

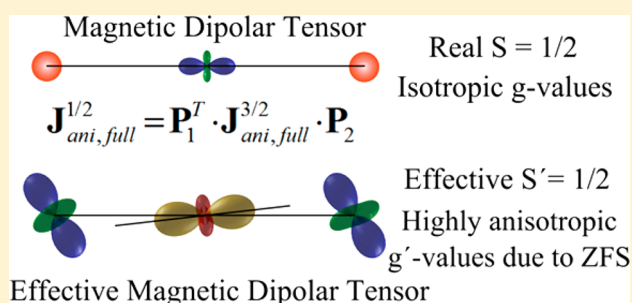
# Effective Anisotropic Interactions in Spin Pairs Containing High-Spin Ions with Large Zero-Field Splitting

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Supporting Information

**ABSTRACT:** Analytic and numeric derivations are made of the effective exchange and dipolar magnetic interactions between spin pairs containing  $S = 3/2$  ions, such as high-spin Co(II),  $S = 5/2$  ions, such as high-spin Fe(III) ions, experiencing zero-field splittings much larger than the interion interactions, or  $J = 15/2$  ions such as Dy(III) with crystal-field splittings much larger than the interion interaction. These formulas allow for a simpler analysis of the magnetic properties of dimers containing high-spin ions.



## INTRODUCTION

The study of magnetic interactions between paramagnetic ions or molecules, molecular magnetism, has been of great interest in the fields of inorganic<sup>1,2</sup> and bioinorganic chemistry.<sup>3–7</sup> EPR spectroscopy has played an important role in the first and a major role in the second discipline. In the case of interactions between  $S = 1/2$  spins, the theoretical framework allowing interpretation of EPR results is well understood, remaining mostly improvements in quantum-mechanical calculations of the magnitudes of different magnetic interactions and further development of advanced methods (i.e., high-frequency and pulsed EPR) for elucidation of subtle or difficult to resolve interactions. The story is very different in the case of high-spin ions such as Co(II) ( $S = 3/2$ ) and Fe(III) ( $S = 5/2$ ) which, in addition to having a large spin, usually present partially unquenched orbital momentum, which under the effect of spin–orbit coupling, produce a zero-field splitting (ZFS) of the spin sublevels. This ZFS does not only give rise to very anisotropic effective  $g'$  matrices, but also conveys high anisotropy to magnetic interactions between these types of ions. A similar situation is observed for some lanthanides such as Dy, which present highly anisotropic effective  $g'$  matrices ( $g'_{xy} \approx 0$ ,  $g'_z \approx 10–20$ ) and have lately been the focus of intense research efforts.<sup>8–10</sup> One of the problems in studying anisotropic magnetic interactions is that magnetic susceptibility or magnetization studies, which are usually performed on powder samples, do not always allow us to reliably obtain the anisotropic parts of the interactions, with some exceptions.<sup>11</sup> While EPR performed on powder samples does give anisotropic information, when systems with more than one ion with a high spin are studied, usually the number of parameters associated with the magnetic interactions is so large that approximations have to be made and the extracted information is limited. Finally, although single-crystal EPR can

be used to extract full anisotropic interactions, the difficulties associated with measurements (large ( $\sim 0.5^3$  mm<sup>3</sup>) stable crystals have to be grown, morphology has to be determined to align the crystals, and long times of data analysis) have diminished the number of this kind of studies. In the case of metalloproteins, single-crystal EPR studies are very scarce. Our aim in this work is to derive general equations for anisotropic effective interactions in pairs involving high-spin ions, which can confidently be used to analyze EPR, thus considerably diminishing the number of unknown parameters and simplifying the problem. Furthermore, these relations could be used to more reliably relate EPR results, which are usually (but not always) analyzed as effective spin 1/2 systems, to magnetization and magnetic susceptibility results, which are usually treated using real-spin Hamiltonians.

