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# Connecting bright and dark states through accidental degeneracy caused by lack of symmetry

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Coupled excitonic structures are found in natural and artificial light harvesting systems where optical transitions link different excitation manifolds. In systems with symmetry, some optical transitions are allowed, while others are forbidden. Here we examine an excitonic ring structure and identify an accidental degeneracy between two categories of double-excitation eigenstates with distinct symmetries and optical transition properties. To understand the accidental degeneracy, a complete selection rule between two arbitrary excitation manifolds is derived with a physically motivated proof. Remarkably, symmetry analysis shows that the lack of certain symmetry elements in the Hamiltonian is responsible for this degeneracy, which is unique to rings with size  $N = 4l + 2$  ( $l$  being an integer). *Published by AIP Publishing.* <https://doi.org/10.1063/1.5026116>

## I. INTRODUCTION

Symmetry of the Hamiltonian leads to degeneracy in its eigenspace. In simple chemical systems such as molecules, degeneracies can often be assigned to geometrical symmetries and characterized by symmetry groups of the molecular Hamiltonian. Other types of symmetries, e.g., time reversal symmetry and translational symmetry, can also produce degenerate eigenstates. However, not every degeneracy can be explained by simple symmetries of the Hamiltonian. Accidental degeneracy is commonly associated with some unidentified hidden symmetry of the system. Notable examples of accidental degeneracy include the bound state degeneracy in a hydrogen atom,<sup>1</sup> the degeneracy in an infinite square potential well,<sup>2</sup> and the Landau level degeneracy in cyclotron motion.<sup>3</sup> Accidental degeneracy, in addition to theoretical interest,<sup>4</sup> has potential applications in material design.<sup>5–7</sup> In this study, we examine an accidental degeneracy found in a coupled excitonic ring structure. Coupled excitonic structures are found in natural and artificial light harvesting systems, in which delocalized quantum states are extensively studied for their potential effect on energy transfer efficiency.<sup>8–23</sup> These quantum states have selection rules determined by symmetry which, for the single-excitation manifold, separate the optically active bright state from the optically inactive dark states. The dark states are of particular interest because they can potentially reduce radiative recombination and enhance excitation transport efficiency.<sup>24–26</sup> Since the dark states cannot be accessed optically, they are usually populated through phononic dissipation from the bright state. In this work, we show the possibility of connecting the bright and dark states with

optical transitions. In a ring structure made of identical local two-level systems, the boundary coupling condition is dependent on the parity of the number of excitations on the ring. Therefore, the double-excitation manifold is related to the single-excitation manifold in a unique way. Below, we show that the double-excitation manifold of an excitonic ring has an accidental degeneracy between two categories of eigenstates with distinct symmetries such that the first category only couples to the bright state, while the second category only couples to the dark state through optical transitions. These degenerate eigenstates may potentially mix without additional energy cost, producing hybrid eigenstates that optically connect to both the bright and dark states. This could have an important implication in the dynamics of exciton transfer on the ring structure, as it adds a channel in addition to phononic dissipation for the dark states to be populated. The accidental degeneracy is unique to a ring with  $N = 4l + 2$  ( $l$  being an integer) sites. Analysis of the relationship between the geometry of the ring and the eigenstates reveals that the accidental degeneracy is due to the absence of certain symmetry elements in the Hamiltonian.

## II. THEORY

In this study, we consider a ring structure composed of identical local exciton-supporting sites. Excitons are hardcore bosons that cannot occupy the same quantum state. The creation and annihilation operators  $a_j^\dagger$  and  $a_k$  of hardcore bosons observe the bosonic commutation relation  $[a_j^\dagger, a_k] = 0$  when  $j \neq k$ , but when  $j = k$ , they observe the fermionic anticommutation relation  $\{a_j^\dagger, a_j\} = 0$ . Obviously, the Pauli raising and lowering operators satisfy these conditions if we identify  $a_j^\dagger$  with  $\sigma_j^+$  and  $a_k$  with  $\sigma_k^-$ . The Hamiltonian of the ring is

