Excitation decay in one-dimensional disordered systems with paired traps

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Incoherent transport of excitations in one-dimensional disordered lattices with pairs of traps placed at random is studied by numerically solving the corresponding master equation. Results are compared to the case of lattices with the same concentration of unpaired traps, and it is found that pairing of traps causes a slowdown of the decay rate of both the mean square displacement and the survival probability of excitations. We suggest that this result is due to the presence of larger trap-free segments in the lattices with paired disorder, which implies that pairing of traps causes less disruption on the dynamics of excitations. In the conclusion we discuss the implications of our work, placing it in a more general context.

I. INTRODUCTION

Transport properties of randomly disordered systems are a subject of long-lasting interest both from fundamental and applied viewpoints.[1,2] This issue arises in largely different physical contexts, many of which can be conveniently mapped onto the problem of random walks on random lattices. These include particle or excitation diffusion in a random one-dimensional (1D) material, low-temperature properties of the random 1D Heisenberg ferromagnet, the 1D tight-binding electron problem with diagonal and off-diagonal disorder, electrical transmission lines, and excitation transfer along a 1D array of traps of random depth (see Ref. 1 and references therein). This wide range of applications is the reason why random walks on random lattices have become a standard model to study transport in disordered media; in fact, although most of those applications belong to the field of condensed matter physics, there have been many parallel pure mathematical and interdisciplinary (biology, chemistry, and physics) developments.[2] In addition, quantum tight-binding chains with pair correlated off-diagonal disorder are equivalent to phonon (or magnon) uncorrelated disorder ($E \to -\omega^2$), and to classical diffusion ($E \to i\omega$); therefore, pair correlations in the classical diffusion case might be useful to understand longer-range correlated quantum tight-binding chains. On the other hand, in recent years we have witnessed a great deal of work that tends to undermine well-established beliefs among researchers on the topic of transport in disordered systems. In particular, studies on quasiparticle dynamics in 1D systems with correlated disorder[3–13] have shown that localization of all eigenstates in 1D disordered systems is not a general result. Correlated disorder means that the random parameters of the system are not independent within a given correlation length. This correlation leads to a competition between the short-range order and the underlying long-range disorder. Such competition is ultimately responsible for the occurrence of unexpected phenomena like, e.g., whole bands of extended electron states.[11,13] In the few years elapsed in this decade these results for disordered models exhibiting nonlocalization properties have been put on solid grounds. The question then arises as to what are the deep physical reasons for this behavior.

Pursuing further the above line of research, in this paper we concern ourselves with the study of the decay of *incoherent* excitations in disordered systems, comparing their time decay when correlations are present to that of purely random systems. We will use both names *excitation* and *exciton* to describe our results on quasiparticle dynamics, since they apply in a more general context. Note that this problem is described by a random walk on a random lattice in the way discussed in the previous paragraph. We have recently carried out the time-domain analysis of *coherent* (quantum) motion of Frenkel excitons in 1D systems in the presence of paired correlated traps, randomly placed in an otherwise perfect lattice.[12] By comparing with the dynamics of 1D lattices with the same number of unpaired traps, we found that pairing of traps leads to a slowdown of the survival probability due to the occurrence of larger segments of the lattice which are free of traps. This fact is experimentally relevant since, as we have argued recently,[14] correlated disorder causes the occurrence of characteristic lines in the optical spectra of these systems which are not shared by uncorrelated disorder. Furthermore, Scher *et al.* have shown how for short and intermediate times 1D transport may be relevant even for three-dimensional systems.[15] Then it becomes interesting to elucidate whether this enhacement of the survival probability due to pairing of traps is restricted to the coherent motion or, on the contrary, it can be also expected in incoherent motion of excitons. This question could be also phrased in terms of the increase of the survival probability being a quantum effect or being a general one. This is the motivation of this work; we report on it in this paper according to the following scheme. In Sec. II we describe our model and the quantities we are going to use to characterize it. In Sec. III we present our results on survival probability, mean square displacement, and long-decay asymptotics, and discuss how they can be interpreted. We will present numerical simulations that clearly indicate that pairing of traps leads to a slowdown of the time decay of incoherent excitations in 1D random systems. Also, pairing dramatically affects the excitation size, measured by its mean square displacement, as a function of time. Thus, the main conclusion of the above mentioned calculations is that structural correlations cause less disruption of the lattice, and so the quasiparticle dynamics is less affected than it would be expected for the same concentration of traps in a purely random system. Section IV concludes the paper with a brief summary of our work and some comments on implications of its results, which may be of interest in a more general physical context.