Half-integer spins, in the presence of an axial ZFS, have  $(2S + 1)/2$  Kramers doublets separated by an energy difference  $D(2|M_S| + 1)$  between the  $(|M_S| + 1)$  and  $|M_S|$  doublets. When the ZFS is large enough, each of these doublets can be considered an effective  $S' = 1/2$  with an effective  $g'$  matrix. When the ZFS is not axial the doublets are not pure  $M_S$  states and the energy separation between them is modified, but still an effective spin and  $g'$  matrix can be assigned to each doublet. Pilbrow's equations<sup>12</sup> relate the real  $g$  matrix associated with the real spin ( $S = 3/2$  or in some cases  $S = 5/2$ ) and the rhombicity parameter  $E/D$  of the zero-field splitting  $\mathbf{D}^{ZFS}$  tensor with the effective  $g'$  matrix associated with each of the Kramer's doublets arising from the total spin and separated in energy by the ZFS. The general form of these equations is

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$$g'_u = g_u \alpha_u(E/D) \quad (1)$$

where  $u = x, y, z$  and the expressions for  $\alpha_u(E/D)$  for  $S = 3/2$  are given in the SI. For  $S = 5/2$  and higher the  $\alpha_u$  factors have to be calculated numerically and plotted in the form of rhombograms<sup>13,14</sup>. The same can be stated in matrix form as  $\mathbf{g}' = \mathbf{gP}$ , where  $\mathbf{P}$  is the diagonal matrix with  $\alpha_u$  coefficients. In this work we extend our previous relations<sup>15</sup> to obtain general formulas for the effective anisotropic exchange and magnetic dipolar interactions within pairs containing  $S = 3/2$  and  $S = 5/2$  ions and, more preliminarily, to  $J = 15/2$  ions such as Dy(III). The form of these interactions makes it easy to see that the expressions are valid for any kind of spin pair and allows us to more accurately study interactions in any magnetic system with more than one spin. In particular, these equations will allow researchers to more accurately measure distances in spin-labeled metalloproteins using the dipolar interaction as a ruler.

## THEORETICAL METHODS

There is a simple theoretical deduction, which will be shown below, of the equations relating the real interspin interactions  $J_{\text{iso}}^{\text{HS}}$ ,  $J_{\text{ani}}^{\text{HS}}$ , and  $\mathbf{D}_{\text{dip}}^{\text{HS}}$  (isotropic and anisotropic exchange and magnetic dipolar interaction, respectively), with the effective interion interactions  $J_{\text{ani}}^{1/2}$  and  $\mathbf{D}_{\text{dip}}^{1/2}$  (the effective isotropic interaction  $J_{\text{iso}}^{1/2}$  can be obtained as 1/3 of the trace of the effective anisotropic interactions). Assuming for simplicity that all matrices involved are coaxial and given the real Hamiltonian for  $S = 3/2$  or  $5/2$  ions

$$\hat{H}^{3/2} = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}}^{\text{HS}} + D \left( (S_z^{\text{HS}})^2 - \frac{S(S+1)}{3} \right) + E \left( (S_x^{\text{HS}})^2 - (S_y^{\text{HS}})^2 \right) \quad (2)$$

with HS meaning high spin; if  $D \gg h\nu$ , each Kramers' doublet can be described by an effective  $S' = 1/2$  spin and the following Zeeman Hamiltonian

$$\hat{H}_Z^{1/2} = \mu_B \mathbf{B}^T \mathbf{g}' \hat{\mathbf{S}}^{1/2} = \mu_B \mathbf{B}^T \mathbf{gP} \hat{\mathbf{S}}^{1/2} \quad (3)$$

