

Description of molecular nanomagnets by the multiorbital Hubbard model with correlated hopping

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We present a microscopic description of molecular magnets by the multiorbital Hubbard model, which includes the correlated hopping term, i.e., the dependence of the electron hopping amplitude between orbitals on the degree of their occupancy. In the limit of large Coulomb on-site interaction, we derive the spin Hamiltonian using the perturbation theory. We determine the magnetic coupling constant between two ions in two different ways: (a) from the expression obtained in the perturbation calculus and (b) from the analysis of distances between the lowest levels of the energy spectrum obtained by diagonalization of the multiorbital Hubbard model. The procedure we use can be applied to various nanomagnets, but we perform the final calculations for the molecular ring Cr_8 . We show that the correlated hopping can reduce the antiferromagnetic exchange between ions, which is essential for a proper description of Cr_8 .

DOI: [10.1103/PhysRevB.104.014431](https://doi.org/10.1103/PhysRevB.104.014431)**I. INTRODUCTION**

Molecular nanomagnets (MNMs) are molecules containing a core of a finite number of d or f ions whose spins are magnetically coupled. These systems are becoming more and more popular due to their potential use in the construction of, among other things, quantum computers and high-performance magnetic memory [1–3].

In the theoretical studies of MNMs, a key issue is the calculation of the coupling parameters between magnetic ions. This is quite a difficult task due to the presence of unfilled d or f shells and dynamical electron correlations, which can be described by Hubbard-type models. However, it turns out that typical spectra of low-energy excitations of MNMs determined experimentally correspond (approximately) to the excitation spectra obtained for models of localized spins with dominant isotropic Heisenberg-type coupling [4]. For this reason, the efforts of many researchers have been directed towards determining the exchange coupling constants in a system-appropriate version of the Heisenberg model. The calculations are usually performed with methods based on the density functional theory (DFT), which enables determination from first principles of various microscopic parameters for specific materials [4–7]. In fact, there are many variants of the DFT-based method, and the literature on this subject is extensive (see, for example, Refs. [5,8–13]). However, in some cases the DFT-based methods do not give satisfactory results. For example, in some *chromium-based rings* the excitation energies derived from the DFT calculations substantially outweigh values measured in experiments [14,15].

In this case, the problem with finding the correct value of the exchange parameter seems to arise from the difficulty in determining the eigenstates of the Heisenberg model.

Indeed, the presence of spin-flipping terms in the Heisenberg model ensures that the fixed spin configurations (except the ferromagnetic one) are not eigenstates of the Heisenberg Hamiltonian; therefore, their energies are not fixed. Consequently, calculations in which the exchange parameter is determined on the basis of the energy difference of states with fixed spin configurations (e.g., the ferromagnetic and the Néel-type antiferromagnetic configuration) do not lead to the correct results. However, quite recently, it was reported that the magnetic couplings calculated using the symmetry-broken version of DFT [16] are close to those deduced from the experimental data [17].

In general, the problem with obtaining correct magnetic coupling values by DFT-based methods stems from the lack of consideration of electron dynamics and the resulting electron correlations in these methods. A possible remedy to this problem was proposed, e.g., in [8], where the LDA++ method (a scheme for first-principles calculations of the electronic structure with the local correlation effects being included), which “deals with the thermodynamic potential as a functional of Green function rather than electron density,” was presented. An extension of this approach referred to as the DFT + Dynamical Mean Field Theory (DMFT) method is presented in [18].

In fact, the problem of electron dynamics and correlation is one of the central issues of condensed-matter theory, and we will not discuss it further here. For more information on the advantages and limitations of different variants of the DFT method used in the calculation of the exchange constants of different MNMs, see, e.g., Refs. [19,20]. The authors of those papers also proposed describing MNMs using the multiorbital Hubbard model (HM) combined with DFT calculations [19,20]. In their approach, which they named the DFT + MB method (where MB stands for many body), they first determined the microscopic parameters of the multiorbital HM, and only then did they calculate the exchange constant using the second-order perturbation theory.

