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Density of states and localization properties of a one-dimensional Frenkel Hamiltonian with off-diagonal disorder

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Abstract

We study a one-dimensional Frenkel Hamiltonian with off-diagonal disorder, focusing our attention on the physical nature of the zero-energy peak of the density of states. The character of excitonic states (localized or delocalized) is also examined in the vicinity of this peak. It is shown that the state being responsible for the peak is localized.

Keywords: Frenkel exciton; Density of states; Localization

1. Introduction

Two decades ago, Theodorou and Cohen established [1] that the density of states (DOS) of a one-dimensional (1D) tight-binding Hamiltonian with nearest-neighbor (NN) interaction and random off-diagonal elements presents a singularity at the center of the band. In Ref. [1] it was also stated that the corresponding state is delocalized. This contradicts the theorem of Mott and Twose [2] that all states in one dimension are localized in the presence of disorder. Adding some amount of diagonal disorder (in the presence of off-diagonal randomness) makes all states to be localized [3]. Remarkably, calculations done for 1D tight-binding Hamiltonians with only diagonal disorder do not reveal any singularity in the DOS [4].

Recently, Fidder et al. have found by numerical diagonalization of the 1D Frenkel Hamiltonian with off-diagonal disorder that, notwithstanding the singularity of the DOS, the corresponding state is localized when one includes the long-range (LR) interaction due to dipolar coupling between different sites [5]. This finding seems to be in contradiction with the point of view raised in Ref. [1] suggesting that the state corresponding to the singularity of the DOS is delocalized. In this paper, we examine the conclusions of Ref. [1]. We present arguments demonstrating that the zero-energy state is localized even in the nearest-neighbor problem. This conclusion, based on analytical considerations, is then confirmed by numerical simulations of systems with different sizes and degrees of disorder.

2. Is the zero-energy state delocalized?

In this section we briefly restore the arguments of Ref. [1] leading to the conclusion that the state at center of the band is delocalized. We present other

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arguments suggesting the opposite point of view and, what is most important, numerical simulations confirming our statement.

Let us consider a tight-binding Hamiltonian with only nearest-neighbor interaction

$$H = \sum_n U_{n,n+1}(|n\rangle\langle n+1| + |n+1\rangle\langle n|), \tag{1}$$

where $U_{n,n+1} = -U/|\xi_m - \xi_n|^3$, $-U$ being the dipole–dipole coupling of nearest-neighbors and $\xi_m = m + \delta_m$, with δ_m being a stochastic variable distributed according to the Gaussian law with variance σ^2

$$P(\delta_m) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \exp\left[-\frac{\delta_m^2}{2\sigma^2}\right]. \tag{2}$$

The randomness in δ_m affects the interactions $U_{n,n+1}$, whose distribution function can be found in Ref. [5].

The state vector $|n\rangle$ represents an excitation at site n. All site energies are set to zero since no diagonal disorder is included. The eigenvalue problem of the NN-model reads

$$U_{n,n+1}a_{n+1} + U_{n,n-1}a_{n-1} = Ea_n, \tag{3}$$

where the set $\{a_n\}$ represents the real eigenvector corresponding to the eigenenergy E. For zero energy Eq. (3) gives the recurrence relation $a_{n+1} = -(U_{n,n-1}/U_{n,n+1})a_{n-1}$. Using this relation one can find

$$a_{2n+1} = \left(-\frac{U_{2n,2n-1}}{U_{2n,2n+1}}\right) \times \left(-\frac{U_{2n-2,2n-3}}{U_{2n-2,2n-1}}\right)\cdots\left(-\frac{U_{2,1}}{U_{2,3}}\right)a_1, \tag{4}$$

whereas the amplitudes at even positions equal zero. The eigenvector given by Eq. (4) represents the zero-energy state for a chain with odd number of sites. Defining the localization length $L(E=0)$ by the expression

$$\frac{1}{L(E=0)} = -\lim_{n\to\infty}\frac{1}{2n}\ln\left|\frac{a_{2n+1}}{a_1}\right|, \tag{5}$$