The  $\mathbf{P}$  matrix contains the coefficients  $\alpha_u$  relating the real and effective  $\mathbf{g}$  matrices, and it is written explicitly to show that the real  $\hat{\mathbf{S}}^{\text{HS}}$  operator can be replaced by the effective  $\mathbf{P} \hat{\mathbf{S}}^{1/2}$  on its action within each Kramer's doublet. Therefore, in the effective spin-1/2 space of two interacting ions the real-spin operators in the pair spin Hamiltonian

$$\hat{H}_{12} = (\hat{H}_{Z,1} + ZFS_1) + (\hat{H}_{Z,2} + ZFS_2) + (\hat{\mathbf{S}}_1^{\text{HS}})^T \mathbf{D}_{12}^{\text{HS}} (\hat{\mathbf{S}}_2^{\text{HS}})$$

where  $ZFS_{1,2}$  represents the zero-field splitting terms for each center, can be replaced by the effective spin operator as follows (note that the  $ZFS_{1,2}$  terms will now contribute a constant value because of the effective spin-1/2 operators and so can be disregarded)

$$\begin{aligned} \hat{H}_{12} &= \hat{H}_{Z,1} + \hat{H}_{Z,2} + (\mathbf{P}_1 \hat{\mathbf{S}}_1^{1/2})^T \mathbf{D}_{12}^{\text{HS}} (\mathbf{P}_2 \hat{\mathbf{S}}_2^{1/2}) \\ &= \hat{H}_{Z,1} + \hat{H}_{Z,2} + (\hat{\mathbf{S}}_1^{1/2})^T \mathbf{P}_1^T \mathbf{D}_{12}^{\text{HS}} \mathbf{P}_2 (\hat{\mathbf{S}}_2^{1/2}) \\ &= \hat{H}_{Z,1} + \hat{H}_{Z,2} + (\hat{\mathbf{S}}_1^{1/2})^T \mathbf{D}_{12}^{1/2} (\hat{\mathbf{S}}_2^{1/2}) \end{aligned} \quad (4)$$

where  $\hat{H}_{Z,i}$  represents the effective Zeeman interaction for each spin and  $\mathbf{D}_{12}^{\text{HS}}$  and  $\mathbf{D}_{12}^{1/2}$  represent the real and effective interaction between the spins. The effect of multiplication by the  $\mathbf{P}_i$  matrices on the interaction matrix is shown in eq 5 for a general exchange (isotropic plus anisotropic) and dipolar interaction. If one of the spins is a 1/2 spin, then its effective and real  $\mathbf{g}$  matrices will be the same (or its  $\mathbf{P}_i$  matrix will be the unit matrix).

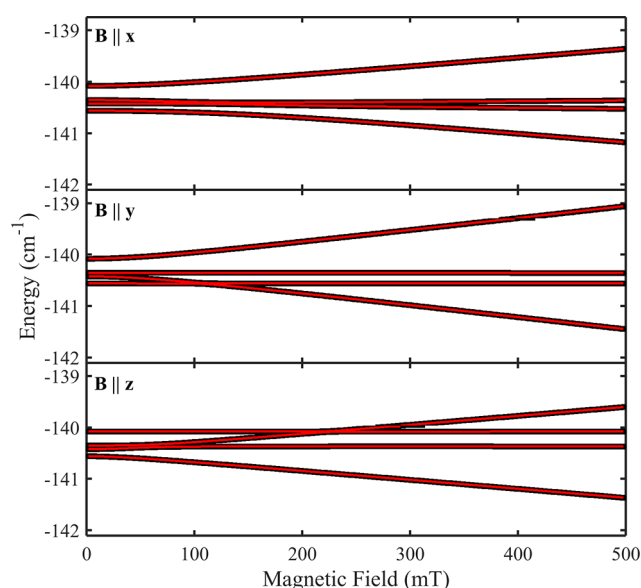
## RESULTS AND DISCUSSION

The equations derived in the SI and in the preceding section allowed us to obtain the following general formulas for the effective anisotropic exchange interaction and the effective magnetic dipolar interaction.

