfrac{3}{2}. \qquad (4.4)
\end{aligned}$$

It must be stressed that the coordinates $\vec{r}$ and ζ appearing in the hole Bloch functions are still electronic coordinates. Furthermore, all the preceding functions are assumed to be normalized to unity.

In order to classify the nonperturbed charged exciton states, we restrict ourselves to symmetric Γ_1 Ψ_{X^-, X_2^+} envelope functions which lead to the most-stable states. The crystalline functions are then antisymmetric with respect to the two identical particles. For small $\vec{K}_0$ vectors, the charged exciton states and the crystalline functions belong to the same irreducible representation of the point group, and we get for both substances

$$\begin{aligned}
&\text{CuCl:} \quad \begin{cases} X^-: & (\Gamma_6 \times \Gamma_6)_- \times \Gamma_7 = \Gamma_7,\\ X_2^+: & \Gamma_6 \times (\Gamma_7 \times \Gamma_7)_- = \Gamma_6; \end{cases}\\
&\text{CuBr:} \quad \begin{cases} X^-: & (\Gamma_6 \times \Gamma_6)_- \times \Gamma_8 = \Gamma_8,\\ X_2^+: & \Gamma_6 \times (\Gamma_8 \times \Gamma_8)_- = \Gamma_6 + \Gamma_7 + 2\Gamma_8, \end{cases}
\end{aligned} \qquad (4.5)$$

where we have used the reduced form of the antisymmetrized products

$$\begin{aligned}
&(\Gamma_6 \times \Gamma_6)_- = (\Gamma_7 \times \Gamma_7)_- = \Gamma_1,\\
&(\Gamma_8 \times \Gamma_8)_- = \Gamma_1 + \Gamma_3 + \Gamma_5.
\end{aligned} \qquad (4.6)$$

In Appendix A, we have reported the different crystalline functions $f_{X^-, X_2^+}^{r-, i}(\xi_1, \xi_2, \xi_3)$ expressed in terms of the electron and hole Bloch functions C_α, W_β^7, and W_β^8. In the case of X_2^+ in CuBr, we remark that two independent sets of basis functions correspond to the representation Γ_8. But these two basis sets are orthogonal so that the crystal Hamiltonian, neglecting the electron-hole exchange contribution, does not mix the two sets of Γ_8 states, which remain degenerated.

Let us first look at the short-range electron-hole exchange contribution. Using the orthogonality and completeness properties of the basis functions, we may write the short-range exchange matrix elements $H_{X^-, X_2^+; \text{SR}}^{rs, ij}$ in terms of the parameter:

$$\Theta_{X^-, X_2^+;\, s} = 2\Omega_0 I_{X^-, X_2^+}^{+} J_0, \qquad (4.7)$$

where J_0 denotes the "atomic" exchange integral

$$J_0 = N^2 \int_{\Omega_0^2} d^3r_1\, d^3r_2\, \phi^*(r_1)\psi_0^*(r_1) \times \frac{e^2}{|r_1 - r_2|}\phi(r_2)\psi_0(r_2). \qquad (4.8)$$

As a result, the matrix $H_{X^-, X_2^+; \text{SR}}^{rs, ij}$ is diagonal for both complexes X^- and X_2^+ in the case of CuCl, and for X^- in CuBr. But, in the case of X_2^+ in CuBr, the two states Γ_8 are mixed and the $\Gamma_8 - \Gamma_8$ degeneracy is already lifted by the short-range contribution. After diagonalization, the two Γ_8 representations lead to two four-times-degenerate levels, which we will still note "Γ_8" for convenience, although they do not transform like Γ_8 functions. Thus, we may write the short-range exchange contribution

$$\Delta E_{X^-, X_2^+; \text{SR}}^{r} = Z_{X^-, X_2^+}^{r}\Theta_{X^-, X_2^+, s}, \qquad (4.9)$$

where the numerical factors Z^r depend on the irreducible representation under consideration, and are listed in Table I. It is interesting to compare the exchange energy (4.9) with the analog one that we obtain in the case of the exciton

$$\Delta E^r_{X,\mathrm{SR}} = \Omega_0 |\Psi_X(0)|^2 Z^r_X J_0 , \tag{4.10}$$

where $|\Psi_X(0)|^2 = 1/\pi a_X^3$, a_X being the ground-state excitonic Bohr radius. The numerical coefficients Z_X have the same meaning as the analogous Z_{X^-}, $Z_{X_2^+}$ ones. The values that we have confirm those reported previously[21,22]:

$$\begin{aligned} &\text{CuCl:}\quad Z_X^{\Gamma_2} = 0 , \quad Z_X^{\Gamma_5} = \tfrac{2}{3} ; \\ &\text{CuBr:}\quad Z_X^{\Gamma_3,\Gamma_4} = 0 , \quad Z_X^{\Gamma_5} = \tfrac{4}{3} . \end{aligned} \tag{4.11}$$

