

Many-Body Models for Molecular Nanomagnets

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We present a flexible and effective *ab initio* scheme to build many-body models for molecular nanomagnets, and to calculate magnetic exchange couplings and zero-field splittings. It is based on using localized Foster-Boys orbitals as a one-electron basis. We apply this scheme to three paradigmatic systems, the antiferromagnetic rings Cr₈ and Cr₇Ni, and the single-molecule magnet Fe₄. In all cases we identify the essential magnetic interactions and find excellent agreement with experiments.

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Clusters made of a finite number of interacting spins are ideal test beds to investigate fundamental issues in quantum mechanics. One of the first physical realizations are molecular nanomagnets (MNMs), molecules containing a core of *d* or *f* ions, whose spins are coupled by magnetic interactions; MNMs form crystals which behave like an ensemble of identical and almost noninteracting magnetic units. During the last years sophisticated experiments and targeted research activities have unveiled a variety of fundamental quantum phenomena and potential technological applications of MNMs [1–7]. The two most promising classes have been identified in the single-molecule magnets (SMMs), like Mn₁₂ [1], Fe₈ [1] and Fe₄ [1,8,9], and the antiferromagnetic rings (AFRs), like Cr₈ [10,11], shown in Fig. 1, Cr₇Ni [6,12,13] and Fe₆ [1]. While SMMs have opened the perspective of storing information in single molecules and building high-density magnetic memories, AFRs are of great interest in the field of quantum information processing [6,7,13–15].

At the synthetic level, thanks to the huge progresses made in the last years in coordination chemistry, it is now possible to reach a high degree of control on the molecular structure and on the topology of magnetic interactions. At the theoretical level, one of the main obstacles to further progress remains the lack of a flexible and systematic approach to build *ab initio* system-specific models for the magnetic interactions; such models should describe on the same footing chemistry and many-body effects within the partially filled *d* or *f* shells of the magnetic ions.

MNMs are typically described through Heisenberg-like spin Hamiltonians. If the form of the spin Hamiltonian is known, the magnetic couplings can be in principle extracted from total-energy density-functional theory calculations for different spin configurations [16–19]. This approach can become unpractical if many parameters have to be determined, as, e.g., in heterometallic compounds or anisotropic SMMs; furthermore, subtle interactions, which could greatly influence, e.g., the relaxation dynamics, can

be easily overlooked. An alternative consists in computing the couplings via energy variations at small spin rotations [20]. However, at a more fundamental level, a common problem of all these approaches is that the most used density-functional theory functionals (the local-density approximation (LDA) and its simple extensions), do not properly describe strong correlation effects in open *d* or *f* shells, while LDA + *U* or hybrid functionals include them only at the static mean-field level. Recently, it has been suggested that Hubbard-like models could be more appropriate [21,22], but an efficient and flexible scheme to calculate the parameters of such models *ab initio*, no

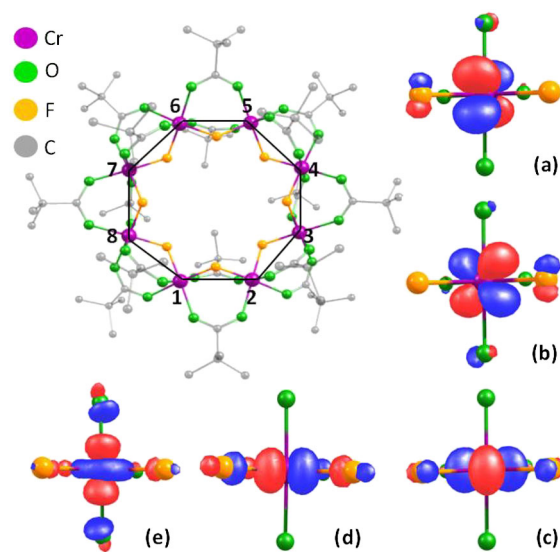


FIG. 1 (color online). The Cr₈ antiferromagnetic ring and its Cr *d* crystal-field orbitals for site 1, in order from (a) to (e) of increasing energy. Red (blue) orbital lobes are positive (negative). The covalent *p* tails on the neighboring ligands carry the information on the molecular structure and are crucial for the magnetic exchange couplings. We define *z* as the axis perpendicular to the ring and pointing outwards. All Cr sites are approximately equivalent. H atoms are not shown for clarity.

matter the complexity of the system, has not been implemented so far.