$$\begin{aligned} \mathbf{J}_{\text{ani,full}}^{1/2} &= \mathbf{R}_1 \cdot \begin{pmatrix} g'_{xA} \\ g_{xA} \\ g'_{yA} \\ g_{yA} \\ g'_{yA} \\ g_{yA} \end{pmatrix} \cdot \mathbf{R}_1^T \mathbf{J}_{\text{ani,full}}^{3/2} \cdot \mathbf{R}_2 \cdot \begin{pmatrix} g'_{xB} \\ g_{xB} \\ g'_{yB} \\ g_{yB} \\ g'_{yB} \\ g_{yB} \end{pmatrix} \cdot \mathbf{R}_2^T \\ D_{\text{dip,eff}}^{1/2} &= \mu_B^2 \hbar^2 \frac{\mu_0}{4\pi r^3} (\mathbf{g}'_1 \cdot \mathbf{g}'_2 - 3 \cdot (\mathbf{g}'_1 \cdot \hat{\mathbf{r}})(\hat{\mathbf{r}} \cdot \mathbf{g}'_2)) \end{aligned} \quad (5)$$

where  $\mathbf{R}_{A,B}$  are the column eigenvector matrices of the effective  $\mathbf{g}'$  matrices from sites A and B,  $\hat{\mathbf{r}}$  is the unit vector connecting spins A and B, and all other symbols have the usual meanings. These equations have been derived for cases of high symmetry, in which the  $xyz$  system defined by the ZFS matrix is coincident with the axis system of either the anisotropic or dipolar interaction, but the shape of the equations obtained made us propose, in a heuristic approach, that they are indeed general to any arbitrary mutual orientation of each site's ZFS matrices. The easiest way to prove if this was indeed so was simulation of the energy levels in both the full  $S \otimes S$  space (with  $S = 5/2$  or  $S = 3/2$ ) and the effective  $(S' = 1/2) \otimes (S' = 1/2)$  subspace, choosing arbitrary orientations for the different matrices. Figure 1 shows a simulation of the energy levels of a pair of high spin Co(II) ions with positive ZFS, treated as real  $S = 3/2$  spins and as effective  $S' = 1/2$  spins. The simulation parameters are listed in Table 1.

Equation 5, which is the primary result of this study, is the equivalent of Pilbrow's equations for the interaction between spins, at least one of which is higher than  $S = 1/2$ . The idea of an effective exchange interaction is not at all new,<sup>15,17–20</sup> but previous formulas were limited to special symmetries or either only discussed an effective isotropic exchange or used effective  $\mathbf{g}'$  matrices in dipolar interactions without a theoretical justification. In particular, Lines' important 1971 paper<sup>17</sup> studied the effective exchange interaction between  $S = 3/2$  Co(II) ions in cubic symmetry, arriving to an effective isotropic interaction  $J_{\text{iso}}^{1/2} = (25/9)J_{\text{iso}}^{3/2}$ . Lines' approach has been applied to many studies, but this work is not useful in most systems containing HS Co(II), which are distorted from cubic symmetry, particularly in biological systems. Specifically, the isotropic part of the effective interaction is not 25/9 times larger than the real isotropic interaction. In general, the factor  $\alpha_{\text{iso}}$  in the formula  $J_{\text{iso}}^{1/2} = \alpha_{\text{iso}} J_{\text{iso}}^{\text{HS}}$  depends on the rhombicity factor (E/D), as shown in Table 2, but for a pair of high-spin Co(II) ions this factor equals 3 independently from E/D. The ratios between the isotropic part of the effective exchange and



**Figure 1.** Energy levels of a dimer of  $S = 3/2$  ions and the corresponding dimer of effective  $S' = 1/2$  ions, with the magnetic field in the  $x$ ,  $y$ , and  $z$  directions. Simulation parameters are given in Table 1.