Comparing Eqs. (4.9) and (4.10), we obtain

$$\Delta E^r_{X^-,X_2^+;\mathrm{SR}} = 2 \frac{Z^r_{X^-,X_2^+} I^+_{X^-,X_2^+}}{Z_X^{\Gamma_5} |\psi_X(0)|^2} \Delta E^{\Gamma_5}_{X,\mathrm{SR}} . \tag{4.12}$$

The short-range exciton exchange energies $\Delta E^{\Gamma_5}_{X,\mathrm{SR}}$ have been computed using the following experimental data for[23] CuCl and[24,25] CuBr:

$$\begin{aligned} &\text{CuCl:}\quad \begin{cases} h\nu_X(\Gamma_5^L) = 25\,870 \text{ cm}^{-1} , \\ h\nu_X(\Gamma_5^T) = 25\,850 \text{ cm}^{-1} , \\ h\nu_X(\Gamma_2) = 25\,808 \text{ cm}^{-1} ; \end{cases} \\ &\text{CuBr:}\quad \begin{cases} h\nu_X(\Gamma_5^L) = 24\,026 \text{ cm}^{-1} , \\ h\nu_X(\Gamma_5^T) = 23\,946 \text{ cm}^{-1} , \\ h\nu_X(\Gamma_3, \Gamma_4) = 23\,912 \text{ cm}^{-1} , \end{cases} \end{aligned} \tag{4.13}$$

which lead us to the values $\Delta E^{\Gamma_5}_{X,\mathrm{SR}} = 49 \text{ cm}^{-1}$ and 61 cm^{-1} for CuCl and CuBr, respectively. [Recent indirect luminescence measurements[26] in CuCl using recombination of biexcitons lead to $h\nu_X(\Gamma_5^L) - h\nu(\Gamma_5^T) = 39 \text{ cm}^{-1}$ at high-density regime. The computations done below are relative to the low-density regime.] The charged-exciton exchange corrections $\Delta E^r_{X^-,X_2^+;\mathrm{SR}}$, as well as the corresponding corrected binding energies

$$W^r_{X^-,X_2^+;\mathrm{SR}} = W_{X^-,X_2^+} + \Delta E^r_{X^-,X_2^+} \tag{4.14}$$

are listed in Table I. We recall that W_{X^-}, $W_{X_2^+}$ are the binding energies previously obtained[6-8] without taking into account the electron-hole exchange interaction. In conclusion, we may say that charged excitons remain stable enough to be observed in CuCl and CuBr, when taking into account the short-range exchange energy correction only.

In order to get the actual corrected binding energies $W_{X^-,X_2^+;\mathrm{exch}}$ we must also include the long-range contribution (3.16) to the exchange matrices (3.18). To this purpose, we have expressed in Appendix B the effective dipole matrix elements (3.15) in terms of the "atomic" matrix elements

$$\mu_0 = N \int_{\Omega_0} d^3r\, \phi(\vec{r}) e x_i \Phi_{x_i}(\vec{r}) , \quad x_i = x, y, z . \tag{4.15}$$

We remark that there are many dipole vectors corresponding to a given charged exciton and that their polarizations appear to be linear along z or circular (forward or backward) in the x-y plane,

TABLE I. Binding energies of charged excitons in CuCl and CuBr. W corresponds to the binding energies previously obtained (Refs. 6 and 8) without taking into account the exchange interaction, using the following input parameters: CuCl (Ref. 20): $m_e^*/m_0 = 0.415$; $m_h^* = 20 m_0$; $\epsilon^* = 5.41$; CuBr (Ref. 20): $m_e^*/m_0 = 0.2323$; $m_h^* = 23 m_0$; $\epsilon^* = 5.23$. Due to the importance of the polarization effects, we have used an effective dielectric constant ϵ^* which takes these effects partially into account.

				SR exchange correction				Total exchange correction		
Substance	Complex	W (cm^{-1})	$\frac{I}{\lvert\psi_x(0)\rvert^2}$	Symmetry	Z	ΔE_{SR} (cm^{-1})	W_{SR} (cm^{-1})	Symmetry or degeneracy	ΔE_{exch} (cm^{-1})	W_{exch} (cm^{-1})
CuCl	X^-	−83	0.5131	Γ_7	$\frac{1}{2}$	38	−45	Γ_7	38	−45
	X_2^+	−229	0.6099	Γ_6	$\frac{1}{2}$	45	−184	Γ_6	45	−184
CuBr	X^-	−50	0.5134	Γ_8	$\frac{1}{2}$	23	−27	2	34	−16
								2	13	−37
	X_2^+	−152	0.6186	Γ_7, "Γ_8"	$\frac{1}{6}$	9	−143	2	80	−72
				Γ_6	$\frac{1}{2}$	28	−124	2	45	−107
				"Γ_8"	1	57	−95	2	25	−127
								2	8	−144
								2	7	−145
								2	5	−147

whereas in the case of the exciton the dipole vector is unique and corresponds always to a linear polarization. The lattice sum (3.17) may be summed in the limit of small $\vec{K}_0$ vectors. Indeed, following Cohen and Keffer,[13] we have in the case of cubic symmetry

