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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · OCTOBER 2011

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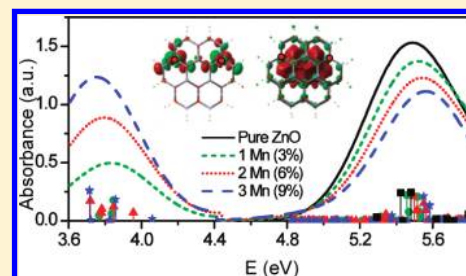
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Characterization of Excited-State Magnetic Exchange in  $\text{Mn}^{2+}$ -Doped ZnO Quantum Dots Using Time-Dependent Density Functional Theory

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**ABSTRACT:** Absorption spectra of  $\text{Mn}^{2+}$ -doped ZnO quantum dots have been studied with the linear-response time-dependent density functional theory. Spectral changes caused by excited state dopant-carrier and dopant–dopant magnetic exchange couplings are investigated. The excitonic transition maximum shifts to higher energy and decreases in intensity with increasing  $\text{Mn}^{2+}$  concentration. The lowest excitonic transitions split in the spin-up and spin-down manifolds due to  $sp$ – $d$  magnetic exchange between the  $\text{Mn}^{2+}$  and ZnO conduction and valence band carriers. Increased  $\text{Mn}^{2+}$  concentration leads to a broadening and increase in the intensity of the midgap charge-transfer electronic absorption band. The charge-transfer band broadening results from excited-state splitting arising from double exchange magnetic interactions involving  $\text{Mn}^{2+}$  ions and the photogenerated hole. The excited-state double exchange leads to stabilization of the ferromagnetic configuration in the charge-transfer state. The strength of this ferromagnetic double exchange interaction depends on the inter- $\text{Mn}^{2+}$  distance within the quantum dot.



## I. INTRODUCTION

Semiconductor nanocrystals doped with transition metal ions (diluted magnetic semiconductor quantum dots, DMS QDs) have recently drawn considerable attention due to their potential applications in magneto-optical and magneto-electronic devices,<sup>1–5</sup> bioimaging,<sup>6,7</sup> as photocatalytic and antibacterial agents,<sup>8</sup> and in solar energy conversion.<sup>9</sup> II–VI DMSs based on  $\text{Mn}^{2+}$  have been the most extensively studied, but among these,  $\text{Mn}^{2+}$ -doped ZnO ( $\text{Mn}^{2+}:\text{ZnO}$ ) represents a special class.<sup>10</sup> The occupied  $\text{Mn}^{2+}$  3d levels reside inside the semiconductor bandgap (midgap). This unique electronic structure gives rise to midgap “photoionization” or metal-to-ligand charge-transfer ( $\text{ML}_{\text{CB}}\text{CT}$ ) excited states (eq 1).<sup>11–15</sup>



The charge-transfer nature of the midgap transitions observed experimentally in  $\text{Mn}^{2+}:\text{ZnO}$  QDs is supported by a variety of spectroscopic studies.<sup>11,16–18</sup> Theoretical efforts have also been carried out to provide insights into the characteristics of this important midgap band.<sup>17–19</sup> Our previous theoretical work showed that the broad  $\text{ML}_{\text{CB}}\text{CT}$  band consists of electronic excitations from  $\text{Mn}^{2+}$   $d_e$  and  $d_{t2}$  orbitals to the conduction band (CB) of ZnO. Because of their energetic proximity to the ZnO band-to-band transitions, these CT transitions are mixed with the excitonic band, resulting in partial delocalization of the photo-excited hole. Quantum confinement effects in doped QDs have been observed both theoretically and experimentally to shift the semiconductor band edges relative to the pinned transition metal  $d$ -levels, resulting in diameter-dependent  $\text{ML}_{\text{CB}}\text{CT}$  energies.<sup>17,20</sup>

Many of the proposed applications of DMSs are based on intrinsic interactions between the localized impurity spins and