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then

$$H = \omega \sum_{i=1}^N \sigma_i^+ \sigma_i^- + S \sum_{i=1}^N (\sigma_i^+ \sigma_{i+1}^- + \sigma_{i+1}^+ \sigma_i^-), \quad (1)$$

where  $\hbar = 1$ ,  $\omega$  is the site energy,  $S$  is the coupling strength, and  $\sigma_{N+1}^\pm = \sigma_1^\pm$ . Under the Jordan-Wigner transformation, the Hamiltonian becomes

$$H_{JW} = \omega \hat{n} + S \sum_{j=1}^{N-1} (c_j^\dagger c_{j+1} + c_{j+1}^\dagger c_j) - S (c_N^\dagger c_1 + c_1^\dagger c_N) e^{i\pi \hat{n}}, \quad (2)$$

where  $\hat{n}$  is the number operator for the total number of excitations on the ring and  $c_j^\dagger$  and  $c_j$  are the transformed fermionic creation and annihilation operators, respectively. Note that here we are only considering the nearest-neighbor interactions. When long-range couplings (beyond tight-binding) are present, the Jordan-Wigner transformation would produce non-local terms<sup>27</sup> such as  $c_i^\dagger \exp\left(i\pi \sum_{n=i}^{j-1} c_n^\dagger c_n\right) c_j$ , creating a Hamiltonian whose solution remains an open problem. On the other hand, for an excitonic system, the coupling is usually dipole-dipole interaction in nature and scales with the third power of the distance. Consequently a next-nearest-neighbor interaction is about  $2^3 = 8$  smaller than a nearest-neighbor interaction and is reasonably negligible. The solution to Eq. (2) is dependent on the parity of the excitation number due to the  $e^{i\pi \hat{n}}$  term in the boundary condition. For a given excitation number  $n$ , we first find the creation operators for the single excitation component states (referred to as the component states thereafter),

$$C_k^+ = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i \frac{k\pi}{N} j} c_j^\dagger \quad \text{if } n \text{ is odd,} \quad (3)$$

$$C_k^+ = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i \frac{(k+1)\pi}{N} j} c_j^\dagger \quad \text{if } n \text{ is even,}$$

where  $k$  is an even number from 0 to  $2N - 2$ . We then construct the  $n$ -excitation eigenstates by selecting  $n$  number of  $C_k^+$  operators to operate successively on the ground state,

$$|\psi_{k_1 k_2 \dots k_n}\rangle = C_{k_1}^+ C_{k_2}^+ \dots C_{k_n}^+ |0\rangle, \quad (4)$$

where  $k_1 \neq k_2 \neq \dots \neq k_n$ . The energies of the  $n$ -excitation eigenstates are given by  $E_{k_1 k_2 \dots k_n} = \sum_{i=1}^n \left(\omega + 2S \cos \frac{k_i \pi}{N}\right)$  if  $n$  is odd and  $E_{k_1 k_2 \dots k_n} = \sum_{i=1}^n \left(\omega + 2S \cos \frac{(k_i+1)\pi}{N}\right)$  if  $n$  is even, where the total energy is the sum of the energies of the individual component states. For example, the single-excitation eigenstates are

$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i \frac{k\pi}{N} j} c_j^\dagger |0\rangle, \quad (5)$$

where each  $|\psi_k\rangle$  has the energy  $E(k) = \omega + 2S \cos \frac{k\pi}{N}$ . The component states that are building blocks for the double-excitation states have the expression

$$|\phi_k\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i \frac{(k+1)\pi}{N} j} c_j^\dagger |0\rangle, \quad (6)$$

where the energy of an individual  $|\phi_k\rangle$  is  $\varepsilon(k) = \omega + 2S \cos \frac{(k+1)\pi}{N}$  and the double-excitation state formed by  $|\phi_{k_1}\rangle$  and  $|\phi_{k_2}\rangle$  has the energy  $E(k_1, k_2) = \varepsilon(k_1) + \varepsilon(k_2)$ . Without loss of generality, in the following discussion, we set  $\omega = 0$ .