In this Letter we show that this can be achieved by using localized Foster-Boys orbitals [23] as a one-electron basis to construct molecule-specific generalized Hubbard models. We use the constrained local-density approximation (cLDA) scheme [24] to calculate the screened Coulomb interactions in such a Foster-Boys basis. We obtain the spin Hamiltonians systematically by using a canonical transformation [25] to eliminate charge fluctuations, without any *a priori* assumption on the form of the final spin Hamiltonian. We implement this scheme in the NWChem quantum-chemistry code [26], and apply it to three prototype molecules, representative of the two main classes of MNMs: the AFRs Cr₈ (Fig. 1) and Cr₇Ni and the SMM Fe₄ (Fig. 2). These systems have been extensively investigated experimentally [8–10,12,27] and the magnetic exchange couplings are now well known. In all cases, we find excellent agreement with experiments, and identify the microscopic mechanisms that lead to the empirical spin models commonly adopted to describe them.

The procedure we adopt is the following. First we perform LDA calculations for the experimental structures reported in Refs. [28]; in this step we use as basis a triple-zeta valence set of Gaussians. Next, we identify the transition-metal *d*-like molecular orbitals; by means of Foster-Boys localization [23], we construct a set of localized orbitals, which are centered on the transition-metal ions and span such *d*-like states; using these orbitals as basis we build the corresponding generalized Hubbard model

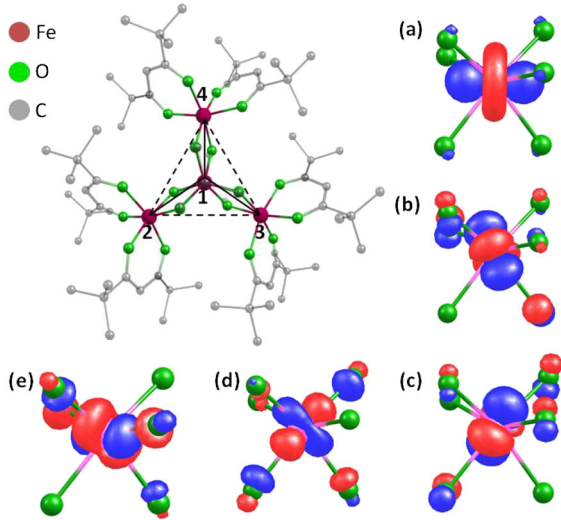


FIG. 2 (color online). Structure of Fe₄ and Fe *d* crystal-field orbitals localized on the central Fe (D_3 symmetry): The a_1 singlet (a), and the two e doublets (b), (c) and (d), (e), in order of increasing energy. Heisenberg couplings: $\Gamma^{1,2}$ (full line) and $\Gamma^{2,3}$ (dashed line). We define z as the axis perpendicular to the triangle, and pointing outwards. H atoms are not shown for clarity.

$$H = -\sum_{ii'\sigma} \sum_{mm'} t_{m,m'}^{i,i'} c_{im\sigma}^\dagger c_{i'm'\sigma} + \frac{1}{2} \sum_{ii'\sigma\sigma'} \sum_{mm'pp'} U_{mpm'p'}^{i,i'} c_{im\sigma}^\dagger c_{ip\sigma'}^\dagger c_{i'p'\sigma'} c_{i'm'\sigma} + \sum_i \lambda_i \mathbf{S}_i \cdot \mathbf{L}_i - H_{\text{DC}}. \quad (1)$$

