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HAL Id: jpa-00209606
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Submitted on 1 Jan 1983

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Excitons in a 1-D crystal with an electron-hole interaction of variable range and strength

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Abstract. — The competition between strength and range of the electron-hole (e-h) interaction is introduced to develop a description of « intermediate » excitons, which can interpolate between Wannier and Frenkel limits. A model is proposed for which a variational equation is deduced to obtain the pair bound states. The model is specialized to one-dimensional crystals and, thus, generalizes the well accepted results of Egri. It is shown that the number of bound states is an intricate function of the interaction range and strength. As a consequence domains exist characterized by the number of such states. The boundaries between these domains are computed for an exponential interaction. For a zero-range interaction the concept of a Frenkel exciton is justified by a limiting procedure : the interaction range has to be taken equal to zero before the band width. For an infinite-range interaction, and finite band width, a quasi-continuum of bound states is obtained, which may be separated from the unbound pair continuum if the interaction strength is sufficient. The case of a Coulombic interaction is also investigated, and it is shown that it leads to a hydrogenic spectrum, possibly truncated with missing states. Finally the dynamics of an e-h pair created on a same site at some initial time is investigated. For an ultra long-range interaction (quasi-continuum of bound pairs), a dynamical charge density wave appears, oscillating in time as the pair looses its « Frenkel » character, its size increasing.

1. Introduction. — Egri [1] has examined the problem of finding a unified scheme describing excitonic states and accounting for both Frenkel and Wannier limits. His treatment is based on a Hamiltonian proposed by Anderson [2] and linearized by the use of the RPA.

Egri considered only contact interaction between the electron and the hole, hence he found a single bound state, whereas the Wannier exciton is characterized by a hydrogenic like spectrum. Moreover, his model assumes the site to site transfer matrix element to be non-zero only when the electron and the hole are located on the same site.

It seems, therefore, of interest to develop a less
restrictive analysis allowing for arbitrary coupling range. Indeed, the fundamental distinction between Wannier and Frenkel excitons is more to be found in an interplay between the range of the electron-hole interaction and the magnitude of the binding energy. This reflects in the energy spectrum which displays either a single bound state or a series of levels, so that, in the « range-magnitude » plane, there exist domains characterized by the number of bound states. In order to handle this problem, one may start from a Schrödinger equation with an effective electron-hole interaction potential. But this method does not allow one to take easily into account the effect of the lattice on the electron and hole so that, generally, one describes the embedding lattice by a continuum. To be sure, this description is likely to be more valid for the Wannier situation where the relevant lengths are sufficiently large to allow for the description of the surrounding medium by a dielectric constant. Another way of doing is to start from a Hamiltonian in the site configuration with hopping transfer elements for electrons and holes. This is the spirit of Anderson's Hamiltonian and, consequently, of Egri's work.

In part 2, we use this kind of approach and extend it by introducing arbitrary range hopping elements and electron-hole interaction. We next derive, by a variational procedure, an equation for the wave function describing the internal motion of the electron-hole pair.

In part 3, the equation is solved for a one-dimensional model in several limits, with an exponentially decreasing interaction:

1) Zero-range interaction. — We clearly recover here Egri's result : there exists only one bound state, whatever the binding energy characterized by the dimensionless parameter

\[ b \sim \frac{\hbar \omega}{t} \]

where \( \hbar \omega \) measures the two-particle interaction energy and \( t \) the band width, as long as \( b \) remains finite.

2) Short-range interaction. — We solve the equation approximately and derive the boundary between one, two, three, ... bound states structures as a function of \( b \) and of the range \( 1/\alpha \). As expected, for a given \( \alpha \), the number of bound states increases with \( b \) and, conversely, for a given \( b \), increases with the range. By examining the \( \alpha \to \infty \) limit, the concept of Frenkel exciton is then re-discussed.

3) Arbitrary-range interaction. — We solve the equation numerically in order to obtain, for a given range, the thresholds for the appearance of a new bound state when \( b \) is varied. This allows us to draw a « phase diagram » in the \( (b, \alpha) \) plane.

Actually \( b \) is \( k \) dependent, so that the number of bound states may vary from one point to another in the Brillouin zone. This is an interesting feature which may play a role in the dissociation of excitons by interaction with phonons.

4) Ultra long-range interaction. — In this case, the above numerical procedure does not converge properly. By another technique, however, we can compute exactly the limit for a strictly infinite range. It is shown that a continuum of bound states is obtained, whatever the value of \( b \), which is separated from the continuum by a gap \( \epsilon_0(0) - 2 \langle k \rangle \), as soon as this quantity is positive.

5) Coulomb like interaction and continuous description. — The case of a Coulomb interaction is of physical interest, but cannot be treated by the same method. Indeed the Coulomb potential is long range but sufficiently decreasing in order to prevent a calculation of the type 4). We, thus, resort to a continuous description for the lattice which naturally, albeit non-trivially, yields a hydrogenic like spectrum with possible missing states.

In part 4 we investigate some features of the exciton motion when one creates the electron and the hole on the same site. We compute the projection of this initial state on the lowest bound states and show that it decreases with \( b \). Since the bound state occupation rules the radiative transition, this could be linked with the fact that, often, no luminescence is observed.

We also fully compute the behaviour of such an electron-hole pair created on the same site in the case 4) of an ultra long-range interaction. We show that, during the first step, the exciton keeps on its « Frenkel » character, i.e. the electron and hole move together, staying closely spaced; later on the distance between the particles increases. As a result, a dynamical charge density is obtained, the amplitude of which decreasing as \( t^{-1} \).

2. Model Hamiltonian and variational equations. —

2.1 Model Hamiltonian. — We start from the Hamiltonian

\[ H = H_0 + H_{\text{int}} \]

\( H_0 \) is the non-interacting electron-hole Hamiltonian, namely:

\[ H_0 = \sum_q E_q C_q^+ C_q - \sum_q E_b(q) d_q^+ d_q \quad (2.1) \]

where \( C \) (resp. \( d \)) is the electron (resp. hole) annihilation operator and \( q \) the wave vector in the first Brillouin zone. It may be equivalently rewritten as:

\[ H_0 = \sum_{\mathbf{R}, \beta} (T_{\mathbf{R} + \beta, \beta} C_{\mathbf{R} + \beta}^+ C_{\mathbf{R}} + T_{\mathbf{R} + \beta, \beta}^* d_{\mathbf{R} + \beta}^+ d_{\mathbf{R}}) \quad (2.1a) \]

where \( T^* \) (resp. \( T^b \)) are the site to site hopping elements for the electron (resp. hole). \( \mathbf{R} \) is a site location and \( \beta \) a translation of the lattice. Equations (2.1), (or 2.1a), takes into account the effect of the lattice and of the interaction between electrons and between...
holes, but not the electron-hole interaction properly, which is included in \( H_{\text{int}} \). Therefore \( H_{\text{int}} \) is written as:

\[
H_{\text{int}} = -\sum_{\mathbf{R}} \sum_{\mathbf{p}} \sum_{\mathbf{a}, \mathbf{a}' \neq 0} W(\beta, \mathbf{a}, \mathbf{a}') C_{\mathbf{R}+\mathbf{a}}^{+} d_{\mathbf{R}+\mathbf{p}+\mathbf{a}}^{+} C_{\mathbf{R}} d_{\mathbf{R}+\mathbf{p}} (2.1b)
\]

where \( \mathbf{a} \) and \( \mathbf{a}' \) are lattice translations.

\( H_{\text{int}} \) is much too complicated to be treated as such. We consequently make the following simplifying assumptions:

a) first we single out the extended Hubbard type electron-hole interaction, namely:

\[
H_1 = -\sum_{\mathbf{R}} \sum_{\mathbf{p}} U(\beta) C_{\mathbf{R}}^{+} d_{\mathbf{R}+\mathbf{p}}^{+} C_{\mathbf{R}} d_{\mathbf{R}+\mathbf{p}} (2.2a)
\]

b) we then add the following «transfer» contribution:

\[
H_2 = -\sum_{\mathbf{R}} \sum_{\mathbf{p}} V(\beta, \mathbf{a}) C_{\mathbf{R}+\mathbf{a}}^{+} d_{\mathbf{R}+\mathbf{p}+\mathbf{a}}^{+} C_{\mathbf{R}} d_{\mathbf{R}+\mathbf{p}}.
\]

(2.2b)

This last term assumes that a pair is transferred «rigidly» (i.e. \( \mathbf{a} = \mathbf{a}' \)). This restriction could be released in order to take into account some enlargement or shrinking of a pair during the transfer. But this will introduce extra parameters at the expense of simplicity and clarity, and with not much gain of physical insight.

Indeed, \( H_1 \) ensures that the electron-hole distance may vary, and since \( |V| \ll |U| \), the conservation of length in the transfer of a pair does not seem to be a much too drastic shortage.

