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# Microscopic derivation of Frenkel excitons in second quantization

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Starting from the microscopic Hamiltonian describing free electrons in a periodic lattice, we derive the Hamiltonian appropriate to Frenkel excitons. This is done through a grouping of terms different from the one leading to Wannier excitons. This grouping makes the atomic states appear as a relevant basis to describe Frenkel excitons in the second quantization. Using them, we derive the Frenkel exciton creation operators as well as the commutators which rule these operators and which make the Frenkel excitons differ from elementary bosons. The main goal of the present paper is to provide the necessary grounds for future works on Frenkel exciton many-body effects, with the composite nature of these particles treated exactly through a procedure similar to the one we have recently developed for Wannier excitons.

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## I. INTRODUCTION

The absorption of photons in a dielectric solid can lead to delocalized excitations called excitons. These excitons are essentially of two types: the Wannier excitons[1] and the Frenkel excitons.[2]

Wannier excitons are formed in inorganic semiconductors. The relative motion of the electron and the hole from which the excitons are made encompasses hundreds of unit cells. This leads to a small binding energy ($\simeq 10$ meV) and a large Bohr radius ($\simeq 10$ nm). As a consequence, Wannier excitons start to interact at relatively low densities, giving rise to a large variety of many-body effects associated with optical nonlinearities, which makes these conventional semiconductors usable in today's technologies.

The second type of exciton, known as Frenkel exciton, is commonly found in organic crystals. These crystals are of potential importance for future electronic devices, which makes them under current intensive studies.[3–8] Frenkel excitons are formed with electron and hole localized on a small scale, of the order of a single molecular block ($\simeq 1$ nm), the typical binding energy being of the order of 1 eV. Due to interactions between blocks, these single molecule excitations are transferred from site to site, giving rise to a wave known as a Frenkel exciton.

These pictures can be qualitatively understood by noting that, in conventional (inorganic) semiconductors, the relative dielectric constant is rather large ($\simeq 10$), which makes the screening of the interaction between carriers quite strong. As a result, the attraction between electrons and holes is weak, which explains the large extension of their relative motion wave function. On the contrary, the small relative dielectric constant of molecular crystals ($\simeq 1$) leads to a strong electron-hole attraction which localizes the pair on a system unit cell.

The separation between Wannier and Frenkel excitons, of course, is not very sharp. The limitations of the simple Frenkel picture for excitons in organic semiconductors are well known, see, e.g., the review in Ref. 9 and the recent work in Ref. 5. Under certain conditions, it is necessary to introduce "charge-transfer exciton" in which the electron and the hole are located in different sites, with similarity to Wannier excitons for which the distance between electron and hole is large compared to the ion-ion distance. Usually, the lowest energy charge-transfer exciton has a wave function extended over two nearest neighbor sites, the electron being localized on the acceptor and the hole on the donor. Along the same line, recent progresses in device nanofabrication now allow one to obtain an organic-inorganic semiconductor structure in which the hybridization between Frenkel and Wannier excitons can be produced.[3,4]

Due to their small exciton Bohr radius, interactions between Frenkel excitons are expected to occur at a much larger density than the one at which many-body effects between Wannier excitons start to be noticeable. This comes from the fact that the dimensionless parameter which controls these many-body effects is

$$\eta = N(a_x/L)^D, \tag{1.1}$$

where $a_x$ is the exciton Bohr radius, $L$ the sample size, $D$ the space dimension, and $N$ the exciton number, the exciton density being $n = N/L^D$.

Most likely, as for Wannier excitons, interactions between Frenkel excitons are going to be of importance in electronic devices constructed with organic semiconductors. This is why a correct treatment of these interactions is highly desirable. Being made of indistinguishable carriers, Frenkel excitons, like Wannier excitons, are not well-defined objects, which makes the proper identification of the interactions *between* excitons not possible. As a direct consequence, one cannot describe these interactions through a potential, as usually done because of lack of a correct procedure.

Over the past few years, we have developed a many-body theory[10,11] for Wannier excitons, in which the composite nature of the particles is treated exactly. We have shown that Wannier excitons predominantly interact through the Pauli exclusion principle which exists between their fermionic components. This exclusion gives rise to very many carrier exchanges between excitons which are nicely visualized through Shiva diagrams,[12] rather different from Feynman

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diagrams due to the composite character of the particles. All our works on Wannier excitons end with the same conclusion: it is not possible to replace composite excitons by elementary excitons, as commonly done through sophisticated bosonization procedures;[13] either one misses terms as large as the ones kept or, in optical nonlinear effects, one even misses the dominant terms.[14] This can be readily seen from a dimensional argument: the Pauli scatterings associated with carrier exchanges are dimensionless, while the Coulomb scatterings are energylike quantities, so that they have to appear with an energy denominator, which can only be a photon detuning. This makes these Coulomb terms completely negligible in front of the pure exchange terms (missed with bosonized excitons) when unabsorbed photons have a large detuning.

The development of a similar procedure for Frenkel excitons requires that a second quantization formalism for these excitons be settled on a clean basis in order to possibly keep their composite boson nature exactly all over the calculations. Note that the second quantization formalism for Frenkel excitons is already used in Refs. 15–20. We discuss differences between the results of these papers and our results in Sec. VII.

In this work on Frenkel excitons, we propose a microscopic approach to the description of these excitons based on a second quantization formalism, starting from the Hamiltonian of free electrons in a periodic lattice. Through a grouping of terms different from the one leading to Wannier excitons, we introduce the atomic states as a physically relevant one-electron basis for Frenkel excitons and we rewrite the system Hamiltonian in terms of electrons and holes localized on atomic sites in order to have a precise description of the interactions. Since we use a second quantization scheme in terms of electrons and holes separately and not in terms of their product $B_n^\dagger$ as usually done, our approach automatically takes into account the fermionic composite nature of the particles forming the Frenkel excitons. This is going to be of crucial importance for a proper study of many-body effects involving these excitons. The present preliminary work actually provides the necessary grounds for further works on Frenkel exciton systems. In a forthcoming publication, we are going to use this second quantization formalism to derive the Coulomb and Pauli scatterings of two Frenkel excitons: these are the elementary scatterings on which all many-body effects dealing with excitons are based. We will then use these scatterings to calculate the ground state energy of $N$ Frenkel excitons in the low density limit, a physical quantity of basic relevance.

The present paper is organized as follows. In Sec. II, we start with the first quantization description of a periodic system made of interacting ions and electrons. We discuss the conceptual difference between Wannier and Frenkel excitons which leads to a different grouping of terms in the Hamiltonian. We introduce the atomic states as the appropriate one-electron basis for the problem when the tight-binding approximation, which neglects the overlaps between the atomic wave functions for electrons on different sites, is valid. We also discuss the conceptual difficulty associated with the atomic basis compared to the free electron and hole basis used in the case of Wannier excitons. In Sec. III, we derive the semiconductor Hamiltonian appropriate to Frenkel excitons in second quantization using this atomic basis. In Sec. IV, we switch to holes and we reduce the Hamiltonian to the terms which conserve the number of electron-hole pairs. We then discuss all these terms with particular attention to the one responsible for the excitation transfer from site to site. In Sec. V, we identify the lowest excited states of the Hamiltonian in the absence of interactions between sites and we show that they form a degenerate subspace. This degeneracy is split to give rise to Frenkel excitons by the intersite interactions. They are introduced in Sec. VI, which is devoted to the precise derivation of the creation operators for Frenkel excitons and the commutation rules which govern these operators. The precise handling of these commutators are at the basis of the many-body theory we are going to construct. We show that, like Wannier excitons, Frenkel excitons are composite bosons, their commutation rules differing from the ones of elementary bosons due to the fermionic nature of the electrons and holes forming these excitons. Previous works on Frenkel excitons in second quantization are discussed in Sec. VII. In Sec. VIII, we collect the main results of this paper and conclude.

## II. FIRST QUANTIZATION DESCRIPTION

### A. Semiconductor Hamiltonian in first quantization

Let us consider $N_s$ electrons with charge $-|e|$, located at $\mathbf{r}_i$, and $N_s$ ions with charge $+|e|$, located at $\mathbf{R}_n$, with $i$ and $n$ running from 1 to the number of sites $N_s$. In this work on Frenkel excitons, we are going to forget all spin degrees of freedom for the sake of simplicity. This physically corresponds to all the electrons having the same spin. This also means that we drop all degeneracies coming from the orbital part of the electronic levels. These spin and orbital degrees of freedom generate very interesting polarization effects. They, however, lead to heavy notations which are wise to avoid in a first work.