The single-excitation states can be classified by their symmetry group representations which determine their optical transition possibilities. Here, we categorize the single-excitation states according to the possibility that they will optically transition to the ground state via the optical coupling operator  $J^+ = \sum_{i=1}^N \sigma_i^+$ . In this way, we can easily connect the theoretical model to its practical application in excitonic systems. By simple algebraic evaluation of Eq. (5), only the  $|\psi_0\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N c_j^\dagger |0\rangle$  state has finite coupling to the ground through optical transitions: the optical transition dipole is  $\Gamma_{kg} = \left| \langle \psi_k | \sum_{i=1}^N \sigma_i^+ |0\rangle \right|^2 = N \delta_{k0}$ , where  $\delta_{k0}$  is the Kronecker delta.  $|\psi_0\rangle$  is therefore the bright state and all other  $|\psi_k\rangle$  are dark states. Similarly, the double-excitation states can also be categorized according to how they optically connect to the single-excitation states. The first category of double-excitation states are those optically coupled to the bright state but not the dark states; the second category of double-excitation states are those optically coupled to the dark states but not the bright state. To identify each double-excitation state by its category, we invoke a complete selection rule between the  $n$ -excitation manifold and the  $(n+1)$ -excitation manifold.

If an  $n$ -excitation state is  $|\psi_{t_1 t_2 \dots t_n}\rangle = C_{t_1}^+ C_{t_2}^+ \dots C_{t_n}^+ |0\rangle$ , where the component states  $C_{t_i}^+$ 's have quantum numbers  $t_i$ 's, and an  $(n+1)$ -excitation state is  $|\psi_{s_1 s_2 \dots s_{n+1}}\rangle = C_{s_1}^+ C_{s_2}^+ \dots C_{s_{n+1}}^+ |0\rangle$ , where the component states  $C_{s_i}^+$ 's have quantum numbers  $s_i$ 's, then  $|\psi_{t_1 t_2 \dots t_n}\rangle$  is optically coupled to  $|\psi_{s_1 s_2 \dots s_{n+1}}\rangle$  if

$$\sum_i t_i - \sum_i s_i = 2mN, \quad m = 0, \pm 1, \pm 2, \dots \quad (7)$$

Note that here the quantum numbers  $t_i$ 's and  $s_i$ 's are slightly different from the  $k_i$ 's in Eqs. (3) and (4), in which each  $k_i$  is always even, but when it enters the exponent of  $C_{k_i}^+$ , it becomes  $(k_i + 1)$  when  $n$  is even and remains  $k_i$  when  $n$  is odd. In  $C_{t_i}^+$  or  $C_{s_i}^+$ , each  $t_i$  or  $s_i$  enters the exponent as itself, but the parity of  $t_i$  or  $s_i$  can change depending on the parity of  $n$ . If  $n$  is odd, then  $t_i$ 's are even and  $s_i$ 's are odd; if  $n$  is even, then  $t_i$ 's are odd and  $s_i$ 's are even.

Equation (7) can be extracted from pure algebraic calculations,<sup>28</sup> but here we emphasize that the selection rule is a consequence of the rotational symmetry of the ring. For a ring consisting of  $N$  identical local sites with the same coupling strength, a physical equivalence exists among different sites because there is no fundamental difference between one site and another. In the [supplementary material](#), we prove in detail that the selection rule is indeed a phase matching condition imposed by the physical equivalence among local sites, thus giving Eq. (7) a physically motivated explanation.