We shall also restrict the model to the one-dimensional case and assume that the transfer element is limited to the next nearest-neighbours, labelled by \( \langle \mathbf{a}_i \rangle \). Due to translational and symmetry invariance, \( V(\beta, \langle \mathbf{a}_i \rangle) \) depends only on \( \beta \) and the total Hamiltonian reads:

\[
H = H_0 + H_1 + H_2.
\]

(2.3)

In Fourier space, the model interaction \( H_1 + H_2 \) takes the form:

\[
H_1 + H_2 = -\frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{q}} \hbar \Omega_\mathbf{q}(\mathbf{q}'' - \mathbf{q}''') \times \nabla^k \times C_{\mathbf{q}'''}^{+} C_{\mathbf{q}''} d_{\mathbf{q}''' + \mathbf{k}}^{+} d_{\mathbf{q}''} (2.3a)
\]

where

\[
\Omega_\mathbf{q}(\mathbf{K}) = \sum_{\beta} \omega_\beta(\mathbf{q}) e^{i\mathbf{K}\beta}
\]

(2.3b)

\[
\hbar \omega_\beta(\mathbf{q}) = U(\beta) + V(\beta) \sum_{\langle \mathbf{a}_i \rangle} e^{i\mathbf{a}_i \cdot \mathbf{j}}.
\]

(2.3c)

Note that Egri's model is obtained by retaining only the \( \beta = 0 \) term in equations (2.3).

2.2 VARIATIONAL EQUATIONS. — We shall proceed to a variational calculation in which we look for solutions of the form of an exciton, i.e. we introduce the exciton creation operator by:

\[
B_\mathbf{q}^+ = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sum_{\beta} e^{i\mathbf{R}\beta} f_\beta(\mathbf{q}) B_{\mathbf{R},\beta}^+ (2.4a)
\]

where

\[
B_{\mathbf{R},\beta}^+ = C_{\mathbf{R}}^{+} d_{\mathbf{R}+\beta} (2.4b)
\]

is the operator corresponding to the electron-hole pair located on \( (\mathbf{R}, \mathbf{R} + \beta) \), where \( f_\beta(\mathbf{q}) \) describes the relative motion of the hole and electron in the pair.

Using the Fourier transform for \( C \) and \( d \), equations (2.4) yield:

\[
B_\mathbf{q}^+ = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} F_\mathbf{q}(\mathbf{q}) C_{\mathbf{q} + \mathbf{q}'}^{+} d_{\mathbf{q}'' - \mathbf{q}'} (2.4c)
\]

\[
F_\mathbf{q}(\mathbf{q}) = \sum_{\beta} e^{i\beta\mathbf{q}} f_\beta(\mathbf{q}).
\]

(2.4d)

In order that the wave function be normalized to unity, one imposes:

\[
\sum_{\beta} |f_\beta(\mathbf{q})|^2 = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} |F_\mathbf{q}(\mathbf{q})|^2 d\mathbf{q} = 1 (2.4e)
\]

where \( a \) is the atomic distance.

The form of \( B_\mathbf{q}^+ \) has been retained in order to allow for an explicit \( k \) dependence of the internal motion.

Let us designate by \( |\text{vac} \rangle \) the exact ground state of the system. Since it corresponds to the absence of holes, we have:

\[
d_{\mathbf{q}} |\text{vac} \rangle = 0, \quad \forall \mathbf{k}.
\]

(2.5a)

Therefore the function

\[
B_\mathbf{q}^+ |\text{vac} \rangle
\]

is orthogonal to \( |\text{vac} \rangle \) and may be taken as a variational function to describe the first electronic excitations. The variational procedure then amounts to determine the minimum for:

\[
\bar{H} = \langle \text{vac} | \mathbf{H} \mathbf{B}^+_{\mathbf{q}} | \text{vac} \rangle - E(k) \langle \text{vac} | B_\mathbf{q} B_\mathbf{q}^+ | \text{vac} \rangle (2.6a)
\]

i.e.

\[
\frac{\delta}{\delta F_\mathbf{q}} \bar{H} = 0.
\]

(2.6b)

\( E(k) \) is a Lagrange multiplier which will give the energy of the excited state.

The calculation proceeds as ordinarily, and one obtains readily:
The minimization equation takes the following Fredholm form (1)

$$F_k(q) = G_k(q) \frac{a}{2 \pi} \int_{-\pi/a}^{\pi/a} dq' \ h\Omega_k(q' - q') F_k(q')$$

(2.7a)

with

$$G_k(q) = [E_k(q) - E_h(q - k) - E(k)]^{-1}.$$  

(2.7b)

It is interesting to rewrite equations (2.7) in the direct space, since $Q_k(q' - q'')$ depends only on $q' - q''$, or, expressed in more sophisticated terms since (2.7a) is a separable Fredholm integral equation. This leads to the matrix equation:

$$f_k(\beta) = \sum_{\beta'} M_{\beta\beta'} f_k(\beta')$$

(2.8a)

where $M$ is the matrix of elements

$$M_{\beta\beta'} = h\omega_k(\beta') \frac{a}{2 \pi} \int_{-\pi/a}^{\pi/a} dq' e^{i\beta' - \beta} G_k(q').$$

(2.8b)

Equations (2.8) implies that the equation:

$$\det(M - I) = 0$$

be satisfied. This, of course, determines the energy $E(k)$.

It is to be noted that Egri [8] has obtained the same type of equation as (2.7a) by using the R.P.A.

(2.7) or (2.9) are not ordinary eigenvalue equations, so that they have not always adequate solutions (i.e. $E(k)$ real). Each time such a solution appears, it corresponds to a bound state, i.e. an exciton. To this exciton corresponds an exciton binding energy defined as the difference between the lowest energy of an unbound pair (i.e. the bottom of the continuum of the dissociated pairs, hereafter designated as «the continuum ») and $E(k)$.

2.3 MODEL. — In order to proceed we shall retain the following model:

a) for the electron and the hole bands a tight-binding description is used, namely:

$$E_e(q) = t_0 - t_e \cos qa$$

(2.10a)

$$E_h(q) = -t_0 + t_h \cos qa.$$  

(2.10b)

The energy $\epsilon_k(q)$ of an unbound pair is then

$$\epsilon_k(q) = E_e(q) - E_h(q - k) = 2 t_0 - t(k) \cos [(q - k) a]$$

(2.11a)

where

$$t(k) = [t_e^2 + t_h^2 + 2 t_e t_h \cos ka]^{1/2}$$

(2.11b)

$$\sin k_0 a = \frac{t_b}{t(k)} \sin ka; \quad \cos k_0 a = \frac{t_e + t_h \cos ka}{t(k)}. \quad (2.11c)

It is seen that the unbound continuum is defined by:

$$\epsilon_1(k) = 2 t_0 - t(k) \leq \epsilon_k(q) \leq \epsilon_2(k) = 2 t_0 + t(k)$$

(2.12)

$2 t(k)$ is thus the width and $\epsilon_1$ the bottom of this continuum. Setting:

$$\cosh u(k) = \frac{2 t_0 - E(k)}{t(k)}$$

(2.13)

the exciton binding energy reads:

$$E_{exc} = \epsilon_1(k) - E(k) = 2 t(k) \sinh \frac{u(k)}{2} \quad (2.14)$$

while:

$$M_{\beta\beta'} = h\omega_k(\beta') e^{ik_0(n' - n)} \frac{e^{-|n'| |u|}}{\sinh u}.$$  

(2.15)

We have introduced the atomic distance $a$, set:

$$\beta = na, \quad \beta' = n'a \quad (n, n' \text{ integers})$$

and used the mathematical relations:

$$\frac{1}{2 \pi} \int_{-\pi}^{\pi} dx \left(1 - \frac{\cos x}{\cosh u}\right)^{-1} e^{iux} = \frac{e^{-|n|u}}{\tanh u}$$

(2.16a)

$$(\cosh u - \cos x)^{-1} = \sum_{n=0}^{+\infty} \frac{e^{-|n|u}}{\sinh u} e^{iux}.$$

(2.16b)

b) In most cases we shall use, for the interaction potential, an exponential form, namely:

$$\omega_k(\beta) = \omega(0) e^{-|n|\beta} \quad (\beta = na).$$

(2.17)

The range of the interaction is thus $a/|\beta|$.

Within the framework of this assumption, we can introduce the dimensionless parameter:

$$b(k) = \frac{2 h\omega(0)}{t(k)}$$

(2.18)

as a mesure of the interaction strength.
The two dimensionless parameters $b$ and $a$ picture the essential features of the model.

