

Future applications of artificially-synthesized organic molecules containing transition-metal atoms

Selma Mayda ^{a,b}, Zafer Kandemir ^a, Nejat Bulut ^a

^a*Department of Physics, Izmir Institute of Technology, Urla 35430, Turkey*

^b*Department of Materials Science and Engineering, Izmir Institute of Technology, Urla 35430, Turkey*

Abstract

Artificially-synthesized organic molecules which contain transition-metal atoms offer new possibilities for applications in the electronics, pharmaceutical and chemical industries. Hence, developing an understanding of the electronic properties of this kind of organic molecules is important. With this purpose, here we study the electronic properties of metalloproteins, metalloenzymes and Ru-based dye molecules as examples for this kind of organic molecules. In particular, we perform combined Hartree-Fock (HF) and quantum Monte Carlo (HF+QMC) calculations as well as combined density functional theory (DFT) and quantum Monte Carlo (DFT+QMC) calculations to study the electronic properties of these molecules. Our results show that new electronic states named as impurity bound states (IBS) form in metalloproteins, metalloenzymes and Ru-based dye molecules. We show that the electron occupancy of IBS is critically important in determining the low-energy electronic properties of these molecules. In this respect, the IBS may play a central role in developing new applications based on artificially-synthesized organic molecules containing transition-metal atoms.

Keywords: metalloproteins, metalloenzymes, Haldane-Anderson model, quantum Monte Carlo, strongly interacting electrons, impurity bound state

1. Introduction

Artificially-synthesized organic molecules which contain transition-metal atoms offer new opportunities for applications in the electronics, pharmaceutical and chemical industries. In this respect, it is interesting to note that this kind of molecules already exist and are used widely in nature. For example, about one third of proteins and enzymes contain metal atoms, (Pratt, 1972); (Krautler et al., 1998); (Banerjee, 1999); (Brown, 2005) which are called as metalloproteins and metalloenzymes. These molecules, which have been developed by evolution, play an essential role in the chemical reactions taking place in all organisms. In this article, we will discuss the electronic properties of metalloproteins and metalloenzymes with the purpose of using what we learn here in the design of new artificially-synthesized organic molecules.

We study the electronic properties of metalloproteins and metalloenzymes by using the framework of the Haldane-Anderson model of a transition-metal impurity in a semiconductor host material (Kandemir et al., 2016); (Mayda et al., 2017). In particular, as an example for metalloenzymes we study the electronic structure of vitamin B₁₂, which contains a cobalt atom and also has an energy gap in the excitation spectrum as in a semiconductor. We use the combined Hartree-Fock (HF) and quantum Monte Carlo (HF+QMC) methods as well as the combined density functional theory (DFT) and quantum Monte Carlo (DFT+QMC) methods. Our results show that new electronic states, which are named as impurity bound states (IBS), are formed in these molecules and they play an important role in determining the low-energy electronic properties. We see that small changes in occupancy of IBS lead to important changes in the electronic state and the magnetic correlations.

We also study the electronic properties of the Ru-based dye molecules which are used in dye-sensitized solar cell applications. In these dye molecules, the local atomic environment around the transition-metal atom is similar to these in the metalloproteins and metalloenzymes. We have performed DFT+QMC calculations for the Ru-based dye molecules and we find that the IBS also exists in them and might be playing an important role in the functioning of these molecules.

In view of our results, we think that the IBS will also play a central role in the electronic structure and functioning of new artificially-synthesized organic molecules. Hence, we suggest that the magnetic and electronic properties

of the IBS can be exploited in the design of new synthetic catalyzers and enzymes, or other functional molecules. Such molecules may be utilized in electronics, chemical and pharmaceutical industries.

1.1. Molecular structure of vitamin B₁₂

Vitamin B₁₂, which contains a Co transition-metal atom, is an example for metalloenzymes. It is important in the production of the red blood cells and in the functioning of the nervous system in addition to taking place in various other chemical reactions. The vitamin B₁₂ has three known co-factors. They are cyanocobalamin (CNCbl), adenosylcobalamin (AdoCbl) and methylcobalamin (MeCbl). Here, we will concentrate on CNCbl which contains 181 atoms. Its molecular structure is shown in Fig. 1(a).