The semiconductor Hamiltonian can be written as

$$H = H_{kin} + V_{e\text{-}ion} + V_{ee} + V_{ion\text{-}ion}. \qquad (2.1)$$

The one-body operator $H_{kin}$ describes the electron kinetic energy,

$$H_{kin} = \sum_{i=1}^{N_s} \frac{p_i^2}{2m}, \qquad (2.2)$$

where $m$ is the *free* electron mass. The second term of Eq. (2.1), which describes the electron-ion Coulomb attraction, is also a one-electron operator. It reads as

$$V_{e\text{-}ion} = \sum_{i=1}^{N_s} \sum_{n=1}^{N_s} \frac{-e^2}{|\mathbf{r}_i - \mathbf{R}_n|}. \qquad (2.3)$$

The third operator $V_{ee}$ describes the Coulomb repulsion between electrons. This two-body operator is given by

$$V_{ee} = \frac{1}{2} \sum_{i \neq j} \sum \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \qquad (2.4)$$

The last term, $V_{ion\text{-}ion}$, which describes the Coulomb interaction between ions, is a constant with respect to the electron motion. It is, however, necessary to keep it in order to work with the Hamiltonian of a fully neutral system. This is required for the convergence of the Coulomb terms in the large sample limit. We will see below the importance of this point.

## B. Conceptual difference between Wannier and Frenkel excitons

### 1. Wannier excitons

Wannier excitons are constructed on delocalized electrons excited from the valence band to the conduction band. These semiconductor bands result from the periodic ionic structure of the semiconductor lattice. A simple way to make these bands appear is to add and substract a one-electron operator,

$$\bar{V}_{ee} = \sum_i \bar{v}_{ee}(r_i), \tag{2.5}$$

to the semiconductor Hamiltonian $H$. Although arbitrary, $\bar{V}_{ee}$ physically represents a mean electron-electron interaction. We will show below the appropriate way of choosing it.

This leads us to rewrite the semiconductor Hamiltonian $H$ [given by Eq. (2.1)] as

$$H = H_0^{(W)} + V_{Coul}, \tag{2.6}$$

where $V_{Coul}$, usually called the "semiconductor Coulomb interaction," corresponds to the difference

$$V_{Coul} = V_{ee} - \bar{V}_{ee}.$$

The zero order Hamiltonian for Wannier excitons $H_0^{(W)}$ is a sum of one-electron operators. It can thus be written as

$$H_0^{(W)} = H_{kin} + V_{e\text{-}ion} + \bar{V}_{ee} + V_{ion\text{-}ion} = \sum_i h_i^{(W)}, \tag{2.7}$$

where the one-electron operator $h_i^{(W)}$ is given by

$$h_i^{(W)} = \frac{p_i^2}{2m} + \sum_n \frac{-e^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \bar{v}_{ee}(r_i) + \frac{1}{N_s} V_{ion\text{-}ion} = \frac{p_i^2}{2m} + v(\mathbf{r}_i). \tag{2.8}$$

This one-electron operator has the lattice periodicity if $\bar{v}_{ee}(r)$ is chosen with such a periodicity. Besides this requirement, we must also enforce $\bar{v}_{ee}(r)$ to be such that the resulting interaction $v(r)$ defined in Eq. (2.8) fulfills

$$\int d\mathbf{r}\, v(\mathbf{r}) = 0 \tag{2.9}$$

in order for $H_0^{(W)}$ to be the Hamiltonian of a fully neutral system. The simplest choice for $\bar{v}_{ee}(r)$ is to take it as a constant, through the so-called positive jellium, namely, $\bar{v}_{ee}(r) = N_s^{-1} V_{ion\text{-}ion}$.

Due to the periodicity of the potential $v(r)$, the eigenstates of $h_i^{(W)}$ are made of delocalized states separated by band gaps. The relevant ones for the physics of Wannier excitons belong to the last filled band, called the valence band, and the first empty band, called the conduction band. Close to these band extrema, the eigenstate energies can be written as $\Delta + \hbar^2\mathbf{k}^2/2m_c$ and $\hbar^2\mathbf{k}^2/2m_v$, where $\Delta$ is the band gap, while $m_c$ and $m_v$ are the electron masses for the conduction and valence bands dressed by the lattice periodic potential. Note that the effective mass for valence electrons, which are close to a maximum, is negative, so that the resulting valence hole mass, defined as $m_h = -m_v$, is positive.

The eigenstates $|\nu k\rangle$ of the Hamiltonian $h_i^{(W)}$ with $\nu$ equal to $v$ or $c$ for valence and conduction states,

$$(h_i^{(W)} - \varepsilon_{\nu k})|\nu k\rangle = 0, \tag{2.10}$$

are then used as a one-electron basis to rewrite the semiconductor Hamiltonian $H$ in the second quantization.

### 2. Frenkel excitons

The situation for Frenkel excitons is totally different: while Wannier excitons are constructed on delocalized valence and conduction electron states, the physical picture of the semiconductor excitations giving rise to Frenkel excitons is a set of electrons tight to their ions, these electrons switching from the atomic ground state to the atomic first excited level. Consequently, the physically relevant one-electron states for Frenkel excitons are not the free (delocalized) electrons in a periodic lattice used in the case of Wannier excitons but instead the electron localized atomic states associated with the various ion sites.

In order to make these physically relevant atomic states appear, we are led to perform a grouping of terms in the semiconductor Hamiltonian $H$ [given in Eq. (2.1)] different from the one we have done for Wannier excitons. This new grouping of terms is

$$H = H_0^{(F)} + V_{e\text{-}e} + V_{ion\text{-}ion}. \tag{2.11}$$

The zero order Hamiltonian for Frenkel excitons $H_0^{(F)}$ is still a one-electron operator, but it now contains the electron kinetic contribution plus the electron-ion potential, so that it differs from the zero order Hamiltonian for Wannier excitons $H_0^{(W)}$. It precisely reads as

$$H_0^{(F)} = H_{kin} + V_{e\text{-}ion} = \sum_i h_i, \tag{2.12}$$

where $h_i$ is now given by

$$h_i = \frac{p_i^2}{2m} - \sum_{n=1}^{N_s} \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_n|}. \tag{2.13}$$

## C. Atomic states

We can note that, in the one-electron Hamiltonian $h_i$, the interactions of the electron $i$ with *all* the ions $n$ enter, so that $h_i$ differs from a simple atomic Hamiltonian. Nevertheless, it is rather clear that the physically relevant one-electron states for Frenkel excitons are going to be these atomic states, i.e., the eigenstates of one electron in the presence of *one* ion. Let us introduce them.

(i) The atomic states $|\nu\rangle$ for one ion located at $R=0$, associated with the Hamiltonian

$$h_{atom} = \frac{p^2}{2m} - \frac{e^2}{r}, \tag{2.14}$$

are such that

$$(h_{atom} - \varepsilon_\nu)|\nu\rangle = 0, \tag{2.15}$$

their wave functions being $\varphi_\nu(\mathbf{r}) = \langle \mathbf{r}|\nu\rangle$. As the Hamiltonian eigenstates form an orthogonal set, we do have

$$\langle \nu'|\nu\rangle = \int d\mathbf{r}\varphi^*_{\nu'}(\mathbf{r})\varphi_\nu(\mathbf{r}) = \delta_{\nu'\nu}. \tag{2.16}$$

(ii) If we still consider one ion but located at $R_n$ instead of $R=0$, the corresponding atomic Hamiltonian reads as

$$h^{(n)} = \frac{p^2}{2m} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_n|}. \tag{2.17}$$

Due to translational invariance, the eigenstates of $h^{(n)}$ in terms of the atomic Hamiltonian states $(\varepsilon_\nu, |\nu\rangle)$ read as

$$(h^{(n)} - \varepsilon_\nu)|\nu n\rangle = 0,$$

their wave function being such that

$$\langle \mathbf{r}|\nu n\rangle = \varphi_{\nu n}(\mathbf{r}) = \varphi_\nu(\mathbf{r} - \mathbf{R}_n). \tag{2.18}$$

For a given ion $R_n$, the bound and extended states of the Hamiltonian $h^{(n)}$ form a complete basis for one-electron states, so that we do have

$$\langle n\nu'|\nu n\rangle = \delta_{\nu'\nu}, \tag{2.19a}$$

$$I = \sum_\nu |\nu n\rangle\langle n\nu|, \tag{2.19b}$$

with the sum restricted to the atomic levels $\nu$.

(iii) If we now turn to the Hamiltonian $H_0^{(F)}$ [given in Eq. (2.13)], we see that it differs from a bare sum of atomic Hamiltonians, since each electron feels the interaction of all the other ions. This is a real difficulty: unlike Wannier excitons, in which the eigenstates of $H_0^{(W)}$ can be obtained exactly, the diagonalization of the one-body part of $H_0^{(F)}$ for Frenkel excitons can only be approximated due to this multiple ion interaction. As shown below, this will force us to make assumptions on the atomic wave function extensions, the Frenkel exciton picture being appropriate when the tight-binding approximation is valid.

Due to the sum over all ions contained in the one-body Hamiltonian $H_0^{(F)}$ given in Eq. (2.13), it is, on the one hand, clear that the states $|\nu n\rangle$ for a *fixed* $n=n_0$ [which form a complete set for one-electron states due to Eqs. (2.19a) and (2.19b)] cannot be a physically relevant basis to describe Frenkel excitons made of excitations on all possible ion sites. On the other hand, it is also clear that if we leave $n$ running over all the ion positions, the states $|\nu n\rangle$ for all $\nu$ and all $n$ form an overcomplete set—the states $|\nu n\rangle$ for one particular $n$ forming a complete set already. As a bare consequence of this overcompleteness, the states $|\nu n\rangle$ with different $n$ are not exactly orthogonal.