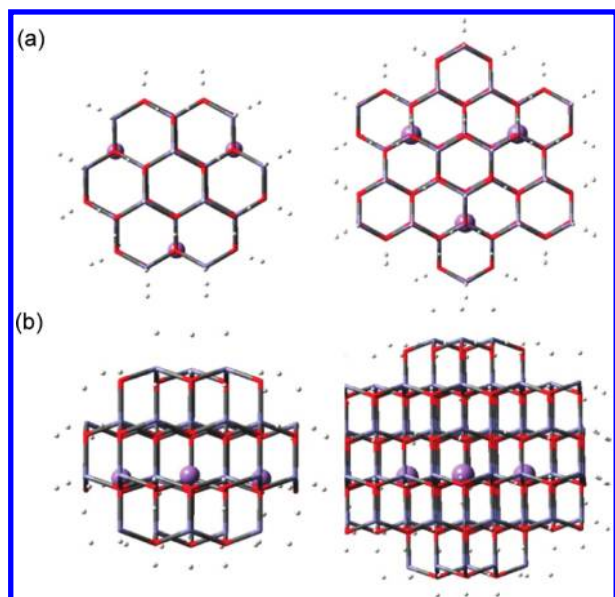
the semiconductor band-like charge carriers. For example, dopant-carrier magnetic exchange gives rise to “giant” Zeeman splittings of the semiconductor band structure, the signs and magnitudes of which are intimately linked to the energies of dopant-centered CT configurations.<sup>21</sup> In addition, high- $T_{\text{C}}$  ferromagnetism in oxide DMSs has also been proposed to be related to the energies of various  $\text{ML}_{\text{CB}}\text{CT}$  configurations.<sup>22–25</sup> Experimentally, however, the effects of dopant concentration and spin state on CT transitions in  $\text{Mn}^{2+}:\text{ZnO}$  have been difficult to analyze quantitatively because of inhomogeneous broadening and overlapping transitions. Experimental difficulties have also lead to inconsistent interpretations of the effect of concentration on the optical properties of  $\text{Mn}^{2+}:\text{ZnO}$ . For example, a red shift in the band gap absorption energies of  $\text{Mn}^{2+}:\text{ZnO}$  nanorods has been reported and attributed to strong  $p$ – $d$  exchange between  $\text{Mn}^{2+}$  3d electrons and ZnO valence band (VB) spins.<sup>26</sup> A red shift of the band-to-band transition was observed with increasing  $\text{Mn}^{2+}$  concentration for  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  QDs when  $x < 0.02$ , while a blue shift was reported for larger  $x$ .<sup>27</sup> On the other hand, a blue shift of the excitonic absorption with increasing  $x$  was reported for  $\text{Mn}^{2+}:\text{ZnO}$  epitaxial thin films,<sup>13,28,29</sup> nanopowders,<sup>30</sup> nanorods,<sup>16</sup> and nanowires.<sup>31,32</sup> This blue shift has been attributed to the intrinsically larger bandgap of wurtzite  $\text{MnO}$  ( $E_{\text{g}} \sim 4$  eV)<sup>33–35</sup> compared to wurtzite ZnO ( $E_{\text{g}} \sim 3.4$  eV).

Density functional calculations have also been used to understand the role of  $\text{Mn}^{2+}$  concentration and magnetic exchange interactions in  $\text{Mn}^{2+}:\text{ZnO}$ .<sup>19,28,36</sup> The relative energies of  $\text{Mn}^{2+}$  levels and ZnO bands in the ground-state electronic structure

Received: July 12, 2011

Revised: September 20, 2011

Published: September 22, 2011

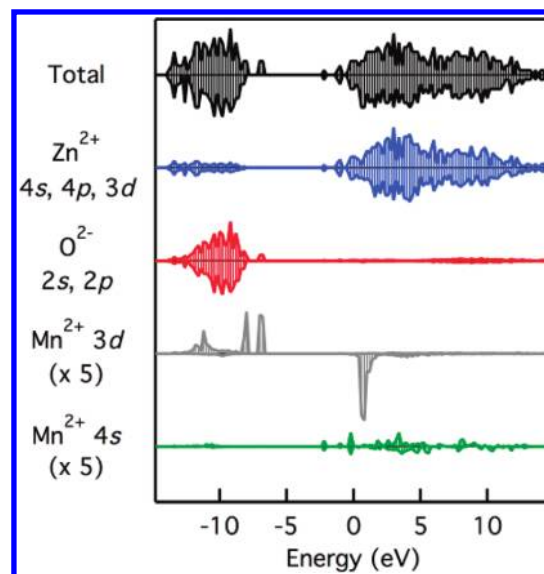


**Figure 1.** Structure of  $\text{Mn}^{2+}:\text{ZnO}$  QDs with the  $C_3$ -axis oriented (a) out of the page and (b) vertically in the plane of the page (left,  $\text{Zn}_{30}\text{Mn}_3\text{O}_{33}$ ; right,  $\text{Zn}_{81}\text{Mn}_3\text{O}_{84}$ ).  $\text{Mn}^{2+}$  dopants are located at second-nearest neighbor sites, as indicated by the purple spheres.

have been used to elucidate the mechanisms of dopant-centered magnetic exchange interactions. Although ground-state orbital splittings are informative, electronic structure calculations of excited states offer more insight into the dopant–carrier interactions that are directly related to experimental magneto-optical measurements. Here, we report the application of linear-response time-dependent density functional theory (TDDFT) to examine the influence of  $\text{Mn}^{2+}$  concentration and spin orientation on the absorption spectra of  $\text{Mn}^{2+}$ -doped ZnO quantum dots. This work builds upon our previous efforts to understand the spectral features in  $\text{Mn}^{2+}:\text{ZnO}$  QDs using TDDFT, now focusing on the spectral splittings arising from dopant–carrier magnetic exchange interactions.