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The DFT + MB method seems to be universal because, starting from the multiorbital HM, it takes into account the most important microscopic processes affecting the value of the exchange constant in the effective spin model, including the dynamical electron correlations [18]. The correctness of this method seems to be confirmed by the results of the calculation of the exchange constants for several MNMs, which are given in [19].

For example, for the Cr₈ ring, the exchange constant $\Gamma = 1.65$ meV appeared to be substantially lower than 3.5 meV obtained from previous DFT calculations. However, this value is still clearly greater than predicted from the experiments $\Gamma = 1.46$ meV [17] and also greater than that obtained from the DFT calculations reported in [16].

To explain this discrepancy, here we extend the description of the system by including in the Hamiltonian the *correlated hopping* (CH) term [21,22] (also known as *correlated hybridization* [23]), in which the amplitudes of the electron hopping between the orbitals depend on their occupancies. More specifically, higher occupancies correspond to lower amplitudes. The reduction of the amplitude results from the fact that the hopping of an electron between two orbitals is hindered by the presence of another electron with opposite spin at the initial or final orbital. Obviously, it leads to a reduction of the hopping amplitude between orbitals if the sum of their occupancies is larger than 1 and, consequently, to a reduction in the antiferromagnetic exchange constant. In fact, CH has already been considered in the earlier works [24].

In real materials CH is always present, but its effect on the physical properties of a given system are not always known because it is rarely taken into account in theoretical descriptions. The reason is that the magnitude of the part of the Coulomb interaction associated with CH is usually much smaller than the main part, which corresponds to the interaction between electrons located on the same orbital with opposite spins. At the same time, however, many authors admit that in spite of its relatively small strength it may play an essential role in the correct description of some systems [21–30]. For example, Ref. [21] suggested that CH “may be essential for the complete understanding of the metal-insulator transition in V_{2-y}O₃ and Ca_{1-x}Sr_xVO₃,” while Ref. [23] demonstrated that CH “may possibly provide a means to significant spin polarization of currents through transition-metal based molecular transistors in modest magnetic fields” and that matrix elements resulting from CH “could significantly change the parameters in effective single-band models for transition-metal oxides.”

In the case of 3d electrons in transition metals, Hubbard has already estimated the different contributions of the Coulomb interaction [31]. Then other authors also estimated these parameters for various materials [21,23,27–29]. These estimates suggest that the correlated and direct hopping amplitudes have comparable magnitude, but typically, the ratio of the former to the latter is less than 0.4.

In this contribution, we investigate the effect of CH on the value of the magnetic coupling constant between Cr ions in the molecular ring Cr₈. Here we focus on Cr₈ because for this system we found data relevant to our calculations, but we suppose our considerations can be applied to other molecular nanomagnets as well.

Taking advantage of the fact that the hopping amplitudes are much smaller than the on-site Coulomb couplings, we first constructed the effective spin Hamiltonian using perturbation theory. In this way we obtained the Heisenberg model with the exchange constant equal to Γ . Then we diagonalized the Hamiltonian (1) for the system of two Cr ions, and based on the analysis of the obtained exact energy spectrum, we deduced another value Γ^* for the exchange constant, which turned out to be slightly greater than Γ .

The perturbative calculus for the multiorbital HM was also applied in Ref. [19], but CH was not considered there in constructing the effective Hamiltonian and was also not included in our earlier comparative analysis of the multiorbital HM and the Heisenberg model [32].

The remainder of this paper is organized as follows. In Sec. II we present the model. In Sec. III we present the exact solution for a single ion, and in Sec. IV we give our main results regarding the interaction between two ions. Section V contains a brief summary and conclusions.