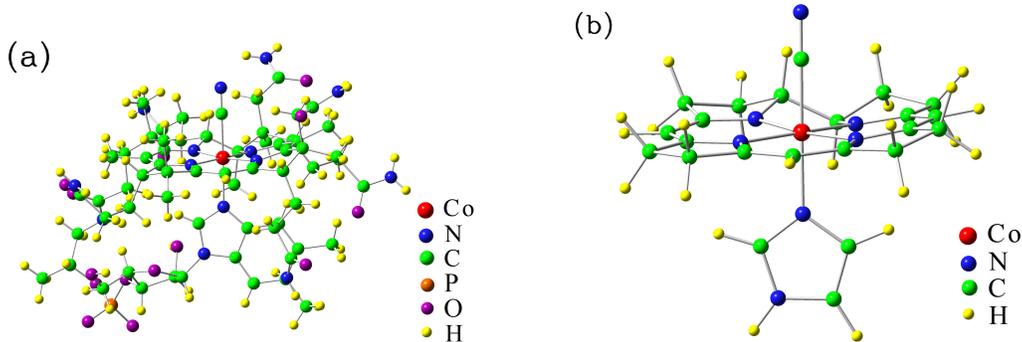


Figure 1: (a) Molecular structure of CNCbl ($C_{63}H_{88}CoN_{14}O_{14}P$). (b) Truncated molecular structure for $Im-[Co^{III}(corrin)]-CN^+$.

In our studies on CNCbl molecule, we have first performed HF+QMC calculations for a simplified, truncated molecule ($Im-[Co^{III}(corrin)]-CN^+$) containing 56 atoms (Kandemir et al., 2016) which is illustrated in Fig. 1(b). In these calculations, we have used the multi-orbital Haldane-Anderson model but we neglected the inter-orbital Coulomb interactions. Next, we have performed DFT+QMC calculations for the full CNCbl molecule with 181 atoms included but without including the inter-orbital Coulomb interactions (Mayda et al., 2017). Finally, we have also performed DFT+QMC calculations for the full CNCbl molecule including the inter-orbital Coulomb interactions along with the Hund's coupling. In all of these three different computational approaches, we have observed the existence of the IBS and that it controls

the magnetic correlations in CNCbl. Here, we find that the existence of the IBS is robust for CNCbl. Below in Section 2.1 and 2.2, we will discuss the results from the HF+QMC for the truncated molecular structure without inter-orbital Coulomb interactions and also from the DFT+QMC for the full CNCbl including the inter-orbital Coulomb interactions.

1.2. Molecular structure of the Ru-based dye molecules

Ru-based dye molecules which are used in solar cells applications have attracted attention in recent years due to their low-cost production and high efficiency. Figure 2 shows the molecular structure of N719 which is an example for the Ru-based dye molecules. As seen in this figure, Ru is located at the center of the molecule and six N atoms are attached to it. Comparing Figure 1 and Figure 2, we observe that the local atomic environment around the transition-metal impurity is similar in these two different types of molecules. In Section 2.3, we show results from DFT+QMC calculations including inter-orbital Coulomb interactions and observe that the IBS also exists in the electronic structure of the Ru-based dye molecules.

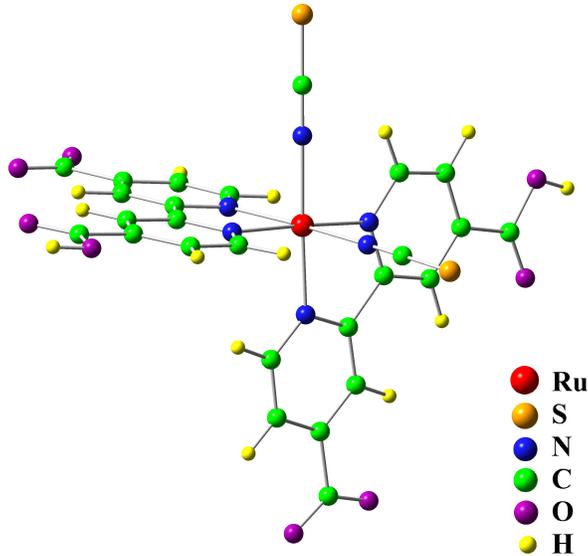


Figure 2: Molecular structure of the N719 Ru-based dye molecule $[\text{C}_{26}\text{H}_{14}\text{N}_6\text{O}_8\text{RuS}_2]^{-2}$.