II. MODEL

We consider a 1D lattice whose time evolution is described by the following master equation for the probability $P_k(t)$ to find the exciton at site k:

$$\frac{d}{dt}P_k = F(P_{k+1} + P_{k-1} - 2P_k) - G_k P_k, \tag{1}$$

where $F > 0$ is the intersite rate constant, which will be assumed to be independent of k hereafter. Although we restrict ourselves to zero temperature, thermal effects can be easily included choosing intersite rate constants depending on temperature according to the Boltzmann distribution.[1] Here $G_k = G$ if there is a trap at site k and otherwise $G_k = 0$, where $G > 0$ is the trapping rate. Such a master equation is quite close to those studied in Refs. 1, 2 as general random trapping models. These have been used as simple theoretical approaches to discuss the time-dependent effect in fluorescent line-narrowing experiments concerned with investigations of spectral transfer within inhomogeneously broadened optical lines (see, for instance, Ref. 16).

The magnitude of interest in luminescence experiments is the survival probability $n(t)$ defined as

$$n(t) = \left\langle \sum_k P_k(t) \right\rangle, \tag{2}$$

where the index k runs over all lattice sites and $\langle \cdots \rangle$ means ensemble average over all possible arrangements of traps. Moreover, assuming that the excitation is initially at site k_0 [$P_k(0) = \delta_{kk_0}$], we can also calculate the mean square displacement of the excitation as follows:

$$R^2(t) = \left\langle \sum_k (k - k_0)^2 P_k(t) \right\rangle, \tag{3}$$

where the lattice spacing is taken to be unity hereafter. These two functions characterize the exciton dynamics in the lattice. For instance, in the absence of traps ($G = 0$) it can be shown that $n(t) = 1$ and $R^2(t) = 2Dt$ in infinite lattices, D being the difusion coefficient.[17] We have used those results to test the reliability of our numerical calculations. We note that our choice for the initial condition corresponds to an optical pulsed excitation experiment where a nonequilibrium localized excitation distribution is created at site k_0 at $t = 0$; other possible choices are relevant in different contexts. Finally, the correlated disorder is introduced as follows: We suppose that traps are randomly distributed along the lattice but with the additional constraint that they only appear in pairs of neighboring sites (and hence the correlation length is roughly the lattice spacing). Hereafter, we define the fraction of traps c as the ratio between the number of sites with a trap associated with it and the total number N of sites in the lattice.

III. NUMERICAL RESULTS AND DISCUSSIONS

We have numerically solved the master equation (1) for lattices of $N = 1000$ sites using an implicit (Crank-Nicholson) integration scheme.[18] In order to avoid recombinations at free ends, spatial periodic boundary conditions are introduced. The initial condition is, as mentioned before, $P_k(0) = \delta_{kk_0}$, with $k_0 = 500$. The trapping rate G will be measured in units of F whereas time will be expressed in units of F^{-1}. The maximum integration time and the integration step were 250 and 5×10^{-4}, respectively. Smaller time steps led to similar results. Since we are mainly interested in the effects due to the presence of paired traps rather than in the effects of the different parameters in the incoherent motion of excitations, we will fix the values of F and G, focusing our attention on the defect concentration c. Thus we have set $F = 1$ and $G = 0.2$ henceafter as representative values. The defect concentration c ranged from 0.1 up to 0.9, and for each lattice a random distribution of paired traps was chosen. The ensembles comprised a number of realizations varying from 50 to 200 to check the convergence of the computed mean values. The convergence was always satisfactory between all the ensembles. In what follows the results we present correspond to 50 averages. In addition lattices with unpaired traps have been studied and compared with lattices containing the same fraction of paired traps. This enabled us to separate the effects merely due to incoherent trapping in one dimension from those aspects that manisfest the peculiarities of the correlation between random traps.