II. MULTIORBITAL HM WITH CORRELATED HOPPING

The multiorbital HM with CH H_{HMcor} that we use here has the following form:

$$H_{HMcor} = H_0 + H_1, \quad (1)$$

with the single-ion part

$$\begin{aligned} H_0 = & U \sum_{im} n_{im\downarrow} n_{im\uparrow} \\ & + \frac{1}{2} \sum_{i,m \neq m',\sigma} [U' n_{im\sigma} n_{im'\bar{\sigma}} + U'' n_{im\sigma} n_{im'\sigma}] \\ & + \frac{1}{2} \sum_{i,m \neq m',\sigma} [J c_{im\sigma}^\dagger c_{im'\bar{\sigma}}^\dagger c_{im\bar{\sigma}} c_{im'\sigma} + J c_{im\sigma}^\dagger c_{im'\sigma}^\dagger c_{im'\bar{\sigma}} c_{im\bar{\sigma}}] \end{aligned}$$

and the intersite hopping term

$$H_1 = \sum_{\substack{i \neq j \\ m, m', \sigma}} t_{mm'}^{ij} [1 - a(n_{im} + n_{jm'} - 1)] c_{im\sigma}^\dagger c_{jm'\sigma}.$$

In the above formulas i and j denote nearest-neighbor sites, m, m' label orbitals, $\sigma, \bar{\sigma}$ label spins of electrons ($\bar{\sigma} = -\sigma$), $c_{im\sigma}^\dagger$ ($c_{im\sigma}$) denotes the creation (annihilation) operator of an electron, $n_{im\sigma} = c_{im\sigma}^\dagger c_{im\sigma}$ is the occupation number, and $n_{im} = n_{im\downarrow} + n_{im\uparrow}$. U, U' , and U'' describe the Coulomb-type on-site interactions between two electrons: U describes electrons on the same orbital, and U' (U'') describes electrons on different orbitals with opposite (parallel) spins. J represents the on-site exchange coupling resulting from the first Hund's rule. Here we adopt the following relations between parameters of the model: $U' = U - 2J$ and $U'' = U - 3J$. They result from the requirements of rotational symmetry [33]. The parameter $t_{mm'}^{ij}$ is the hopping amplitude ($i \neq j$) from orbital m' at site j to orbital m at site i or the energy $\varepsilon_m^i \equiv t_{mm}^ii$ of orbital m at site i ($i = j$ and $m = m'$), and a is the correlated hopping parameter.

The parameter a in (1) is a measure of the reduction of the electron hopping amplitude between two orbitals when the sum of their occupancies exceeds 1. In real systems the degree

TABLE I. Eigenstates of H_0 forming the ground state quartet $S = 3/2$ for a single ion with three electrons and three orbitals.

S_z	State representation
3/2	$(\uparrow \uparrow \uparrow \uparrow)$
1/2	$\frac{1}{\sqrt{3}}[(\downarrow \uparrow \uparrow \uparrow) + (\uparrow \downarrow \uparrow \uparrow) + (\uparrow \uparrow \uparrow \downarrow)]$
-1/2	$\frac{1}{\sqrt{3}}[(\downarrow \downarrow \uparrow \uparrow) + (\downarrow \uparrow \uparrow \downarrow) + (\uparrow \downarrow \uparrow \downarrow)]$
-3/2	$(\downarrow \downarrow \downarrow \downarrow)$

of this reduction may be different for different pairs of orbitals. Consequently, the parameter a may acquire appropriate indexes and may be replaced by the table of parameters $a_{mm'}^{ii'}$. However, since, currently, these quantities are not known from independent calculations, to avoid introducing many new parameters $a_{mm'}^{ii'}$, we assume here that for all relevant pairs of orbitals they have the same value $a_{mm'}^{ii'} = a$. In fact, in all the studies that included CH we have noticed so far [21–23,25–30], only systems of identical ions with one orbital per ion were considered; thus, we have never seen in the scientific literature the parameter a with indexes. But of course, the value of a depends on the material we are dealing with, and as we already mentioned, the most common estimates are $0 < a < 0.4$ [21–23,25–30].

In our calculations a plays the role of an effective CH parameter which is the only adjustable quantity, while all other parameters of the Hamiltonian (1) are taken from Ref. [19]. We take into account five orbitals per ion because Cr ions in the molecular ring Cr₈ have five d orbitals. Their energies split due to the crystal field to form a lower-energy quasitriplet and a higher-energy quasidoublet. The energy splitting of the quasitriplet is about 0.1 eV, and that of the quasidoublet is about 0.05 eV, with the doublet energy being about 2 eV higher than the triplet energy [19]. Since there are three d electrons per Cr ion, it is obvious that at the lowest temperatures they occupy orbitals belonging to the quasitriplet, whereas the states of the quasidoublet are left unoccupied.