1.3. Comparison with the diluted magnetic semiconductors

Vitamin B₁₂ and Ru-based dye molecule N719 exhibit energy gaps in their spectrum and contain transition-metal atoms. In this respect, they are similar to an entirely different class of materials which are named as diluted magnetic semiconductors (DMS) (Ohno et al., 1992); (Ohno et al., 1996). The DMS materials are obtained by substituting transition-metal impurities into a semiconductor host. For example, (Ga,Mn)As is obtained by substituting Mn impurities for Ga in the GaAs semiconductor.

DMS materials have attracted much attention because of their magnetic and semiconducting properties. They display high Curie temperatures. In addition, an impurity bound state, which is a sharp resonant state in the single-particle spectrum, exists 110 meV above the top of the valence band in the semiconducting gap (Jungwirth et al., 2007). The impurity bound state consists of spectral weight from both the Mn impurity and the host. Calculations performed by using the Haldane-Anderson model show that this new electronic state is important in determining the electronic and magnetic properties of (Ga,Mn)As (Ichimura et al., 2006); (Bulut et al., 2007); (Tomoda et al., 2009). In particular, long-range ferromagnetic correlations exist among Mn impurities when the chemical potential is located between the top of the valence band and IBS. These ferromagnetic correlations disappear rapidly as the IBS becomes occupied by electrons. Due to these electronic and magnetic properties, the DMS materials have potential for new device applications (Munekata et al., 1989) for example in spintronics (Maekawa, 2006); (Žutić et al., 2004) .

When studied within the framework of the Haldane-Anderson model (Haldane and Anderson, 1976), the vitamin B₁₂, the Ru-based dye molecules and the DMS materials have similar electronic structures; they have semiconducting energy gaps, they contain transition-metal impurities. In addition, we observe that all these different classes of materials have impurity bound states in the electronic spectrum which control the magnetic properties. Hence, we think that the IBS will also play an important role in determining the electronic properties of future artificially-synthesized organic molecules which contain transition-metal atoms.

1.4. Haldane-Anderson Model

The Haldane-Anderson model was introduced in order to describe the electronic state of a transition-metal impurity placed in a semiconductor host (Haldane and Anderson, 1976). In this model, the 3d orbitals of the transition-metal atom are named as the impurity and the remaining orbitals are named as the host.

In our calculations for metalloproteins, metalloenzymes and the Ru-based dye molecules, we employ an extended multi-orbital single-impurity Haldane-Anderson model which is given by

$$\begin{aligned}
H &= \sum_{m\sigma} (\varepsilon_m - \mu) c_{m\sigma}^\dagger c_{m\sigma} + \sum_{\nu,\sigma} (\varepsilon_{d\nu} - \mu) n_{\nu\sigma} \\
&+ \sum_m \sum_{\nu,\sigma} V_{m\nu} (c_{m\sigma}^\dagger d_{\nu\sigma} + h.c.) \\
&+ \sum_{\nu} U n_{\nu\uparrow} n_{\nu\downarrow} \\
&+ \sum_{\nu>\nu'} [U' n_{\nu\sigma} n_{\nu'-\sigma} + (U' - J) n_{\nu\sigma} n_{\nu'\sigma}]. \tag{1}
\end{aligned}$$

Here, $c_{m\sigma}^\dagger$ ($c_{m\sigma}$) creates (annihilates) an electron in host state m with spin σ , $d_{\nu\sigma}^\dagger$ ($d_{\nu\sigma}$) is the creation (annihilation) operator for a localized electron with spin σ at the 3d orbital, and $n_{\nu\sigma} = d_{\nu\sigma}^\dagger d_{\nu\sigma}$. In addition, ε_m and $\varepsilon_{d\nu}$ are the energies of the host and the 3d impurity states, respectively, The hybridization matrix element between these states is $V_{m\nu}$. The intra-orbital Coulomb repulsion is U . Furthermore, U' and $U' - J$ are the Coulomb interactions between the two 3d electrons located at different orbitals with opposite and parallel spins, respectively. Here, J is the Hund's coupling term. Finally, a chemical potential μ is introduced since the QMC calculations are performed in the grand canonical ensemble. We note that the Haldane-Anderson model was first used within the Hartree-Fock approximation by (Yamauchi et al., 2003) for describing the electronic structure of hemoglobin, which is a metalloprotein.