Setting

$$\phi_n = e^{i k n a} f_k(\beta = na)$$

(2.19)

the matrix equation (2.8) takes the new form (we drop the $k$ index to simplify notation):

$$\phi_n = \frac{b}{2 \sinh u} \sum_{n=-\infty}^{n=\infty} e^{-|n| u} e^{-|n-k| u} \phi_{n'}$$

(2.20)

or equivalently:

$$A(u) B(\alpha) \phi = \frac{2 \sinh u}{b} \phi$$

(2.21)

where:

$$A(u)_{n,n'} = e^{-|n-n'| u}$$

(2.21a)

$$B(\alpha)_{n,n'} = e^{-|n| \alpha} \delta_{n,0}$$

(2.21b)

Equation (2.21) is an ordinary secular equation if we consider $2 \sinh u/b$ as the eigenvalue. It leads, when solved, to an implicit relation for $u$, i.e. for the bound state energy. Its discussion is, however, much simplified if (2.21) is rewritten as:

$$b B(\alpha) \phi = 2 \sinh u A^{-1}(u) \phi$$

(2.22)

Indeed, $A(u)$ is easily seen to be:

$$A(u) = 1 + \sum_{p=1}^{\infty} e^{-p u} (T_p + (-)^p T_{-p})$$

(2.23)

where $T_{\pm p}$ are $\pm p$th Jacobi matrices (i.e. matrices, the elements of which being zero but on the $\pm p$th parallel to the main diagonal, where their value is 1).

We have the relation:

$$T_p = (T_{-p})^{-1} = T_1^p$$

(2.24)

so that (2.21) reads:

$$[(T_1 + T_1^{-1}) + b B(\alpha)] \phi = 2 \cosh u \phi$$

(2.25)

One is thus led to find the eigenvalues and vectors of the very simple matrix $H$:

\[
\begin{array}{cccccccc}
\vDash & \vDash & \vDash & \vDash & \vDash & \vDash & \vDash & \vDash \\
\vdash & 0 & 0 & 0 & 1 & be^{2s} & 1 & 0 & 0 \\
\vDash & 0 & 0 & 1 & b & 0 & 1 & 0 & 0 \\
\vdash & 0 & 0 & 0 & 1 & be^{s} & 1 & 0 & 0 \\
\vDash & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\vDash & 0 & 0 & 0 & 0 & 1 & be^{-s} & 1 & 0 \\
\vDash & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\vDash & \vDash & \vDash & \vDash & \vDash & \vDash & \vDash & \vDash \\
\end{array}
\]

Solving (2.25) yields an equation between $b$, $a$ and $u$:

The matrix $b B(\alpha) + (T_1 + T_1^{-1})$ is real, symmetric; its eigenvalues are therefore real. Let us call them $\lambda_i(b, a)$. The equation determining the $i$th bound state is:

$$\lambda_i(b, a) = 2 \cosh u$$

(2.26)

This equation has real $u$ solutions, i.e. corresponds to a physical bound state only when $\lambda_i \geq 2$. Setting

$$\lambda_i(b, a) = 2$$

(2.27)

gives a relation between $b$ and $a$ determining the threshold for the appearance of the $i$th bound state. This will be extensively exploited in the next section.

3. Existence of bound states. — 3.1 Zero-range interaction. — For a contact interaction, the matrix equation (2.8a) simplifies to: $(\beta' = 0$, in (2.8b))

$$f_1(\beta) = f_1(0) \int_{-\infty}^{\infty} dq \frac{e^{iq\beta}}{\delta(q) - E(k)}$$

(3.1)

The eigenvalue is obtained by setting $\beta = 0$ in this equation, namely:

$$1 = \frac{b(k)}{2 \sinh u(k)}$$

(3.2a)

For the tight-binding model of the bands (see (2.11a) and (2.13)), the integral is readily performed and yields:

$$1 = \frac{b(k)}{2 \sinh u(k)}$$

(3.2b)

Consequently, whatever the value of $b$, there is always one and only one bound state, the Egri's state $E_0(k)$ corresponding to:

$$u_0(k) = \sinh^{-1} \left( \frac{b(k)}{2} \right)$$

(3.3a)

of binding energy:

$$E_0^{(0)}(k) = \lambda(k) \left\{ \left( \frac{b^2}{4} + 1 \right)^{1/2} - 1 \right\}$$

(3.3b)

From now on, except when explicitly needed, we shall drop the $k$ index and write $b$ for $b(k)$, $E$ for $E(k)$, etc.

Note that $E_0$ is below the continuum, of bottom $\varepsilon_1$, since:

$$\varepsilon_1 - \lambda_{0}(0) \leq E_0 \leq \varepsilon_1$$

if $\lambda_{0}(0) < \varepsilon_2 - \varepsilon_1$

$$\varepsilon_1 - \lambda_{0}(0) \leq E_0 \leq \varepsilon_2 - \lambda_{0}(0)$$

if $\lambda_{0}(0) > \varepsilon_2 - \varepsilon_1$

Using equation (2.16) we write explicitly the eigenfunctions, namely:

$$f_1(\beta) \sim \int \frac{e^{iq\beta}}{\cos u_0 - \cos (q - k_0) a} dq \sim e^{ink_0 \cos q} e^{-|q|\infty}$$

(3.4)

As expected, we recover Egri's result.
3.2 ULTRA SHORT-RANGE INTERACTION.

We now explicitly resort to the exponential interaction and use equation (2.20). For $\alpha \gg 1$, we proceed by successive approximations.

a) Zeroth order

We retain only the term $n' = 0$ in the r.h.s. summation of equation (2.20), and we clearly recover the results of the preceding section.

\[ \phi_0 = \frac{b}{2 \sinh u} \left[ \phi_0 + e^{-u} e^{-s}(\phi_1 + \phi_{-1}) \right] \]
\[ \phi_1 + \phi_{-1} = \frac{b}{2 \sinh u} \left[ 2e^{-u} \phi_0 + (1 + 2e^{-s}) e^{-2s}(\phi_1 + \phi_{-1}) \right] \]
\[ \phi_1 - \phi_{-1} = b e^{-u} e^{-s}[\phi_1 - \phi_{-1}] \]

The solutions of this set are:

i) $\phi_0 = 0; \phi_1 = - \phi_{-1}$;
\[ e^u = b e^{-s} \]  (3.6a)

ii) $\phi_1 = \phi_{-1}$;
\[ \frac{2 \sinh u - b}{2 \cosh u - b} = e^{-u} e^{-s} b . \]  (3.6b)

It is seen that (3.6a) corresponds to antisymmetric solutions, while (3.6b) to symmetric ones.

As usual, $\phi_1$ in i) and $\phi_0$ in ii) are arbitrary and are to be fixed by normalization. When this is done, $f_0(\beta)$ is deduced from equation (2.19).

As explained at the end of section 2, setting $u = 0$ in the equation for $u$, gives the relation between $b$ and $\alpha$ which corresponds to a new solution. It is seen that three critical values exist, namely:

\[ b^{(1)}_{cr} = 0; \quad b^{(2)}_{cr} = e^s; \quad b^{(3)}_{cr} = e^s + 2 \]  (3.7)

and thus determine the domains of existence of solutions:

- $b^{(1)}_{cr} < b < b^{(2)}_{cr}$: one symmetric solution
- $b^{(2)}_{cr} < b < b^{(3)}_{cr}$: one symmetric + one antisymmetric solution
- $b^{(3)}_{cr} < b < ?$ : one symmetric + one antisymmetric + one symmetric solution.

Evidently enough, the lowest symmetric solution is the extension of the zeroth order. It takes explicitly the form:

\[ u^{(1)}_0 = u^{(0)}_0 + 2 e^{-u_0} \tanh u^{(0)}_0 e^{-s} \]  (3.8a)

($u^{(0)}_0$ is Egri's value) while the antisymmetric solution is:

\[ u^{(1)}_1 = \log b - \alpha . \]  (3.8b)

The corresponding exciton binding energies are:

\[ E^{(0)}_{exc} \simeq 2 t(k) \left\{ \frac{b^2(k)}{4} + \frac{1}{2} \right\}^{1/2} - 1 + O(e^{-s}) \]  (3.9a)

(b) First order

We now retain $n' = 0, \pm 1$, in the same summation. This yields three equations:

\[ E^{(1)}_{exc} \simeq 2 t(k) \left\{ \frac{e^s}{2b(k)} - 1 + \frac{b(k)}{2} e^{-s} \right\} \]  (3.9b)

(remind that $e^{-s} \ll 1$ and $b e^{-s} > 1$ so that $b \gg 1$).

We do not investigate the behaviour of the second symmetric solution, since we are going to discuss the general features of the bound states for an arbitrary exponential interaction.

3.3 ARBITRARY-RANGE INTERACTION.

For arbitrary-range interaction we return to equation (2.25). We have not been able to find a closed analytic form for the eigenvalues of the matrix:

\[ \mathcal{M} = (T_1 + T^{-1}_1) + bB(x) \]  (3.10)

despite its apparent simplicity. We have therefore used a numerical computation, the procedure of which is explained in appendix A.