III. ATOMIC LIMIT: SINGLE-ION RESULTS

The Hilbert space dimension for three electrons occupying three orbitals is equal to 20. Due to the intraion exchange couplings, the diagonalization of the single-ion part H_0 of the Hamiltonian (1) within this space results in the formation of two quartets and six doublets. One of these quartets, corresponding to spin $S = 3/2$, is the ground state. Its energy E_0 is equal to

$$E_0 = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + 3U - 9J, \quad (2)$$

where $\varepsilon_m \equiv t_{mm}^{ii}$ (here we used the same notation for energies of orbitals $m = 1, 2, 3$ as given in Ref. [19]). The eigenstates belonging to this quartet are displayed in Table I, where their representations are given in the graphically intuitive basis of the form (orbital 1|orbital 2|orbital 3). These states can be used to build up the 4^N times degenerate N -ion ground state of N ions in the $t_{mm}^{ii} = 0$ limit. The full Hilbert space is then a tensor product of N spaces, each of which is spanned by the states given in Table I but corresponding to different ions.

IV. INTERACTION BETWEEN TWO IONS

In the model (1), the interaction between ions results from electron jumps between orbitals belonging to adjacent ions. If the amplitudes of these jumps are small enough with respect to U , then we can use the perturbative calculus. In the case of two ions the ground state of the unperturbed Hamiltonian H_0 is 16-fold degenerate, and its energy is equal to $2E_0 = 2(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) + 6U - 18J$. Electron jumps reduce this degeneration because an effective exchange interaction (kinetic exchange) between total spins $S = 3/2$ of the ions is then formed.

In our case, electrons can jump either between quasitriplet states or from a quasitriplet to an empty quasidoublet and back to the quasitriplet. There are nine amplitudes $t_{mm'}^{ij}$ ($m, m' = 1, 2, 3$) describing electron jumps from ion 2 to ion 1 and nine amplitudes $t_{mm'}^{21}$ describing jumps from ion 1 to ion 2. So there are altogether 18 amplitudes describing electron hops between the quasitriplet states, but due to the symmetry relationships $t_{mm'}^{ij} = t_{m'm}^{ji}$, only nine of them are independent. Since in the ground state the orbitals belonging to the quasitriplets are singly occupied, the electron hops are allowed only when their spins are antiparallel, and the CH effect is present then. On the other hand, there is no CH effect for electron hops from the quasitriplet to unoccupied quasidoublet orbitals.

Taking into account the electron jumps in the second-rank perturbative calculus applied to (1) in the limit of small $t_{mm'}^{ii'}$, one gets an effective Heisenberg Hamiltonian of interacting spins $S = 3/2$ with the antiferromagnetic superexchange coupling $\Gamma_{SE}^{ii'}$. If, following the discussion in [19], we take into account a direct ferromagnetic Coulomb exchange term $\Gamma_{CE}^{ii'}$ between the ions [not present in the Hamiltonian (1) but obtained independently via the constrained LDA], the final form of the effective Hamiltonian H_{eff} is as follows:

$$H_{\text{eff}} = \frac{1}{2} \sum_{i,i'} \Gamma^{ii'} S_i \cdot S_{i'}, \quad (3)$$

where $\Gamma^{ii'} = \Gamma_{CE}^{ii'} + \Gamma_{SE}^{ii'}$ and the sum is over all pairs (not ordered) of adjacent magnetic ions.

