PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983

Eigenstates of N excitons and one hole

R. Schilling* and D. C. Mattis
Physics Department, University of Utah, Salt Lake City, Utah 84112
(Received 29 September 1982)

We solve for the eigenstates and energy eigenvalues of N immobile Frenkel excitons (a relatively trivial proposition) and of N such excitons plus one hole (which for large N can only be done in one dimension). We also guess that a charged globule, consisting of N excitons and $O(N)$ holes, can be stable if, in any number of dimensions, m_h^* for holes is much larger than m_e^* for electrons.

INTRODUCTION

This paper deals with excitons and holes (or electrons) in a certain limiting approximation in which the many-body problem can be solved in closed form. First, the excitons normally thought of as bound electron-hole pairs are so strongly bound that the electron in the conduction band and the hole in the valence band *must* reside on the same atomic cell. In this limit the composite particle is a Frenkel exciton.[1] We investigate what happens when two or more such excitons are present, especially when one or more extra holes are introduced.

The case of two or more such excitons is trivial and solvable in any number of dimensions (d). The "*trion*" (one exciton and one extra hole or electron) can also be solved in any d, as shown in an earlier publication.[2] The "*penton*," "*septon*," etc., can be solved only for $d=1$ by a method of transfer matrices that we outline in the present paper. We find an interesting result in this case, viz., one extra hole can bind *any number* of excitons in one dimension (1D).

The method is reminiscent of, yet differs from, Bethe's *ansatz*, the currently popular tool[3] in one-dimensional many-body problems.

We start by the study of excitons, then excitons plus one hole (under the assumption that the conduction bandwidth exceeds that of the valence band—the usual situation; otherwise, excitons + 1 electron), and finish with a conjecture concerning N excitons + P holes, where $P=O(N)$.

EXCITONS ONLY

We note that if the motional energy is entirely due to the one-body matrix elements constituting the conduction and valence bands, then the tightly bound exciton is incapable of motion because the intermediate state, where the electron is ahead of the hole or vice versa, is prohibited. This is illustrated in Fig. 1., reproduced from Ref. 2. The many-exciton state is then, simply,

$$|R_1,R_2,\ldots,R_N\rangle=\prod_{j=1}^{N}(c_j^\dagger v_j)|0\rangle=\prod_{j=1}^{N}e_j^\dagger|0\rangle\ , \tag{1}$$

where $|0\rangle$ is the ground state (filled valence band, empty conduction band), $c_j^\dagger$ creates an electron in the conduction band at site R_j, and v_j destroys an electron (i.e., creates a hole) in the valence band at the same site; $e_j^\dagger$ is the composite operator which creates an exciton there. State (1) is independent of dimensionality. We are ignoring spin variables here and throughout for simplicity.

We also note that if certain two-body translational matrix elements are included,[4] an exciton at R_j can move resonantly to a neighboring site R_m with matrix element $W(R_{jm})$. The Fourier transform of this

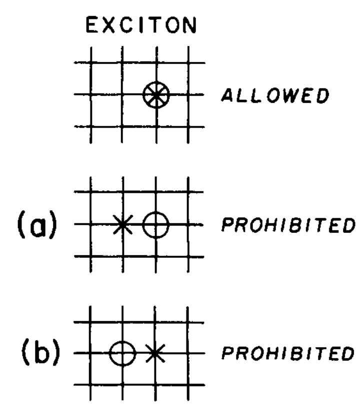

FIG. 1. Demonstration of the impossibility of motion of a Frenkel exciton with only one-body transfer-matrix elements.

quantity, $\hat{W}(k)$, is the motional energy of the exciton of wave vector $\vec{k}$. Its wave function on a lattice of L sites can be characterized as

$$|k)=L^{-1/2}\sum_{\text{all } j} e_j^{\dagger} e^{i\vec{k}\cdot\vec{R}_j}|0)\equiv e_k^{\dagger}|0) \ . \tag{2}$$

The many-body state *cannot* now be written as $\prod e_k^{\dagger}|0)$ because of the effective "hard-core" interaction prohibiting two excitons from occupying the same site. In 1D the many-exciton state is expressible in terms of the complete set (1) as

$$|k_1,k_2,\ldots)=\sum_{R_1}\sum_{R_2}\cdots\sum_{\cdots} D(k_1,k_2,\ldots|R_1,R_2,\ldots)|R_1,R_2,\ldots) \ , \tag{3}$$

where $D(k_1,\ldots|R_1,\ldots)$ is a determinantal function. Here, as in two dimensions (2D) or three dimensions (3D), the many-exciton problem maps exactly onto the well-studied X-Y model[5] for spins of $\frac{1}{2}$, in which guise it has received much attention lately.[6] We note that the energy eigenvalue of (3) is

$$E_{\text{total}}=\sum_{k_i}\hat{W}(k_i) \ . \tag{4}$$

The eigenstates of two excitons can be found in arbitrary d by transforming to center-of-mass coordinates and using a Green-function technique. We have nothing more to say about this and turn our attention now to the novel cases.