The physically interesting information is the appearance of new bound states. As explained at the end of section 2, this amounts to finding the relation between

Fig. 1. — « Phase diagram » for the number (%) of bound states as a function of the strength $b$ and the range $z = e^{-s}$ of the interaction. The full lines represent the boundaries as defined by eq. (2.27).
band so that the $i$th eigenvalue of $\mathcal{K}$ be equal to 2 (i.e. $u = 0$). The results of the numerical calculations are given in figures 1 and 2. In the $(b, a)$ plane we obtain regions with one, two, etc. bound states. Clearly when the $p$th new bound state appears, it is symmetric, or antisymmetric, according to the parity of $(p - 1)$.

For $a \gg 1$ we recover the limiting calculation developed in the preceding section. Note, however, that for a given $a \gg 1$ but $\neq \infty$, there exist an infinite sequence of critical values $b_{cr}^{(p)}$ for $b$ ($p = 1, 2, \ldots, \infty$), so that one can obtain a great number of bound states even for a very short-range interaction. It is easily seen that for $a \gg 1$, these critical values behave as

$$b_{cr}^{(p)} \sim \exp(E(p/2) \alpha) \quad (3.11a)$$

where

$$E(p/2) = \begin{cases} \frac{p}{2} & \text{for even } p \\ \frac{p - 1}{2} & \text{for odd } p \end{cases} \quad (3.11b)$$

The number of bound states thus depends strongly on the value of $b$ and for a given $\omega$ on the band width. For a zero band width, $b \to \infty$ so that an infinite number of bound states is obtained, even for a quasi-contact interaction. This shows that Frenkel's idea, which retains a contact interaction with a zero band width, is somewhat disputable since it corresponds to a limiting procedure in which the range of interaction is taken equal to zero before the band width.

An infinite number of bound states for a zero band width is plausible. Indeed, in this case, the electrons and holes are strongly localized (their effective masses are infinite) and a pair, when formed, is bound to remain as such. The energy of the pair will depend on the e-h distance. Therefore one expects an infinite countable set of such pairs, i.e. of bound states. To be sure, one should take into account the possibility of a variation of the pair distance by retaining in the

Fig. 2. — Number of bound states for a given $z = e^{-\alpha}$ as a function of $b$.

Fig. 3. — Variation of the bound-state energies as a function of the wave number.

(3a) $U(0) = 5$, $V(0) = 1$, $t_e = 4$, $t_h = 2$, $z = e^{-\alpha} = 0.5$. Three bound states are obtained for all values of $ka$. (3b) The number of bound states varies with $ka$. For the sake of clarity two different scales have been used for the first (right scale) and the second (left scale) bound state. The second bound state merges in the continuum for $ka \sim 110^\circ$ and reemerges for $ka \sim 160^\circ$. 
starting Hamiltonian $H_2$ a distance dependent transfer term, i.e. of the form:

$$H_2 = -\sum_{R} \sum_{\beta} \sum_{a_i} V(\beta, a_i, a_j) C_{R+\beta+a_i}^* d_{R+\beta+a_j} C_{R} d_{R+\beta}$$

so that new channels of dissociation would be open. Note that this is a higher approximation term.

In real situations the number of bound states, if large, is finite since range and band width, if small, are never zero.

When the range increases, the boundaries of the various domains come close together and, eventually, seem to converge for infinite range $(\alpha = 0)$ towards the point $b = 0, \alpha = 0$.

This means that for $\alpha \to 0$ the number of bound states tends towards infinity whatever the value of $b$, a plausible result indeed.

Close to $\alpha = 0$ (long-range), the numerical procedure does not converge rapidly, and we have been forced to restrict our computation to ranges of 0 to 10 atomic distances (i.e. $0 \leq e^{-\alpha} \leq 0.9$). In order to demonstrate the announced behaviour of the boundaries, we have to resort to another technique. This is the subject of the next section.

For a given value of $b$ and $\alpha$, one can compute the corresponding values of possible $u$'s, i.e. the binding energies of the various bound states. Remember that $b$ is actually $k$ dependent (see Eq. (2.18)), and thus is $u$. An interesting feature appears: when $k$ is varied the value of $b$ will change. In some cases the number of bound states may vary in the zone when a threshold is crossed: a new bound state may be peeled out from the continuum, or, conversely, the highest bound state may merge into it (Fig. 3a et Fig. 3b). To be sure, close to such a point, the description of the system becomes more involved: one should take into account other processes such as the effect of phonons, or even renormalize the continuum itself. We nevertheless believe that this effect may play a role in non-radiative transitions.

### 3.4 Ultra Long-Range Interaction.

For $\alpha \sim 0$, one would be tempted to start from the matrix equation (2.25) and try to find an expansion of the eigenvalue in power series of $\alpha$. Unfortunately, one is faced with a fundamental difficulty: $e^{-i \alpha}$ is not correctly represented by $1 - |n| \alpha$ even for small $\alpha$, since there always exist $n$ such that $|n| > 1/\alpha$. The matrix has to be taken in its full extent. Here again we encounter the mathematical reason responsible for the bad numerical convergence mentioned in the preceding section. One could set up some kind of truncation technique but the result will depend on the truncation itself, except for the strict limit $\alpha \to 0$.

Since we can reach this limit by another method, we did not try truncation-type evaluation. Indeed, starting from equation (2.7a), one remarks that $\Omega(q', q)$ is strongly peaked around $q' = q$ for $\alpha \to 0$. In fact

$$\frac{1}{2 \pi \omega_k(0)} \Omega(q' - q) = \frac{1}{2 \pi} \cosh \frac{\alpha}{2} \sinh \frac{\alpha}{2}$$

$$= \frac{1}{2 \pi} \cosh \frac{\alpha}{2} \sinh \frac{\alpha}{2}$$

generates, for $\alpha \to 0$, the $\delta$ function $\delta[(q' - q) a]$.

(This is easily seen by setting $\sinh \frac{\alpha}{2} = \frac{e^\alpha - 1}{2}$ and expanding $\sin \left[ \frac{(q' - q) a}{2} \right]$ as $(q' - q) a$ or, equivalently, by investigating equation (2.3b). To be sure, this identification requires that the dimension of the crystal is made infinite \textit{before} the range interaction.)

The equation for $F(q)$ takes then the simple form:

$$F(q) = \tilde{G}(q) a \int \delta[(q' - q) a] F(q') \, dq' = \tilde{G}(q) F(q)$$

where $\tilde{G} = \hbar \omega_k(0) G$. This yields:

$$F(q) = 0$$

or

$$\tilde{G}(q) = 1$$

(3.14b) is evidently the only equation of interest, it gives:

$$\cosh u = \frac{b}{2} + \cos \left[ (q - k_0) a \right].$$

For a given value of $b$, there always exists an infinite number of $q$ values for which $\cosh u \geq 1$. Indeed this requires:

$$\cos \left[ (q - k_0) a \right] \geq 1 - \frac{b}{2}$$

which is always satisfied as soon as $b \geq 0$.

In other words, the limiting point for the domain boundaries is $\alpha = 0, b = 0$, as announced in the preceding section.

For a given $b$ the values of $q$ are restricted to the band:

$$\left\{ \begin{array}{l} 1 - b/2 \\ -1 \end{array} \right\} \leq \cos (q - k_0) a \leq 1.$$  (3.17a)

As a result the energies are such that:

$$\left\{ \begin{array}{l} b/2 - 1 \\ -1 \end{array} \right\} \leq \cosh u \leq b/2 + 1$$  (3.17b)

i.e.

$$\omega_k(0) - 2 \pi(k) \leq E_{\text{exc}} \leq \omega_k(0).$$  (3.18)
It is seen that for $b > 2$ no restriction is imposed to $q - k_0$ which may vary from $-\pi/a$ to $n/a$.

$b > 2$ corresponds to $\omega_b(0) > 2 \tau(k)$. In this situation the band of bound states is separated by the gap $\Delta_k = \omega_b(0) - 2 \tau(k)$ from the continuum. For a given $q$, say $q_{bs}$, there corresponds one value $u_b(k)$ for $u$. The corresponding eigenfunction $F_{bs}^b(q)$ is actually the $\delta$ function:

$$F_{bs}^b(q) = \delta(q - q_{bs}).$$  \hfill (3.19)

In the $q$ space, the bound states are thus constituted by an infinite set of strongly localized functions. In the direct space, however, each bound state of energy $E_{bs}^b = 2 \tau(k) \sinh^2 \frac{u_b(k)}{2}$ is a non-localized plane wave of the form $\exp(q_{bs} a)$. This is plausible since, in the case of an infinite-range interaction, one expects non-localized bound states or, equivalently, that the average radius of the pairs be infinite.