Here $c_{im\sigma}^\dagger$ ($c_{im\sigma}$) creates (annihilates) an electron with spin σ in the Boys orbital m at site i . The parameters $t_{m,m'}^{i,i'}$ are the hopping integrals ($i \neq i'$) or the crystal-field matrix ($i = i'$), while $U_{mpm'p'}^{i,i'}$ are the screened Coulomb integrals (Table I). The term H_{DC} is the double counting correction, which removes the part of the Coulomb interaction already included and well accounted for in the LDA; λ_i is the spin-orbit coupling. The results presented in this work are obtained using the rotational invariant form of the Coulomb vertex, including spin-flip and pair hopping terms but (for simplicity) no Coulomb anisotropy; thus all Coulomb parameters can be expressed as a function of the averaged screened Coulomb couplings $U^{i,i}$ and $J^{i,i}$ [29]. We determine the latter by using the cLDA [24] approach in the Foster-Boys basis, keeping the basis frozen in the self-consistency loop. For H_{DC} we adopt the common [30] expression $H_{\text{DC}} = \frac{1}{2} \sum_i U^{i,i} n_d^i (n_d^i - 1) - \frac{1}{4} \sum_i J^{i,i} n_d^i (\frac{1}{2} n_d^i - 1)$, where n_d^i is the number of *d* electrons at site i . For homonuclear systems H_{DC} amounts to a shift

TABLE I. Top: Crystal-field energy levels and hopping integrals (LDA) for Cr₈ (in eV). The latter are given in the basis of crystal-field orbitals, and for sites $i = 1$ and $i' = 2$ in Fig. 1. The energy of the Fermi level is set to zero. Bottom: Screened Coulomb integrals $U^{i,i}$ and $J^{i,i}$ (in eV) obtained via cLDA and spin-orbit couplings λ_i (in meV). Sites i are defined in Figs. 1 and 2.

Cr ₈							
ε_n	$ n\rangle$	$t_{n,n'}^{i,i+1}$					
		$ n\rangle$	$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$
$ 1\rangle$	-0.071	$ 1\rangle$	-0.231	0.041	-0.001	0.056	0.028
$ 2\rangle$	-0.061	$ 2\rangle$	-0.057	0.085	-0.061	-0.019	0.010
$ 3\rangle$	0.040	$ 3\rangle$	0.011	0.021	0.033	-0.154	-0.160
$ 4\rangle$	2.021	$ 4\rangle$	-0.092	-0.128	-0.171	0.094	0.164
$ 5\rangle$	2.070	$ 5\rangle$	0.001	-0.053	-0.011	0.114	-0.033
Cr ₈ Fe ₄ Cr ₇ Ni							
	$U^{1,1}$	5.98	5.22	6.32 (Ni)			
	$U^{2,2}$	5.98	5.03	5.98 (Cr)			
	$J^{1,1}$	0.26	0.24	0.21 (Ni)			
	$J^{2,2}$	0.26	0.22	0.26 (Cr)			
	λ_1	16.5	34.3	33.5 (Ni)			
	λ_2	16.5	37.0	16.5 (Cr)			

of the d levels and can be incorporated into the chemical potential; in the case of Cr_7Ni , instead, the shift due to H_{DC} has to be taken into account explicitly. Finally, we extract the spin-orbit coupling λ_i by comparing the one-electron part of Hamiltonian (1) obtained with and without spin-orbit interaction. Once we have obtained the parameters of the Hubbard model (Table I), by using a canonical transformation, we eliminate charge fluctuations and derive the corresponding low-energy spin model. In this step, it is convenient to work in the basis of crystal-field states, obtained by diagonalizing the on-site matrix $t_{m,m'}^{i,i}$; we denote their energies ε_n with $\varepsilon_n \leq \varepsilon_{n+1}$. The crystal-field states are shown in Fig. 1 for Cr_8 and Fig. 2 for Fe_4 . At all sites but the central Fe in Fe_4 , the environment of the magnetic ion is approximately octahedral; thus the crystal-field orbitals split into a lower energy t_{2g} -like quasitriplet and a 1–2 eV higher energy e_g -like quasideublet. The central Fe site of Fe_4 has D_3 symmetry; its crystal-field levels (Fig. 2) split into a a_1 ground state and two excited e doublets, ~ 0.6 eV and ~ 1.7 eV above.