We can, however, note that, for atomic states $\nu$ and $\nu'$ highly localized compared to the ion-ion distance, the wave function overlap between different atoms is essentially zero,

$$\varphi^*_{\nu'}(\mathbf{r} - \mathbf{R}_{n'})\varphi_\nu(\mathbf{r} - \mathbf{R}_n) \simeq 0 \quad \text{for } n' \neq n, \tag{2.20}$$

whatever $r$ is. Consequently, the scalar product of such atomic states reduces to

$$\langle n'\nu'|\nu n\rangle = \int d\mathbf{r}\varphi^*_{\nu'}(\mathbf{r} - \mathbf{R}_{n'})\varphi_\nu(\mathbf{r} - \mathbf{R}_n) \simeq \delta_{n'n}\delta_{\nu'\nu} \tag{2.21}$$

due to Eq. (2.16): The states $|\nu n\rangle$ for highly localized $\nu$ are thus quasiorthogonal.

(iv) In spite of these difficulties, linked to the overcompleteness of the states $|\nu n\rangle$ with $n$ running over all ion sites, the $|\nu n\rangle$ states have to play a role in the Frenkel exciton physics. This is why we are going to use them in the second quantization description of Frenkel excitons.

Before going further, let us add some comments on using these states $|\nu n\rangle$ as a basis for second quantization. It is clear that Eq. (2.20) is not valid for atomic extended states nor even for the highest bound levels. The states $|\nu n\rangle$ can, however, be seen as an acceptable basis for one-electron states if the problem at hand relies on the highly localized (lowest) atomic states for which the overlaps between atomic wave functions for different ions are negligible. This is actually the case for conventional Frenkel excitons in which the $\nu$ of interest reduce to the ground state ($\nu=0$) and the first excited state ($\nu=1$).

A somewhat cleaner way to present the use of these overcomplete states $|\nu n\rangle$ is to say that we can always add to the two sets of atomic states of physical interest, namely, $|\nu=0,n\rangle$ and $|\nu=1,n\rangle$, other states constructed "in an appropriate way" in order to form a complete orthogonal basis when added to the set of two states $|\nu=(0,1),n\rangle$. In problems physically controlled by the two lowest atomic states, these additional "appropriate states" are not going to play a role in the final results. This is why it is far simpler not to consider them at all and to stay with the full overcomplete set of states $|\nu n\rangle$ for all $n$ and all $\nu$, the $\nu$ different from (0,1) playing no role in the end. As a direct consequence, in the following, the sums over $\nu$ will have to be considered as sums over $\nu=(0,1)$.

## III. FRENKEL EXCITON HAMILTONIAN IN THE SECOND QUANTIZATION

### A. One-electron creation operators relevant to Frenkel excitons

Let $a^\dagger_{\nu n}$ be the creation operator for the atomic state $|\nu n\rangle$ on site $n$ and atomic level $\nu$,

$$|\nu n\rangle = a^\dagger_{\nu n}|v\rangle. \tag{3.1}$$

Since the state $|\nu n\rangle$ can be expanded on the plane wave basis $|\mathbf{k}\rangle$ as $|\nu n\rangle = \Sigma_\mathbf{k}|\mathbf{k}\rangle\langle\mathbf{k}|\nu n\rangle$, the atomic state creation operator $a^\dagger_{\nu n}$ in terms of the free electron creation operator $a^\dagger_\mathbf{k}$ reads as

$$a^\dagger_{\nu n} = \sum_\mathbf{k} a^\dagger_\mathbf{k}\langle\mathbf{k}|\nu n\rangle. \tag{3.2}$$

By using the fact that the electron operators anticommute, $[a_{\mathbf{k}},a^{\dagger}_{\mathbf{k}'}]_{+}=\delta_{\mathbf{k}\mathbf{k}'}$, it is easy to show, using the above relation, that the anticommutator for atomic state destruction operators is exactly zero,

$$[a_{\nu'n'},a_{\nu n}]_{+}=0, \tag{3.3}$$

while for the lowest highly localized states $\nu=(0,1)$, we do have [due to Eq. (2.21)]

$$[a_{\nu'n'},a^{\dagger}_{\nu n}]_{+}=\sum_{\mathbf{k}}\langle\nu'n'|\mathbf{k}\rangle\langle\mathbf{k}|\nu n\rangle=\langle\nu'n'|\nu n\rangle\simeq\delta_{\nu'\nu}\delta_{n'n},$$

so that, within the tight-binding approximation, the operators $a^{\dagger}_{\nu n}$ follow the standard commutation relations for fermion operators.

### B. One-body part of the Frenkel exciton Hamiltonian

Let us now use these operators to rewrite the part $H_0^{(F)}$ of the semiconductor Hamiltonian given by Eq. (2.12). Since $H_0^{(F)}$ is a sum of one-body operators, it can be written in terms of the creation operators for the one-electron states $|\nu n\rangle$ relevant to Frenkel excitons as

$$H_0^{(F)}=\sum_{\nu'n'\nu n}\varepsilon(\nu'n',\nu n)a^{\dagger}_{\nu'n'}a_{\nu n}. \tag{3.4}$$

According to the second quantization procedure, the prefactor $\varepsilon(\nu'n',\nu n)$ is given by

$$\varepsilon(\nu'n',\nu n)=\int d\mathbf{r}\varphi^{*}_{\nu'n'}(\mathbf{r})\left[\frac{\mathbf{p}^2}{2m}-\sum_{m=1}^{N_s}\frac{e^2}{|\mathbf{r}-\mathbf{R}_m|}\right]\varphi_{\nu n}(\mathbf{r}). \tag{3.5}$$

Due to Eq. (2.18), this prefactor also reads as

$$\varepsilon(\nu'n',\nu n)=\int d\mathbf{r}\varphi^{*}_{\nu'n'}(\mathbf{r})\left[\varepsilon_{\nu}-\sum_{m\neq n}\frac{e^2}{|\mathbf{r}-\mathbf{R}_m|}\right]\varphi_{\nu n}(\mathbf{r}), \tag{3.6}$$

so that, for highly localized states, as the ones of physical interest, it reduces [due to Eq. (2.20)] to

$$\varepsilon(\nu'n',\nu n)\simeq\delta_{nn'}[\varepsilon_{\nu}\delta_{\nu\nu'}+v(\nu',\nu)], \tag{3.7}$$

where $v(\nu',\nu)$ comes from the interactions with all the other ions. Due to the translational invariance of the Hamiltonian leading to Eq. (2.18), $v(\nu',\nu)$ can be rewritten as

$$\begin{aligned}v(\nu',\nu)&=\sum_{m\neq n}\int d\mathbf{r}\varphi^{*}_{\nu'}(\mathbf{r})\sum_{m\neq n}\frac{-e^2}{|\mathbf{r}-(\mathbf{R}_m-\mathbf{R}_n)|}\varphi_{\nu}(\mathbf{r})\\&=\left\langle\nu'\left|\sum_{R\neq0}\frac{-e^2}{|\mathbf{r}-\mathbf{R}|}\right|\nu\right\rangle,\end{aligned} \tag{3.8}$$

where the vectors $\mathbf{R}$ in the sum correspond to all possible distances between ions. The one-body part of the semiconductor Hamiltonian appropriate to Frenkel excitons then ends by reading as

$$H_0^{(F)}=\sum_{\nu,n}\tilde{\varepsilon}_{\nu}a^{\dagger}_{\nu n}a_{\nu n}+\sum_{n,\nu'\neq\nu}v(\nu',\nu)a^{\dagger}_{\nu'n}a_{\nu n}, \tag{3.9}$$

where $\tilde{\varepsilon}_{\nu}=\varepsilon_{\nu}+v(\nu,\nu)$. As seen from the definition of $v(\nu',\nu)$, given by Eq. (3.8), the second term in $H_0^{(F)}$ describes the fact that the electron of a given site can change its atomic level from $\nu$ to $\nu'$ while staying on the same site, due to its interaction with the ions of all the other sites. For states $\nu=(0,1)$ highly localized compared to the ion-ion distance, these $v(\nu',\nu)$ scatterings, however, are extremely small.