The fact that $F_{bs}^b(q)$ behaves as a $\delta$ function does not allow for a simple perturbation calculation for $\alpha \sim 0$, but not strictly zero. Indeed, a conventional procedure would use the fact that $\Omega(q' - q)$ is strongly peaked to try to replace $F(q')$ in the integral (2.7a) by some expansion in power series of $q' - q$, i.e.

$$F(q') \sim F(q) + (q' - q) F'(q) + \frac{(q' - q)^2}{2} F''(q) + \cdots$$

and derive from this a differential equation of finite order for $F(q)$. However, it is readily seen that for $\alpha \sim 0$ (but not 0) the various moments of $\Omega$ are of order sinh $\alpha$, so that the proposed procedure does not converge properly. This, of course, pictures the fact that $F(q)$ tends towards a $\delta$ function for $\alpha \to 0$.

Yet, one can safely interpolate, at least for the lowest bound states, between the numerical procedure and the $\alpha = 0$ limit by some graphical drawing.

This is represented by dotted lines in figure 1, giving the boundaries between domains of different numbers of bound states in the $(b, \alpha)$ plane. Notice that, for a very long range, one can safely use the infinite-limit result as long as the radius of a pair is much smaller than the actual range. This, again, means that our results are valid for the lowest bound states.

### 3.5 COULOMB INTERACTION AND CONTINUOUS REPRESENTATION

It is interesting to investigate the case of a Coulomb interaction which is not taken into account in the preceding model. In its simplest form, it varies $\sim |x|^{-1}$. It is known to occur in various cases (Bounds and Siebrand [3]). One could also imagine a screened Coulomb interaction, say of the form $\exp(-|x|)/(|x| + x_0)$. In this last case, one could retain for $\Omega_b(\kappa)$ the following form:

$$\Omega_b(\kappa) = \omega_b(0) + 2 \omega \sum_{n=1}^{\infty} \frac{e^{-\eta_0 n a}}{n + \eta_0} \cos \kappa n a$$

$$\left(0 < \eta_0 < 1\right).$$  \hfill (3.20)

The bare Coulomb potential is obtained for the limit $\alpha \to 0^+$, $\eta_0 \to 0$. We retain this form, for the time being, with $\eta_0 = 0$, in order to discuss some features of the Coulomb like potentials since it leads to simple mathematical calculations. Indeed for $\eta_0 = 0$, the summation in (3.20) is easily performed and one finds:

$$\Omega_b(\kappa) = \omega_b(0) - \omega \left\{ \log \left[ 2(\cosh \alpha - \cos \kappa a) \right] - \alpha \right\}.$$  \hfill (3.21)

For $\alpha \to 0$, the most singular part of this expression is $\sim \log (1 - \cos \kappa a)$ which is not a $\delta$ function of $\kappa$. This pictures the fact that the Coulomb like potentials, albeit long-range, are still sufficiently decreasing in the direct space. (Clearly this conclusion would remain valid for $\eta_0 \neq 0$.) Let us now return to equation (2.8a) in the direct space and assume that $f_c$ is a sufficiently slowly varying function of $n$, so that it can be considered as the mean value of some function $f(x)$ in the interval $[\frac{n - 1}{2} a, (n + \frac{1}{2}) a]$. If this is the case (to be checked at the end of the calculation), the matrix equation is easily transformed into an integral equation for $f(x)$. Using (2.8a) and (2.15) and setting $g(x) = f(x) \exp ik_0 x$ this integral equation is obtained as:

$$g(x) = \frac{1}{2 a \sinh u} \times$$

$$\times \int_{-\infty}^{\infty} \exp \left( - u \frac{|x - x'|}{a} \right) b(x') g(x') \, dx'$$  \hfill (3.22a)

where

$$b(x) = 2 \frac{\gamma_{\omega_b}(x)}{\tau(k)}$$  \hfill (3.22b)

$\omega_b(x)$ being the continuous generalization of $\omega_b(\beta)$ appearing in equations (2.3) for $\Omega$. Clearly, the continuous approximation to be valid requires that the expected eigenvalue parameter $u$ be sufficiently small, so that the exponential kernel varies sufficiently slowly (in other words $a/u \gg a$).

By differentiating twice with respect to $x$, the integral equation transforms into:

$$g''(x) + \frac{u}{a^2 \sinh u} b(x) g(x) = \frac{u^2}{a^2} g(x).$$  \hfill (3.23a)

This is a second-order differential equation with boundary condition

$$g(x) \to 0 \text{ for } |x| \to \infty.$$  \hfill (3.23b)

Notice, however, that $u$ appears in a very intricate way in the « potential » $\frac{u}{a^2 \sinh u} b(x)$, and as « eigenvalue » $u^2/a^2$. Moreover, the exciton binding energy is related to $u$ by equation (2.14), so that no simple prediction can be made from a superficial examination of (3.23).
In order to be more precise, we have to introduce an explicit form for \( b(x) \). We retain expression (3.20) for \( \Omega \), with \( a = 0 \) and \( \omega_k(0) = \omega/\eta_0 \), i.e.

\[
\omega_k(n) = \frac{\omega}{|n| + \eta_0}
\]

so that the continuous generalization is

\[
\omega_k(x) = \frac{a\omega}{|x| + x_0}
\]

(3.25)

where \( x_0 \) is some truncation distance that we assume to be much smaller than \( a \), and which is introduced only to avoid spurious divergencies at \( x = 0 \).

Formally equation (3.23) may be rewritten as a Schrödinger equation:

\[
-\frac{\hbar^2}{2m} g''(x) - \frac{A\omega}{|x| + x_0} g(x) = Eg(x)
\]

(3.26)

i.e. a Schrödinger equation for a one-dimensional hydrogen atom, as studied by Haines and Roberts [4] and Care [5] to describe the effect of a strong magnetic field. These authors found that the ground state energy \( E_0 \) is finite, but diverges towards \(-\infty\) when \( x_0 \to 0 \). The spectrum consists in a series of levels, embedded in a continuum, which becomes a hydrogenic succession when \( x_0 \to 0 \). Remember, however, that we are looking for \( u \) which is related to \( \Lambda \).

The best is to solve directly equation (3.26), which is easily done by using the conventional Laplace method. Setting

\[
z = \frac{2x}{a \sinh u} \quad g(x) = P(z) \exp\left(-u \frac{|x|}{a}\right)
\]

(3.27a)

\[
P(z) = \int e^{iz} \phi_z(t) \, dt \quad (\pm \text{ for } x \geq 0)
\]

(3.27b)

one obtains

\[
\phi_z(t) = t^\left(1 + \frac{b}{2 \sinh u}\right) \left(t \pm i \frac{u}{\sinh u}\right)^{-1 + \frac{b}{2 \sinh u}}
\]

(3.27c)

The integral for \( P \) has to be taken clockwise on a small contour around the origin. (Notice that in the expression for \( g \) we have retained the condition \( x_0 \ll a \).

Imposing the boundary condition (3.23b) yields:

\[
\frac{b}{2 \sinh u} = n \text{ (non-negative integer)}
\]

(3.28a)

\[
P(z) \quad \text{polynomial in } z \text{ of degree } n.
\]

(3.28b)

\( n = 0 \) cannot be retained in (3.28a) since for this solution \( g(x) \) behaves as \( \delta(x) \) which is, by no means, to be considered as a slowly varying function! The exciton binding energy is therefore

\[
E_{\text{exc}}(k) = \frac{\hbar^2}{2 m} \left(1 + \frac{b^2}{4 n^2}\right)^{1/2} - 1
\]

(3.29a)

for each value of

\[
u = u_n = \sinh^{-1}\left(\frac{b}{2 n}\right)
\]

(3.29b)

while the wave function is

\[
g_n(x) = P_n\left(\frac{b |x|}{na}\right) \exp\left(-\frac{b |x|}{2 na}\right)
\]

(3.29c)

where \( P_n \) is the polynomial

\[
P_n(z) \sim z^{n-1} \sum_{p=0}^{n-1} \frac{(-)^p}{(p+1)!} \left(\frac{P}{n-1}\right) \left(\frac{u_n}{\sinh u_n}\right)^{zp} z^p.
\]

(3.29d)

The requirement that \( g(x) \) be a slowly varying function of \( |x| \) imposes:

\[
\frac{u_n}{\sinh u_n} \ll 1 \quad \text{or} \quad \frac{b}{2 n} \ll 1.
\]

(3.30)

When condition (3.30) is satisfied, \( E_{\text{exc}} \) becomes the hydrogenic spectrum:

\[
E_{\text{exc}}(k) \sim t(k) \left(\frac{b^2}{8 n^2}\right) = \frac{\hbar^2 \omega_0^2(0)}{2 \mu t(k) n^2}.
\]

(3.31)

Note that for \( n = 1 \), one recovers the lowest eigenvalue of the ultra short-range interaction, but with a quite different wave function. We suspect that this somewhat surprising result is related to the lowest bound of the eigenvalues of the matrix \( M \) in equation (2.9), but we have no definite proof of this conjecture.