In our computations we have found that $n(t)$ decays faster as the fraction of traps increases, in both paired and unpaired traps cases, as shown in Fig. 1(a) and Fig. 1(b), respectively. This is expected since trapping should reduce the probability of finding the excitation in any point of the discrete lattice, and this reduction is obviously increased on increasing the number of centers able to trap. In the high concentration limit $c \to 1$

it is not difficult to demonstrate from (1) and (2) that trappping is simply exponential, $n(t) = \exp(-Gt)$, because in this limit the trap distribution exhibits translational symmetry and equations can be exactly solved. It is worth mentioning that such dependence on time agrees with the coherent potential approximation (CPA), which is known to be exact in the high concentration limit.[19] However, this is not the case for a random distribution of traps ($c < 1$), as seen in Fig. 1. The presence of disorder causes a nonexponential decay of excitations in systems with either paired or unpaired traps. We discuss the differences between both kinds of spatial distribution of traps below.

We have found that another important parameter to describe the time behavior of excitations is the mean square displacement. Our results are shown in Fig. 2(a) for paired traps and Fig. 2(b) for unpaired ones. In all cases it becomes apparent that the time evolution of $R^2(t)$ arises from the competition between two processes, namely, diffusion (the exciton is transferred from site to site, starting at k_0) and trapping (the exciton decays in time due to trapping). At short times, the first mechanism dominates since the exciton is still close to the initial position and consequently there are small chances to be trapped. On increasing time, the probability of trapping also increases because the exciton can be found in a larger segment of the lattice. This competition explains the occurrence of a well-defined maximum in $R^2(t)$, whose position depends not only on the concentration of traps but also on the spatial distribution of traps. Moreover, the fact that $R^2(t)$ is not a linear function of time is a consequence of the way we have posed the problem, starting from a nonequilibrium distribution.[2] We elaborate further on these points later on.

Having described the main features of the incoherent exciton dynamics and decay due to the presence of traps, we now consider the effects of pairing of traps in comparison to results obtained in 1D lattices with unpaired traps. This comparison will be carried out for systems with the same fraction of traps, and so the differences come simply from the particular distribution of trapping centers in each kind of lattice. The main result we found is that, in all cases considered, we have observed that the exciton decay is slower in the presence of paired traps. This is illustrated in Fig. 3 for two different values of c,

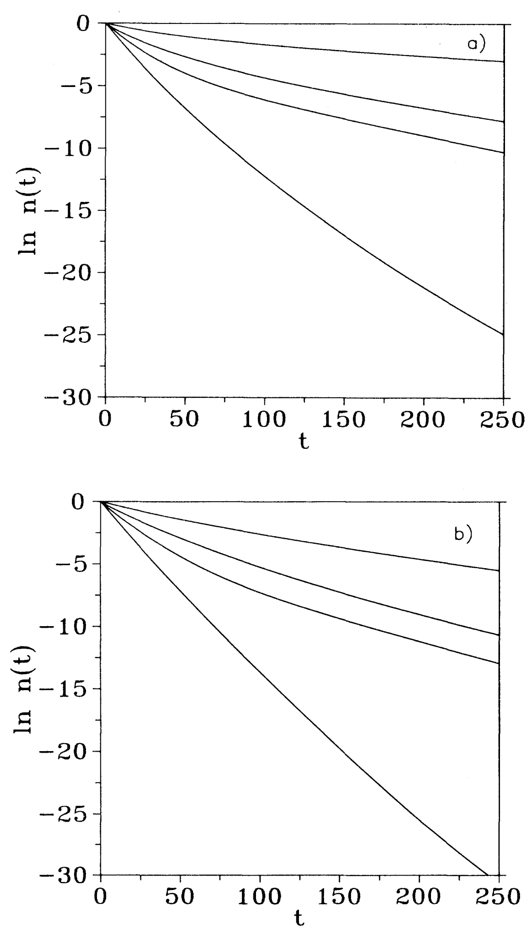

FIG. 1. Logarithm of the survival probability of excitons as a function of time for lattices of $N = 1000$ sites with (a) paired and (b) unpaired traps. The fraction of traps is $c = 0.2$, 0.4, 0.6, and 0.8 from top to bottom. Each curve comprises the results of 50 averages.