N EXCITONS PLUS ONE HOLE

We examine this problem in 1D, setting the motional energy W (or $\hat{W}$) to zero. Thus there is no interaction between an exciton and a hole beyond that due to the motion of the electron from the exciton to the hole when they are neighbors.

We fix the N excitons at $n_1,n_2,\ldots,n_N$ with m the position of the hole to the left of n_1 ($m<n_1<n_2,\ldots$). We identify $N+1$ sectors, depending on the subsequent position of the free hole. Sector 1 has $m<n_1$, sector 2 has $n_1\leq m<n_2,\ldots,$ and finally, sector $N+1$ has $m\geq n_N$. The exclusion principle prevents an extra hole being present at the sites of the excitons (so $m=n_1$ or n_2, etc. is forbidden) although, as is obvious, these sites change by ±1 whenever an electron has the opportunity to jump to a nearest-neighbor free hole.

We assume that $-V$ is the matrix element for the transfer of a particle in the valence band from any given site to a neighboring site, and $-C$ is the same for the conduction band. ($m_h^*\propto 1/V$ and $m_e^*\propto 1/C$ are the respective "effective masses," but we do not use these except for illustrative, qualitative purposes.)

For $m\neq n_i-1$ and n_{i-1}, the equation of motion is

$$-V[F_i(m+1)+F_i(m-1)]=EF_i(m) \ . \tag{5}$$

We denote the amplitude of a hole in sector i by $F_i(m)$, and E is the energy eigenvalue,

At $m=n_{i-1}$ the hole is on the same site as the electron, therefore the *extra* hole must be at $n_{i-1}-1$. The special equation in that case is

$$-VF_i(n_{i-1}+1)-CF_{i-1}(n_{i-1}-1)=EF_i(n_{i-1}) \ . \tag{6}$$

Similarly, when $m=n_i-1$,

$$-VF_i(n_i-2)-CF_{i+1}(n_i)=EF_i(n_i-1) \ . \tag{7}$$

Equations (6) and (7) can be cast in the form of (5) if the following conditions are met:

$$CF_{i+1}(n_i)=VF_i(n_i)$$

and

$$VF_{i+1}(n_i-1)=CF_i(n_i-1) \ . \tag{8}$$

From (8) one can construct 2×2 "transfer matrices" as follows.

BOUND STATES

In region 1,

$$F_1(m)=a_1\exp[\lambda(m-n_1)] \ , \tag{9}$$

with $\lambda>0$, while in successive regions,

$$F_i(m)=a_i\exp[\lambda(m-n_i)] + b_i\exp[-\lambda(m-n_i)] \ , \tag{10}$$

until at the end,

$$F_{N+1}(m)=b_{N+1}\exp[-\lambda(m-n_N)] \ . \tag{11}$$

Thus let us define the vectors ζ_i as follows:

$$\begin{bmatrix} a_i \\ b_i \end{bmatrix}\equiv\zeta_i \tag{12}$$

in terms of which (8) becomes

$$\underline{S}_i\zeta_{i+1}=\underline{T}_i\zeta_i \ , \tag{13}$$

where $\underline{S}_i$ and $\underline{T}_i$ are 2×2 matrices:

$$\underline{S}_i=\begin{bmatrix} e^{\lambda(n_i-n_{i+1})} & e^{-\lambda(n_i-n_{i+1})} \\ e^{\lambda(n_i-n_{i+1}-1)} & e^{-\lambda(n_i-n_{i+1}-1)} \end{bmatrix} \tag{14}$$

for $i < N$, and for $\underline{S}_N$ setting $n_{N+1}=n_N$ in the above. We write

$$\underline{T}_i = \begin{bmatrix} \nu & \nu \\ \frac{e^{-\lambda}}{\nu} & \frac{e^{\lambda}}{\nu} \end{bmatrix} \tag{15}$$

for all $i \leq N$. In the above, we have used $\nu \equiv V/C$ as the bandwidth ratio parameter. In Ref. 2 we have shown that the trion ($N=1$) has a bound state for $0 \leq |\nu| < 1$. We now can find bound states for arbitrary N. The energy is

$$E = -2V\cosh\lambda \ , \tag{16}$$

making use of Eq. (5), but there may be many roots λ obtained as the solutions of the two equations in two unknowns, a_1 and b_{N+1},

$$\begin{bmatrix} 0 \\ b_{N+1} \end{bmatrix} = \underline{S}_N^{-1}\underline{T}_N\underline{S}_{N-1}^{-1}\underline{T}_{N-1} \cdots \underline{S}_1^{-1}\underline{T}_1 \begin{bmatrix} a_1 \\ 0 \end{bmatrix} \ . \tag{17}$$

The first nontrivial result comes at $N=2$. Figure 2 shows the solutions of the above equation as a function of the size of the *penton*, n_2-n_1. At large separation the upper bound state and the lower one merge at a common value, that of the trion bound state. It is easy to understand that at large separations the penton breaks up into either of two degenerate trions: one at n_1 with a free exciton at n_2 or one bound trion at n_2 with the free exciton at n_1. However, at finite separation the lower of the penton states is stable against breakup into a trion + an exciton.