$$\sum_{l\neq 0}\exp(i\vec{K}'\cdot\vec{R}_l)\,\frac{3X_lY_l}{|R_l|^5}\simeq -\tfrac{4}{3}\pi N^2\times 3\frac{K'_xK'_y}{K'^2},$$

$$\sum_{l\neq 0}\exp(i\vec{K}'\cdot\vec{R}_l)\frac{R_l^2-3Z_l^2}{|R_l|^5}\simeq \tfrac{4}{3}\pi N^2\left(-1+3\frac{K_z'^2}{K'^2}\right), \tag{4.16}$$

where

$$\vec{K}'=\frac{m_e^*+m_h^*}{M_0}\vec{K}_0$$

and X_l, Y_l, Z_l are the components of the lattice vector $\vec{R}_l$, while $\vec{K}'$ is a "reduced" charged exciton wave vector. Taking the Z axis along the wave vector $\vec{K}_0$ we obtain the long-range exchange matrix elements (3.16) in terms of the parameter

$$\Theta_{X^-,X_2^+;L}=2\Omega_0 I^+_{X^-,X_2^+}\times \tfrac{4}{3}\pi N^2\mu_0^2. \tag{4.17}$$

We have reported in Appendix C the exchange matrices (3.18) for X^- and X_2^+ in both substances. We remark that the long-range contribution vanishes in CuCl for X^- and X_2^+. In the case of CuBr, this contribution is diagonal for X^-, whereas for X_2^+ there appears a strong coupling in the two following sets of states: (Γ_6, Γ_6, Γ_8) and (Γ_7, Γ_8, Γ_8). The values of the exchange parameters Θ_S and Θ_L are estimated using the experimental excitonic exchange correction deduced from the results (4.13) by means of the theoretical excitonic exchange shifts formulas[15]

$$\begin{aligned}\Delta E_X^r&=\Omega_0|\psi_X(0)|^2Z_X^r(J_0-\tfrac{4}{3}\pi N^2\mu_0^2)\\ &\qquad\text{(transverse excitons)},\\ \Delta E_X^r&=\Omega_0|\psi_X(0)|^2Z_X^r(J_0+\tfrac{8}{3}\pi N^2\mu_0^2)\\ &\qquad\text{(longitudinal exciton)}.\end{aligned} \tag{4.18}$$

So we obtain

$$\begin{aligned}&\text{CuCl:}\ \begin{cases}X^-: & \Theta_S=76\ \text{cm}^{-1},\\ X_2^+: & \Theta_S=90\ \text{cm}^{-1};\end{cases}\\ &\text{CuBr:}\ \begin{cases}X^-: & \Theta_S=47\ \text{cm}^{-1},\quad \Theta_L=21\ \text{cm}^{-1},\\ X_2^+: & \Theta_S=56\ \text{cm}^{-1},\quad \Theta_L=25\ \text{cm}^{-1}.\end{cases}\end{aligned} \tag{4.19}$$

The exchange energy corrections may then be written as follows:

$$\begin{aligned}&\text{CuCl:}\ \begin{cases}\Delta E_{X^-}^{\Gamma_7,\pm1/2}=\Delta E_{X^-,SR}^{\Gamma_7,\pm1/2}=Z_{X^-}^{\Gamma_7}\Theta_{X^-,S}=38\ \text{cm}^{-1},\\ \Delta E_{X_2^+}^{\Gamma_6,\pm1/2}=\Delta E_{X_2^+}^{\Gamma_6,\pm1/2}=Z_{X_2^+}^{\Gamma_6}\Theta_{X_2^+,S}=45\ \text{cm}^{-1};\end{cases}\\ &\text{CuBr:}\ \begin{cases}\Delta E_{X^-}^{\Gamma_8,\pm1/2}=Z_{X^-}^{\Gamma_8}(\Theta_{X^-,S}+\Theta_{X^-,L})=34\ \text{cm}^{-1},\\ \Delta E_{X^-}^{\Gamma_8,\pm3/2}=Z_{X^-}^{\Gamma_8}(\Theta_{X^-,S}-\Theta_{X^-,L})=13\ \text{cm}^{-1}.\end{cases}\end{aligned} \tag{4.20}$$

The diagonalization of the X_2^+ matrix in CuBr has been done numerically and leads to the following results:

$$\begin{aligned}&\Delta E_1^{\Gamma_7,2\Gamma_8}=80\ \text{cm}^{-1},\\ &f_{1,\pm}^{\Gamma_7,2\Gamma_8}=0.8116f^{\Gamma_8',\pm3/2}\\ &\qquad -0.5515f^{\Gamma_8,\pm3/2}\mp0.1927f^{\Gamma_7,\mp1/2};\\ &\Delta E_2^{\Gamma_7,2\Gamma_8}=7\ \text{cm}^{-1},\\ &f_{2,\pm}^{\Gamma_7,2\Gamma_8}=\mp0.0889f^{\Gamma_8',\pm3/2}\\ &\qquad \mp0.4426f^{\Gamma_8,\pm3/2}+0.8923f^{\Gamma_7,\mp1/2}\\ &\Delta E_3^{\Gamma_7,2\Gamma_8}=5\ \text{cm}^{-1},\\ &f_{3,\pm}^{\Gamma_7,2\Gamma_8}=0.5773f^{\Gamma_8,\pm3/2}\\ &\qquad +0.7071f^{\Gamma_8',\pm3/2}\pm0.4082f^{\Gamma_7,\mp1/2}\end{aligned}$$