## II. METHODS

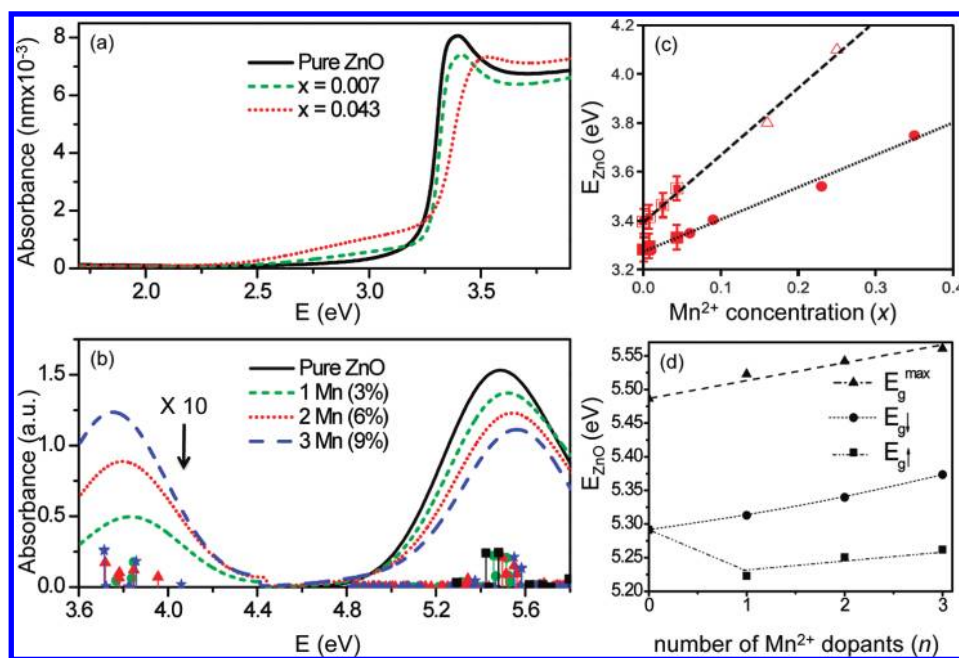
All calculations were performed with the development version of the Gaussian program suite.<sup>37</sup> QD electronic structures were obtained with the PBE1PBE hybrid DFT functional.<sup>38–40</sup> The short-range screened hybrid HSE1PBE<sup>41–43</sup> functional and the long-range corrected LC-wPBE<sup>44</sup> functional were also used to check for possible spurious delocalization. The Los Alamos double- $\zeta$  pseudocore potential (LANL2DZ)<sup>45–48</sup> and the associated basis set were used for all atoms with the  $\text{Zn}^{2+}$  ( $3p$ ,  $4s$ ,  $3d$ ),  $\text{Mn}^{2+}$  ( $3s$ ,  $3p$ ,  $4s$ ,  $3d$ ) and  $\text{O}^{2-}$  ( $1s$ ,  $2s$ ,  $2p$ ) electrons treated as valence electrons. Nearly spherical wurtzite ZnO QDs ( $\text{Zn}_{33}\text{O}_{33}$  and  $\text{Zn}_{84}\text{O}_{84}$ ) as shown in Figure 1a and b) were constructed with the  $C_{3v}$  symmetry constraint.<sup>49</sup> The diameters of these QDs are about 1.2 and 1.8 nm, respectively. The lattice parameters were obtained from experimental data:  $a = 3.249 \text{ \AA}$ ,  $c = 5.204 \text{ \AA}$ , and  $u = 0.382$ .<sup>50</sup> The dangling bonds on the surfaces of the QDs were passivated with pseudohydrogen atoms, which have a modified nuclear charge of 0.5 and 1.5 to terminate surface  $\text{O}^{2-}$  and  $\text{Zn}^{2+}$  ions, respectively. A partial optimization of the O–H and Zn–H bond lengths was performed for all QD sizes. This pseudohydrogen capping scheme leads to a well-defined bandgap and stable



**Figure 2.** Total and projected density of states (DOS) for a  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QD with  $\text{Mn}^{2+}$  dopants in second-nearest neighbor sites with parallel spin alignment. Positive and negative values represent the spin-up and spin-down DOS, respectively. Note the  $5\times$  magnification of the  $\text{Mn}^{2+}$   $3d$  and  $4s$  projected DOS.