and applying the central-limit theorem the authors of Ref. [1] obtained $1/L(E=0) = 0$. From this result, they concluded that the state at center of the band was delocalized. This statement seems rather strange since there are at least two reasons for the vanishing of $1/L(E=0)$ which have nothing to do with delocalization of the zero-energy state. The first and simplest one is precisely that the amplitude a_n decreases (or increases) with n slower than exponential. For example, in Ref. [6] it was claimed (to tell the truth, with no evidence) that $a_n \sim \exp(c\sqrt{n})$, where c is a constant. If one accepts for a moment this result, then one should conclude that the zero-energy state is rather localized than extended, in contradiction with the statement of Ref. [1]. The second reason concerns the application of the central-limit theorem. The quantity $\ln|a_{2n+1}/a_1|$ itself, although being a sum of stochastic variables distributed around zero, goes to zero on increasing n because of the same theorem. In this sense, the result $1/L(E=0) = 0$ means nothing.

Now we present our arguments as regards to the problem of interest, from which it follows the opposite conclusion to that claimed in Ref. [1]. To check the localized or delocalized character of the zero-energy state we examine the behavior of a_n^2 averaged over realizations of the NN-interactions $U_{n,n+1}$. Then, the fact that the mean value $\langle a_{2n+1}^2\rangle$ increases (or decreases) exponentially (or in some other way but steeply enough) as a function of n can be regarded as an indication that the corresponding state is localized. Contrary to that, a constant value of $\langle a_{2n+1}^2\rangle$ will imply delocalization. Let us apply this result to establish the character of the zero-energy state.

Let $p\ (U_{n,n+1})$ be the distribution function of the NN-interaction. Introducing the magnitude

$$\alpha = \int p\ (x)p\ (y)\left(\frac{x}{y}\right)^2 \mathrm{d}x\,\mathrm{d}y, \tag{6}$$

one can then obtain from Eq. (4)

$$\langle a_{2n+1}^2\rangle = \alpha^n a_1^2, \quad n = 0,1,2,\ldots \tag{7}$$

We assumed here that a_1 equals some fixed, nonzero value and that the integral $\int y^{-2}p(y)\mathrm{d}y$ exists. Our main goal now is to evaluate the magnitude of α. If $\alpha \neq 1$ then the zero-energy state have an

exponential dependence against n and, therefore, the zero-energy state is localized. On the contrary, if $\alpha = 1$ this state is delocalized. From the identity

$$\alpha = \int p(x)p(y)\left(\frac{x}{y}\right)^2 dx\,dy$$

$$= 1 + \frac{1}{2}\int p(x)p(y)\left(\frac{x^2 - y^2}{xy}\right)^2 dx\,dy, \quad (8)$$

it definitely follows that $\alpha > 1$. Thus, one can conclude that $\langle a_n^2 \rangle$ increases exponentially with n, contrary to Ref. [1] as well as to Ref. [6].

3. Numerical simulations and discussion

We will mainly focus our attention on the normalized density of states $\rho(E)$ and on the degree of localization (inverse participation ratio, IPR) for the states at energy E. They are defined, respectively, as follows:

$$\rho(E) = \frac{1}{N}\left\langle \sum_k \delta(E - E_k) \right\rangle, \quad (9a)$$

$$\mathscr{L}(E) = \frac{1}{N\rho(E)}\left\langle \sum_k \delta(E - E_k)\left(\sum_{n=1}^{N} a_{kn}^4\right) \right\rangle, \quad (9b)$$

where the angular brackets indicate an average over an ensemble of disordered linear chains and the a_{kn} and E_k are the solution of the eigenvalue problem given by Eq. (3). From its definition, it can be seen that the IPR is expected to behave as $1/N$ for delocalized states, while localized states have much larger values. In the extreme case, when the exciton is localized at a single site, Eq. (9b) implies that the IPR becomes unity. At this point it is worth mentioning that the IPR by itself does not longer suffice to elucidate the true extended or localized character of eigenstates. This would require a complete multifractal analysis, accomplished by studying the scaling of the IPR (and the other moments of the probability distribution) with the system size. We have not intended to perform such a scaling analysis although the IPR will be quite useful to discuss the localization properties of states with different energies for the same values of the physical parameters.