In our calculations for CNCbl molecule, we took the atomic coordinates from the Protein Data Bank (Berman et al., 2000). For the Ru-based dye molecule N719, we used the molecular structure given by Ref.(Schiffmann et al., 2010). The Anderson model parameters ε_m , $\varepsilon_{d\nu}$ and $V_{m\nu}$ were estimated by using

both the HF approximation and the DFT. For the Coulomb parameters U and J we used the well known estimates and also took $U' = U - 2J$.

The resulting extended multi-orbital Haldane-Anderson model is studied with the QMC technique developed by Hirsch and Fye (Hirsch and Fye, 1986). With this technique, we obtain the electron occupancy numbers and the effective magnetic moments for all of the 3d orbitals along with the host orbitals. We also calculate the magnetic correlation functions among the various host and 3d orbitals.

2. Quantum Monte Carlo results on vitamin B₁₂ and the Ru-based dye molecule N719

2.1. HF+QMC results for Im-[Co^{III}(corrin)]-CN⁺

We begin by presenting QMC data for the truncated CNCbl structure (Im-[Co^{III}(corrin)]-CN⁺) (Kandemir et al., 2016). We have performed HF+QMC calculations to obtain the electronic properties of this molecule without including the inter-orbital Coulomb interaction terms U' and $U' - J$. Here, we study the electronic structure of the Anderson Hamiltonian by varying the chemical potential as a free parameter. Figure 3(a) shows QMC results on the electron occupation number $\langle n_\nu \rangle$ of the Co($3d_\nu$) orbitals as a function of the chemical potential μ . Similarly, the square of the magnetic moment $\langle (M_\nu^z)^2 \rangle$ at the Co($3d_\nu$) orbitals is shown in Fig. 3(b) as a function of μ . In these figures, the solid black and dashed lines denote the highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level found by DFT, respectively.

We observe in Fig. 3(a) that $\langle n_\nu \rangle$ exhibits a jump at $\mu \approx -45$ eV for xz , $x^2 - y^2$ and yz orbitals, because the $\varepsilon_{d\nu}$ values are located near -45 eV for these orbitals. These orbitals remain singly occupied upto $\mu \approx -10$ eV. Near $\mu = -10$ eV, they become nearly doubly occupied. We see in Fig. 3(b) that the magnetic moments at xz , $x^2 - y^2$ and yz orbitals have their maximum value at around $\mu = -10$ eV. Above $\mu = -10$ eV, these moments decrease rapidly due to double occupancy of the orbitals.