The superexchange coupling $\Gamma_{SE}^{ii'}$ resulting from electrons kinetics can be expressed as the sum of the following two contributions:

$$\Gamma_{SE}^{ii'} = \Gamma_0^{ii'} + \Delta\Gamma^{ii'}, \quad (4)$$

where the main part, $\Gamma_0^{ii'}$, comes from jumps of electrons between singly occupied states belonging to the quasitriplets,

$$\Gamma_0^{ii'} = \frac{2}{9} \sum_{n=1}^3 \sum_{n'=1}^3 \frac{|t_{nn'}^{ii'}|^2 + |t_{nn'}^{i'i}|^2}{U + 2J + \varepsilon_n - \varepsilon_{n'}} (1 - a)^2, \quad (5)$$

and the second part, $\Delta\Gamma^{ii'}$, results from electron jumps between singly occupied states belonging to the quasitriplet and unoccupied states belonging to the quasidoublet,

$$\Delta\Gamma^{ii'} = \frac{2}{9} \sum_{n'=1}^3 \sum_{n=4}^5 \frac{|t_{nn'}^{ii'}|^2 + |t_{nn'}^{i'i}|^2}{U + \varepsilon_n - \varepsilon_{n'}} - \frac{2}{9} \sum_{n'=1}^3 \sum_{n=4}^5 \frac{|t_{nn'}^{ii'}|^2 + |t_{nn'}^{i'i}|^2}{U - 3J + \varepsilon_n - \varepsilon_{n'}}. \quad (6)$$

The factor $(1 - a)^2$ associated with the effect of CH occurs only in the formula for $\Gamma_0^{ii'}$ because only in this case does an electron hop to the orbital which is already occupied by another electron with an opposite spin. On the other hand, $\Delta\Gamma^{ii'}$ does not depend on the parameter a because then the electron hops to an unoccupied orbital. As a result, only $\Gamma_0^{ii'}$, and not $\Delta\Gamma^{ii'}$, is reduced due to the effect of CH. The simple forms of the denominators in (5) and (6) result from the simple expression for energy [see Eq. (2)] of the ground state multiplet displayed in Table I.

Since we assume that the interactions between adjacent Cr ions in Cr_8 are the same, from now on we omit the upper indexes i, i' in the coupling constants Γ , Γ_0 , and $\Delta\Gamma$. And if we do not take into account the CH effect by assuming that $a = 0$ and put into formula (5) the parameters taken from Table I in Ref. [19], then it turns out that Γ_0 is equal to 4.847 meV. Taking into account in the calculations the hoppings of electrons between states belonging to the quasitriplet and quasideublet on adjacent ions results in the formation of a small ferromagnetic contribution of about -0.334 meV [resulting from (6)], which slightly reduces the Γ value. Another reduction in Γ is due to the direct ferromagnetic exchange between ions [not included in the Hamiltonian (1)], whose value estimated in Ref. [19] amounts to $\Gamma_{CE} = -0.34$ meV. After these reductions we get $\Gamma = 4.17$ meV, which is much more than 1.46 meV, the value resulting from the experimental data.

Quite recently, it was found that the value of the electron hopping amplitude t_{11}^{ij} given in Ref. [19] is overestimated, and instead of $t_{11}^{ij} = -0.231$ eV, it should be $t_{11}^{ij} = -0.131$ eV [34]. If we include in our calculations this new value of the parameter t_{11}^{ij} , then we get $\Gamma = 1.7$ meV, which is still too large. Therefore, we expect that for the correct description of this system, the effect of CH cannot be ignored.

There is no doubt that in real systems this effect occurs and that in our case it will lead to a decrease in the value of some $t_{mm'}^{ii'}$ amplitudes and thus to a diminution in the Γ value. However, we are not aware of any calculations made for Cr_8 that would allow us to estimate the size of the CH parameter a . Of course, such calculations would be appreciated, but as long as they are not available to us, we fit the value of a in such a way as to obtain Γ close to 1.46 meV. However, we suggest performing *ab initio* calculations that would allow us to verify whether the value of the parameter a that we got from fitting to the experimental data can be obtained by an *ab initio* method.

Let us add that when we derive the value of the magnetic coupling constant not from expressions (4)–(6) for Γ_{SE} but directly from the diagonalization of the multiorbital HM Hamiltonian given in (1), then in order to meet the condition for $\Gamma^* = 1.46$ meV we get a slightly higher value of $a \approx 0.06$. The reason is that the distances between energy levels determined by the diagonalization of the multiorbital HM (1) are slightly larger than the distances obtained from the diagonalization of H_{eff} (3).