QD geometry (see references 17 and 49 for a detailed discussion). When doped into a ZnO QD,  $\text{Mn}^{2+}$  ions were substitutionally introduced into the lattice, such that the total charge of the cluster remained neutral. Excited-state energies and oscillator strengths were calculated with the linear-response time-dependent density functional theory (TDDFT)<sup>51</sup> at the PBE1PBE/LANL2DZ level of theory. Our recent work has demonstrated that the TD-PBE1PBE method provides consistent results compared to range-separated and long-range corrected functionals.<sup>18</sup> Absorption spectra were obtained by dressing excited-state peaks from TDDFT calculations with Gaussian functions having a broadening constant of 0.16 eV. Natural transition orbital (NTO)<sup>52</sup> analysis based on the calculated transition densities between the ground and excited states was used to describe the electronic characteristics of the excited states. The NTO approach provides a compact representation of the electronic transitions in terms of an expansion into single-particle orbitals (electron and hole) by diagonalizing the transition density matrix associated with each excitation. For the closed-shell calculation, an excitation can be described by a pair of spin-independent transition orbitals. In the case of an open-shell calculation, two sets of spin-transition orbitals must be considered for a given excitation (spin-up and spin-down manifolds). All NTOs presented here were produced with an isosurface value of 0.02.

Because the QD is a confined system, both the ground-state energies and the absorption spectra of the doped QDs are highly sensitive to inter- $\text{Mn}^{2+}$  distances and to  $\text{Mn}^{2+}$  positions relative to the QD center.<sup>53</sup> Experimentally, this dependence introduces inhomogeneous broadening of the spectral lines, which complicates the analysis of the effect of concentration on the absorption spectrum. To avoid this complication here, calculations involving multiple  $\text{Mn}^{2+}$  ions were performed by placing these ions in symmetrically equivalent positions relative to the QD center, either as nearest neighbors or as second-nearest neighbors with respect to each other (Figure 1a,b). The ferromagnetic (FM) and antiferromagnetic (AFM) configurations were optimized by



**Figure 3.** (a) Experimental absorption spectra of epitaxial  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  films, adapted from ref 13, with  $x = 0$  (black solid), 0.007 (green dashed), and 0.043 (red dotted). (b) Absorption spectra of  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs computed at the TD-PBE1PBE/LANL2DZ level of theory, for  $n = 0$  (black solid), 1 (green dashed), 2 (red dotted), and 3 (blue long-dashed), corresponding to concentrations of  $x = 0, 0.03, 0.06$ , and  $0.09$ , respectively. The lower energy  $\text{ML}_{\text{CB}}\text{CT}$  transition region is amplified 10-fold. Vertical lines correspond to TDDFT excited-state energies and oscillator strengths. TDDFT peaks are dressed with Gaussian functions with a broadening parameter of  $0.16$  eV. (c) Experimental change of ZnO bandgap with  $\text{Mn}^{2+}$  concentration, adapted from ref 13. The energies were obtained from the intercept between the  $\text{ML}_{\text{CB}}\text{CT}$  and excitonic bands (■, ●), and from the first band-to-band absorption maxima (□, △). (d) Calculated excitonic excitation energies with  $\text{Mn}^{2+}$  concentration in a  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QD, where  $E_g^{\text{max}}$  (▲) is the excitonic absorption maximum estimated from the calculated spectra in (b),  $E_g^{\uparrow}$  (■) is the lowest spin-up (majority spin) excitonic excited state, and  $E_g^{\downarrow}$  (●) is the lowest spin-down excitonic excited state.  $\text{Mn}^{2+}$  3d electrons are in the all-spin-up (ferromagnetic) configuration. Any two  $\text{Mn}^{2+}$  ions are positioned at second nearest-neighbor sites (Figure 1a,b; inter- $\text{Mn}^{2+}$  distance of  $3.25$  Å).

restricting the total spin multiplicity to 11 and 1, respectively, and finding a state where each  $\text{Mn}^{2+}$  site has a local spin  $S_{\text{Mn}} = 5/2$ .