For all systems analyzed, we find that the essential spin interactions are described by the spin Hamiltonian

$$H = \frac{1}{2} \sum_{ii'} \Gamma^{i,i'} \mathbf{S}_i \cdot \mathbf{S}_{i'} + \sum_i D^i \left[S_{iz}^2 - \frac{1}{3} S_i(S_i + 1) \right], \quad (2)$$

where $\Gamma^{i,i'}$ are the isotropic magnetic couplings and D^i a zero-field splitting (ZFS) parameter, which is negative if z is an easy axis; the z direction is defined as the axis perpendicular to the ring (Fig. 1) or to the triangle (Fig. 2). The coupling $\Gamma^{i,i'} = \Gamma_{\text{CE}}^{i,i'} + \Gamma_{\text{SE}}^{i,i'}$ is the sum of a ferromagnetic (FM) screened Coulomb exchange term, $\Gamma_{\text{CE}}^{i,i'}$, which we obtain directly via cLDA calculations, and a superexchange term $\Gamma_{\text{SE}}^{i,i'}$, which can be FM or anti-ferromagnetic (AFM), and it is obtained by integrating out charge fluctuations via the canonical transformation.

In Fig. 3 we show the calculated $\Gamma_{\text{SE}}^{i,i'}$ for Cr_8 ($3d^3$, $S = 3/2$) as a function of $U = U^{i,i}$ and $J = J^{i,i}$. The figure can be understood from the analytical expression of $\Gamma_{\text{SE}}^{i,i'}$ in the limit in which only density-density Coulomb interactions and leading order terms are retained,

$$\begin{aligned} \Gamma_{\text{SE}}^{i,i'} \sim & \frac{2}{9} \sum_{n'=1}^3 \sum_{n=4}^5 \frac{|t_{n',n}^{i,i'}|^2 + |t_{n,n'}^{i,i'}|^2}{U + \varepsilon_n - \varepsilon_{n'}} \\ & + \frac{2}{9} \sum_{n'=1}^3 \sum_{n=1}^3 \frac{|t_{n',n}^{i,i'}|^2}{U + 2J + \varepsilon_n - \varepsilon_{n'}} \\ & - \frac{2}{9} \sum_{n'=1}^3 \sum_{n=4}^5 \frac{|t_{n',n}^{i,i'}|^2 + |t_{n,n'}^{i,i'}|^2}{U - 3J + \varepsilon_n - \varepsilon_{n'}}. \end{aligned} \quad (3)$$

Equation (3) shows the competition between the first two terms, which yields a positive, i.e., AFM contribution and the FM third term, arising from excitations to empty states

(see the Supplemental Material [31]). For realistic parameters, $\Gamma_{\text{SE}}^{i,i'}$ is small and AFM.

The ZFS term D^i in Eq. (2) originates from the combined action of crystal-field and spin-orbit interactions. In the case of Cr_8 it is given by

$$\begin{aligned} D^i = & \frac{1}{2} \sum_m \frac{\langle \frac{3}{2}, \pm \frac{3}{2} | H_{\text{SO}} | m \rangle \langle m | H_{\text{SO}} | \frac{3}{2}, \pm \frac{3}{2} \rangle}{E_{3/2} - E_m} \\ & - \frac{1}{2} \sum_m \frac{\langle \frac{3}{2}, \pm \frac{1}{2} | H_{\text{SO}} | m \rangle \langle m | H_{\text{SO}} | \frac{3}{2}, \pm \frac{1}{2} \rangle}{E_{3/2} - E_m}. \end{aligned} \quad (4)$$

Here $|S, M\rangle$ are many-electron states in the $S = 3/2$ ground multiplet with energy $E_{3/2}$, while $|m\rangle$ are all the excited multiplets connected to $|S, M\rangle$ by the spin-orbit interaction H_{SO} , and have energy E_m . Our calculations yield the full ZFS tensor, and thus we can identify the easy magnetization axis, which in general is site-dependent. Remarkably, we find that the molecular global z axis (see above) is a nearly-easy axis for all sites.