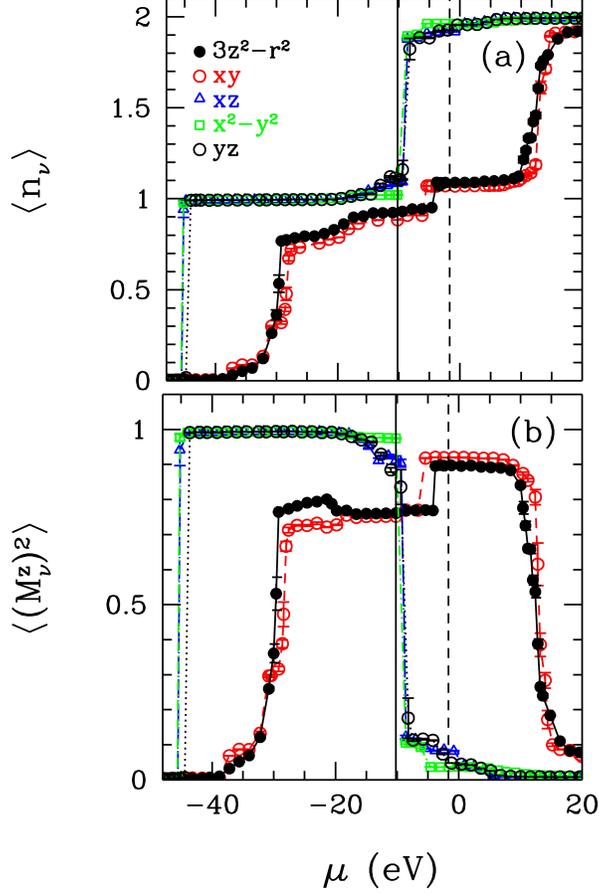


Figure 3: (a) Electron occupation number $\langle n_\nu \rangle$ of the $\text{Co}(3d_\nu)$ orbitals plotted as a function of the chemical potential μ . (b) Square of the local magnetic moment $\langle (M_\nu^z)^2 \rangle$ at the $\text{Co}(3d_\nu)$ orbitals versus the chemical potential μ . These results are from the HF+QMC calculations for $\text{Im}[\text{Co}^{\text{III}}(\text{corrin})\text{-CN}^+$ performed by using $U = 36$ eV. Here, the inter-orbital Coulomb interactions are ignored. In addition, the vertical solid and dashed lines denote the HOMO and the LUMO levels found by the HF approximation, respectively.

The situation is different for the xy and $3z^2 - r^2$ orbitals. In Figure 3(a), we see that $\langle n_\nu \rangle$ for xy and $3z^2 - r^2$ orbitals increases rapidly around $\mu \approx -30$ eV where the ε_{d_ν} values are located. It is important to point out that these orbitals have less than one electron until μ reaches about -5.5 eV, where $\langle n_{xy} \rangle$ exhibits a sudden increase of about 0.2 electrons. Similarly, for the $3z^2 - r^2$ orbital, a sudden increase occurs at $\mu \approx -4$ eV. It is important to note in Fig. 3(b) that the magnetic moments of the xy and $3z^2 - r^2$

orbitals also increase suddenly at $\mu \approx -5.5$ eV and $\mu \approx -4$ eV, respectively. These sharp increases both in $\langle n_\nu \rangle$ and in $\langle (M_\nu^z)^2 \rangle$ correspond to impurity bound states as found in the Hartree-Fock approximation for the Haldane-Anderson model (Ichimura et al., 2006). Hence, we find that the IBS exists in Im-[Co^{III}(corrin)]-CN⁺ at energies -5.5 eV and -4 eV for the xy and $3z^2 - r^2$ orbitals, respectively. Above $\mu \approx 10$ eV, the xy and $3z^2 - r^2$ orbitals become doubly occupied, and the magnetic moments rapidly decrease.

In Figure 4(a) and (b), we present QMC data on the host electron number $\langle n_m \rangle$ versus μ and the square of the magnetic moment $\langle (M_m^z)^2 \rangle$ versus μ for the $m = 111$ and $m = 114$ 'th host states, respectively. These host orbitals consist mainly of the C(2p) and N(2p) orbitals neighbouring the Co atom. Here, we choose these host states because they have the highest hybridization values with the Co(3d _{ν}) xy and $3z^2 - r^2$ orbitals, respectively. Here we observe that, because of hybridization, these host orbitals have partial occupancies and develop magnetic moments. In particular, both $\langle n_\nu \rangle$ and $\langle (M_\nu^z)^2 \rangle$ exhibit sudden increases at the IBS locations, as expected within the HF approximation.

We have also studied the magnetic correlation function $\langle M_\nu^z M_m^z \rangle$ between the Co(3d) electrons and the host states $m = 111$ and $m = 114$ as a function of the chemical potential μ . In Figure 5(a), we observe that the xy orbital develops antiferromagnetic (AF) correlations with the $m = 111$ 'th host state. These AF correlations diminish rapidly at $\mu \approx -5.5$ eV. Figure 5(b) shows similar results for the $3z^2 - r^2$ orbital. In these figures, we observe that AF correlations exist between these host states and 3d orbitals, and that these correlations vanish rapidly as the IBS becomes occupied by electrons.