(3.29c) and (3.31) are the eigenfunction and energy of a hydrogenic system of mass:

\[
\mu_k = \left(\frac{a_0}{a}\right)^2 \frac{e^2}{a_0} t(k) m
\]

and of dielectric constant:

\[
e_k = \left(\frac{a_0}{a}\right)^2 \frac{e^2}{a_0} \hbar \omega_0(0)
\]

\( a_0 = 0.53 \text{ Å} \) is the Bohr radius, \( e \) and \( m \) the electron charge and mass. Apart from the scaling factor \( a_0/a \), \( \mu_k \) is simply the inverse of the band width of the unbound-electron hole continuum, as expected. Note, however, that \( \mu_k^{-1} \) is not \( m_e^{-1} + m_h^{-1} \) but is \( k \) dependent and varies between \( m_e^{-1} \pm m_h^{-1} \) (where \( m_{e,h} = \frac{\hbar^2}{2 \pi a^2} t_{e,h} \)).

As an illustration, let us take \( t \sim 10 \text{ eV}, \hbar \omega_k \sim 1 \text{ eV} \). This leads to \( b \sim 0.2 \) and \( u \sim \sinh u \), even for \( n = 1 \).
so that the computation is valid for all \( n \). The binding energy is \( 0.05/n^2 \) eV and with \( a \sim 3 \, \text{Å}, \ e \sim 2-3, \ \mu \sim 10^{-2} \, \text{W} \). Let us conclude by a remark on the condition \( b/2 \, n \ll 1 \).

The simple way to fulfill it is to impose \( b \ll 2 \). This corresponds to a weakly interacting e-h pair, as compared to the band width. Remember that the Wannier exciton concept assumes more or less a continuum approximation for the lattice, as expressed by a dielectric constant.

For moderate values of \( b \), the condition \( b/2 \, n \ll 1 \) may be violated for the first values of \( n \), up to a certain value \( n_0 \).

\[
\sinh u \text{ is a rapidly increasing function value of } u,
\]
so that the solution \( n < n_0 \) of the continuous approximation have no counterpart in the original formulation. In other words, one would obtain a truncated hydrogenic spectrum.

For practical cases, however, \( b \) cannot be too large so that it is likely that there will be only one missing state, if any, corresponding to \( n = 1 \).

4. Dynamics of excitons. — Experimentally, one usually creates excitons by irradiating a crystal with photons. When no spectral precautions are taken, one will obtain a mixture of the various bound states, possibly with some exclusions due to symmetry selection rules. In principle, there is no phase coherence between the various involved states.

On the contrary, if one uses coherent photons in a broad band, one can obtain a coherent superposition of bound states. The most simple experimental situation would be to create an electron-hole pair located on a same site. If this situation corresponds to an eigenstate of the system, it remains as such for all times, and no dynamics results. This is evidently never the case. Another simple situation arises when the electron and hole created on the same site experience a zero-range interaction. Then, one expects Frenkel excitons to exist. The subsequent dynamics is well known [6]. Remember, however, that this requires that the range is made zero before any other relevant parameter (e.g. the band width).

For an arbitrary-range interaction, the Frenkel exciton will not correspond to an eigenstate of the system, so that the created pair will not « stay together ». Another kind of dynamics occurs which we now investigate. For a non-Coulombic interaction, several bound states are available for each \( k \) (see sections 3.1 to 3.3). The prepared state \( \left| \psi(0) \right> \) (i.e. electron and hole located on the same site at \( t = 0 \)) will subsequently behave as a superposition of all these states. The decomposition is unique and time independent, of the form:

\[
\left| \psi(t) \right> = \sum_{n} c_n \left| \psi_n \right> e^{i \omega_n t} + \\
+ \text{integral over the continuum}.
\]

The coefficients are readily obtained by the projection of \( \left| \psi(0) \right> \) on the bound states. We have computed

\[
P_1 = \frac{a}{2 \pi} \int_{-\pi/a}^{\pi/a} \, dk \left| C_1(k) \right|^2.
\]

\[
C_1, \text{ i.e. the projection coefficient on the lowest bound state, for each value of } k, \text{ assuming for simplicity that the range is sufficiently short, so that we can use the zeroth-order approximation (Eq. (3.8a)) for } u(k) \text{ and the wave function. It is found that}:
\]

\[
| C_1(k) | = \left| \langle B_1 \, B_{10}^* \rangle \right| = \frac{1}{\sqrt{N}} \left| f(k) \right| \simeq
\]

\[
\simeq \frac{1}{\sqrt{N}} \tanh u_0^2(k) \quad (4.2)
\]

(see Eq. (3.4), the \( \tanh \) term comes from the normalization of \( f \)). The probability for the exciton to be in the lowest bound state is:

\[
P_1 = \frac{a}{2 \pi} \int_{-\pi/a}^{\pi/a} \, dk \left| C_1(k) \right|^2.
\]

We have computed \( P_1 \) as a function of \( U(0), \ V(0), \ t_e \) and \( t_h \) (see Eqs. (2.3c), (2.11) and (2.18) for the definition of these quantities). Figure 4 shows a typical variation of \( P_1 \). We have assumed for simplicity \( t_e = t_h = t_w, \ U(0) \) and \( V(0) \) fixed. As expected, \( P_1 \) decreases when \( t_w \), i.e. the band width, is increased. For other cases, a similar behaviour is observed.

All this is somewhat self-evident; notice, however, that one could infer from this result that, for a broad band, the fluorescence from the lowest bound states could be weak.

More interesting is the case of a long-range interaction, since one expects a quasi-continuum of bound states, as shown in section 3.4. The existence of this continuum pictures the fact that the correlation between the electron is long-ranged : peculiar features of the motion are likely to occur due to the close vicinity of the bound states.

The behaviour of a pair created on some site, say \( R = 0, \, \beta = 0, \) at \( t = 0 \), is conveniently described by the Green function:

\[
G_{R,\beta}(t) = \left< B_{R,\beta}(t) \, B_{0\beta}^*(0) \right>.
\]

In order to compute this quantity we shall use the ultra long-range results of section 3.4. Remember that
the eigenfunction $F_k(q)$ is a $\delta$ function, $\delta(q - q_{bs})$ (Eq. (3.19)). To each state (labelled by $q_{bs}$) corresponds the annihilation operator

$$B_{k,q_{bs}}(0) = \frac{1}{\sqrt{N}} \sum_K e^{-ikR} \sum_\beta e^{-ik\beta} e^{-iq_{bs}\beta} B_{R,\beta}(0). \quad (4.5)$$

As explained in the text, the values of $q_{bs}$ are limited by the condition:

$$\cos(q_{bs} - k_0) \geq 1 - b/2. \quad (4.6)$$

If $b < 2$, the bound state continuum is not separated from the unbound electron-hole continuum. The time behaviour of the pair is not easily describable. The two continua have to be treated on the same footing. In other words, (4.5) is difficult to invert.

For $b > 2$, on the contrary, a gap opens between the two continua and they can be treated independently. We restrict ourselves to this case and obtain ($q_{bs}$ is no more limited):

$$B_{R,\beta}(0) = \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dq_{bs} \times$$

$$\times e^{ikR} e^{ik\beta} e^{iq_{bs}\beta} B_{k,q_{bs}}(0). \quad (4.7)$$

(We have used the fact that $q_{bs}$ takes continuous values between $-\pi/a + k_0$ and $\pi/a + k_0$ and that the various functions are periodic in the reciprocal space.) The Green function (4.4) turns out to be:

$$G_{R,\beta}(t) = \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dq_{bs} \times$$

$$\times e^{ik(R+\beta)} e^{iq_{bs}\beta} \exp\left(-\frac{i}{\hbar} E_{q_{bs}} t\right) \quad (4.8)$$

where

$$E_{q_{bs}} = E_1 - E_{exc}(k, q_{bs}) = 2t_0 - \hbar\omega_0(0) - \lambda(k) \cos q_{bs} a$$

is the bound state energy.

For the sake of simplicity, we shall assume a flat band for the hole, i.e. $t_0 = 0$. Setting $R = na$, $\beta = va$ ($n$ and $v$ integers), it is seen that (4.8) introduces Bessel functions through integrals of the form:

$$J_p(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-iyx} e^{i\pi y} dy \quad (4.9)$$

so that:

$$|G_{n,v}(t)| = |J_p(\psi) J_{n+}(\phi)| \quad (4.10a)$$

where

$$\phi = \frac{2}{\hbar} V(0) t = \frac{2}{t_1} t_1, \quad \psi = \frac{t}{\hbar} t = \frac{t}{t_2}. \quad (4.10b)$$

We have set:

$$t_1 = \frac{\hbar}{V(0)}; \quad t_2 = \frac{\hbar}{t_e} \quad (4.11)$$

$V(0)$ is the value of $V(\beta = 0)$ appearing in equation (2.3c).

$t_1$ and $t_2$ are the two time scales of the problem.