### C. Electron-electron interaction

Let us now turn to the two-body operator $V_{ee}$ [defined in Eq. (2.4)]. The standard second quantization procedure leads us to write it on the atomic basis $|\nu n\rangle$ as

$$V_{ee}=\frac{1}{2}\sum_{\{\nu,n\}}V\begin{pmatrix}\nu_2'n_2' & \nu_2n_2\\ \nu_1'n_1' & \nu_1n_1\end{pmatrix}a^{\dagger}_{\nu_1'n_1'}a^{\dagger}_{\nu_2'n_2'}a_{\nu_2n_2}a_{\nu_1n_1}, \tag{3.10}$$

where the prefactor is given by

$$\begin{aligned}V\begin{pmatrix}\nu_2'n_2' & \nu_2n_2\\ \nu_1'n_1' & \nu_1n_1\end{pmatrix}&=\int d\mathbf{r}_1d\mathbf{r}_2\varphi^{*}_{\nu_1'n_1'}(\mathbf{r}_1)\varphi^{*}_{\nu_2'n_2'}(\mathbf{r}_2)\\&\quad\times\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\varphi_{\nu_2n_2}(\mathbf{r}_2)\varphi_{\nu_1n_1}(\mathbf{r}_1).\end{aligned} \tag{3.11}$$

For $\nu$ and $\nu'$ equal to (0,1), this prefactor is nonzero for $n_1'=n_1$ and $n_2'=n_2$ only due to Eq. (2.20). If we then use the translational invariance of atomic wave functions [namely, Eq. (2.18)], it is easy to see that $V_{ee}$ can be written as

$$V_{ee}=\frac{1}{2}\sum_{\substack{n_1\nu_1'\nu_1\\ n_2\nu_2'\nu_2}}V_{R_{n_1}-R_{n_2}}\begin{pmatrix}\nu_2' & \nu_2\\ \nu_1' & \nu_1\end{pmatrix}a^{\dagger}_{\nu_1'n_1}a^{\dagger}_{\nu_2'n_2}a_{\nu_2n_2}a_{\nu_1n_1}, \tag{3.12}$$

where the electron-electron scattering depends on the distance $R$ between ions through

$$\begin{aligned}V_R\begin{pmatrix}\nu_2' & \nu_2\\ \nu_1' & \nu_1\end{pmatrix}&=V_{-R}\begin{pmatrix}\nu_1' & \nu_1\\ \nu_2' & \nu_2\end{pmatrix}\\&=\int d\mathbf{r}_1d\mathbf{r}_2\varphi^{*}_{\nu_1'}(\mathbf{r}_1)\varphi^{*}_{\nu_2'}(\mathbf{r}_2)\\&\quad\times\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2+\mathbf{R}|}\varphi_{\nu_2}(\mathbf{r}_2)\varphi_{\nu_1}(\mathbf{r}_1).\end{aligned} \tag{3.13}$$

### D. Restricted Hamiltonian for Frenkel excitons

The atomic states $(\nu=0,n)$ and $(\nu=1,n)$ are the equivalents of the valence and the conduction band states for Wannier excitons. By noting that the energy of the atomic ground state $\varepsilon_{\nu=0}$ is very different from the one of the first excited level, $\varepsilon_{\nu=1}$, we are led to think that the physically relevant

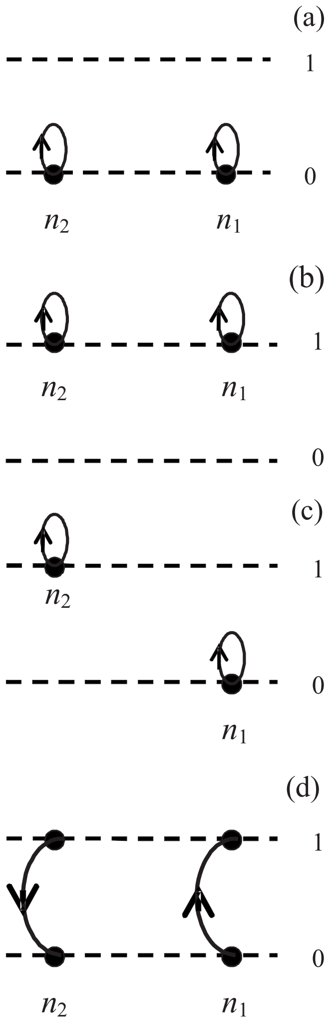

FIG. 1. Electron-electron potentials [given in Eq. (3.15)]. (a) Terms in $a_{0n_1}^\dagger a_{0n_2}^\dagger a_{0n_2} a_{0n_1}$, in which the two electrons stay in their atomic ground state $\nu=0$. (b) Terms in $a_{1n_1}^\dagger a_{1n_2}^\dagger a_{1n_2} a_{1n_1}$, in which the two electrons stay in their atomic excited state $\nu=1$. (c) Terms in $a_{0n_1}^\dagger a_{1n_2}^\dagger a_{1n_2} a_{0n_1}$, in which one electron stays in the ground state, while the another one stays in the excited state. (d) Terms in $a_{1n_1}^\dagger a_{0n_2}^\dagger a_{1n_2} a_{0n_1}$, in which the electron on site $n_1$ is excited from the ground state $\nu=0$ to the excited state $\nu=1$, while the electron on site $n_2$ returns to its ground state. In these four processes, the number of electrons in the ground state and in the excited state are separately conserved.

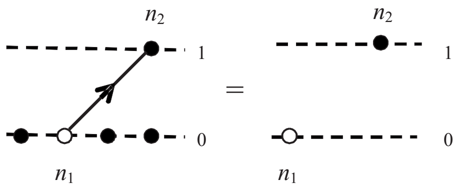

FIG. 2. Excitation of an electron from the ground state on site $n_1$ to the excited state on site $n_2$: this corresponds to the creation of an electron-hole pair on sites $(n_2, n_1)$.

part of the Hamiltonian corresponds to processes in which the number of electrons in the $\nu=0$ level and the number of electrons in the $\nu=1$ level are separately conserved. This is equivalent to processes which keep the number of conduction electrons and the number of valence electrons fixed for Wannier excitons. This leads us to drop terms with $\nu \neq \nu'$ in $H_0^{(F)}$. The latter then reduces to the first sum of Eq. (3.9), namely,

$$H_0^{(F)} \simeq H_0 = \tilde{\varepsilon}_0 \sum_n a_{0n}^\dagger a_{0n} + \tilde{\varepsilon}_1 \sum_n a_{1n}^\dagger a_{1n}. \qquad (3.14)$$

If we now turn to the Coulomb interaction $V_{ee}$ [given in Eq. (3.12)] and we also keep terms which conserve the number of $\nu=0$ and $\nu=1$ electrons separately, we see that they are of two kinds. (i) $V_{ee}$ contains intra-atomic processes, in which the electron of a given site stays on the same level. These processes correspond to terms such as $a_{\nu n}^\dagger a_{\nu n'}^\dagger a_{\nu n'} a_{\nu n}$ with $\nu$ equal to 0 or 1. $V_{ee}$ also contains terms such as $a_{0n}^\dagger a_{1n'}^\dagger a_{1n'} a_{0n}$ with 0 and 1 possibly exchanged—which makes such a term appear with a factor of 2. (ii) In addition, $V_{ee}$ contains interatomic processes, in which the electron of one site jumps from $\nu=0$ to $\nu=1$, while the electron of another site goes from $\nu=1$ to $\nu=0$, namely, terms such as $a_{0n}^\dagger a_{1n'}^\dagger a_{0n'} a_{1n}$, with 0 and 1 possibly exchanged—which makes this term also appear with a factor of 2.

Consequently, $V_{ee}$ for Frenkel excitons ends by reading $V_{ee} \simeq V_{00} + V_{11} + V_{01}^{dir} + V_{01}^{exch}$ with

$$V_{00} = \frac{1}{2} \sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} a_{0n_1}^\dagger a_{0n_2}^\dagger a_{0n_2} a_{0n_1},$$

$$V_{11} = \frac{1}{2} \sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} a_{1n_1}^\dagger a_{1n_2}^\dagger a_{1n_2} a_{1n_1},$$

$$V_{01}^{dir} = \sum_{n_1 n_2} V_{R_{n_1}-R_{n_2}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} a_{0n_1}^\dagger a_{1n_2}^\dagger a_{1n_2} a_{0n_1},$$

$$V_{01}^{exch} = \sum_{n_1 n_2} V_{R_{n_1}-R_{n_2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} a_{1n_1}^\dagger a_{0n_2}^\dagger a_{1n_2} a_{0n_1}. \qquad (3.15)$$

Note that the last two terms differ from zero for $n_1=n_2$, while the first two terms are equal to zero for $n_1=n_2$; this is why we have explicitly excluded $n_1=n_2$ from the first two sums.

These four terms are shown in Fig. 1.

## IV. ELECTRON-HOLE HAMILTONIAN FOR FRENKEL EXCITONS

### A. Electron and hole creation operators

As for Wannier excitons, it is appropriate to introduce the concept of a hole. This will allow us to start with a $|0\rangle$ state, in which the electrons of all sites are in the atomic ground state ($\nu=0$), and to speak in terms of excitations with respect to this ground state, i.e., in terms of the small number of sites in which the electron has jumped into the excited state, this number being 1 for one exciton, 2 for two excitons, and so on. Such an elementary electron-hole excitation is shown in

Fig. 2. Due to the electron-hole attraction and the cost in electrostatic energy induced by the electron and hole separation, we expect the lowest energy excited states to correspond to $n_1 = n_2$. As a direct consequence, the Frenkel excitons are going to be made from electron-hole pairs on the same site. Let us now recover this obvious result.