In the next paragraphs we discuss the results of our calculations (Table II), in comparison with experiments. Let us start with the AFR Cr_8 . Figure 3 shows that, for realistic U and J values, the superexchange coupling $\Gamma_{\text{SE}}^{i,i+1}$ is AFM and of the order of few meV. By using the value of U and J obtained in cLDA (Table II) we obtain $\Gamma_{\text{SE}}^{i,i+1} = 1.99$ meV. We find that the ferromagnetic direct Coulomb exchange is $\Gamma_{\text{CE}}^{i,i+1} = -0.34$ meV. Hence, the total Heisenberg exchange constant is $\Gamma^{i,i+1} = 1.65$ meV, AFM and in excellent agreement with experiments [10]. In addition, we find that the next-nearest neighbors exchange interaction is tiny ($\Gamma^{i,i+2} \approx 10^{-2} \Gamma^{i,i+1}$); this explains why all experimental data can be interpreted on the basis of a nearest-neighbor spin Hamiltonian. Beside the dominant isotropic exchange coupling, we also find a sizable single-ion ZFS term. Our calculations yield a significant easy-axis anisotropy in the z direction ($D^i < 0$); nonaxial terms are an order of magnitude smaller than D^i ,

TABLE II. Top: Calculated superexchange couplings. Bottom: Calculated total magnetic couplings [32] and zero-field splitting (Th) versus experiments (Exp). Sites $i = 1, 2, 3$ are defined in Fig. 1 and 2. In Cr_7Ni the Ni ion is on site 1 of Fig. 1. All numbers are in meV.

	Cr ₈		Fe ₄		Cr ₇ Ni	
$\Gamma_{\text{SE}}^{1,2}$	1.99		3.25		2.10	
$\Gamma_{\text{SE}}^{2,3}$	1.99		0.15		1.99	
	Th	Exp [10]	Th	Exp [8]	Th	Exp [12]
$\Gamma^{1,2}$	1.65	1.46	2.45	2.05	1.75	1.70
$\Gamma^{2,3}$	1.65	1.46	-0.08	-0.09	1.65	1.46
D^1	-0.06	-0.03	-0.03		-0.48	-0.35
D^2	-0.06	-0.03	-0.06		-0.06	-0.03

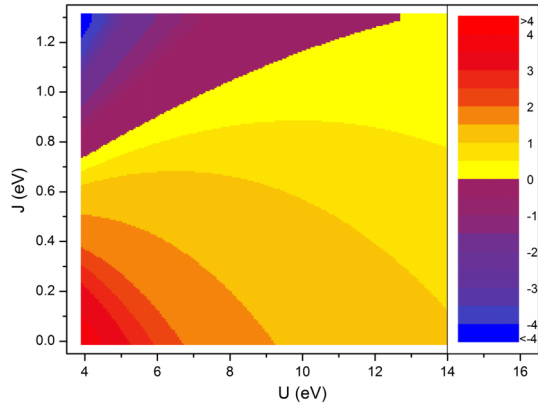


FIG. 3 (color online). Cr_8 : Calculated superexchange coupling (in meV) between nearest neighbors [32], $\Gamma_{\text{SE}}^{i,i+1}$, as a function of the Coulomb parameters J and U . Calculations are performed using the rotationally invariant Coulomb interaction. The cLDA values of the screened Coulomb integrals are $U \sim 6$ eV and $J \sim 0.26$ eV. Around these values $\Gamma_{\text{SE}}^{i,i+1} > 0$ (AFM).

in line with experiments. The calculated D^i is twice the value extracted from inelastic neutron scattering data, a remarkably good agreement given the small value of D^i .