The procedure we used to determine Γ^* by diagonalizing the multiorbital HM (1) was as follows. First, we constructed the Hilbert spaces of states for the system of two ions with five orbitals per ion and fixed values of the z coordinate of the total

spin S_z . In our case, the dimensions of these spaces amount to 14 400, 9450, 2520, and 210 for $S_z = 0, \pm 1, \pm 2, \pm 3$, respectively.

If there is no electron hopping between ions, then all these ground state multiplets (quartet for $S_z = 0$, triplet for $S_z = \pm 1$, doublet for $S_z = \pm 2$, and singlet for $S_z = \pm 3$) have the same energies. When the hopping is switched on, the multiplets split, and for small hopping amplitudes the structure of the split multiplets is close to that for the Heisenberg model. Let us recall that for two spins $S = 3/2$ that are coupled antiferromagnetically with the coupling constant Γ the energy spectrum forms four levels: $E = 0, \Gamma, 3\Gamma$, and 6Γ .

The spectrum is similar in the case of the multiorbital HM when the hopping amplitudes are small enough. Indeed, for $S_z = 0$, the four lowest energy levels then approximately have a distribution in the form of $0, \Gamma^*, 3\Gamma^*, 6\Gamma^*$, but Γ^* is slightly larger than Γ ($\Gamma^* > \Gamma$). Thus, the difference in energy between the lowest two levels can be assigned the coupling values Γ^* . In practice, it is more convenient to diagonalize HM not in the configuration space $S_z = 0$, but in $S_z = 2$, because then we are dealing with a number of states equal to 2520 and not 14 400. However, then the difference between the lowest two energy levels is approximately $3\Gamma^*$.

In Fig. 1 we display the evolution of the total interionic exchange couplings Γ and Γ^* with an increase in the CH coefficient a when the on-site coupling parameters U and J , as well as the amplitudes $t_{mm'}^{ii'}$, take the values reported in Ref. [19] (with the corrected value of $t_{11}^{ij} = -0.131$ eV). After viewing Fig. 1 it is clear that $a \approx 0.05$ meets the condition $\Gamma = 1.46$ meV, whereas a slightly larger $a \approx 0.06$ meets the condition $\Gamma^* = 1.46$ meV. Indeed, we get $\Gamma(a = 0) \approx 1.7$ meV and $\Gamma^*(a = 0) \approx 1.75$ meV, whereas $\Gamma(a = 0.05) \approx \Gamma^*(a = 0.06) \approx 1.46$ meV.

The impact of CH can also be seen in Fig. 2, where curves with a constant value of $\Gamma = 1.46$ meV for a few values of a

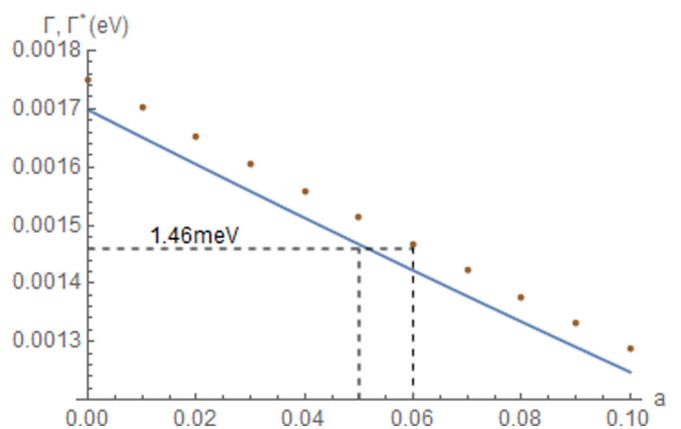


FIG. 1. The total exchange couplings: Γ derived from perturbation theory (solid line) and Γ^* derived from the exact diagonalization calculations (dots) in Cr_8 as a function of the CH parameter a for $U = 5.98$ eV, $J = 0.26$ eV, and the set of $t_{mm'}^{ii'}$ amplitudes reported in Ref. [19] with the corrected value of $t_{11}^{ij} = -0.131$ eV. The intersection points of the dashed lines indicate that the experimental value $\Gamma = 1.46$ meV is attained for either $a \approx 0.05$ or $a \approx 0.06$, as obtained with the perturbation or exact diagonalization calculations, respectively.