In the absence of spin degrees of freedom, the electron and hole creation operators are simply linked to the $\nu=0$ and $\nu=1$ atomic state level creation operators through

$$a_{1n}^{\dagger} = a_n^{\dagger},$$

$$a_{0n} = b_n^{\dagger}. \tag{4.1}$$

By using the anticommutation relations for electrons in atomic states given by Eq. (3.3), it is straightforward to show that $[a_{n'}, a_n]_+ = 0$, while

$$[a_{n'}, a_n^{\dagger}]_+ = [a_{1n'}, a_{1n}^{\dagger}]_+ = \langle 1n' | 1n \rangle \simeq \delta_{nn'} \tag{4.2}$$

for highly localized atomic states compared to the interatomic distance, which makes Eq. (2.21) valid. In the same way, $[b_{n'}, b_n]_+ = 0$, while

$$[b_{n'}, b_n^{\dagger}]_+ = [a_{0n'}^{\dagger}, a_{0n}]_+ = \langle 0n' | 0n \rangle \simeq \delta_{n'n}. \tag{4.3}$$

If we now turn to the anticommutator between electron and hole operators, we find that

$$[a_{n'}, b_n^{\dagger}]_+ = [a_{1n'}, a_{0n}]_+ = 0,$$

$$[a_{n'}, b_n]_+ = [a_{1n'}, a_{0n}^{\dagger}]_+ = \langle 1n' | 0n \rangle \simeq 0 \tag{4.4}$$

for highly localized atomic states, this last anticommutator being exactly equal to zero for $n=n'$ due to Eq. (2.19a).

### B. One-body operator $H_0$ in terms of electrons and holes

In order to rewrite the part $H_0$ of the Frenkel exciton Hamiltonian given in Eq. (3.14) in terms of electron and hole operators, we first note that $a_{0n}^{\dagger} a_{0n} = b_n b_n^{\dagger} = 1 - b_n^{\dagger} b_n$, so that

$$H_0 = N_s \tilde{\varepsilon}_0 + \sum_n (\tilde{\varepsilon}_1 a_n^{\dagger} a_n - \tilde{\varepsilon}_0 b_n^{\dagger} b_n). \tag{4.5}$$

Due to other contributions in $a_n^{\dagger} a_n$ and $b_n^{\dagger} b_n$ coming from the electron-electron interaction, the electron energy and the hole energy are going to differ from $\tilde{\varepsilon}_1$ and $(-\tilde{\varepsilon}_0)$, as will now be shown.

### C. Electron-electron interaction in terms of electrons and holes

We now turn to the electron-electron interactions given in Eq. (3.15). Since $a_{1n} = a_n$, the second term of this equation [shown in Fig. 3(a)] readily gives the Coulomb repulsion between two electrons as

$$V_{11} = \tilde{V}_{ee} = \frac{1}{2} \sum_{n_1 \neq n_2} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} a_{n_1}^{\dagger} a_{n_2}^{\dagger} a_{n_2} a_{n_1}. \tag{4.6}$$

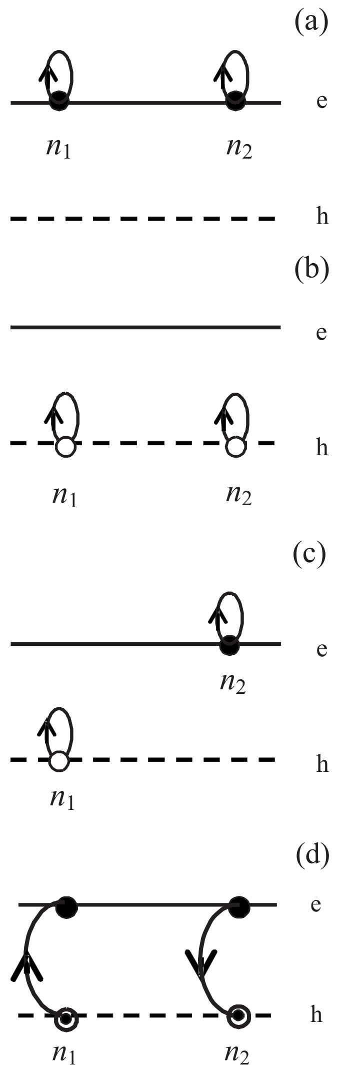

FIG. 3. (a) Electron-electron interaction $\tilde{V}_{ee}$ [given in Eq. (4.6)]. (b) Hole-hole interaction $\tilde{V}_{hh}$ [given in Eq. (4.13)]. (c) Direct electron-hole interaction $V_{eh}^{(dir)}$ [given in Eq. (4.8)]. (d) Exchange electron-hole interaction $V_{eh}^{(exch)}$ [given in Eq. (4.10)].

In order to rewrite the third term of Eq. (3.15), we first note that $a_{0n_1}^{\dagger} a_{1n_2}^{\dagger} a_{1n_2} a_{0n_1} = b_{n_1} a_{n_2}^{\dagger} a_{n_2} b_{n_1}^{\dagger} = a_{n_2}^{\dagger} a_{n_2} (1 - b_{n_1}^{\dagger} b_{n_1})$, so that this third term gives two contributions,

$$V_{01}^{dir} = V_{eh}^{(dir)} + \sum_{n_2} a_{n_2}^{\dagger} a_{n_2} \sum_{n_1} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix}. \tag{4.7}$$

The second term of $V_{01}^{dir}$, which comes from the Coulomb interaction between one electron in an atomic excited level and all the atomic ground states, is going to dress the bare electron energy $\tilde{\varepsilon}_1$ [appearing in Eq. (4.5)]. The first term of $V_{01}^{dir}$, given by

$$V_{eh}^{(dir)} = - \sum_{n_1 n_2} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} b_{n_1}^{\dagger} a_{n_2}^{\dagger} a_{n_2} b_{n_1}, \tag{4.8}$$

describes a direct electron-hole attraction, the electron and the hole staying on their sites [see Fig. 3(c)].

In the same way, the fourth term of Eq. (3.15) gives two contributions since $a_{1n_1}^\dagger a_{0n_2}^\dagger a_{1n_2} a_{0n_1} = a_{n_1}^\dagger b_{n_2} a_{n_2} b_{n_1}^\dagger = -a_{n_1}^\dagger (\delta_{n_2 n_1} - b_{n_1}^\dagger b_{n_2}) a_{n_2}$, so that it reads as

$$V_{01}^{exch} = V_{eh}^{(exch)} - V_{R=0}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\sum_n a_n^\dagger a_n. \tag{4.9}$$

The second term of $V_{01}^{exch}$ is also going to dress the electron energy $\tilde{\varepsilon}_1$, while the first term, given by

$$V_{eh}^{(exch)} = \sum_{n_1 n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} a_{n_1}^\dagger b_{n_1}^\dagger b_{n_2} a_{n_2} \tag{4.10}$$

and shown in Fig. 3(d), corresponds to the destruction of one electron-hole pair on the site $n_2$ and to its recreation on the site $n_1$. Let us stress that, while the direct electron-hole Coulomb interaction $V_{eh}^{(dir)}$ in Eq. (4.8) corresponds to an attraction, this exchange electron-hole Coulomb interaction $V_{eh}^{(exch)}$ is repulsive.

We now turn to the first term of Eq. (3.15) between two ground state electrons $\nu=0$. We first note that, due to Eqs. (3.3) and (3.4),

$$\begin{aligned} a_{0n_1}^\dagger a_{0n_2}^\dagger a_{0n_2} a_{0n_1} &= b_{n_1} b_{n_2} b_{n_2}^\dagger b_{n_1}^\dagger \\ &= 1 - b_{n_1}^\dagger b_{n_1} - b_{n_2}^\dagger b_{n_2} + b_{n_2}^\dagger b_{n_1}^\dagger b_{n_1} b_{n_2}, \end{aligned} \tag{4.11}$$

so that, by grouping the two terms with a minus sign, $V_{00}$ generates three contributions,

$$\begin{aligned} V_{00} = {}& \frac{1}{2}\sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix} \\ & - \sum_n b_n^\dagger b_n \sum_{n' \neq n} V_{R_n - R_{n'}}\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix} + \tilde{V}_{hh}. \end{aligned} \tag{4.12}$$

The last term of $V_{00}$, shown in Fig. 3(b), corresponds to a hole-hole repulsion. It precisely reads as

$$\tilde{V}_{hh} = \frac{1}{2}\sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix} b_{n_1}^\dagger b_{n_2}^\dagger b_{n_2} b_{n_1}. \tag{4.13}$$

The first term of $V_{00}$ is a bare constant which describes all Coulomb interactions between ground state atomic levels. It produces a band gap renormalization. The second term of $V_{00}$ comes from the interaction between one particular ground state electron (in the site $n$) and the other ground state electrons. This term has to appear when the site $n$ is empty, i.e., occupied by a hole, in order to compensate for the electron-electron repulsion already included in the constant term of $V_{00}$. This second term is going to dress the atomic ground state energy $\tilde{\varepsilon}_0$ (when speaking in terms of holes) as fully reasonable, since all interactions between atomic ground state electrons are by construction forgotten when we turn to electrons and holes. These interactions actually appear through the renormalization of the atomic ground state and excited state energies, the electron and the hole being more subtle objects that just one electron in the atomic excited state and one electron absence in the atomic ground state.