### III. RESULTS AND DISCUSSION

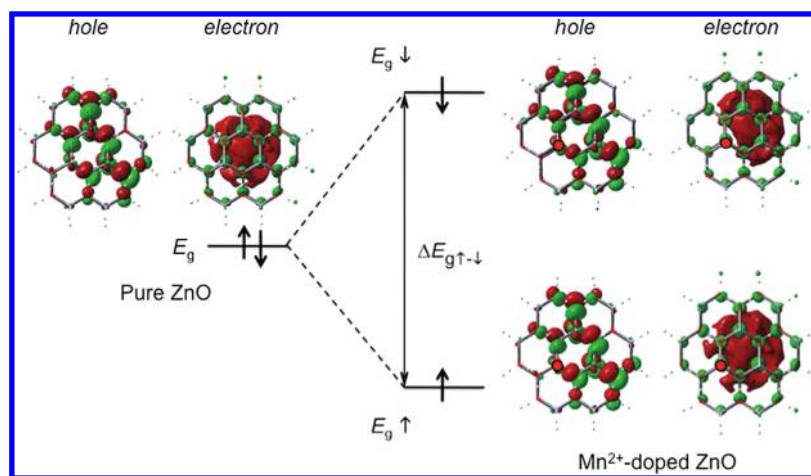
Figure 2 illustrates the density of states (DOS) of a  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QD (1.2 nm in diameter) obtained using one-electron orbitals from the DFT ground-state calculation. The VB of ZnO is formed primarily from  $\text{O}^{2-}$  2p orbitals, whereas the CB edge predominantly consists of  $\text{Zn}^{2+}$  4s and 4p character. The occupied  $\text{Mn}^{2+}$  3d levels are localized at the top edge of the VB and are split into  $t_2$  and  $e$  sets separated by  $\sim 1$  eV due to the pseudotetrahedral crystal field of the wurtzite structure. This description agrees well with photoemission spectra<sup>13,54</sup> and with recent LSDA+U calculations of  $\text{Mn}^{2+}:\text{ZnO}$ .<sup>55</sup> The unoccupied  $\text{Mn}^{2+}$  3d levels are found at  $\sim 3$  eV above the CB edge for the  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QD. This energy difference increases with increasing QD diameter because  $\text{Mn}^{2+}$  3d level positions are pinned while the CB and VB edges shift with QD size due to quantum confinement effects.<sup>17,20</sup>  $\text{Mn}^{2+}$  4s levels reside  $\sim 2$  eV above the CB edge but also contribute to the lowest unoccupied molecular orbital (LUMO) through hybridization. From the ground-state electronic structure point of view, an increase in the  $\text{Mn}^{2+}$  concentration yields an increase in the density of  $\text{Mn}^{2+}$  3d levels and can lead to d-band broadening as a result of the Coulomb and exchange interactions between  $\text{Mn}^{2+}$  ions.<sup>53</sup>

Figure 3 shows the effect of  $\text{Mn}^{2+}$  concentration on the electronic absorption spectra, comparing TDDFT calculations (Figure 3b,d) with recent experimental data for epitaxial

$\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x = 0, 0.007$ , and  $0.043\%$ ) films (Figure 3a,c).<sup>13</sup> Experimentally, the excitonic ( $\text{ZnO VB} \rightarrow \text{CB}$ ) absorption-band maximum is located at  $\sim 3.4$  eV, and a broad midgap shoulder is observed tailing into the visible energy region. This midgap absorption has been assigned to a  $\text{ML}_{\text{CB}}\text{CT}$  excitation, or donor-type photoionization transition, of  $\text{Mn}^{2+}$  in  $\text{ZnO}$ .<sup>13</sup> The calculated absorption spectra for the  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QD ( $n = 0-3$ , corresponding to concentrations of  $x = 0, 3, 6$ , and  $9\%$ , respectively) exhibit very similar spectral features. Both the excitonic and  $\text{ML}_{\text{CB}}\text{CT}$  bands are shifted to higher excitation energies than in the experimental spectra due to quantum confinement (see ref 17 for details on the quantum confinement effect). Increasing the  $\text{Mn}^{2+}$  concentration leads to a more intense  $\text{ML}_{\text{CB}}\text{CT}$  band and a less intense excitonic transition. These effects are discussed in detail below.

**A. Excitonic Transitions.** The  $\text{ZnO VB} \rightarrow \text{CB}$  transitions give rise to the most intense absorption peak, occurring at  $\sim 5.3-5.5$  eV in strongly quantum-confined  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs (Figure 3b). NTOs for the lowest excitonic transition of the undoped and  $\text{Mn}^{2+}$ -doped ZnO QDs are shown in Figure 4. In the excitonic excited state, the photogenerated hole resides mainly in  $\text{O}^{2-}$  2p orbitals that are antibonding with respect to cation–anion interactions. The photogenerated electron resides primarily in  $\text{Zn}^{2+}$  4s orbitals and has a spherical s-like density distribution with its maximum near the QD center. Upon introduction of a  $\text{Mn}^{2+}$  dopant, the electron's wave function is strongly modified in the region around the dopant, while the hole's distribution is nearly unchanged. As the  $\text{Mn}^{2+}$  concentration increases, more  $\text{Zn}^{2+}$  4s electronic levels in the lower edge of the ZnO CB are replaced with





**Figure 4.** Electron and hole natural transition orbitals (NTO) for excitonic transitions in  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs. Left: electron and hole NTOs for the lowest excitonic transition in a  $\text{Zn}_{33}\text{O}_{33}$  QD. Right: electron and hole NTOs of the spin-up ( $E_{g\uparrow}$ ) and spin-down ( $E_{g\downarrow}$ ) manifolds for the lowest excitonic transition in a  $\text{Zn}_{32}\text{MnO}_{33}$  QD. The  $\text{Mn}^{2+}$  positions are indicated by black circles (red dots).