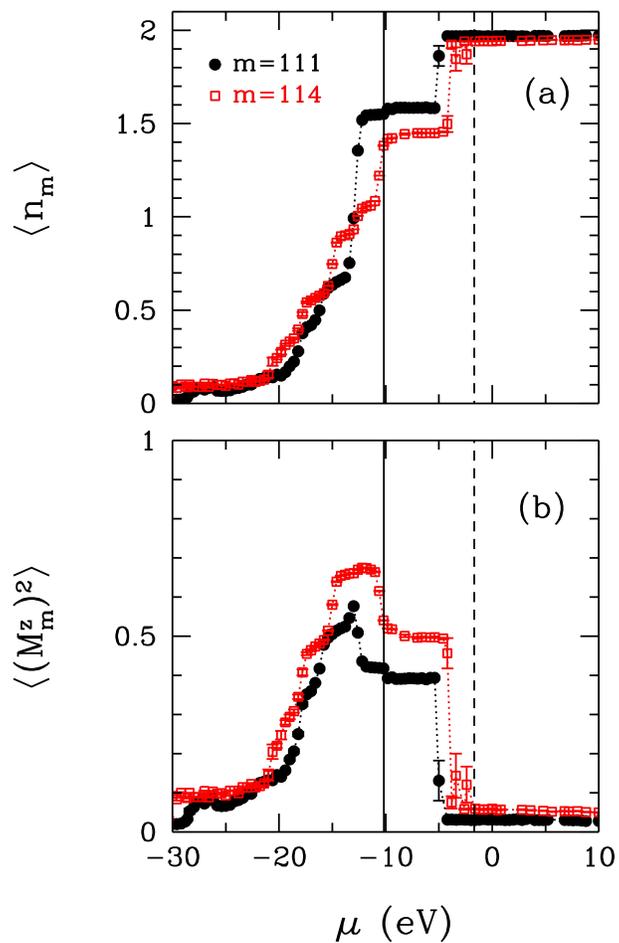


Figure 4: (a) Occupation of the m 'th host eigenstate $\langle n_m \rangle$ versus μ . (b) Square of the magnetic moment of the m 'th host eigenstate $\langle (M_m^z)^2 \rangle$ versus μ . These results are from the HF+QMC calculations for Im-[Co^{III}(corrin)]-CN⁺ performed by using $U = 36$ eV. Here, the inter-orbital Coulomb interactions are ignored. In addition, the vertical solid and dashed lines denote the HOMO and the LUMO levels found by the HF approximation, respectively.

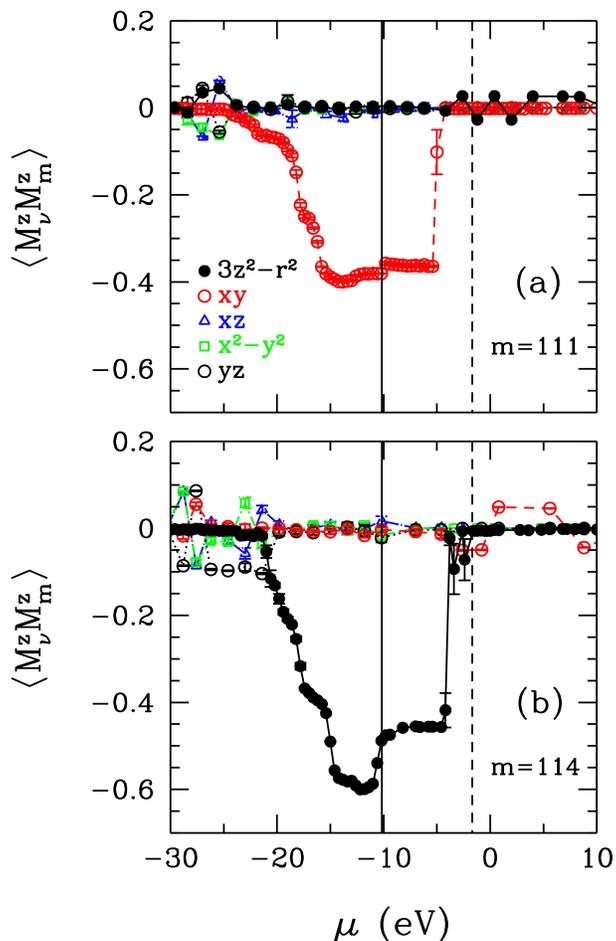


Figure 5: Magnetic correlation function $\langle M_\nu^z M_m^z \rangle$ between the m 'th host eigenstate and the various the $\text{Co}(3d_\nu)$ orbitals. Here results are shown for host states (a) $m = 111$ and (b) 114. These results are from the HF+QMC calculations for $\text{Im}[\text{Co}^{\text{III}}(\text{corrin})]\text{-CN}^+$ performed by using $U = 36$ eV. Here, the inter-orbital Coulomb interactions are ignored. In addition, the vertical solid and dashed lines denote the HOMO and the LUMO levels found by the HF approximation, respectively.