### D. Electron-hole Hamiltonian

If we now collect all these terms, we end by writing the part of the semiconductor Hamiltonian appropriate to Frenkel excitons $H_0 + V_{00} + V_{11} + V_{01}^{dir} + V_{01}^{exch} + V_{ion\text{-}ion}$ as

$$H^{(F)} = \Delta + H_{eh} + V_{intra} + V_{inter}. \tag{4.14}$$

(i) $\Delta$ is a constant which contains contributions from the atomic level ground states only. It precisely reads as

$$\begin{aligned} \Delta = {}& N_s \varepsilon_0 + N_s v(0,0) + \frac{1}{2}\sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix} \\ & + \frac{1}{2}\sum_{n_1 \neq n_2} \frac{e^2}{|\mathbf{R}_{n_1} - \mathbf{R}_{n_2}|} \\ = {}& N_s(\varepsilon_0 + \varepsilon_0^{(Coul)}), \end{aligned} \tag{4.15}$$

where $N_s$ is the number of ion sites. By using Eqs. (3.8) and (3.13), the Coulomb contribution to this band gap renormalization (given by the bracket of the above expression) can be rewritten as

$$\begin{aligned} \varepsilon_0^{(Coul)} = \sum_{R \neq 0} \int d\mathbf{r}\, d\mathbf{r}' |\varphi_0(\mathbf{r})|^2 |\varphi_0(\mathbf{r}')|^2 \Bigg[ & \frac{-e^2}{|\mathbf{r} - \mathbf{R}|} \\ & + \frac{1}{2}\frac{e^2}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}|} + \frac{1}{2}\frac{e^2}{R} \Bigg], \end{aligned} \tag{4.16}$$

where the $R$'s are the possible distances between two ions. Note that the last term ($e^2/R$), which comes from the ion-ion interaction and which makes the system at hand neutral, allows for the convergence of $\varepsilon_0^{(Coul)}$ in the large sample limit.

(ii) The second term of Eq. (4.14) is a one-body operator which can be written as

$$H_{eh} = \varepsilon_e \sum_n a_n^\dagger a_n + \varepsilon_h \sum_n b_n^\dagger b_n. \tag{4.17}$$

It describes the electron and hole kinetic energies. These energies, given by

$$\varepsilon_e = \varepsilon_1 + v(1,1) + \sum_R V_R\begin{pmatrix}1 & 1\\ 0 & 0\end{pmatrix} - V_{R=0}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \tag{4.18}$$

$$-\varepsilon_h = \varepsilon_0 + v(0,0) + \sum_{R \neq 0} V_R\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix}, \tag{4.19}$$

differ from the atomic bare ground and excited state energies $-\varepsilon_0$ and $\varepsilon_1$ due to Coulomb interactions with all the atomic ground states. These contributions have to appear when we speak in terms of holes since all Coulomb interactions among these atomic ground state levels are then forgotten by construction.

(iii) The third term $V_{intra}$ of Eq. (4.14) corresponds to $V_{eh}^{(dir)} + V_{eh}^{(exch)}$ taken for $n_1 = n_2$. It precisely reads as

$$V_{intra} = -\delta \sum_n a_n^\dagger b_n^\dagger b_n a_n, \tag{4.20}$$

where $-\delta$ is given by

$$-\delta = -V_{R=0}\begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} + V_{R=0}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{4.21}$$

By using the Coulomb matrix elements [given in Eq. (3.13)], we see that this quantity also reads as

$$\delta = \int d\mathbf{r}_1 d\mathbf{r}_2 [\varphi_1^*(\mathbf{r}_2)\varphi_0^*(\mathbf{r}_1) - \varphi_0^*(\mathbf{r}_2)\varphi_1^*(\mathbf{r}_1)] \times \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_1^*(\mathbf{r}_2)\varphi_0^*(\mathbf{r}_1). \tag{4.22}$$

This shows that $\delta$ is a positive constant, since $\langle \nu | \nu \rangle = 1$, while $\langle 0 | 1 \rangle = 0$. This energy $\delta$ physically corresponds to the energy decrease when the site $n$ is occupied by an electron-hole pair, i.e., when the site $n$ is neutral. This is going to make the potential $V_{intra}$ responsible for the fact that excitons are made from linear combinations of electrons and holes located on the same site.

(iv) The last term of Eq. (4.14) $V_{inter}$ is made of all Coulomb interactions *between* sites. It contains the electron-electron and hole-hole contributions $\tilde{V}_{ee}$ and $\tilde{V}_{hh}$ given by Eqs. (4.6) and (4.13), which are interactions between sites by construction, since a given site cannot accommodate two electrons or two holes due to the Pauli exclusion principle. It also contains the part of the direct electron-hole potential $V_{eh}^{(dir)}$, taken for $n_1 \neq n_2$. Using Eq. (4.8), this direct electron-hole exchange interaction between sites precisely reads as

$$\tilde{V}_{eh}^{(dir)} = -\sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} b_{n_1}^\dagger a_{n_2}^\dagger a_{n_2} b_{n_1}. \tag{4.23}$$

It finally contains the part of the electron-hole exchange potential $V_{eh}^{(exch)}$ given in Eq. (4.10), also taken for $n_1 \neq n_2$. This part has a very special role since it allows the excitation transfer from one site to the other. Let us isolate this transfer term from the other Coulomb terms and call it $V_{trans}$,

$$V_{trans} = \sum_{n_1 \neq n_2} V_{R_{n_1}-R_{n_2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} a_{n_1}^\dagger b_{n_1}^\dagger b_{n_2} a_{n_2}. \tag{4.24}$$

All these lead us to write $V_{inter}$ in Eq. (4.14) as

$$V_{inter} = V_{trans} + V_{Coul},$$

$$V_{Coul} = \tilde{V}_{ee} + \tilde{V}_{hh} + \tilde{V}_{eh}^{(dir)}. \tag{4.25}$$

The four contributions of this $V_{inter}$ operator are shown in Fig. 4, with $(n_1 \leftrightarrow n_2)$ exchanged.

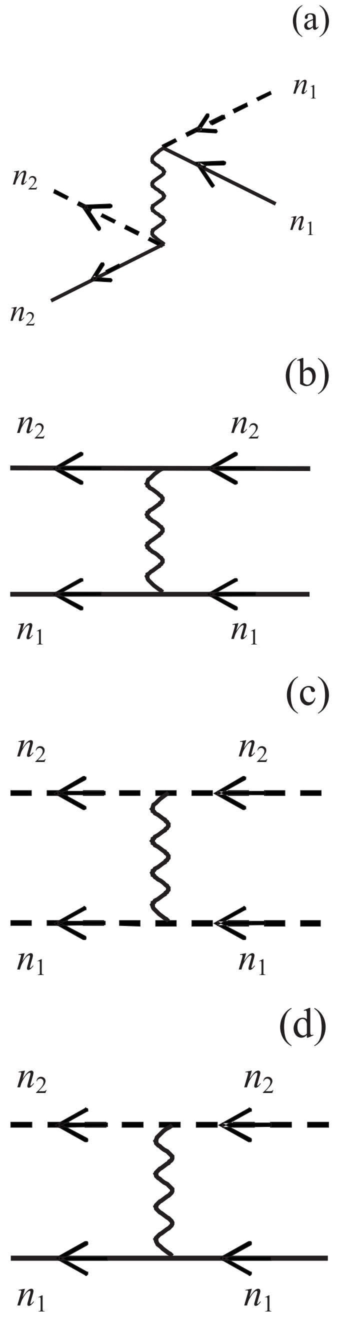

FIG. 4. Interaction between sites, described by $V_{inter}$, given in Eq. (4.25). (a) The part $V_{trans}$ [given in Eq. (4.24)] describes the destruction of an electron-hole pair on site $n_1$ and its recreation on site $n_2$. (b) Direct interactions between two electrons, corresponding to $\tilde{V}_{ee}$ [given in Eq. (4.6)], (c) between two holes, corresponding to $\tilde{V}_{hh}$ [given in Eq. (4.13)], and (d) between one electron and one hole, corresponding to $\tilde{V}_{eh}^{(dir)}$ [given in Eq. (4.23)].

### E. Discussion

The expression of the semiconductor Hamiltonian appropriate to Frenkel exciton $H^{(F)}$ in terms of electrons and holes [given in Eq. (4.14)] allows an easy comparison between highly localized states leading to Frenkel excitons and extended states leading to Wannier excitons. We first see that the electron and the hole energies for Frenkel excitons appearing in $H_{eh}$ are constant, while they depend on $\mathbf{k}$ for Wannier excitons: the electrons and holes for Wannier excitons, which belong to the conduction and valence bands, are delocalized over the whole sample, so that their energies must depend on momentum. In addition, the "electron-hole exchange," i.e., the possibility for one electron-hole pair to recombine while another pair is created, plays essentially no role for Wannier excitons: it is just responsible for a small splitting between Wannier excitons when the spin degrees of freedom are included, the dark excitons $S=\pm 2$ achieving the lowest energy. On the contrary, this electron-hole exchange is crucial in the case of highly localized states as it is the only process which allows an excitation transfer between sites: this makes the operator $V_{trans}$ entirely responsible for the Frenkel exciton formation, as we will now show.