$\text{Mn}^{2+}$  4s levels.  $\text{Mn}^{2+}$  4s levels occur much higher in energy than  $\text{Zn}^{2+}$  4s levels and, hence, are poorly suited for resonance, leading to a reduction of the transition dipole moment,  $\langle\psi_{\text{VB}}|\hat{r}|\psi_{\text{CB}}\rangle$ . The oscillator strength of the excitonic transition thus decreases with increasing  $\text{Mn}^{2+}$  concentration. For the same reasons, the position of the first excitonic absorption maximum ( $E_g^{\text{max}}$ ) also blue shifts (Figure 3c,d) with increasing  $\text{Mn}^{2+}$  concentration.

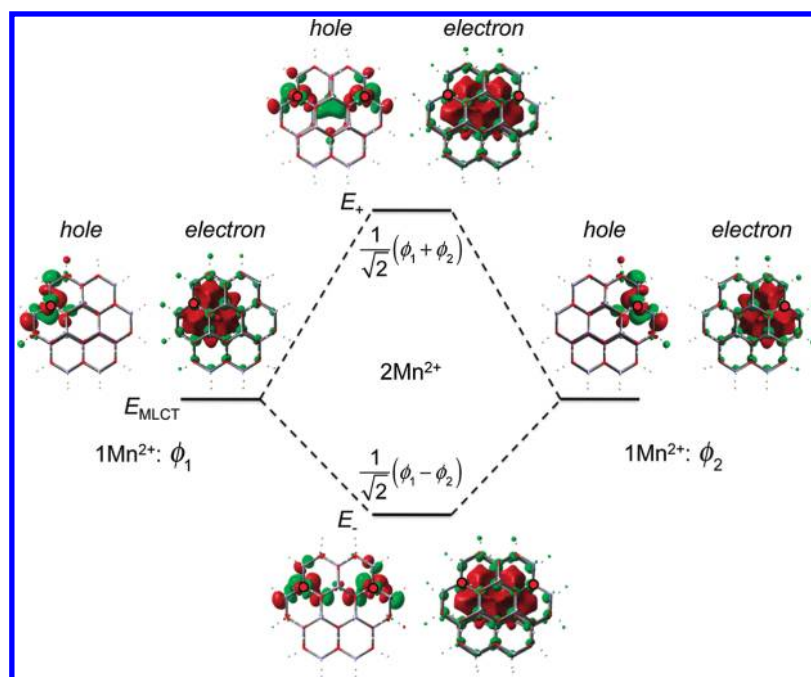
Figure 3d also plots the splitting of the lowest excitonic excited states in the  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs. In the absence of a magnetic field, the spin-up and spin-down excitonic transitions are degenerate for an undoped ZnO QD. When  $\text{Mn}^{2+}$  is introduced, spin-up ( $E_{g\uparrow}$ , majority spin) and spin-down ( $E_{g\downarrow}$ , minority spin) excitonic transitions split due to  $sp-d$  exchange interactions between  $\text{Mn}^{2+}$  3d electrons and photogenerated charge carriers in the semiconductor bands. This energy difference between spin-up and spin-down manifolds of the excitonic transitions,  $\Delta E_{g\uparrow\downarrow} = E_{g\uparrow} - E_{g\downarrow}$ , is related to the excitonic Zeeman splitting observed experimentally in magneto-optical spectroscopies of DMSs. TDDFT calculations of the  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs (1.2 nm in diameter) show that  $\Delta E_{g\uparrow\downarrow}$  grows from 0.101 eV for  $n = 1$  to 0.141 when  $n = 3$ , for  $\text{Mn}^{2+}$  ions in the nearest-neighbor configuration. In the  $\text{Zn}_{84-n}\text{Mn}_n\text{O}_{84}$  QDs (1.8 nm diameter), the excitonic splitting energies decrease to 0.031 eV for  $n = 1$  and 0.044 eV for  $n = 3$ . This reduction in excitonic Zeeman splitting with increased QD diameter is due to the decrease in the excitonic wave function amplitude at the dopant sites shown in Figures 1a and b, which leads to decreased magnetic exchange coupling strengths between the charge carriers and the  $\text{Mn}^{2+}$  3d electrons localized at those sites.