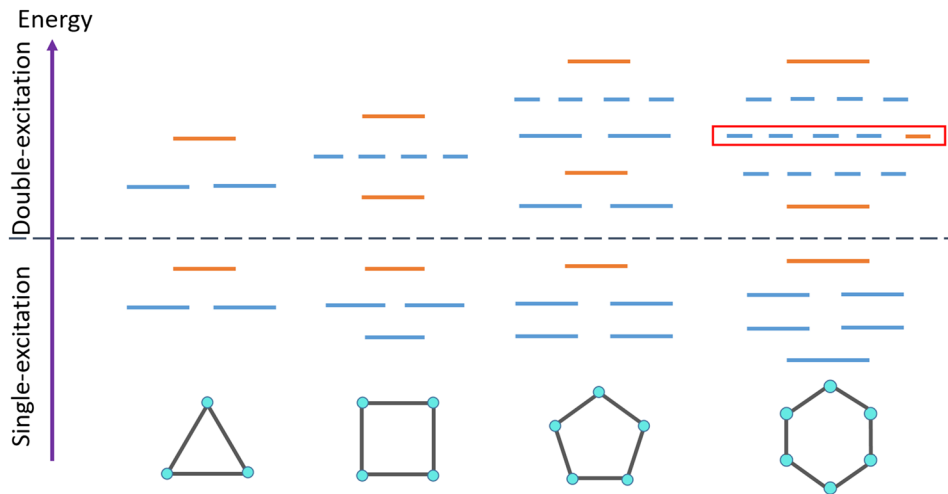


FIG. 1. Energy ladder structure of the single-excitation and double-excitation eigenstates for rings with  $N = 3$  to  $N = 6$  sites. Single-excitation and double-excitation states are shown below and above the dashed line, respectively. The bright states and their optically connected double-excitation states are in orange (first category); the dark states and their optically connected double-excitation states are in blue (second category). The red box highlights the degeneracy between the two categories that is unique to the 6-sited ring.

Applying Eq. (7) to the single-excitation manifold and the double-excitation manifold, we identify each double-excitation state by its category on the energy ladder in Fig. 1.

In Fig. 1, we see that the double-excitation manifold can be partitioned into two categories: (1) states optically coupled to the bright state and (2) states optically coupled to the dark states. For rings with 3–5 sites, the first category double-excitation states are non-degenerate, while the second category double-excitation states are evenly degenerate. For the 6-sited ring, however, there is a level on the double-excitation manifold with degeneracy five that contains states from both categories. This is an important property of the energy ladder because degeneracy may potentially allow states with different symmetries and optical transition properties to mix, producing hybrid eigenstates without additional energy cost. For example, if the degenerate states in the red box in Fig. 1 are allowed to mix, the hybrid states would be able to mediate optical connection between the bright state and the dark states, which is otherwise forbidden due to symmetry mismatch. Note if only optical transition is possible, the bright state would first be populated, then select the state with the bright-matching symmetry from the degenerate level, and there will be no coherent mixing with the state of the other

category. However, if there is any other mechanism that can cause dephasing among the degenerate states, then coherent mixing is possible. For example, phononic dephasing could be the mechanism that enables such coherent mixing because it does not observe the optical symmetry rules. Note there is only one basis representation—the one favored by optical transition—that forbids the coherent mixing between the double-excitation states with distinct symmetries. Any other basis representation would allow the optical connection between the bright and dark states, and when a dephasing mechanism is present, the coherent mixing of the degenerate states should be entropically favorable.

To find out how the states from two categories are degenerate for the 6-sited ring, we consider how the double-excitation states are formed from the component states as defined in Eq. (6). The energy ladder structure of the component states is shown in Fig. 2.

Figure 2 clearly shows how the two categories of double-excitation states are separated. The first category states are formed by component states of the same energy and are non-degenerate for rings with 3–5 sites. These states can optically couple to the bright states, but not the dark states, because their symmetry only allows phase matching with the bright

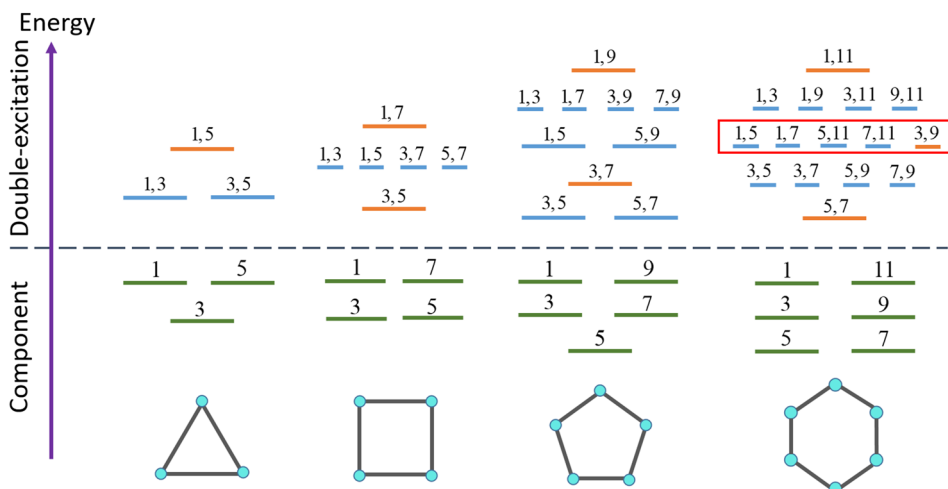


FIG. 2. Energy ladder structure showing how the double-excitation states are formed by the component states. Below the dashed line, the component states are labeled by single numbers corresponding to the  $(k + 1)$  values in Eq. (6). Above the dashed line, the double-excitation states are labeled by double numbers corresponding to their respective component states. The special level of degeneracy five is enclosed in the red box. Double-excitation states in the first category (orange) are formed by component states of the same energy; double-excitation states in the second category (blue) are formed by component states of different energies.