Note that

$$\sum_{n,v} |G_{n,v}(t)|^2 = 1.$$

As usual, the various quantities of interest are obtained from $G$. For instance the electron and hole charge densities at site $R_n = na$ are given respectively by:

$$\rho_{R_n}(t) = \sum_{v=-\infty}^{+\infty} |G_{n,v}(t)|^2 \quad (4.12a)$$

$$\rho_{R_n}^h(t) = \sum_{v=-\infty}^{+\infty} |G_{n,-v}(t)|^2. \quad (4.12b)$$

The total charge density on the same site is thus

$$\rho_{R_n}(t) = \rho_{R_n}^e(t) - \rho_{R_n}^h(t) =$$

$$= \sum_{v=-\infty}^{+\infty} \left( |G_{n,v}(t)|^2 - |G_{n,-v}(t)|^2 \right). \quad (4.12c)$$

The probability that the electron and hole be separated by the distance $va$ reads:

$$P_x(t) = \sum_{n=-\infty}^{+\infty} |G_{n,v}(t)|^2 \quad (4.13a)$$

so that the mean-square e-h distance $\bar{r}_{exc}$ is:

$$\bar{r}_{exc}^2 = \sum_{v=-\infty}^{+\infty} a^2 v^2 P_x(t) = a^2 \sum_{n,v} v^2 |G_{n,v}(t)|^2. \quad (4.13b)$$

Another quantity of interest is the mean-square dispersion of the exciton $\bar{r}_x$ defined by:

$$\bar{r}_x^2 = a^2 \sum_{n,v} |G_{n,v}(t)|^2. \quad (4.13c)$$

Using (4.10a) several of these quantities may be computed easily, if one uses the well-known relation

$$\sum_{p=-\infty}^{+\infty} J_p^2(z) e^{ipx} = J_0 \left(2 z \sin \frac{x}{2}\right).$$

The charge densities for electron and hole are:

$$\rho_{R_n}^e(t) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx e^{inx} J_0 \left(2 \phi \sin \frac{x}{2}\right) J_0 \left(2 \psi \sin \frac{x}{2}\right) \quad (4.14a)$$

$$\rho_{R_n}^h(t) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx e^{inx} J_0 \left(2 \phi \sin \frac{x}{2}\right) J_0^2(\phi). \quad (4.14b)$$
It is instructive to compute the spatial moments of the distributions:
\[ M_{p}^{uh}(t) = \sum_{n=-\infty}^{\infty} (na)^p \rho_{n}^{uh}(t). \] (4.15)

For \( p \) odd, these moments vanish as expected. For \( p = 2 \), one has:
\[ M_{2}^{uh}(t) = -a^2 \left( \frac{4}{t_1^2} + \frac{1}{2t_2^2} \right) t^2. \] (4.16a)
\[ M_{2}^{bh}(t) = a^2 \frac{4}{t_1^2} t^2. \] (4.16b)

This shows that the electron moves faster than the hole. This evidently results from the fact that \( t_b \) has been taken equal to zero.

For the total charge the second moment is:
\[ M_{2}(t) = -\frac{1}{2} a^2 \frac{t^2}{t_2^2}. \] (4.16c)

\( M_{2} \) does not depend on \( t_1 \) (i.e. on \( V(0) \)). This comes from the « rigid » site to site transfer of the pair (\( \beta \) remains constant in \( H_2 \)).

The mean-squared exciton radius is given by:
\[ \bar{r}_{exc} = \frac{at}{\sqrt{2t_2}}. \] (4.17a)

The Frenkel character of the exciton is pictured by the probability \( P_F \) that the electron and the hole are still on a same site, namely
\[ P_{F}(t) = \sum_{n=-\infty}^{\infty} |G_{n,0}(t)|^2 = J_{2} \left( \frac{t}{t_2} \right). \] (4.17b)

This shows that this character is preserved for times \( \lesssim t_2 \), since \( \bar{r}_{exc} \sim 0 \) and \( P_F \sim 1 \). For \( t \gg t_2 \), \( \bar{r}_{exc} \) tends towards \( \infty \) and \( P_F \) behaves as:
\[ P_{F}(t) \approx \frac{t_2}{nt} \cos \left( \frac{2t}{t_2} - \frac{\pi}{4} \right). \] (4.18)

The Frenkel character is lost in a damped (\( \sim t^{-1} \)) oscillatory (period \( \sim t_2 \)) way.

It is also instructive to consider the charge densities on a given site \( R_n \). To be sure, they are given by formulae (4.12), which are not so transparent. In order to make them more palatable, we shall suppose \( t_1 \ll t_2 \). Physically this corresponds to a situation where the electron band is rather flat. As discussed above, this is one of the conditions ordinarily retained for a Frenkel like description.

We return to equation (4.10a) for \( G \).

For \( t \leq t_1 \ll t_2 \), \( J_{n}(\psi = t/t_2) \) can be expanded as a series in powers of \( t/t_2 \). We obtain:
\[ |G_{n,v}(t)| \approx J_{n+1} \left( \frac{2}{t_1} \right) \left| \delta_{v,0} + \frac{\psi}{2} (\delta_{v,1} - \delta_{v,-1}) + \frac{\psi^2}{8} (\delta_{v,2} + \delta_{v,-2} - 2 \delta_{v,0}) \right| \] (4.19)

and:
\[ \rho_{n,v}(t) \approx \frac{t_2^2}{4} \left[ J_{n} \left( \frac{2}{t_1} \right) - J_{n+1} \left( \frac{2}{t_1} \right) - J_{n-1} \left( \frac{2}{t_1} \right) \right] \] (4.20a)
\[ \bar{r}_{exc}^{2} \sim \frac{1}{\sqrt{2}} \frac{t}{t_2} a. \] (4.20b)
\[ \bar{r}_{F}^{2} \sim \frac{\sqrt{2}}{t_2} a. \] (4.20c)

We recover the fact that the Frenkel character is preserved as long as \( t \ll t_2 \). The spreading over the lattice corresponds to the well-known wave like motion of a purely coherent Frenkel exciton [6]. Clearly, during this first step of the motion, the charge density remains quite small. Note that for a truly flat band, \( t_b = 0, t_2 \to \infty \)
\[ \left| G_{n,v}(t) \right| \approx \left| J_{2} \left( \frac{t}{t_2} \right) \right| \delta_{v,0}; \quad P_{F} = 1 \]

so that the Frenkel character persists for all times.

For \( t_1 \ll t \ll t_2 \), \( G_{n,v}(t) \) is approximated by
\[ \left| G_{n,v}(t) \right| \approx \frac{t_2}{\sqrt{\pi t}} \cos \left( \frac{2t}{t_1} - (n + v) \frac{\pi}{2} \right) J_{1} (\frac{t}{t_2}). \]

The local charge densities take the form:
\[ \rho_{n,v}(t) \approx \frac{t_1}{2t} (-y)^{n+1} \left[ 1 - J_{0} \left( \frac{2}{t_2} \right) \right] \sin \frac{4t}{t_1}. \] (4.21a)
\[ \rho_{n,v}(t) \approx \frac{t_1}{2t} (-y)^{n+1} \sin \frac{4t}{t_1}. \] (4.21b)
\[ \rho_{n,v}(t) \approx \frac{t_1}{2t} (-y)^{n+1} J_{0} \left( \frac{2}{t_2} \right) \sin \frac{4t}{t_1}. \] (4.21c)

It is clearly seen that a charge density wave develops:
\[ \text{two neighbouring sites bear opposite charges. For } t \sim t_2 \text{ this wave oscillates rapidly with a period } \sim t_1, \text{ while its amplitude decreases as } t_1/t, \text{ but is also slowly modulated by the electron band width appearing in the argument } t/t_2 \text{ of the Bessel function. (Note that for } t_2 \to \infty, \rho_{n,v}(t) \to 0 \forall t, \text{ as expected.)} \]

In general, the mean distance between the electron and hole will thus increase with time. Consequently the exciton will become more and more sensitive to perturbating effects: phonons, impurities, defects, etc. If \( \delta E \) is the energy linked to such a perturbation the mean life time of an exciton \( \tau_{exc} \) will be such that:
\[ \hbar \omega_{k} \bar{r}_{exc} (t = \tau_{exc}) \lesssim \delta E. \] (4.22)

Clearly, the preceding calculation will fail for times \( t \gtrsim \tau_{exc} \).

Before concluding this section, let us recall that our results have been obtained within an infinite-range approximation. Independently of possible perturbations, this requires that any distance of interest (e.g. the pair radius) remains smaller than the actual
finite interaction range. When this requirement is fulfilled, the above description should be physically correct.

5. Conclusion. — In conclusion, we have shown that in a one-dimensional rigid crystal, including two-particle interactions, excitons exist whatever the interaction, weak or strong, short- or long-range. This generalizes Egri's statement. To be sure, this is specific of a low-dimensional system. As is well known, in three dimensions for example, the existence of bound states is certainly much more model dependent.