**B. Charge-Transfer States.** Strong concentration and spin-state dependence is observed in the midgap energy region of  $\text{Mn}^{2+}$ :ZnO. Experimentally, an increase in the midgap absorption intensity is observed with increasing  $\text{Mn}^{2+}$  concentration (Figure 3a). In the calculated absorption spectra shown in Figure 3b, the states that span the energy range between  $\sim 3.6$  eV and  $\sim 5.2$  eV were classified as  $\text{ML}_{\text{CBCT}}$  states in our previous theoretical studies as well as in experimental investigations,<sup>11,17,18,22</sup> although some researchers favor a Zhang-Rice-like description of the midgap states.<sup>19,29</sup> In small  $\text{Mn}^{2+}$ :ZnO QDs, the  $\text{ML}_{\text{CBCT}}$  transitions form two bands: a lower energy  $\text{ML}_{\text{CBCT1}}$  band (3.7–3.9 eV for  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$ ), which involves the excitation of a  $d_{z^2}$  electron into

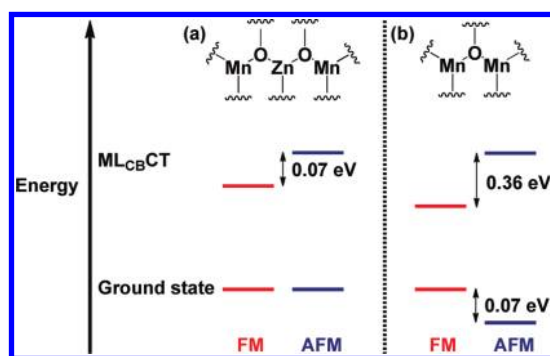
the ZnO LUMO, and a broader  $\text{ML}_{\text{CBCT2}}$  band ( $\sim 4.8$  eV for  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$ ), which includes both excitations of  $\text{Mn}^{2+}$   $d_{z^2}$  electrons to higher lying CB levels as well as  $d_c$ -to-CB transitions.<sup>17</sup>

An increase in the number of  $\text{Mn}^{2+}$  3d levels with increasing dopant concentration leads to a linear increase in the  $\text{ML}_{\text{CBCT}}$  excited-state density and, also, in the transition's integrated intensity. The detailed characteristics of the  $\text{ML}_{\text{CBCT}}$  transitions depend strongly on the spin-configuration of the excited state. To illustrate, we consider the two situations of two  $\text{Mn}^{2+}$  ions positioned at second-nearest-neighbor sites (inter- $\text{Mn}^{2+}$  distance of 6.50 Å, as shown in Figure 1a,b) and positioned at nearest neighbor sites (inter- $\text{Mn}^{2+}$  distance of 3.25 Å).

When two  $\text{Mn}^{2+}$  ions are in second-nearest-neighbor positions in  $\text{Mn}^{2+}$ :ZnO QDs, superexchange coupling between them drops to a negligibly small value,<sup>53,56</sup> and the spectral dependence on dopant concentration can be examined in the absence of ground-state  $\text{Mn}^{2+}$ - $\text{Mn}^{2+}$  exchange coupling. In this scenario, when the two second-nearest-neighbor  $\text{Mn}^{2+}$  ions have their spins aligned in the AFM configuration, their two  $\text{ML}_{\text{CBCT}}$  transitions simply add up to a more intense band at the same frequency compared to the singly doped ZnO QD, that is, they behave independently. When two  $\text{Mn}^{2+}$  ions are in the FM configuration, the  $\text{ML}_{\text{CBCT}}$  absorption is different in both energy and electronic structure characteristics. In our recent work,<sup>18</sup> excited-state double exchange interactions arising from delocalization of the photogenerated hole were shown to stabilize the FM configuration when multiple dopants occupy the same QD. NTOs for such  $\text{ML}_{\text{CBCT}}$  transitions are plotted in Figure 5 and their relative energies are shown in Figure 6. In the FM configuration, the  $\text{ML}_{\text{CBCT}}$  states localized around the two different  $\text{Mn}^{2+}$  ions couple through the double exchange mechanism, giving rise to new delocalized  $\text{ML}_{\text{CBCT}}$  transitions. The wave functions of these delocalized states can be described as  $\phi_- = 1/\sqrt{2}(\phi_1 - \phi_2)$  and  $\phi_+ = 1/\sqrt{2}(\phi_1 + \phi_2)$ , where  $\phi_1$  and  $\phi_2$  are the  $\text{ML}_{\text{CBCT}}$  excited states of the individual uncoupled dopants. The strength and sign of the coupling is determined by the extent of hybridization between  $\text{Mn}^{2+}$  3d orbitals and the VB, which is predominantly  $\text{O}^{2-}$  2p in character. The 3d-oxo orbital interaction defines the parity of the photoexcited hole wave functions in the lowest-energy  $\text{ML}_{\text{CBCT}}$  excited state. The NTOs in Figure 5 show that the lower energy  $\text{ML}_{\text{CBCT}}$  excited state corresponds



**Figure 5.** Schematic illustration of the ferromagnetic interaction between  $\text{Mn}^{2+}$  ions in  $\text{ML}_{\text{CB}}\text{CT}$  excited states of  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QDs. NTOs are plotted for  $\text{ML}_{\text{CB}}\text{CT}$  excited states in  $\text{Zn}_{33-n}\text{Mn}_n\text{O}_{33}$  QDs with  $n = 1$  (left and right sides) and 2 (center, second nearest-neighbors). The  $\text{Mn}^{2+}$  positions are indicated by black circles (red dots).