## V. LOWEST EXCITED STATES IN THE ABSENCE OF INTERACTION BETWEEN SITES

Let us first forget the interactions between sites. The Hamiltonian $H^{(F)}$ [given in Eq. (4.14)] then reduces to

$$H_{pair}=H_{eh}+V_{intra} \tag{5.1}$$

if we drop the irrelevant band gap renormalization $\Delta$.

### A. Ground state and lowest excited states

The ground state of $H_{pair}$ has zero electron-hole pair. Let us call it $|0\rangle$ and choose its energy as 0.

If we now consider the one electron-hole pair state $a_n^\dagger b_{n'}^\dagger|0\rangle$ with an electron on site $n$ and a hole on site $n'$, we see that its energy is $\varepsilon_e+\varepsilon_h$ for $n\neq n'$, while it is $\varepsilon_e+\varepsilon_h-\delta$ for $n=n'$. Since $\delta$ is positive, the lowest excited states of $H_{pair}$ thus have one electron-hole pair on the same site. They read as

$$(H_{pair}-E_{pair})|R_n\rangle=0,$$

$$|R_n\rangle=a_n^\dagger b_n^\dagger|0\rangle=B_n^\dagger|0\rangle, \tag{5.2}$$

with $E_{pair}=\varepsilon_e+\varepsilon_h-\delta$. These states form an $N_s$-degenerate subspace since $n$ can run from 1 to $N_s$.

### B. Commutation rules

Using the anticommutation rules for electrons and holes given in Eqs. (4.2) and (4.4), it is easy to show that the electron-hole pair operators $B_n^\dagger$ behave as bosons with respect to the destruction operators since their commutator reads as

$$[B_{n'},B_n]_-=0, \tag{5.3}$$

while they are composite bosons only since the other commutator is such that

$$[B_{n'},B_n^\dagger]_-=\delta_{n'n}-D_{n'n}, \tag{5.4}$$

the deviation-from-boson operator for electron-hole pairs being equal to

$$D_{n'n}=\delta_{n'n}(a_n^\dagger a_n+b_n^\dagger b_n). \tag{5.5}$$

As standard for deviation-from-boson operator, $D_{n'n}$ gives 0 when acting on the electron-hole pair vacuum.

## VI. FRENKEL EXCITONS

If in the Frenkel exciton Hamiltonian $H^{(F)}$, we now keep the coupling between sites, $V_{inter}=V_{trans}+V_{Coul}$ [defined in Eq. (4.25)], we induce nondiagonal contributions between different sites. They split the degenerate subspace $|R_n\rangle$. The Frenkel excitons result from the diagonalization of the Hamiltonian $H^{(F)}$ in this $|R_n\rangle$ degenerate subspace.

### A. Derivation of the Frenkel excitons

Since the states $|R_n\rangle$ have one electron-hole pair only, the electron-electron and hole-hole parts $\tilde{V}_{ee}$ and $\tilde{V}_{hh}$ of $V_{Coul}$ [defined in Eq. (4.25)] give zero when acting on $|R_n\rangle$. The direct electron-hole interaction $\tilde{V}_{eh}^{(dir)}$ [given in Eq. (4.23)] also gives zero since $b_{n_2}a_{n_1}|R_n\rangle=0$ for $n_1\neq n_2$. Consequently, $V_{Coul}|R_n\rangle=0$, so that the only part of $V_{inter}$ that plays a role in the diagonalization of $H^{(F)}$ in the $|R_n\rangle$ subspace is the electron-hole exchange term $V_{trans}$. Since $b_{n_2}a_{n_2}a_n^\dagger b_n^\dagger|0\rangle=\delta_{n_2 n}|0\rangle$, we readily find

$$V_{trans}|R_n\rangle=\sum_{n_1\neq n}V_{R_{n_1}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}|R_{n_1}\rangle. \tag{6.1}$$

This shows that, if we drop the irrelevant constant $\Delta$, the Frenkel exciton Hamiltonian $H^{(F)}$ acting on $|R_n\rangle$ reduces to

$$H_X^{(0)}=H_{pair}+V_{trans},$$

$$H_X^{(0)}|R_n\rangle=E_{pair}|R_n\rangle+\sum_{n_1\neq n}V_{R_{n_1}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}|R_{n_1}\rangle. \tag{6.2}$$

Let us now show that the following linear combinations of $|R_n\rangle$:

$$|X_Q\rangle=\frac{1}{\sqrt{N_s}}\sum_{n=1}^{N_s}e^{i\mathbf{Q}\cdot\mathbf{R}_n}|R_n\rangle, \tag{6.3}$$

known as Frenkel excitons, are the exact eigenstates of the Hamiltonian $H_X^{(0)}$. To prove it, we first consider $V_{trans}$ acting on $|X_Q\rangle$,

$$V_{trans}|X_Q\rangle=\frac{1}{\sqrt{N_s}}\sum_n e^{i\mathbf{Q}\cdot\mathbf{R}_n}\sum_{n'\neq n}V_{R_{n'}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}|R_{n'}\rangle, \tag{6.4}$$

which also reads as

$$V_{trans}|X_Q\rangle=\frac{1}{\sqrt{N_s}}\sum_{n'}|R_{n'}\rangle\sum_{n\neq n'}e^{i\mathbf{Q}\cdot\mathbf{R}_n}V_{R_{n'}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}. \tag{6.5}$$

In order to calculate the last sum, we rewrite it as

$$\sum_{n\neq n'}e^{i\mathbf{Q}\cdot\mathbf{R}_n}V_{R_{n'}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}$$

$$=e^{i\mathbf{Q}\cdot\mathbf{R}_{n'}}\sum_{n\neq n'}e^{i\mathbf{Q}\cdot(\mathbf{R}_n-\mathbf{R}_{n'})}V_{R_{n'}-R_n}\begin{pmatrix}0&1\\1&0\end{pmatrix}. \tag{6.6}$$

Due to the invariance of the system, the sum in the right hand side cannot depend on $n'$; so that the above equation leads us to

$$\sum_{n\neq n'} e^{i\mathbf{Q}\cdot\mathbf{R}_n} V_{R_{n'}-R_n}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = e^{i\mathbf{Q}\cdot\mathbf{R}_{n'}}\sum_{R\neq 0} e^{-i\mathbf{Q}\cdot\mathbf{R}} V_R\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \tag{6.7}$$

where the sum is taken over all possible distances $R$ between ions. When inserted into Eq. (6.5), this readily leads to

$$V_{trans}|X_Q\rangle = |X_Q\rangle \sum_{R\neq 0} e^{-i\mathbf{Q}\cdot\mathbf{R}} V_R\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \tag{6.8}$$

so that we end with

$$H_X^{(0)}|X_Q\rangle = E_Q|X_Q\rangle, \tag{6.9}$$

where the eigenenergy is given by

$$E_Q = E_{pair} + \sum_{R\neq 0} e^{-i\mathbf{Q}\cdot\mathbf{R}} V_R\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}. \tag{6.10}$$

The above equation shows that the splitting of the $N_s$ degenerate states $|R_n\rangle$ into $N_s$ states $|X_Q\rangle$ is only due to the electron-hole exchange $V_{trans}$ between different sites: $V_{trans}$ is the only part of the Hamiltonian allowing for an excitation transfer from site to site, as necessary for the delocalization of the excitation corresponding to Frenkel excitons.

### B. Frenkel exciton creation operator

Equation (6.3) leads to write the Frenkel exciton creation operator $B_Q^\dagger$ defined as $|X_Q\rangle = B_Q^\dagger|0\rangle$ in terms of the creation operators $B_n^\dagger = a_n^\dagger b_n^\dagger$ for one electron-hole pair on site $n$ as

$$B_Q^\dagger = \frac{1}{\sqrt{N_s}}\sum_{n=1}^{N_s} e^{i\mathbf{Q}\cdot\mathbf{R}_n} B_n^\dagger. \tag{6.11}$$

In the same way as free electron-hole pairs can be written in terms of Wannier excitons, it is possible to write electron-hole pairs localized on site $n$ in terms of Frenkel excitons. This is barely done by noting that

$$\frac{1}{\sqrt{N_s}}\sum_{\mathbf{Q}} e^{-i\mathbf{Q}\cdot\mathbf{R}_n} B_Q^\dagger = \frac{1}{N_s}\sum_{n'=1}^{N_s} B_{n'}^\dagger \sum_{\mathbf{Q}} e^{i\mathbf{Q}\cdot(\mathbf{R_{n'}}-\mathbf{R_n})} = B_n^\dagger, \tag{6.12}$$

since the sum over $\mathbf{Q}$ is equal to 0 for $n'\neq n$ and to $N_s$ for $n'=n$.