**Table 1. Simulation Parameters for the Pair of High-Spin Co(II) Ions Corresponding to Figure 1**

	ZFS	Euler rotation angles <sup>a</sup>	real $g$ matrix	effective $g'$ matrix	
Co1	$D = 70 \text{ cm}^{-1}$	$\alpha = 30^\circ$	$g_x = 2.5$	4.8791	
	$E/D = 0.016$	$\beta = -40^\circ$	$g_y = 2.5$	5.1190	
		$\gamma = 0^\circ$	$g_z = 2.61$	2.6080	
Co2	$D = 70 \text{ cm}^{-1}$	$\alpha = 50^\circ$	$g_x = 2.4$	4.3875	
	$E/D = 0.056$	$\beta = 50^\circ$	$g_y = 2.4$	5.1901	
		$\gamma = 0^\circ$	$g_z = 2.5$	2.4766	
real interaction (MHz) <sup>b</sup>		effective interaction (MHz) <sup>b</sup>			
3011.3	0	-187.4	7919	1000	6529
0	2884.5	0	826	11506	1030
185.4	0	-6021.1	-5945	-1331	-13960

<sup>a</sup> $D$  tensors and real  $g$  matrices for each Co(II) ion are assumed coincident, and the Euler rotation angles are randomly chosen to illustrate the generality of the model. These angles are used in the same way as described in the documentation of the EasySpin program.<sup>16</sup> <sup>b</sup>Simulated interaction is magnetic dipolar (eq 5), with the Co(II)–Co(II) vector chosen in the common frame  $z$  direction and an interion distance of 3 Å. Interaction matrices are both anisotropic and antisymmetric due to the noncoincidence and anisotropy of the  $g$  and  $g'$  matrices.

174 the real exchange for several possible pairs of Co(II) ( $S = 3/2$ ),  
175 Fe(III) ( $S = 5/2$ ) and Cu(II) ( $S = 1/2$ ) are shown in Table 2,  
176 involving different doublets. Where relevant, the  $xyz$  axes of  
177 each ZFS matrix are considered coincident. There are many  
178 other possibilities, but we consider that inclusion of more of  
179 these would not facilitate understanding.

180 Furthermore, Lines<sup>17</sup> and others<sup>20</sup> formulations followed  
181 from considerations that included crystal field and spin–orbit  
182 terms and therefore required a number of implicit and explicit  
183 approximations and assumptions. The formulas presented in  
184 this work are much more general and arise from the spin  
185 Hamiltonian formalism, with the only assumption that  $|D_{ij}| \gg |$   
186  $J_{ij}|$ , which is not necessarily true for molecular magnets but is

almost always true for metalloproteins or any system with high-  
spin ions further away than 4 to 5 Å.

In the case of the effective dipolar interaction, the result that effective  $g'$  matrices have to be used will make it much easier to interpret and extract distance information from EPR measurements in systems with high-spin ions at large distances. If HS Co(II) or Fe(III) spin labels were developed and used in combination with  $S = 1/2$  spin labels such as nitroxides, then distances up to about three times larger could be determined, depending on the relative orientation of the spin–spin vector and the metal effective  $g'$  matrix. This is due to the relation between effective  $g'$  and real  $g$  values for high-spin Co(II) or Fe(III). Figure S5 shows simulated EPR spectra of M-nitroxide spin pairs ( $M = \text{HS Co(II)}$ ,  $\text{HS Fe(III)}$ , and  $\text{Cu(II)}$ ) with metal–nitroxide distances of 15 Å, considering only the magnetic dipolar interaction. It can be observed that high-spin ions with effective  $g'$  matrices cause a larger splitting of the nitroxide signal. The splitting of the high-field nitroxyl signal in the Fe(III)–nitroxyl pair is  $\sim 2$  times larger than in the case of Cu(II)–nitroxyl. This ratio, of course, depends on the relative orientation between the largest  $g'$  values in the metal and the spin–spin vector, and, in principle, up to three to four times larger splittings could be observed in Fe(III)–nitroxyl or Co(II)–nitroxyl pairs in comparison with Cu(II)– or nitroxyl–nitroxyl pairs. The observed splittings for the Fe(III)–nitroxyl pair are in line with results by Eaton and Eaton on iron(III) porphyrins with attached spin labels.<sup>21,22</sup> Fielding et al. analyzed the magnetic interactions present in this Fe(III)–nitroxyl dimer using a dipolar interaction with the Fe(III) anisotropic  $g$  matrix. However, to the best of our knowledge, neither in this paper nor in other work was a theoretical justification given for the use of this effective dipolar tensor. This work provides that justification.