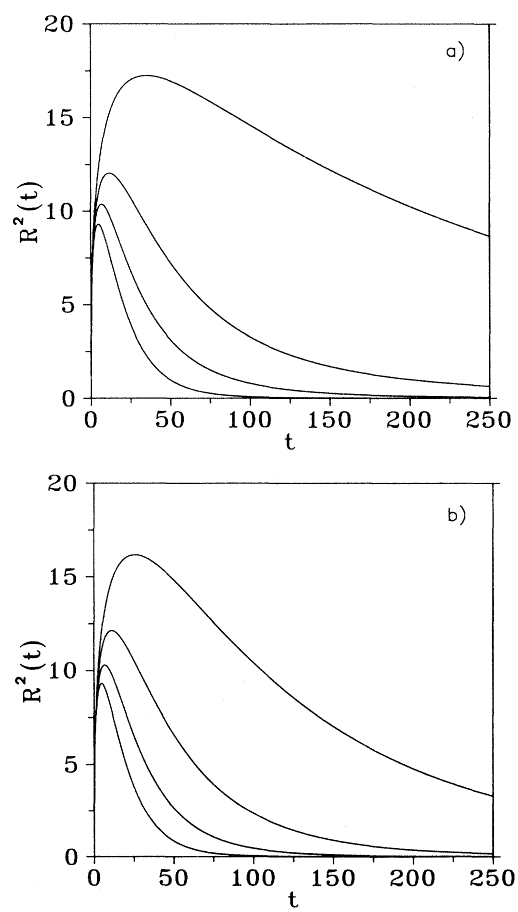

FIG. 2. Mean square displacement of excitons as a function of time for lattices of $N = 1000$ sites with (a) paired and (b) unpaired traps. The fraction of traps is $c = 0.2$, 0.4, 0.6, and 0.8 from top to bottom. Each curve comprises the results of 50 averages.

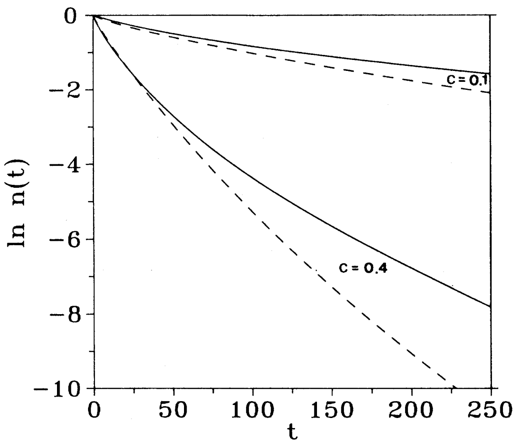

FIG. 3. Logarithm of the survival probability of excitons as a function of time for lattices of $N = 1000$ sites with paired (solid lines) and unpaired (dashed lines) traps. The fraction of traps is indicated on each plot, which comprises the results of 50 averages.

namely, $c = 0.1$ and $c = 0.4$. This result is similar to what we found[12] in the case of quantum transport, as we mentioned in the Introduction, hence suggesting that the origin of this slowdown is similar; that is, pairing of traps causes less disruption of the exciton motion on the lattice because the average length of segments without traps is larger in this situation. This similarity leads us to the following important conclusion: The slowdown is due only to the particular distribution of traps, whereas quantum effects do not play any significant role in these new phenomena.

Another possible way to heuristically understand the above facts is the following: Consider our master Eq. (1) for two sites which form one of the paired traps we are discussing, say, sites k and $k+1$, and define $P' \equiv P_k + P_{k+1}$, i.e., the probability to be in any of the two sites. By using Eq. (1) for sites k and $k+1$ we can write down the following equation for P':

$$\frac{d}{dt}P' = F(P_{k+2} + P_{k-1} - P') - GP', \tag{4}$$

where we have taken into account that $G_k = G_{k+1} = G$ as both sites contain traps. It can be readily seen that Eq. (4) is similar to Eq. (1) but we have renormalized the paired trap sites into a new, single site, with the same trapping rate but smaller intersite constant (which in fact violates detailed balance). From this we learn that the effect of the paired trap is basically as if it were one trap; however, the fact that the intersite rate *out* of the (renormalized) site is reduced forces the excitation to stay longer in it, thus increasing the (effective) probability of being trapped. We see then that the paired trap cannot be trivially compared or dealt with as if it were a single one. We note that this argument is just a heuristic one, as the situation is different if we renormalize one site which belongs to a pair and one which does not, but it can be seen that eventually (they should have to be renormalized once again as they would also be a pair in the renormalized equation) the effect of the pair may be described in the same way we have just argued. Of course, this remains just a plausibility argument, as further theoretical progress on the basis of this renormalization procedure seems hopeless in view of the spatial correlation of the disorder.