These Frenkel excitons are expected to be composite bosons. This is easily seen from their commutation rules. By using Eq. (5.3) for electron-hole pairs on site $n$, we readily find

$$[B_{Q'}, B_Q]_- = 0. \tag{6.13}$$

If we now turn to the other commutator, it reads as

$$[B_{Q'}, B_Q^\dagger]_- = \frac{1}{N_s}\sum_{n'=1}^{N_s}\sum_{n=1}^{N_s} e^{-i\mathbf{Q}'\cdot\mathbf{R}_{n'}} e^{i\mathbf{Q}\cdot\mathbf{R_n}}[B_{n'}, B_n^\dagger]_-. \tag{6.14}$$

We then use Eq. (5.4) for the commutator $[B_{n'}, B_n^\dagger]_-$. The term in $\delta_{nn'}$ gives $N_s^{-1}\Sigma_n e^{i(\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R_n}}$, which is equal to 0 for $\mathbf{Q}\neq\mathbf{Q}'$ and 1 for $\mathbf{Q}=\mathbf{Q}'$, so that we end with

$$[B_{\mathbf{Q}'}, B_{\mathbf{Q}}^\dagger]_- = \delta_{\mathbf{Q}'\mathbf{Q}} - D_{\mathbf{Q}'\mathbf{Q}}, \tag{6.15}$$

where the deviation-from-boson operator $D_{\mathbf{Q}'\mathbf{Q}}$ for Frenkel excitons, which comes from the deviation-from-boson operator for electron-hole pairs $D_{n'n}$ appearing in $[B_{n'}, B_n^\dagger]_-$, reads as

$$D_{\mathbf{Q}'\mathbf{Q}} = \frac{1}{N_s}\sum_{n=1}^{N_s} e^{i(\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R_n}}(a_n^\dagger a_n + b_n^\dagger b_n). \tag{6.16}$$

We can note that, as for Wannier excitons, this deviation-from-boson operator gives 0 when acting on the pair vacuum state,

$$D_{\mathbf{Q}'\mathbf{Q}}|0\rangle = 0. \tag{6.17}$$

This leads us to conclude that, in order to describe the interactions between Frenkel excitons properly, it is necessary to follow a path similar to the one we have used for Wannier excitons, namely to define the Pauli scatterings of two Frenkel excitons for carrier exchanges without Coulomb interaction and the Coulomb scatterings of two Frenkel excitons for carrier interactions without carrier exchange. As for Wannier excitons, the composite nature of the Frenkel excitons makes a clean description of the interactions between two excitons as a potential impossible, the only well-defined quantity again being the "creation potential" of the $Q$ exciton. The calculation of these Pauli and Coulomb scatterings for Frenkel excitons (necessary to handle their many-body physics properly) will be done in a forthcoming publication.

### C. Interacting Frenkel exciton Hamiltonian

If we have more than one electron-hole pair, the Coulomb part $V_{Coul}$ of the Frenkel exciton Hamiltonian [given in Eq. (4.23)] is going to play a role. This leads us to rewrite $H^{(F)}$ as $H^{(F)} = H_X$ with

$$H_X = H_X^{(0)} + V_{Coul}, \tag{6.18}$$

where $H_X^{(0)}$ [given in Eq. (6.2)] corresponds to the pair Hamiltonian $H_{pair}$ plus the part of the Coulomb interaction $V_{trans}$ allowing for the excitation transfer.

The remaining part $V_{Coul}$ [given in Eq. (4.25)] corresponds to all direct Coulomb interactions between two electrons, two holes, and one electron and one hole in different sites. This operator is going to generate all many-body effects between excitons induced by Coulomb interactions. In addition to them, as for Wannier excitons, many-body effects induced by Pauli exclusion through the fact that Frenkel excitons are not elementary bosons, also exist. The scatterings associated with $V_{Coul}$ and to the deviation-from-boson operators will be calculated in a forthcoming publication.

## VII. STATE OF THE ART

As it was mentioned in Sec. I, the second quantization formalism for Frenkel excitons has already been used in

Refs. 15–20. In Refs. 15–18, the Hamiltonian of the periodic molecular crystal is written in terms of creation and destruction operators for excited states of isolated molecules, while we here go one step further by introducing an electron-hole representation conceptually similar to the one commonly used for Wannier excitons. This step is made in Refs. 19 and 20, which also deal with electron-hole representation. In contrast to all these works,[15–20] the detailed derivation presented in this paper allows us to reveal the physical meaning of all the terms entering the Hamiltonian, with a particular emphasis on the transfer term which is responsible for the excitation transfer from site to site. We demonstrate that this term splits the degenerate subspace $B_n^\dagger|0\rangle$ where $n$ runs over all sites. In addition, we introduce exciton creation operator $B_{\mathbf{Q}}^\dagger$ which describes delocalized excitations; we calculate its commutators and show that this exciton operator represents a composite boson. In contrast, Refs. 15–20 stay with the $B_n^\dagger$ operator where $B_n^\dagger$ creates an excitation on site $n$ that is not a delocalized excitation. The further progress of Refs. 15–20 is based on rewriting the original fermionic Hamiltonian in terms of pair operators $B_n^\dagger$ and $B_n$ using certain assumptions. Within our approach, we stick to the original Hamiltonian written in terms of fermionic operators. A precise comparison between our method and the approaches developed by Agranovich and co-workers[15–17] and Mukamel and co-worker,[19,20] in connection to many-body effects, will be discussed in a forthcoming publication.

## VIII. CONCLUSION

In this paper, we have derived the creation operator for Frenkel excitons starting from the microscopic Hamiltonian for free electrons in a periodic lattice. Let us summarize the main steps of the derivation.

(1) We first isolate one ion located on site $n$ and we introduce the atomic states $|\nu n\rangle$, eigenstates for this particular ion. They form a complete basis for one-electron states.

(2) If we let $n$ run over all sites, the states $|\nu n\rangle$ form an overcomplete set. However, if the states of physical interest are the two lowest atomic levels ($\nu=0$ and $\nu=1$), the states $|\nu n\rangle$ with $\nu=(0,1)$ are essentially orthogonal in the tight-binding limit, i.e., when the overlaps of the $\nu=(0,1)$ wave functions on different sites are negligible. This allows us to use the $|\nu=(0,1)n\rangle$ state as a one-electron basis to describe Frenkel excitons in second quantization.

(3) The large energy difference between the atomic states $\nu=(0,1)$ leads us (in the electron-electron interaction written in terms of the creation operators $a_{\nu n}^\dagger$ for these $|\nu n\rangle$ states) to only keep the terms which conserve the number of electrons in state $\nu=0$ and in state $\nu=1$ separately.

(4) When written in terms of electron-hole pairs with $a_n^\dagger=a_{1n}^\dagger$ and $b_n^\dagger=a_{0n}$, the electron-electron interaction generates a constant term, which renormalizes the band gap. It also generates one-body contributions in $b_n^\dagger b_n$ and $a_n^\dagger a_n$ which dress the $\nu=0$ and $\nu=1$ atomic levels, the electron and hole energies differing from the atomic energies due to Coulomb interaction with a kind of jellium having one electron in the ground state of each ion site.

(5) Finally, the electron-electron interaction generates a contribution between sites $V_{inter}$ given in Eq. (4.22) and an intrasite contribution $V_{intra}$ which ensures local neutrality, so that the lowest excited states have one electron and one hole on the *same* site.

(6) The corresponding degenerate subspace $a_n^\dagger b_n^\dagger|0\rangle=B_n^\dagger|0\rangle$ with $n$ running over all sites is split by the transfer part of the contribution between sites $V_{inter}$. This transfer part $V_{trans}$ [given by Eq. (4.21)], allows us to transfer the excitation from one site to the other.

(7) The resulting eigenstates obtained by including this transfer part correspond to a set of delocalized excitations known as Frenkel excitons. Their creation operators read as

$$B_Q^\dagger=\frac{1}{\sqrt{N_s}}\sum_{n=1}^{N_s}e^{i\mathbf{Q}\cdot\mathbf{R}_n}B_n^\dagger,$$

where $N_s$ is the number of ion sites, these ions being located at $\mathbf{R}_n$ on a periodic lattice, the $\mathbf{Q}$ dependence of the energy being

$$\sum_{R\neq 0}e^{-i\mathbf{Q}\cdot\mathbf{R}}V_R\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.$$

(8) Frenkel excitons are composite bosons. Their many-body effects thus have to be handled along a procedure similar to the one we have used for Wannier excitons. Both types of excitons predominantly interact through the Pauli exclusion principle between their electron-hole components which make them differ from elementary bosons and which produce “Pauli scatterings” which describe carrier exchanges without carrier interaction. Frenkel excitons also interact through the $V_{Coul}$ part of the interaction between sites given in Eq. (4.25). It contains electron-electron, hole-hole, and electron-hole direct processes, in which the carriers stay on their site.

The composite boson many-body theory appropriate to Frenkel excitons will be presented in a forthcoming publication, the present work providing the necessary tools to build such a theory on solid grounds.

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