Given the success of the effective interaction approach for HS Co(II) and Fe(III) ions, as evidenced by the simulations shown in Figure 1 and the SI, it is natural to ask if the model would be useful for highly anisotropic lanthanide ions such as Dy(III) ( $J = 15/2$ ). The discussion and simulations presented in Section 7 of the SI show that if the crystal-field splittings acting on Dy(III) ions in a dimer are large compared with the interion magnetic interaction then the effective interaction provides a very good description of the lower energy levels of the dimer. Because of the extremely large anisotropy of Dy(III) in some situations ( $g'_{xy} \approx 0$ ,  $g'_z \approx 10\text{--}20$ ), some very small deviations occur between the real-spin and effective-spin simulations; but in the direction of  $g'_z$ , where the splitting is largest, these differences are negligible. Because Dy(III) is the most anisotropic lanthanide with the highest  $J$ , it is almost certain that the usefulness of the model presented in this work can be extended to other lanthanide ions.

Finally, we think necessary to discuss covalency effects, which at first sight would seem important for ions with highly anisotropic  $g'$  matrices, because spin delocalization into the ligands will reduce the orbital angular momentum contributions to the total electronic angular momentum. The distributed dipole approximation,<sup>23–27</sup> which is an intermediate between the point-dipole and full quantum-mechanical treatment of the dipolar interaction, assumes nonzero spin populations on the metal ligands and calculates the dipolar interaction as a sum of point-dipole terms in the following way

**Table 2.** Effective  $\alpha_{\text{iso}}$  Factor Relating the Isotropic Part of the Effective and Real Exchange Interactions as a Function of Rhombicity for Several Types of Spin Pairs<sup>a</sup>

E/D	3/2,3/2 <sup>b</sup>	3/2,1/2	5/2,5/2 <sup>c</sup>	5/2,1/2 <sup>c</sup>	5/2,3/2 <sup>d</sup>
	( $\pm 1/2, \pm 1/2$ ) ( $\pm 3/2, \pm 3/2$ )	( $\pm 1/2, \pm 1/2$ ) ( $\pm 3/2, \pm 1/2$ )	( $\pm 1/2, \pm 1/2$ ) ( $\pm 3/2, \pm 3/2$ )	( $\pm 1/2, \pm 1/2$ ) ( $\pm 3/2, \pm 1/2$ )	( $\pm 1/2, \pm 1/2$ ) ( $\pm 3/2, \pm 1/2$ )
0	3	1.666	6.333	2.516	4.333
	3	1.000	3.000	1.732	1.000
0.05	3	1.661	6.332	2.516	4.295
	3	1.097	3.068	1.752	1.743
0.10	3	1.647	6.631	2.575	4.325
	3	1.187	3.422	1.849	2.326
0.15	3	1.624	7.053	2.656	4.395
	3	1.269	3.876	1.969	2.752
0.20	3	1.593	7.453	2.730	4.476
	3	1.341	4.282	2.069	3.028
0.25	3	1.557	7.719	2.778	4.542
	3	1.404	4.531	2.129	3.165
0.30	3	1.516	7.777	2.789	4.569
	3	1.457	4.552	2.133	3.174
1/3	3	1.488	7.678	2.771	4.556
	3	1.488	4.419	2.102	3.115