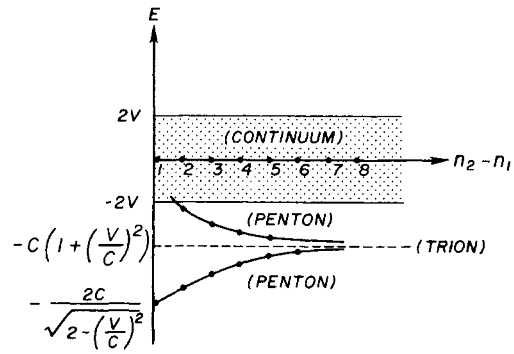

FIG. 2. Energy of the two bound states of the penton (2 excitons + 1 hole) calculated as function of the interexciton distance n_2-n_1. Lower bound state is absolutely stable against breakup into a trion + 1 free exciton at ∞, whereas upper bound state is unstable against this breakup. Note that the greatest binding energy of the lower bound state occurs at minimum allowable separation, $n_2-n_1=1$.

SCATTERING STATES

For E in the range $-2V < E < +2V$, a hole is merely scattered by the assembly of excitons at $n_1, n_2, \ldots,$ and the appropriate quantity to calculate is the transmission (or reflection) coefficient. This is achieved by making the following obvious substitutions in the matrices: λ is replaced by iq, E in (16) becomes $-2V\cos q$, and the initial and final vectors are

$$\zeta_1 = \begin{bmatrix} 1 \\ r^{1/2}e^{i\theta} \end{bmatrix} \tag{18}$$

and

$$\zeta_{N+1} = \begin{bmatrix} t^{1/2}e^{i\phi} \\ 0 \end{bmatrix} \ , \tag{19}$$

replacing those in (17). The initial and final phases θ and ϕ, and the reflection and transmission coefficients r and t, are now found as functions of q (hence of E) from the equation

$$\zeta_{N+1} = \underline{S}_N^{-1}\underline{T}_N \cdots \underline{S}_1^{-1}\underline{T}_1\zeta_1 \ . \tag{20}$$

As the general case depends on the positions $n_1, n_2, \ldots,$ nothing further can be said in all generality. But the special case $V=C$ ($\nu=1$) is solvable by inspection. We set all $F_i(m)=F(m)$ independent of sector i, and obtain the solutions of a free particle as follows:

$$F(m) = e^{iqm} \ , \tag{21}$$

with

$$E = -2V\cos q \ , \tag{22}$$

quite independent of the number N of excitons. Thus, the hole and the excitons are mutually transparent. A similar result follows for two or more holes, from which we may conclude that if the problem were describable by an effective potential its depth would be proportional to $1-\nu$ or $C-V$. Now, in 1D or in 2D, an attractive potential always has a bound state, but in 3D or higher dimensions bound states exist only if the potential exceeds a critical depth.

COMMENTS AND CONCLUSIONS

From the above the following is obvious:

(1) The lowest bound state of 1 hole + N excitons lies lower than the lowest bound state of 1 hole + $(N-1)$ excitons + 1 exciton at ∞.

(2) If one hole binds N excitons, two holes will bind almost twice as well, three almost 3 times as

well, etc., until the Fermi energy and the Coulomb repulsion of P holes makes for diminishing returns. Suppose the attractive energy is $-ANP$ and the repulsive forces plus the Fermi energy is $\frac{1}{2}BP^2$ with A and B two constants. It follows that the minimum-energy charged "globule" will have $P=(A/B)N$ holes, possibly a substantial fraction of N. This notion, that charged globules of excitons and holes might behave as stable particles, should supplement the electron-hole plasma theory propounded by several previous authors.[7]

We have not succeeded in solving the challenging generalization of the many exciton $+1$ hole problem in 2D or 3D (except for $N=1$, see Ref. 2), but perhaps there the qualitative analogy with attractive potential wells may serve. Nor have we been able to include the motional energy W of the excitons for $N>1$. The solution for $N=1$ is given for arbitrary d in a separate publication.[8]

ACKNOWLEDGMENTS

The support of the U. S. Air Force Office of Scientific Research and the travel aid through the National Science Foundation (Grant No. DMR-81-06223) are gratefully acknowledged.

---

*Present address: Institute of Theoretical Physics, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.

[1]R. S. Knox, *The Theory of Excitons* (Academic, New York, 1963).
[2]R. Schilling and D. C. Mattis, Phys. Rev. Lett. 49, 808 (1982).
[3]H. Bethe, Z. Phys. 71, 205 (1931). See various applications in E. Lieb and D. Mattis, *Mathematical Physics in One Dimension* (Academic, New York, 1966).
[4]W. Heller and A. Marcus, Phys. Rev. 84, 809 (1951).
[5]E. Lieb, T. Schultz, and D. Mattis, Ann. Phys. (N.Y.) 16, 407 (1961).
[6]The extensive literature is cited in Chap. 5 of D. Mattis, *The Theory of Magnetism* (Springer, Berlin, 1981), Vol. I.
[7]A review is given by T. M. Rice, in *Solid State Physics* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1977).
[8]R. Schilling and D. Mattis, Phys. Rev. B (in press).