Next we consider the SMM Fe_4 (Fig. 2). This molecule has D_3 symmetry; three Fe^{3+} ions ($3d^5$, $S = 5/2$) are located at the vertices of an equilateral triangle, and the fourth is at its center [9]. We find an AFM isotropic magnetic coupling between the central and external ions ($\Gamma^{1,2}$) and a small FM interaction between the external ions ($\Gamma^{2,3}$), in excellent agreement with the values determined from experiments [8]. We find that the superexchange term is small for the external ions, and thus the FM Coulomb exchange dominates. Finally, we calculate the ZFS tensor and find again a nearly easy-axis anisotropy along z . Our findings for D^i differ of less than a factor 1.5 from the experimental results [33].

As a last case we consider Cr_7Ni , a heteronuclear AFR that can be obtained from Cr_8 by replacing a Cr^{3+} ion with a Ni^{2+} ($3d^8$, $S = 1$). This system is theoretically the most challenging, because two different types of ion (Cr^{3+} and Ni^{2+}) are present. Again, we reproduce well all experimental results. We find that the total Cr-Ni isotropic coupling is AFM, $\Gamma^{1,2} = 1.75$ meV, while the Cr-Cr coupling $\Gamma^{2,2}$ is slightly smaller and close to the value obtained for Cr_8 . The ZFS parameters obtained for Ni^{2+} ion [34] are again negative in sign (easy-axis anisotropy) and much larger than those of Cr^{3+} , in agreement with neutron spectroscopy results [12].

In conclusion, we present an *ab initio* approach to calculate the terms of the spin Hamiltonians for molecular nanomagnets. It is based on the construction of many-body Hubbard-like models, using Foster-Boys orbitals as a one-electron basis [36]. We show that this scheme works remarkably well for MNMs. For all systems considered, our results are closer to the experimental finding than those

obtained by total-energy spin-configurations calculations based on the B3LYP functional [18]. Differently than spin-configurations based approaches, our method allows us to determine the spin models without *a priori* assumptions on the form and the range of the Hamiltonian; furthermore, since it yields the parameters of the Hubbard model, it works also when charge fluctuations are sizable and the spin is not well defined, like for molecules with metal-metal bonds [38], or when electrons are less localized, such as in $4d$ and $5d$ systems, and can be used to calculate spectral functions. This scheme is flexible, its complexity does not increase when the symmetry is low, and it does not rely on the B3LYP or LDA + U approximation to correlation effects. It could become essential for modeling MNMs whose spin Hamiltonian contains many anisotropic terms, in particular if the principal-axis directions and relative magnitude cannot be inferred simply by inspecting the molecular structure, as is often the case for Co or f -electron systems. Finally, the many-body models for small MNMs can still be exactly solvable, allowing us to test approximations often adopted but impossible to check in bulk correlated systems. Thus, we believe that our approach could become the method of choice for exploring fundamental issues and testing approximations, and for identifying and designing new molecules for quantum devices.

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- [30] For a pedagogical derivation see *The LDA + DMFT Approach to Strongly Correlated Materials*, edited by E. Pavarini, E. Koch, D. Vollhardt, and A. Lichtenstein, Reihe Modeling and Simulation Vol. 1 (Verlag des Forschungszentrum Jülich, Jülich, 2011), Chap. 6.
- [31] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.110.157204> for more details on the derivation of spin models from Hubbard models.
- [32] In Cr₈ sites are only approximatively equivalent; the site variation of the exchange parameters is however small ($\sim 4\%$ for $\Gamma^{1,2}$ and $\sim 15\%$ for D^i), and therefore we give the average values.
- [33] Neutron spectroscopy data on the Fe₄ SMM have been interpreted by an effective Hamiltonian for the entire molecule describing the splitting of the $S = 5$ ground manifold. The dominant term is given by $D_{S=5}[S_z^2 - \frac{1}{3}S(S+1)]$, where $D_{S=5} = -55.8$ μeV . We have calculated D using the microscopic D^i parameter in Table II and find $D_{S=5} = -39$ μeV . It should be noted that in the calculation of D we added also the (small) magnetostatic dipole-dipole interaction contribution evaluated in the point-dipole approximation. It amounts to -4.5 μeV .
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