Concerning the exciton mean square displacement, we have also compared results in lattices with the same fraction of paired and unpaired traps. In Fig. 4 we observe that $R^2(t)$ is always larger when traps are paired, and that the relative difference between both cases increases with time. Such differences are also apparent in the maximum of $R^2(t)$, as the time of reaching this maximum is always larger in the case of lattices with paired traps. Since we have assumed that the long-time behavior of $R^2(t)$ is mainly due to trapping effects, these results reinforce our suggestion that the different exciton behavior in both kinds of systems comes mainly from the particular distribution of random traps. There is another feature of Fig. 4 that deserves attention, namely, that $R^2(t)$ is very similar in both paired and unpaired trap systems up to a time around $t \simeq 30$. This similar behavior also shows up in Fig. 3 for $n(t)$. This is easily understood if we recall the diffusion-trapping competition we mentioned in connection with the maximum of the mean square displacement: Excitation transport properties are *diffusion dominated* in the early stages of the evolution. Until a certain time has elapsed, the chances that the excitation has of being trapped are very small, as it has visited very few trapping sites. It is only after this transient that the traps start having a marked effect on the exciton dynamics. Therefore, only when transport becomes *trapping dominated* do the differences between paired and unpaired lattices arise.

Finally, let us consider the asymptotic long-time decay law of excitons in the presence of traps. This is an interesting problem and several theoretical and experi-

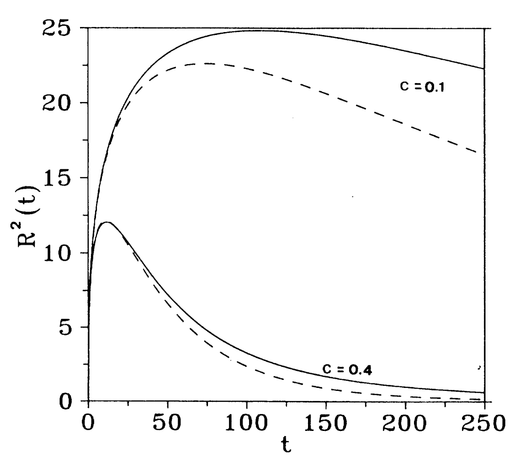

FIG. 4. Mean square displacement of excitons as a function of time for lattices of $N = 1000$ sites with paired (solid lines) and unpaired (dashed lines) traps. The fraction of traps is indicated on each plot, which comprises the results of 50 averages.

mental works have been devoted to finding the relaxation law displayed by excitations in 1D systems. In the case of incoherent motion, theoretical predictions show that the survival probability should decay asymptotically as $\sim \exp(-At^{1/3})$ in the case of a low concentration of unpaired traps,[19,20] whereas there are no available results in the case of paired ones. We have studied exciton decay at long times for lattices with paired as well as unpaired traps. It has to be noticed that our calculations are not in the asymptotic limit, especially at a low concentration of traps, when $n(t)$ decays very slowly, so that a direct comparison with analytical results for $t \to \infty$ could be inconsistent. On the other hand, the results are in the experimental regime, since due to fluorescent decay processes and finite anisotropies one can actually observe one-dimensional diffusion processes for only a finite time span.[1] Plotting $\ln|\ln n(t)|$ versus $\ln t$ in the range from $t = 100$ up to 250 we have confirmed that the survival probability fit stretched exponentials of the form $n(t) \sim \exp(-At^{\alpha})$ in all cases, as shown in Fig. 5. The value of the parameter α is lower in the case of lattices with paired traps, hence confirming the fact that disorder correlation reduces the exciton decay rate even at long time. It is also interesting to mention that α depends on the concentration of traps, and it increases with c in the range of time considered. At low and moderate values of c it becomes of order of 0.6–0.7 whereas at higher concentrations is close to unity. These results should be regarded only as qualitatively correct since at very long times round-off errors increase while the magnitude of $n(t)$ decreases, and hence many averages are actually needed to accurately compute the values of the exponent, which is rather time consuming. It is then clear that a theoretical description would be very valuable for a complete understanding of our results.