**Figure 6.** Energy levels of ferromagnetic (FM) and antiferromagnetic (AFM) configurations for  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QDs.  $\text{Mn}^{2+}$  ions are in (a) second nearest-neighbor positions and (b) nearest-neighbor positions.

to the out-of-phase combination,  $\phi_-$ , which occurs 70 meV below the parent noninteracting  $\text{ML}_{\text{CB}}\text{CT}$  transitions.  $\phi_+$  lies  $\sim 0.24$  eV above  $\phi_-$  and is associated with a lower oscillator strength due to parity selection rules.  $\text{ML}_{\text{CB}}\text{CT}2$  follows the same splitting scheme, but excitations in this band have even more excitonic character because of their energetic proximity to the band-to-band states.

In principle, the double exchange mechanism will have its greatest effect when two  $\text{Mn}^{2+}$  ions are positioned at nearest-neighbor sites connected through an oxygen bridge, that is, a  $\text{Mn}^{2+}-\text{Mn}^{2+}$  dimer. However, AFM superexchange is also at its strongest in the nearest-neighbor geometry. In the ground state, the AFM configuration is stabilized by 70 meV relative to the FM configuration, as shown schematically in Figure 6b. In the  $\text{ML}_{\text{CB}}\text{CT}$  excited state, double exchange and superexchange compete to determine the lowest-energy dimer configuration. TDDFT calculations show that the lowest FM  $\text{ML}_{\text{CB}}\text{CT}$  state is

stabilized by 360 meV compared to the lowest AFM  $\text{ML}_{\text{CB}}\text{CT}$  state for this nearest-neighbor  $\text{Mn}^{2+}-\text{Mn}^{2+}$  dimer in the  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QD. Double exchange is thus much greater for nearest-neighbor  $\text{Mn}^{2+}$  pairs than for next-nearest-neighbor  $\text{Mn}^{2+}$  pairs. TDDFT thus predicts that excited-state double exchange should lead to a red shift of the  $\text{ML}_{\text{CB}}\text{CT}$  band in the absorption spectrum on the order of 360 meV for nearest-neighbor  $\text{Mn}^{2+}-\text{Mn}^{2+}$  pairs and 70 meV for next-nearest-neighbor pairs in  $\text{Zn}_{31}\text{Mn}_2\text{O}_{33}$  QDs, although the experimental observation of this phenomenon could likely be occluded by inhomogeneous broadening.

#### IV. CONCLUSIONS

This work addresses the effects of dopant concentration and spin configuration on the absorption spectra of  $\text{Mn}^{2+}:\text{ZnO}$  QDs from a TDDFT analysis of excited-state dopant–dopant and dopant–carrier magnetic exchange coupling. As the  $\text{Mn}^{2+}$  concentration increases, ZnO excitonic transitions shift to higher energy and decrease in intensity, as observed experimentally. The  $sp-d$  exchange interactions between  $\text{Mn}^{2+}$  3d electrons and band-like charge carriers cause a  $\text{Mn}^{2+}$  concentration-dependent splitting between spin-up and spin-down excitonic excitation energies, that is, the giant excitonic Zeeman splitting that is so characteristic of this class of materials. This excitonic Zeeman splitting increases with increasing  $\text{Mn}^{2+}$  concentration in the QDs.

Midgap  $\text{ML}_{\text{CB}}\text{CT}$  transitions are predicted by the TDDFT calculations. The intensity of the  $\text{ML}_{\text{CB}}\text{CT}$  band in the absorption spectrum is predicted to increase with increasing  $\text{Mn}^{2+}$  concentration. For QDs containing two  $\text{Mn}^{2+}$  ions, the  $\text{ML}_{\text{CB}}\text{CT}$  excited-state energies are shown to depend on the relative  $\text{Mn}^{2+}$  spin orientations. In the FM configuration, double exchange stabilizes the lowest-energy  $\text{ML}_{\text{CB}}\text{CT}$  state. The out-of-phase dimer hole orbital is lower in energy than either the in-phase or

the noninteracting orbitals. This double exchange coupling becomes stronger with decreasing inter-Mn<sup>2+</sup> separation, and it leads to broadening of the ML<sub>CB</sub>CT band in the absorption spectrum.

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## ACKNOWLEDGMENT

This work was supported by the U.S. National Science Foundation (CHE 0628252-CRC to D.R.G. and X.L.). E.B. thanks the UW Center for Nanotechnology for a UIF fellowship. Additional support from Gaussian Inc. and the University of Washington Student Technology Fund is gratefully acknowledged.

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