We solved numerically Eq. (3) for different values of disorder (in our case, it means fluctuation of the NN-distance, $\sigma_{NN} = \sqrt{2}\sigma$) to study the features both of the DOS and of the IPR discussed above. Figs. 1 and 2 represent the results of numerical calculations of the DOS and of the IPR. Analysing these data, one can observe that:

1. when the degree of disorder exceeds a certain threshold value ($\sigma_{NN} \sim 0.02$, for the parameters of our model), a peak in the DOS at zero energy appears, whose amplitude increases with disorder (Fig. 1, left). The percentage of states in the DOS peak is 0.5 and 2.5 for $\sigma_{NN} = 0.08$ and 0.32, respectively;
2. on increasing the degree of disorder the states at the center of the band become more localized (Fig. 1, right),
3. the amplitude of the peak rises noticeably with increasing the number of sites in the chain (Fig. 2, left),
4. it can be seen (Fig. 2, right) that the state belonging to the zero-energy peak of the DOS is no

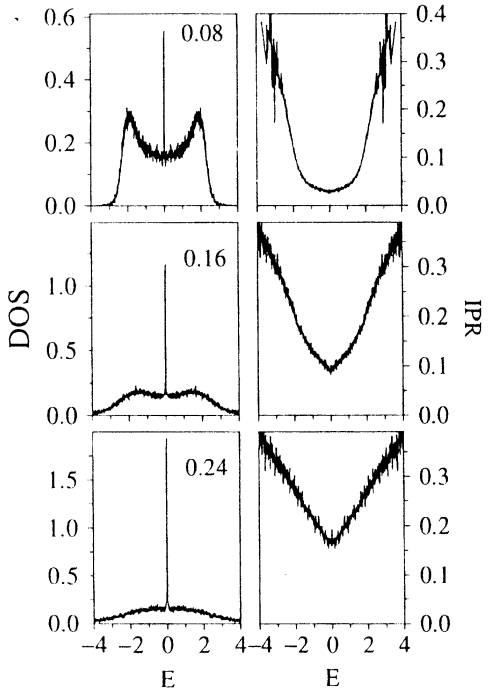

Fig. 1. Plotting of the DOS (left) and of the IPR (right) with increasing disorder, obtained in the frame of NN-coupling by averaging over 160 chains of 500 sites. Labels indicate the average fluctuation of the NN-distance σ_{NN}.

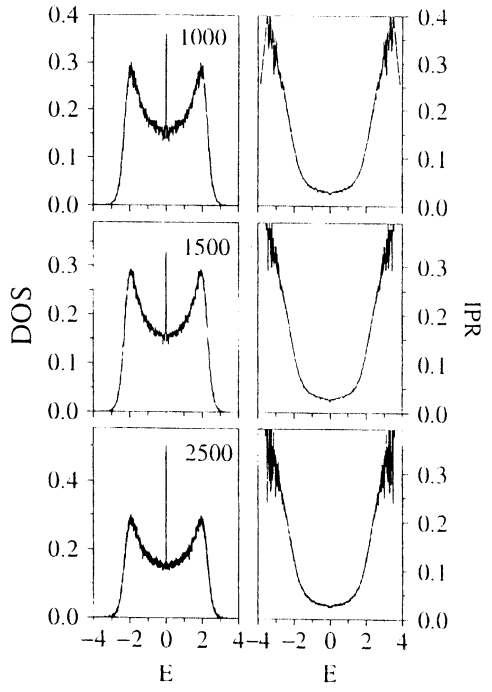

Fig. 2. Plotting of the DOS (left) and of the IPR (right) obtained in the frame of NN-approximation by averaging over 100 chains at the fixed values of disorder, $\sigma_{\alpha\alpha} = 0.08$. Labels indicate the lattice size.

more delocalized as compared to the rest of states. Also notice that its IPR value is independent of the system size.

4. Conclusions

We are led to two main conclusions. The first is that the zero-energy peak of the DOS really exists and tends to convert to δ-singularity with increasing the chain size. The second is that the corresponding eigenstates are localized, as can be drawn from the fact that the IPR increases with the degree of disorder. This remark is further supported by the fact that the IPR at the center of the band remains independent of the chain length, contrary to the expected behavior $1/N$ for extended states.

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