and (4.21)

$$\begin{aligned}&\Delta E_1^{\Gamma_6,2\Gamma_8}=45\ \text{cm}^{-1},\\ &f_{1,\pm}^{\Gamma_6,2\Gamma_8}=0.3963f^{\Gamma_8',\pm1/2}\\ &\qquad +0.7312f^{\Gamma_8,\pm1/2}\mp0.5553f^{\Gamma_6,\pm1/2};\\ &\Delta E_2^{\Gamma_6,2\Gamma_8}=25\ \text{cm}^{-1},\\ &f_{2,\pm}^{\Gamma_6,2\Gamma_8}=\pm0.6563f^{\Gamma_8',\pm1/2}\\ &\qquad \pm0.1974f^{\Gamma_8,\pm1/2}+0.7283f^{\Gamma_6,\pm1/2};\\ &\Delta E_3^{\Gamma_6,2\Gamma_8}=8\ \text{cm}^{-1},\\ &f_{3,\pm}^{\Gamma_6,2\Gamma_8}=0.6421f^{\Gamma_8',\pm1/2}\\ &\qquad -0.6530f^{\Gamma_8,\pm1/2}\mp0.4016f^{\Gamma_6,\pm1/2}.\end{aligned}$$

The two representations Γ_8 and Γ_8' belong, respectively, to $\Gamma_6\times\Gamma_3$ and $\Gamma_6\times\Gamma_5$. The above numerical values of the exchange corrections ΔE as well as the corrected binding energies W_{exch} are listed in Table I. In Fig. 2 we have plotted the corresponding binding energies diagram. In conclusion, charged excitons remain stable under the exchange electron-hole interaction. Furthermore, in CuBr the degeneracy of the X_2^+ levels is lifted due to the long-range exchange interaction. In that case, the remaining X_2^+ levels are only twofold degenerated.

V. DISCUSSION

Though no experimental evidence about the existence of charged excitons has been reported up to now, the binding energies obtained in the previous section show that the charged excitons are stable enough to be observed in CuCl and CuBr. Different radiative processes may be suggested. The most simplest consist in the transitions between free electron or free hole ground states and negative or positive charged exciton states. The free carrier may originate from previous ionization of impurities, band to band transitions or collisions between other quasiparticles. At high excitation intensities, this last process will be predominant. The energy balance corresponding to direct optical transitions reads for both complexes:

$$\begin{aligned} h\nu_{X^-}(\vec{K}_0) &= h\nu_X + W_{X^-,\mathrm{exch}} - \frac{\hbar^2K_0^2}{2m_e^*}\,\frac{\sigma+1}{2\sigma+1}\,, \\ h\nu_{X_2^+}(\vec{K}_0) &= h\nu_X + W_{X_2^+,\mathrm{exch}} - \frac{\hbar^2K_0^2}{2m_h^*}\,\frac{\sigma+1}{\sigma+2}\,. \end{aligned} \tag{5.1}$$

$h\nu_X$ stands for the free Γ_2 (CuCl) or Γ_3, Γ_4 (CuBr) exciton ground-state transitions. An important peculiarity of charged exciton lines consists in that the transition frequency depends on the wave vector $\vec{K}_0$ due to the difference between the free carriers and charged excitons masses. The charged exciton band should be disposed on the low-energy side of the threshold frequency $h\nu_{X^-,X_2^+}(0) = h\nu_X + W_{X^-,X_2^+;\mathrm{exch}}$. Considering only transitions near $\vec{k} \simeq \vec{K}_0 \simeq 0$, we obtain the following transition frequencies:

$$\begin{aligned} &\mathrm{CuCl}\begin{cases} X^-: & \Gamma_7:\ 25\,763\ \mathrm{cm}^{-1}\,, \\ X_2^+: & \Gamma_6:\ 25\,624\ \mathrm{cm}^{-1}\,; \end{cases} \\ &\mathrm{CuBr}\begin{cases} X^-: & \Gamma_8^{\pm 1/2}:\ 23\,896\ \mathrm{cm}^{-1}\,, \\ & \Gamma_8^{\pm 3/2}:\ 23\,875\ \mathrm{cm}^{-1}\,; \\ X_2^+: & 23\,840\ \mathrm{cm}^{-1}\,, \\ & 23\,805\ \mathrm{cm}^{-1}\,, \\ & 23\,785\ \mathrm{cm}^{-1}\,, \\ & 23\,768\ \mathrm{cm}^{-1}\,, \\ & 23\,767\ \mathrm{cm}^{-1}\,, \\ & 23\,765\ \mathrm{cm}^{-1}\,. \end{cases} \end{aligned} \tag{5.2}$$

These levels are twofold degenerate.