states (see the [supplementary material](#)). On the other hand, the second category states are formed by component states of different energies and are evenly degenerate for rings with 3–5 sites. These states can optically couple to the dark states, but not the bright states, because their symmetry only allows phase matching with the dark states (see the [supplementary material](#)). For the 6-sited ring, however, there is an accidental degeneracy between states of the two different categories which cannot be accounted for by simple symmetry of the Hamiltonian. Before we consider a symmetry argument responsible for the accidental degeneracy, notice that the accidental degeneracy happens because three energy levels in the 6-sited ring are evenly spaced in the component energy ladder such that the sum of the energies of  $|1\rangle$  and  $|7\rangle$  is equal to the sum of the energies of  $|3\rangle$  and  $|9\rangle$ . In the [supplementary material](#), we prove with mathematical rigor that this scenario is possible if, and only if, the size of the ring  $N$  satisfies

$$N = 4l + 2 \quad l = 1, 2, 3, \dots \quad (8)$$

Therefore, the 6-sited ring is the first case of the accidental degeneracy—the next case would be the 10-sited ring. For a ring with an even number of sites, energy levels always equally split around zero due to the sublattice symmetry of the Hamiltonian. Sublattice symmetry is immune to changes in the coupling strength  $S$ ; therefore, the equal splitting behavior applies to both the single-excitation eigenstates and the component states, as can be seen from the energy diagrams below the dashed line in both Figs. 1 and 2. In Fig. 2, for both the 4-sited ring and the 6-sited ring, the equally split pairs of component states combine to give zero energy double-excitation states of the second category. The unique accidental degeneracy is brought to the 6-sited ring by the zero energy component states, such as  $|3\rangle$  and  $|9\rangle$ . These zero energy component states combine to give zero energy double-excitation states of the first category, which are only available when the size of the ring is  $N = 4l + 2$ . In Fig. 3, for  $N = 4, 6, 8$ , we present both the single-excitation eigenstates and the component states in

Eqs. (5) and (6) on the complex number plane by representing each state with the factor in the coefficient:  $e^{i\frac{k\pi}{N}}$  for the single-excitation eigenstates and  $e^{i\frac{(k+1)\pi}{N}}$  for the component states.

In Fig. 3, the single-excitation eigenstates form a shape corresponding to the physical geometry of the ring structures, while the component states form the same shape with a  $\frac{\pi}{N}$  rotation. Because the energies of these states are calculated with the cosine function, degenerate states with energy  $\varepsilon$  fall on the same vertical line of  $x = \varepsilon$ . The y-axis is, therefore, the zero energy line with  $x = 0$ . Figure 3 shows that if there are zero energy states on the single-excitation manifold, there will be no zero energy component states. On the other hand, if there are zero energy component states, there will be no zero energy single-excitation state. The  $\frac{\pi}{N}$  rotation between the single-excitation manifold and the component state manifold guarantees that the zero energy degeneracy is only present in one of the two manifolds. When  $N = 4l$ , the zero energy degeneracy is in the single-excitation manifold. When  $N = 4l + 2$ , the zero energy degeneracy is in the component state manifold. The accidental degeneracy between two categories of double-excitation states relies on the existence of degenerate zero energy component states for  $N = 4l + 2$ , which implies that there are no degenerate zero energy single-excitation states. There is a crucial difference between the single-excitation manifold and the component state manifold. The single-excitation states are actual eigenstates of the Hamiltonian such that a degeneracy among them reflects a symmetry element of the Hamiltonian. On the contrary, the component states are not actual eigenstates of the Hamiltonian, and a degeneracy among them is not a symmetry element of the Hamiltonian. *Consequently the lack of zero energy degeneracy in the single-excitation manifold, which is the requirement for the accidental degeneracy, can be interpreted as the lack of certain symmetry in the Hamiltonian.* What exactly is the missing symmetry element in the  $N = 4l + 2$  rings? In Fig. 3, for all three geometries, there are two single-excitation states,  $|\psi_{k=0}\rangle$