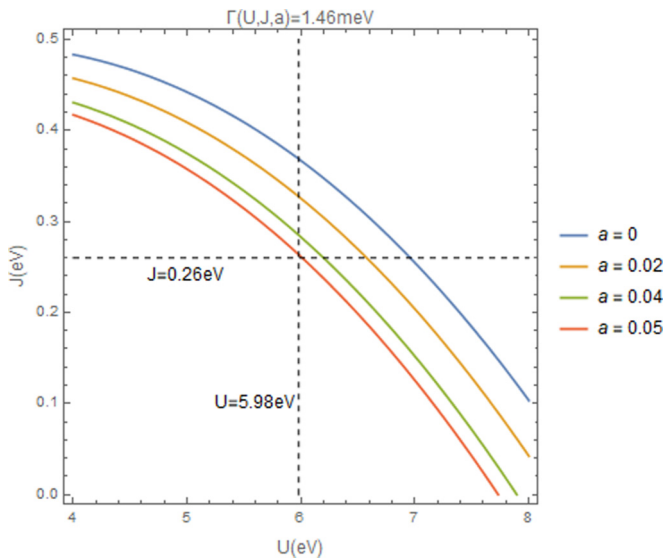


FIG. 2. The curves corresponding to the constant value of the superexchange coupling $\Gamma(U, J) = 1.46$ meV in Cr_8 obtained from the perturbation calculus as a function of the interacting couplings U and J for the amplitudes $t_{mm'}^{ij}$ reported in Ref. [19] with the corrected value of $t_{11}^{ij} = -0.131$ eV and for the following set of the CH parameters: $a = 0.0, 0.02, 0.04, 0.05$ (top to bottom). The intersection point of the dashed lines indicates that the experimental value $\Gamma = 1.46$ meV is attained for $U = 5.98$ eV and $J = 0.26$ eV (the values reported in [19]) when $a \approx 0.05$.

are displayed. In Fig. 2 we can see that in order to get a low enough Γ for fixed U and J , we should increase a to a value of $a \approx 0.05$.

A summary of the results of our calculation of the exchange constant for Cr_8 and compare them with the results obtained in Ref. [19] and those deduced from experiment (Ref. [17]) is given in Table II.

V. SUMMARY AND CONCLUSIONS

In this contribution, we included the CH effect in the microscopic description of MNMs and showed that it reduces

TABLE II. Exchange constants (in meV) related to the Heisenberg model: Γ_{exp} is deduced from the experimental data, $\Gamma_{\text{Ref. [19]}}$ is reported in Ref. [19], Γ is from perturbation theory without CH ($a = 0$) and with CH ($a = 0.05$), and Γ^* is from the exact diagonalization without CH ($a = 0$) and with CH ($a = 0.06$). The results of our calculations are given in the last four columns.

Γ_{exp}	$\Gamma_{\text{Ref. [19]}}$	Γ		Γ^*	
		$a = 0$	$a = 0.05$	$a = 0$	$a = 0.06$
1.46	1.65	1.7	1.46	1.75	1.46

noticeably the value of the exchange constant between the magnetic moments of the ions, thus bringing it closer to the value deduced from experiments. We performed the final calculations for Cr_8 using the data reported in [19]. By changing the parameter a we found that agreement between the value of the exchange coupling Γ calculated from the perturbation calculus and that deduced from the experiment is obtained for $a = 0.05$. A slightly higher value of $a \approx 0.06$ was needed when we performed our calculations by diagonalizing the Hamiltonian, but both these values are quite small, which means that even a tiny CH effect is sufficient to reduce the exchange coupling to the value deduced from the experiment. This is why we believe that the explanation of the decrease in the antiferromagnetic coupling constant by means of CH, as proposed in this work, is justified.

There is no problem with extending these studies to other MNMs with various substitutions. Indeed, both the model and the method used are universal and can be applied to other MNMs, but to obtain quantitative values for the magnetic exchange constants, microscopic parameters such as the local Coulomb coupling, the on-site exchange constant, the CH amplitudes, and the correlated hopping parameters are needed from independent calculations.

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