In CuCl, at low temperature there appear two absorption and emission bands ν_1 (25 814 cm^{-1}) and ν_2 (25 654 cm^{-1}) observed as well at low[27] and high[28] excitation intensities. The energy locations of these two lines seem in good agreement with the calculated absorption and emission thresholds of the charged excitions X^- and X_2^+. The ν_2 line has been previously[29] interpreted as being due to a transition between a neutral acceptor state (A^0) and a bound exciton state (A^0,X) because of a fourfold splitting in a magnetic field. This observed splitting remains consistent with the hypothesis of a transition between a Γ_7 hole and a Γ_6 charged exciton X_2^+. The ν_1 line has not been interpreted up to now at the authors knowledge. Nevertheless, it has been reported[27] that this line disappears at about 77 °K together with an enhancement of the exciton resonance line. The corresponding thermalization energy is quite the same as the X^- binding energy, $W = -45\ \mathrm{cm}^{-1}$, which is also the dissociation energy into an electron and an exciton.

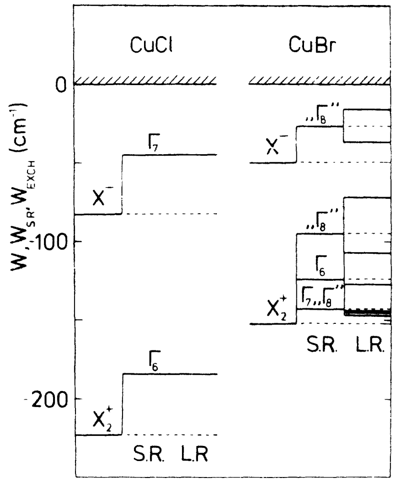

FIG. 2. Binding energies of charged excitons in CuCl and CuBr taking into account short-range (SR) and long-range (LR) electron-hole exchange interaction.

The optical spectrum of CuBr is more complicated. But we may remark that the luminescence spectrum[30] shows a set of close lines located at $h\nu = 23\,766, 23\,791, 23\,806, 28\,939, 23\,847\ \mathrm{cm}^{-1}$, which might be interpretated as being due to the dissociation of positive charged excitons X_2^+. The calculated X^- transition energies fall on the low-energy side of the $(\Gamma_8 - \Gamma_6)$ exciton band, which exhibits a not quite well interpretated structure.

Further, we remark that in CuCl the ν_1 and ν_2 bands appear at high excitation intensities together with the excitonic molecule bands ν_M. We suggest that charged excitons might play the role of intermediate states in the formation of biexcitons. Indeed, the electron-phonon interaction induces a long-range exciton-exciton repulsive interaction,[31-34] whereas the h-X^- and e-X_2^+ interactions are attractive. The previous tentative interpretation have to be supported by further investigations, mainly by splitting experiments under various perturbations and mobility experiments in an electromagnetic field.

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APPENDIX A: CRYSTALLINE WAVE FUNCTIONS OF CHARGED EXCITONS

We restrict ourselves to antisymmetric functions.

1. CuCl

$$f_{X^-}^{\Gamma_7,\beta}(\xi_1,\xi_2,\xi_3)=(1/\sqrt{2})[C_{1/2}(\xi_1)C_{-1/2}(\xi_2)-C_{-1/2}(\xi_1)C_{1/2}(\xi_2)]\,W_\beta^7(\xi_3),\quad \beta=\pm\tfrac{1}{2}\ ;$$

$$f_{X_2^+}^{\Gamma_6,\alpha}(\xi_1,\xi_2,\xi_3)=(1/\sqrt{2})C_\alpha(\xi_1)[W_{1/2}^7(\xi_2)W_{-1/2}^7(\xi_3)-W_{-1/2}^7(\xi_2)W_{1/2}^7(\xi_3)],\quad \alpha=\pm\tfrac{1}{2}\ .$$

2. CuBr

$$f_{X^-}^{\Gamma_8,\beta}(\xi_1,\xi_2,\xi_3)=(1/\sqrt{2})[-C_{-1/2}(\xi_1)C_{1/2}(\xi_2)+C_{1/2}(\xi_1)C_{-1/2}(\xi_2)]\,W_\beta^8(\xi_3),\quad \beta=\pm\tfrac{1}{2},\pm\tfrac{3}{2}\ ;$$

$$\begin{aligned}f_{X_2^+}^{\Gamma_6,\pm1/2}(\xi_1,\xi_2,\xi_3)=\tfrac{1}{2}C_{\pm1/2}(\xi_1)[&W_{-1/2}^8(\xi_2)W_{1/2}^8(\xi_3)-W_{1/2}^8(\xi_2)W_{-1/2}^8(\xi_3)\\&+W_{3/2}^8(\xi_2)W_{-3/2}^8(\xi_3)-W_{-3/2}^8(\xi_2)W_{3/2}^8(\xi_3)]\ ,\end{aligned}$$