<sup>a</sup>Parentheses indicate the considered doublets. <sup>b</sup>High-spin Co(II) ( $S = 3/2$ ) only shows signals arising from the lower energy doublet. If  $D > 0$ , this is the  $M_S = \pm 1/2$ , and if  $D < 0$ , it is the  $M_S = \pm 3/2$ , which is rarely observed. Nevertheless, the  $M_S = \pm 1/2$  option is given above the  $M_S = \pm 3/2$  case. <sup>c</sup>High-spin Fe(III) ( $S = 5/2$ ) usually shows EPR signals arising from the lower  $M_S = \pm 1/2$  doublet and the middle  $M_S = \pm 3/2$  doublet, which have different  $g'$  values. Both options are given, the  $M_S = \pm 3/2$  case below the  $M_S = \pm 1/2$  case. <sup>d</sup>The top possibility is the Co(II)  $M_S = \pm 1/2$ , Fe(III)  $M_S = \pm 1/2$  case and the bottom possibility is the Co(II)  $M_S = \pm 1/2$ , Fe(III)  $M_S = \pm 3/2$  case.

$$\mathbf{D}_{\text{total}} = \sum_{i=1, j=1}^{N_i, N_j} \rho_i \rho_j \mathbf{D}_{ij}(\mathbf{g}_i, \mathbf{g}_j, \mathbf{r}_{ij}) \quad (6)$$

where  $i$  ( $j$ ) runs over the atoms in which there is a spin population  $\rho_i$  ( $\rho_j$ ) due to electron 1 (2).  $\mathbf{r}_{ij}$  is the distance between the corresponding nuclei. One problem with this equation occurs when there are bridging atoms that have spin populations arising from both paramagnetic centers. In this case,  $r_{ij} = 0$  and the dipolar interaction diverges. This is an artifact caused by the semiclassical treatment and could be resolved by an artificial splitting of the spin population of the bridging atom into near but not coincident points. We have previously obtained<sup>27</sup> metal and ligand spin populations  $\rho_i$  in a copper(II) dimer with Cu–Cu separation of 3.34 Å using the distributed dipole approximation and density functional calculations and found for the metals  $\rho_{\text{Cu}} \approx 0.65$  and for the ligands  $\rho_{\text{N,O}} \approx 0.6$  to 0.10. This is a large amount of covalency, and indeed we found that the point dipole approximation was not nearly satisfactory, while the distributed dipole approximation was much better. Density functional theory calculations on a nearly isostructural high-spin Co(II) dimer (unpublished results) show a relatively higher spin-population on the Co(II) atoms ( $\rho_{\text{Co}} \approx 2.7$ ). When the spin  $S = 3/2$  is projected into an  $S = 1/2$  pseudospin, the effective spin population of the Co(II) ions becomes  $\rho'_{\text{Co}} \approx 0.9$ . For the relatively long Co(II)–Co(II) distances for which the interaction is dominated by a dipolar contribution, this relatively large effective spin population should make the point-dipole approximation more valid. However, given the vast diversity of possible situations and varying structural characteristics, simple rules-of-thumb should wait until enough weakly coupled dimeric systems containing high-spin ions are characterized by techniques such as single-crystal or high-field/frequency EPR.

## CONCLUSIONS

We have developed a general set of formulas for analyzing magnetic interactions of exchange and dipolar origin in systems including high-spin ions that can be treated as effective  $S' = 1/2$  spins, including HS Co(II), Fe(III), and Dy(III). The presented formulas do not rely on explicit crystal-field arguments and are easy to apply, given that the effective  $g'$  matrices can be determined or estimated for the individual sites. These formulas provide a bridge between standard frequency (X-band, Q-band) EPR experimental results, usually treated with effective spin-1/2 Hamiltonians, and bulk magnetic measurements, which are usually treated as real-spin systems. We hope that these formulas prove useful to researchers studying magnetic interactions in (bio)inorganic systems containing high-spin ions.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b11908.

Derivation of empirical formulas for the effective  $g$  values of high spin Fe(III) ions; derivations of formulas for the effective magnetic interactions between high-spin ions treated as 1/2 pseudospins, simulations of some spin pairs, and analysis of effective interactions in Dy(III) pairs. (PDF)

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## 313 Notes

314 The author declares no competing financial interest.

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