Therefore, since a system may be quasi one-dimensional in some respects (conductivity, etc.) and two- or three-dimensional in some others (e.g., electron-hole correlation, etc.), one has to be very careful not to draw too hasty conclusions. The question of the relevance of excitons in interpreting experimental data thus requires a thorough examination of various features, albeit idealized models, as the one developed above, demonstrate their general existence.

Our calculation is certainly much too simple. It does not take into account the possible effects of various perturbing agents, such as phonons, impurities, defects, etc. Clearly these would result in finite lifetime for the exciton: this has to be kept in mind when discussing experiments, the more since these effects are to be expected in real crystals, even perfect one (phonons).

All these drawbacks are well known, and are sometimes called up to deny any interest to model calculations. This is not our opinion. Besides the fact that solvable models have an interest of their own, they also help to clarify physical pictures, when taken with the appropriate precautions. We believe that our calculation helps to understand better the difference between Wannier and Frenkel models and to delimitate the validity of these concepts. We estimate that it is interesting to extract, besides general features that could have been predicted on general intuitive physical reasoning, some others which are not so much self evident. It is the case for the fact that the number and the behaviour of bound states depend in a very intricate way on the strength and the range of the interaction. We have seen, for example, that this number may vary in the Brillouin zone: this result is certainly not model dependent (albeit, evidently, in its numerical peculiarities), and may have some importance in some experimental situations, in particular in connection with non-radiative transitions. The possible existence of an infinite number of bound states, which may be so closed as to form a quasi-continuum, is also to be retained since it leads to a very special dynamics in which a charge density wave develops. This sheds new light on the motion of «intermediate» exciton, a subject, which, to our knowledge, has not been so often tackled [7].

Finally, in our model, the Coulombic interaction yields a hydrogenic spectrum only by using a somewhat intricated technique. To, our opinion, this reveals that certain precautions must be taken before predicting an apparent obvious result. We certainly have found the expected hydrogenic spectrum, but, in some cases, truncated with one or several missing states. Once again, this should not be a model dependent conclusion.

Appendix A. — In order to compute the eigenvalues of matrix \( \mathcal{M} \) given in equations (2.25) and (3.10), we remark that it has two kinds of eigenvectors:

a) symmetric ones, for which we can make the change of basis

\[
S_0 = \phi_0; \quad S_n = \frac{1}{\sqrt{2}}(\phi_n + \phi_{-n}) \quad (n = 1, 2, \ldots)
\]  
\[
(A.1a)
\]

b) antisymmetric ones, for which the change of basis is:

\[
A_0 = 0; \quad A_n = \frac{1}{\sqrt{2}}(\phi_n - \phi_{-n}) \quad (n = 1, 2, \ldots).
\]  
\[
(A.2a)
\]

With these new bases, the matrix is divided into two independent blocks:

\[
\mathcal{M}_S = \begin{pmatrix}
\sqrt{2} & 0 & 0 & \ldots \\
0 & \sqrt{2} & bz & 1 & 0 & \ldots \\
0 & 1 & bz^2 & 1 & 0 & \ldots \\
0 & 0 & 1 & bz^3 & 1 & 0 & \ldots
\end{pmatrix}
\]  
\[
(A.3a)
\]

\[
\mathcal{M}_A = \begin{pmatrix}
bz & 1 & 0 & 0 & \ldots \\
1 & bz^2 & 1 & 0 & \ldots \\
0 & 1 & bz^3 & 1 & 0 & \ldots \\
0 & 0 & 1 & bz^4 & 1 & 0 & \ldots
\end{pmatrix}
\]  
\[
(A.3b)
\]

where \( z = e^{-a} \).
The eigenvalue problem corresponds therefore to the sets of infinite homogeneous linear equations:

\[
\begin{align*}
bs_0 + \sqrt{2} s_1 &= \lambda s_0 \\
\sqrt{2} s_0 + b z s_1 + s_2 &= \lambda s_1 \\
s_{n-1} + b z^n s_n + s_{n+1} &= \lambda s_{n} & (n = 2, \ldots) \\
bz A_1 + A_2 &= \lambda A_1 \\
A_{n-1} + b z^n A_n + A_{n+1} &= \lambda A_n & (n = 2, \ldots)
\end{align*}
\tag{A.4a}
\]

and the eigenvalue \( \lambda \) has eventually to be set equal to \( 2 \cosh u \).

For short, we shall expose the principle of the calculation for the antisymmetric subspace \( A \). The symmetric case is treated along the same lines. The set of equations (A.4b2) may be easily rewritten under the form of a continued fraction \( F \) giving the ratio \( A_1/A_2 \) namely:

\[
A_1/A_2 = \lambda - b z^2 - 1/\lambda - b z^3 - 1/\lambda - b z^4 - 1/\lambda - \ldots = F(\lambda).
\tag{A.5}
\]

If \( F \) could be evaluated, the value of \( \lambda \) would be obtained by solving the implicit relation:

\[
F(\lambda) (\lambda - b z) = 1
\tag{A.6}
\]

deduced from comparison of equations (A.4b1) and (A.5).

Thus, the problem reduces to the evaluation of \( F(\lambda) \).

A converging procedure is obtained if one sets \( z^n = 0 \) for \( n > n_0 \), defining an approximate value \( F_{n_0}(\lambda) \) for \( F \) such that:

\[
F_{n_0}(\lambda) = \lambda - b z^2 - 1/\lambda - b z^3 - 1/\lambda - b z^4 - 1/\lambda - \ldots
\tag{A.7}
\]

The partial continued fraction \( \lambda - 1/\lambda - 1/\ldots \) is easily evaluated if one writes \( \lambda = 2 \cosh u \). Its value is \( e^u \).

Therefore

\[
F_{n_0}(\lambda) = 2 \cosh u - b z^2 - 1/2 \cosh u - b z^3 - 1/\ldots - 1/(e^u - b z^{n_0}).
\tag{A.8}
\]

Clearly this procedure amounts to replace the infinite set (A.4b2) by another infinite set for which

\[
\frac{A_{n+1}}{A_n} = e^{-u}; \quad n \geq n_0.
\tag{A.9}
\]

Using the approximate value \( F_{n_0}(\lambda) \) in equation (A.6) would yield an approximate value \( u(n_0) \) for \( u \).

This way of doing would be much too complicated, and it is better to remark that (A.8) and (A.6) are also the solution of a truncated set of \( n_0 \) linear homogeneous equations, the characteristic equation of which being:

\[
\begin{array}{cccccc}
2 \cosh u - b z & - 1 & 0 & 0 & \ldots & \\
- 1 & 2 \cosh u - b z^2 & - 1 & 0 & \ldots & \\
0 & - 1 & 2 \cosh u - b z^3 & - 1 & \ldots & \\
\ldots & \ldots & \ldots & \ldots & \ldots & \\
0 & - 1 & 2 \cosh u - b z^{n_0 - 1} & - 1 & \\
& & & & \ldots & \\
& & & & 0 & - 1 \end{array} = 0.
\tag{A.10a}
\]

For the symmetric case a similar equation is obtained, namely:

\[
\begin{array}{cccccc}
2 \cosh u - b & - \sqrt{2} & 0 & 0 & \ldots & \\
- \sqrt{2} & 2 \cosh u - b z & - 1 & 0 & \ldots & \\
0 & - 1 & 2 \cosh u - b z^2 & - 1 & \ldots & \\
\ldots & \ldots & \ldots & \ldots & \ldots & \\
& & & & \ldots & \\
& & & & 0 & - 1 \end{array} = 0.
\tag{A.10b}
\]

We look for the physical solutions, i.e. \( \cosh u \geq 1 \). As explained in section 2 (see Eqs. (2.26, 27)), setting \( u = 0^+ \) gives the threshold for the appearance of new bound states. Introducing this condition into (A.10) yields a relation between \( b \) and \( z \). When this relation is worked out, one knows the number of eigenvalues \( \cosh u \geq 1 \) for a given couple \((b, z)\). It is then easy to exhaust all the eigenvalues \( u(b, z) \) by solving (A.10).
$n_0$ is the parameter governing the convergence. This is easily checked by comparing different values of $u$
for various $n_0$. Clearly the appropriate value of $n_0$ increases with $z$, i.e. with the range of the interaction. For
example, we found that with $n_0 = 5$ the eigenvalues of interest are correctly computed for $z \leq 0.1$.

When $z \to 1$, the convergence of the procedure becomes poor and $n_0$ increases so quickly that the computa-
tion time becomes prohibitive and the precision disputable. We therefore limited the $z$ values to $z = 0.9$
($z \sim 1/10$, i.e., 10 atomic distances for the range). For this value of $z$ we found that $n_0 = 30$ gives a very good
precision for all the eigenvalues. For values of $n_0 \leq 30$, all the calculations are easily performed using a pocket
size programmable calculator.

As explained in the text, the limit $z = 1$, can be reached by another technique.

References