$$\begin{aligned}f_{X_2^+}^{\Gamma_7,\pm1/2}(\xi_1,\xi_2,\xi_3)=\pm(1/\sqrt{3})\{&C_{\mp1/2}(\xi_1)[W_{\mp3/2}^8(\xi_2)W_{\pm1/2}^8(\xi_3)-W_{\pm1/2}^8(\xi_2)W_{\mp3/2}^8(\xi_3)]\\&+\tfrac{1}{2}C_{\pm1/2}(\xi_1)[W_{3/2}^8(\xi_2)W_{1/2}^8(\xi_3)-W_{1/2}^8(\xi_2)W_{3/2}^8(\xi_3)\\&+W_{-3/2}^8(\xi_2)W_{-1/2}^8(\xi_3)-W_{-1/2}^8(\xi_2)W_{-3/2}^8(\xi_3)]\}\ ,\end{aligned}$$

$$\begin{aligned}f_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_3,\pm1/2}(\xi_1,\xi_2,\xi_3)=\mp\tfrac{1}{2}C_{\mp1/2}(\xi_1)[&W_{-1/2}^8(\xi_2)W_{1/2}^8(\xi_3)-W_{1/2}^8(\xi_2)W_{-1/2}^8(\xi_3)\\&+W_{-3/2}^8(\xi_2)W_{3/2}^8(\xi_3)-W_{3/2}^8(\xi_2)W_{-3/2}^8(\xi_3)]\ ,\end{aligned}$$

$$\begin{aligned}f_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_3,\pm3/2}(\xi_1,\xi_2,\xi_3)=\mp\tfrac{1}{2}C_{\mp1/2}(\xi_1)[&W_{1/2}^8(\xi_2)W_{3/2}^8(\xi_3)-W_{3/2}^8(\xi_2)W_{1/2}^8(\xi_3)\\&+W_{-3/2}^8(\xi_2)W_{-1/2}^8(\xi_3)-W_{-1/2}^8(\xi_2)W_{-3/2}^8(\xi_3)]\ ,\end{aligned}$$

$$f_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_5,\pm1/2}(\xi_1,\xi_2,\xi_3)=(1/\sqrt{2})C_{\mp1/2}(\xi_1)[W_{\mp1/2}^8(\xi_2)W_{\pm3/2}^8(\xi_3)-W_{\pm3/2}^8(\xi_2)W_{\mp1/2}^8(\xi_3)]\ ,$$

$$\begin{aligned}f_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_5,\pm3/2}(\xi_1,\xi_2,\xi_3)=(1/\sqrt{6})\{&C_{\pm1/2}(\xi_1)[W_{\pm3/2}^8(\xi_2)W_{\mp1/2}(\xi_3)-W_{\mp1/2}^8(\xi_2)W_{\pm3/2}^8(\xi_3)]\\&-C_{\mp1/2}(\xi_1)[W_{3/2}^8(\xi_2)W_{1/2}^8(\xi_3)-W_{1/2}^8(\xi_2)W_{3/2}^8(\xi_3)\\&+W_{-3/2}^8(\xi_2)W_{-1/2}^8(\xi_3)-W_{-1/2}^8(\xi_2)W_{-3/2}^8(\xi_3)]\}\ .\end{aligned}$$

APPENDIX B: EFFECTIVE ELECTRIC DIPOLE VECTOR

We express these vectors in an orthonormal basis set $(\vec{e}_x,\vec{e}_y,\vec{e}_z)$. Furthermore, it is convenient to define the vectors $\vec{e}_\pm=(1/\sqrt{2})(\vec{e}_x\pm i\vec{e}_y)$ related to backward and forward circular polarizations.

1. Exciton

It may be shown that the dipole vectors

$$\vec{D}_X^{r,i}=\sum_{\alpha\beta}\gamma_{\alpha\beta}^{r,i}\int d^3\xi\,C_\alpha(\xi)\,e\vec{r}\,k\,V_\beta(\xi)$$

are nonzero only in the case of Γ_5 representations. In that case, we may choose the degenerate eigenstates so that the corresponding dipole vectors are

CuCl:

$$\vec{D}_X^{\Gamma_5,yz}=\sqrt{\tfrac{2}{3}}\,\mu_0\vec{e}_x\ ,$$

$$\vec{D}_X^{\Gamma_5,zx}=-\sqrt{\tfrac{2}{3}}\,\mu_0\vec{e}_y\ ,$$

$$\vec{D}_X^{\Gamma_5,xy}=\sqrt{\tfrac{2}{3}}\,\mu_0\vec{e}_z\ ;$$

CuBr:

$$\vec{D}_X^{\Gamma_5,x}=-\sqrt{\tfrac{4}{3}}\,\mu_0\vec{e}_x\ ,$$

$$\vec{D}_X^{\Gamma_5,y}=\sqrt{\tfrac{4}{3}}\,\mu_0\vec{e}_y\ ,$$

$$\vec{D}_X^{\Gamma_5,z}=-\sqrt{\tfrac{4}{3}}\,\mu_0\vec{e}_z\ .$$

2. Charged excitons

CuCl:

$$\vec{\mathrm{D}}_{X^-}^{\Gamma_7,i}(\alpha):\ \begin{array}{c|cc} {}_{\alpha}\diagdown^{i} & \frac{1}{2} & -\frac{1}{2} \\ \hline \frac{1}{2} & -(i/\sqrt{6})\mu_0\vec{e}_z & -(i/\sqrt{3})\mu_0\vec{e}_+ \\ -\frac{1}{2} & -(i/\sqrt{3})\mu_0\vec{e}_- & (i/\sqrt{6})\mu_0\vec{e}_z \end{array}\ ,\qquad \vec{\mathrm{D}}_{X_2^+}^{\Gamma_6,i}(\beta):\ \begin{array}{c|cc} {}_{\beta}\diagdown^{i} & \frac{1}{2} & -\frac{1}{2} \\ \hline \frac{1}{2} & (i/\sqrt{6})\mu_0\vec{e}_z & (i/\sqrt{3})\mu_0\vec{e}_+ \\ -\frac{1}{2} & (i/\sqrt{3})\mu_0\vec{e}_- & -(i/\sqrt{6})\mu_0\vec{e}_z \end{array}\ .$$

CuBr:

$$\vec{\mathrm{D}}_{X^-}^{\Gamma_8,i}(\alpha):\ \begin{array}{c|cccc} {}_{\alpha}\diagdown^{i} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline \frac{1}{2} & -(i/\sqrt{2})\mu_0\vec{e}_- & (i/\sqrt{3})\mu_0\vec{e}_z & (i/\sqrt{6})\mu_0\vec{e}_+ & 0 \\ -\frac{1}{2} & 0 & -(i/\sqrt{6})\mu_0\vec{e}_- & (i/\sqrt{3})\mu_0\vec{e}_z & (i/\sqrt{2})\mu_0\vec{e}_+ \end{array}\ ,$$

$$\vec{\mathrm{D}}_{X_2^+}^{\Gamma_6,i}(\beta):\ \begin{array}{c|cc} {}_{\beta}\diagdown^{i} & \frac{1}{2} & -\frac{1}{2} \\ \hline \frac{3}{2} & \frac{1}{2}i\mu_0\vec{e}_+ & 0 \\ \frac{1}{2} & -(i/\sqrt{6})\mu_0\vec{e}_z & (i/2\sqrt{3})\mu_0\vec{e}_+ \\ -\frac{1}{2} & -(i/2\sqrt{3})\mu_0\vec{e}_- & -(i/\sqrt{6})\mu_0\vec{e}_z \\ -\frac{3}{2} & 0 & -\frac{1}{2}i\mu_0\vec{e}_- \end{array}\ ,\qquad \vec{\mathrm{D}}_{X_2^+}^{\Gamma_7,i}(\beta):\ \begin{array}{c|cc} {}_{\beta}\diagdown^{i} & \frac{1}{2} & -\frac{1}{2} \\ \hline \frac{3}{2} & -\frac{1}{6}i\mu_0\vec{e}_- & -(i/3\sqrt{2})\mu_0\vec{e}_z \\ \frac{1}{2} & 0 & (i/2\sqrt{3})\mu_0\vec{e}_- \\ -\frac{1}{2} & -(i/2\sqrt{3})\mu_0\vec{e}_+ & 0 \\ -\frac{3}{2} & -(i/3\sqrt{2})\mu_0\vec{e}_z & \frac{1}{6}i\mu_0\vec{e}_+ \end{array}\ ,$$

$$\vec{\mathrm{D}}_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_3,i}(\beta):\ \begin{array}{c|cccc} {}_{\beta}\diagdown^{i} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline \frac{3}{2} & -(i/\sqrt{6})\mu_0\vec{e}_z & \frac{1}{2}i\mu_0\vec{e}_+ & 0 & (i/2\sqrt{3})\mu_0\vec{e}_- \\ \frac{1}{2} & -\frac{1}{2}i\mu_0\vec{e}_- & (i/\sqrt{6})\mu_0\vec{e}_z & (i/2\sqrt{3})\mu_0\vec{e}_+ & 0 \\ -\frac{1}{2} & 0 & (i/2\sqrt{3})\mu_0\vec{e}_- & -(i/\sqrt{6})\mu_0\vec{e}_z & -\frac{1}{2}i\mu_0\vec{e}_+ \\ -\frac{3}{2} & (i/2\sqrt{3})\mu_0\vec{e}_+ & 0 & \frac{1}{2}i\mu_0\vec{e}_- & (i/\sqrt{6})\mu_0\vec{e}_z \end{array}\ ,$$

$$\vec{\mathrm{D}}_{X_2^+}^{\Gamma_8\in\Gamma_6\times\Gamma_5,i}(\beta):\ \begin{array}{c|cccc} {}_{\beta}\diagdown^{i} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline \frac{3}{2} & \frac{2}{3}i\mu_0\vec{e}_z & (i/\sqrt{6})\mu_0\vec{e}_+ & 0 & (i/3\sqrt{2})\mu_0\vec{e}_- \\ \frac{1}{2} & (i/\sqrt{6})\mu_0\vec{e}_- & 0 & (i/\sqrt{2})\mu_0\vec{e}_+ & 0 \\ -\frac{1}{2} & 0 & (i/\sqrt{2})\mu_0\vec{e}_- & 0 & (i/\sqrt{6})\mu_0\vec{e}_+ \\ -\frac{3}{2} & (i/3\sqrt{2})\mu_0\vec{e}_+ & 0 & (i/\sqrt{6})\mu_0\vec{e}_- & -\frac{2}{3}i\mu_0\vec{e}_z \end{array}\ ,$$