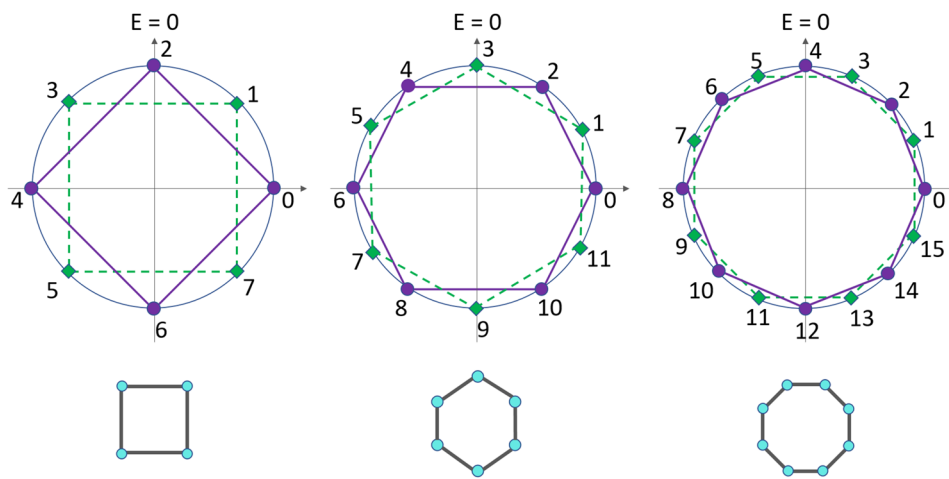


FIG. 3. States are plotted on the complex plane. The  $e^{i\frac{k\pi}{N}}$  points represent the single-excitation states (purple circles labeled by even numbers). The  $e^{i\frac{(k+1)\pi}{N}}$  points represent the component states (green diamonds labeled by odd numbers). The x-axis is the energy axis and the zero energy states fall on the y-axis. The single-excitation states form a shape corresponding to the physical geometry of the ring structures, and the component states form the same shape with a  $\frac{\pi}{N}$  rotation. For the square and octagonal cases, zero energy states are in the single-excitation manifold and are missing from the component state manifold. For the hexagonal case, zero energy states are in the component state manifold and are missing from the single-excitation manifold.

and  $|\psi_{k=N}\rangle$ , on the x-axis, which correspond to the  $A_1$  and  $B_1$  representations, respectively, in the  $D_N$  symmetry groups ( $D_{Nh}$  to be precise, but we do not mind the difference between gerade and ungerade here). For the  $N = 4l$  rings, there are also two single-excitation states,  $|\psi_{k=N/2}\rangle$  and  $|\psi_{k=3N/2}\rangle$ , on the y-axis, which result in a symmetry on the state diagram in Fig. 3 such that if we rotate the shape formed by the single-excitation manifold by  $\frac{\pi}{2}$ , we get exactly the original shape back. Since the shape on the state diagram is the same as the physical geometry of the ring structures, we can relate this  $\frac{\pi}{2}$  rotation to the  $C_4$  symmetry elements in the  $D_{N=4l}$  groups. Indeed, the  $C_4$  symmetry elements are missing from the  $D_{N=4l+2}$  groups. It is remarkable that the absence of certain symmetry elements, not the presence of one, leads to the accidental degeneracy between two categories of double-excitation states of distinct optical transition patterns.