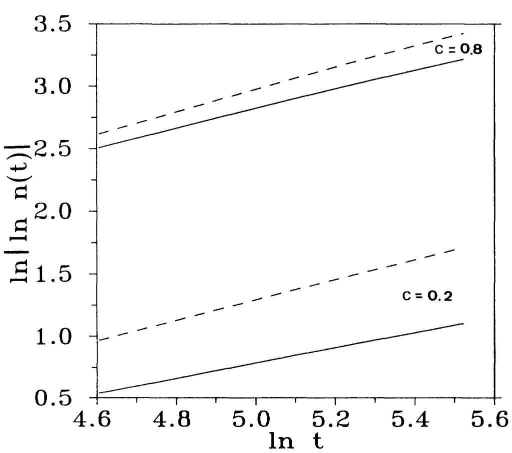

FIG. 5. $\ln|\ln n(t)|$ as a function of $\ln t$ for lattices of $N = 1000$ sites with paired (solid lines) and unpaired (dashed lines) traps. The fraction of traps is indicated on each plot, which comprises the results of 50 averages. From top to bottom, the values of the slopes are $\alpha = 0.88$, 0.79, 0.78, and 0.61.

IV. CONCLUSIONS

The present paper has been devoted to get a more complete and general comprehension of the quasiparticle dynamics in 1D systems with correlated disorder, which is extensively being investigated at present. In particular, we have focused on incoherent exciton transport in 1D random lattices with a certain number of traps appearing in pairs along the lattice, and results have compared to those obtained in the case of unpaired ones. In light of computations, we have concluded that incoherent excitons decay slower when pairing is introduced, in a similar way as we have previously found in the case of (coherent) Frenkel excitons.[12] We have also seen that the paired nature of the traps indeed gives rise to new effects which cannot be simply understood by treating each paired trap separately, because intersite transfer rates are also affected. All these phenomena also manifest themselves in the square mean displacement, which is found to be larger in the case of paired traps at all times, and in the long-time asymptotics, described by a smaller exponent in the stretched exponential dependence. We stress that these differences should be noticeable through optical measurements, as in the case of quantum excitations.[14] Indeed, a most interesting result is that the increasing of the survival probability and the mean square displacement is not a quantum effect, but rather something that comes from the fact that there is spatial correlation between traps.

The previous paragraph summarizes the conclusions that can be extracted from our calculations regarding the specific application of the model to exciton transport properties in solids. In addition, there are some issues of more general character that may be learned from what we have reported. First, in connection with recent work on suppression of localization (see Ref. 11 for a rather exhaustive list of references as well as a summary of results) we see that the consequences of correlation are very different due to the largely disparate characteristics of wave equations versus diffusion equations: Electrons and classical waves delocalize, whereas effects on excitations described by random walks are less dramatically exhibited in longer lifetimes. However, in both cases, and in spite of being very different problems, correlation has very profound effects; this suggests that the influence of having nonwhite disorder as usually assumed may be important in very many fields. Another interesting point is related to applications of random walks on random lattices in condensed matter physics, such as those discussed in the Introduction. The analytical treatments available so far rely heavily on sometimes unrealistic assumptions, i.e., starting from an equilibrium distribution, like the average-T-matrix approximation, or having uncorrelated distributions of traps, like the effective medium approximation.[21] To our knowledge, our results are the first ones on models which verify none of both hypotheses, and theoretical approaches developed to deal with this problem (probably combining some renormalization procedure to remove the correlations or reduce their role followed by a description in the spirit of effective-medium approaches) will be most likely very useful in other subjects in condensed matter physics. Indeed, as the effect of changing the trap pair concentration c on the results is only quantitative, it might be possible to develop a theory in the case of small or large c (CPA-like) which eventually must be valid for any c by an appropriate renormalization of the parameters. In this spirit, it might also be possible to study a single pair of traps, as in Eq. (4), in the same way of the case of adding homogeneous impurity pairs in tight-binding chains. As a final remark from the viewpoint of applications, it can be expected that the calculation presented here will be of use as a means to discern the local spatial structure of active centers in solids, in experiments using pulsed initial excitations. On the other hand, were our results found to be experimentally relevant, they may be employed to design devices with special optical properties. We hope that the numerical work presented here stimulates parallel advances on the theoretical and experimental sides.

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