APPENDIX C: MATRICES OF THE EXCHANGE-COUPLING COEFFICIENTS $H_{X^-,X_2^+}^{rs,ij}$

1. CuCl

$$H_{X^-}^{\Gamma_7,ij}=\tfrac{1}{2}\Theta_{X^-,S}\,\delta_{i,j}\ ,\quad H_{X_2^+}^{\Gamma_6,ij}=\tfrac{1}{2}\Theta_{X_2^+,S}\,\delta_{i,j}\ ,\quad i,j=\pm\tfrac{1}{2}\,.$$

2. CuBr

$$H_{X^-}^{\Gamma_8,ij}=\begin{cases}\tfrac{1}{2}(\Theta_{X^-,S}+\Theta_{X^-,L})\,\delta_{i,j} & \text{if } i,j=\pm\tfrac{1}{2}\\ \tfrac{1}{2}(\Theta_{X^-,S}-\Theta_{X^-,L})\,\delta_{i,j} & \text{if } i,j=\pm\tfrac{3}{2}\,.\end{cases}$$

$H_{X_2^+}^{rs,ij}$: Nondiagonal terms appear between the states $(\Gamma_6, \Gamma_8, \Gamma_8')$ and $(\Gamma_7, \Gamma_8, \Gamma_8')$. We denote Γ_8 and Γ_8' to be representations arising from the direct products $\Gamma_6\times\Gamma_3$ and $\Gamma_6\times\Gamma_5$, respectively. The initial 12×12 matrix may be block-diagonalized into four 3×3 diagonal blocs, which read, with

$\Theta_{X_2^+,S} \equiv \Theta_S$ and $\Theta_{X_2^+,L} \equiv \Theta_L$:

$$\begin{array}{ccc} \Gamma_8'^{3/2} & \Gamma_8^{3/2} & \Gamma_7^{-1/2} \\ \left(\begin{array}{c} \frac{2}{3}(\Theta_S+\Theta_L) \\ \\ \text{H.c.} \end{array}\right. & \begin{array}{c} -(1/\sqrt{6})(\Theta_S+\Theta_L) \\ \frac{1}{2}\Theta_S \\ \end{array} & \left.\begin{array}{c} -\frac{1}{3}\sqrt{2}\,\Theta_L \\ (1/2\sqrt{3})\,\Theta_L \\ \frac{1}{6}\Theta_S \end{array}\right) \end{array}; \quad \begin{array}{ccc} \Gamma_8'^{-3/2} & \Gamma_8^{-3/2} & \Gamma_7^{1/2} \\ \left(\begin{array}{c} \frac{2}{3}(\Theta_S+\Theta_L) \\ \\ \text{H.c.} \end{array}\right. & \begin{array}{c} -(1/\sqrt{6})(\Theta_S+\Theta_L) \\ \frac{1}{2}\Theta_S \\ \end{array} & \left.\begin{array}{c} \frac{1}{3}\sqrt{2}\,\Theta_L \\ -(1/2\sqrt{3})\,\Theta_L \\ \frac{1}{6}\Theta_S \end{array}\right) \end{array};$$

$$\begin{array}{ccc} \Gamma_8'^{1/2} & \Gamma_8^{1/2} & \Gamma_6^{1/2} \\ \left(\begin{array}{c} \frac{2}{3}(\Theta_S-\Theta_L) \\ \\ \text{H.c.} \end{array}\right. & \begin{array}{c} (1/\sqrt{6})(\Theta_S-\Theta_L) \\ \frac{1}{2}\Theta_S \\ \end{array} & \left.\begin{array}{c} 0 \\ -\frac{1}{2}\Theta_L \\ \frac{1}{2}\Theta_S \end{array}\right) \end{array}; \quad \begin{array}{ccc} \Gamma_8'^{-1/2} & \Gamma_8^{-1/2} & \Gamma_6^{-1/2} \\ \left(\begin{array}{c} \frac{2}{3}(\Theta_S-\Theta_L) \\ \\ \text{H.c.} \end{array}\right. & \begin{array}{c} (1/\sqrt{6})(\Theta_S-\Theta_L) \\ \frac{1}{2}\Theta_S \\ \end{array} & \left.\begin{array}{c} 0 \\ \frac{1}{2}\Theta_L \\ \frac{1}{2}\Theta_S \end{array}\right) \end{array}.$$

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