To move from theory to application, the accidental degeneracy on the double-excitation manifold needs to be preserved under two types of disorder: the coupling strength disorder and the site energy disorder. Under disorder in the coupling strength  $S$ , the accidental degeneracy is exactly preserved for  $N = 4l + 2$  with any arbitrary choice of the individual  $S$  values. This remarkable preservation of the accidental degeneracy is guaranteed by the sublattice symmetry. Because the ring is connected through nearest-neighbor couplings, we can separate the Hamiltonian for the component states into two identical blocks with one block containing the odd sites and the other block containing the even sites. This treatment guarantees that each block is disconnected within itself. The coupling between the two blocks then ensures that the energy levels are equally split around zero, which is called the sublattice symmetry. Since the accidental degeneracy is caused by the component states' energy equally split around zero, we see that this condition, and therefore the degeneracy, is preserved by the sublattice symmetry. The sublattice symmetry is itself immune to arbitrary coupling strength disorder because the two blocks remain identical and disconnected within each block. In addition to the sublattice symmetry argument, an alternative analytic proof directly working with the Hamiltonian is given in the [supplementary material](#). When there is a disorder in the site energy  $\omega$ , the perturbation to the Hamiltonian in Eq. (2) is  $V = \sum_{j=1}^N \delta_j c_j^+ c_j^-$ . The unperturbed component states for the double-excitation states of the second category are a pair of  $|C_{k_1}\rangle$  and  $|C_{k_2}\rangle$  of opposite energies. Without loss of generality, we consider the pair  $k_1 = 0$  and  $k_2 = N - 2$ . Both  $|C_{k_1}\rangle$  and  $|C_{k_2}\rangle$  have their own degenerate counterparts and, to find the first order perturbation energy, we need to use the degenerate perturbation theory and diagonalize  $P_{ki}VP_{ki}$ , where  $P_{ki}$  is the projector into the degenerate space of  $|C_{k_i}\rangle$ . The result is a first-order correction of  $\alpha \pm \sqrt{|\beta|^2}$  for both the  $|C_{k_1}\rangle$  and the  $|C_{k_2}\rangle$  degenerate spaces, where  $\alpha = \frac{1}{N} \sum_{j=1}^N \delta_j$  and  $\beta = \frac{1}{N} \sum_{j=1}^N \delta_j e^{i\frac{2\pi j}{N}}$ .

Hence, by picking the eigenstate of energy  $\varepsilon_{k_1} + \alpha + \sqrt{|\beta|^2}$  from the  $|C_{k_1}\rangle$  degenerate space and the eigenstate of energy  $\varepsilon_{k_2} + \alpha - \sqrt{|\beta|^2}$  from the  $|C_{k_2}\rangle$  degenerate space, we can form a double-excitation state of the second category with the

first-order energy correction  $E_I^{(1)} = \varepsilon_{k_1} + \varepsilon_{k_2} + 2\alpha$ . The unperturbed component states for the double-excitation states of the first category are a pair of  $|C_{k_3}\rangle$  and  $|C_{k_4}\rangle$  of the same energy with  $\frac{(k_3+1)\pi}{N} = \frac{\pi}{2}$  and  $\frac{(k_4+1)\pi}{N} = \frac{3\pi}{2}$ . Again, we use the perturbation theory for degenerate states and diagonalize  $P_{k_3}VP_{k_3}$ .

The result is an energy shift of  $\alpha \pm \gamma$ , where  $\gamma = \frac{1}{N} \sum_{j=1}^N \delta_j (-1)^j$ ; therefore, the double-excitation state formed by the eigenstates of  $P_{k_3}VP_{k_3}$  has the first-order energy correction of  $E_{II}^{(1)} = 2\varepsilon_{k_3} + 2\alpha$ . Because  $2\varepsilon_{k_3} = \varepsilon_{k_1} + \varepsilon_{k_2}$ ,  $E_I^{(1)} = E_{II}^{(1)}$ , indeed the accidental degeneracy is preserved up to first order of site energy disorder.

### III. CONCLUSION

In this work, we have identified and investigated an accidental degeneracy on the double-excitation manifold of a coupled excitonic ring structure. The accidental degeneracy occurs between two categories of double-excitation eigenstates which possess distinct symmetries and optical transition patterns to the single-excitation manifold. The accidental degeneracy has been proven to exist if, and only if, the size of the ring is  $N = 4l + 2$ . Using a state diagram relating the geometries formed by the single-excitation manifold and the component state manifold on the complex plane to the actual geometry of the ring, we have shown that, remarkably, the absence of certain symmetry elements is responsible for the accidental degeneracy. Finally the accidental degeneracy is preserved up to first-order site energy disorder and arbitrary coupling strength disorder.

### SUPPLEMENTARY MATERIAL

See [supplementary material](#) for technical details of theoretical discussions, which supports the discussion in the main text.

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