2.2. DFT+QMC results for CNCbl

The charge neutral CNCbl molecule contains 181 atoms and 718 electrons. In this section, we show the DFT+QMC results for the full CNCbl molecule by including the inter-orbital Coulomb interactions with the Hund's coupling. We see from DFT+QMC results that the IBS is formed in the CNCbl

molecule and its existence is not affected by the presence of the Hund’s coupling. Hence, the IBS is a robust feature within this approach.

In our calculations, we find that the vanishing of the AF correlations between the 3d and the host orbitals is the clearest sign for determining the location of the IBS (Kandemir et al., 2016); (Mayda et al., 2017). For this reason and space consideration, in this section we only show results on $\langle M_\nu^z M_m^z \rangle$ vs μ for the $m = 336$ ’th orbital which has high hybridization matrix elements. This host state consists of mainly of the N(2p) orbitals neighbouring the Co atom. Figure 6 shows $\langle M_\nu^z M_m^z \rangle$ vs μ . Here, the black solid line represents the HOMO level and the black dashed line represents the LUMO level obtained by the DFT. We observe in Fig. 6 that the AF correlations which occur between the 3d orbitals and the $m = 336$ ’th host orbital disappear when the IBS is occupied with the electrons.

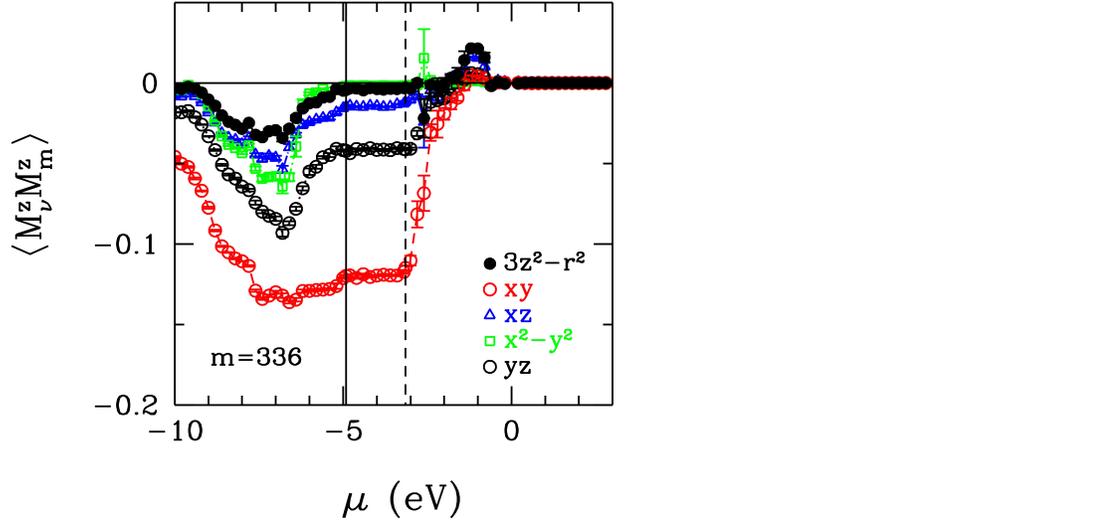


Figure 6: Magnetic correlation function $\langle M_\nu^z M_m^z \rangle$ between the $m = 336$ ’th host state and the $\text{Co}(3d_\nu)$ orbitals. These results are from the DFT+QMC calculations for the full CNCbl molecule. Here, the intra-orbital and inter-orbital Coulomb interactions were taken into account along with the Hund’s coupling. The Coulomb parameters were taken to be $U = 4$ eV and $J = 0.8$ eV. In addition, the vertical solid and dashed lines denote the HOMO and LUMO found by DFT, respectively.

When $\mu = -4.6$ eV, we find that the total electron number is 718. Hence, according to these calculations, the IBS is located about 2 eV above the

HOMO level. Consequently, we expect to see the structures in the excitation spectrum of the CNCbl molecule at these energies.

In this section, we have observed the existence of the IBS in the electronic spectrum for CNCbl using three different computational approaches. This indicates that the existence of the IBS for CNCbl is robust within the framework of the Haldane-Anderson model. In particular, the Hund’s coupling does not smear the IBS.

2.3. DFT+QMC results for the Ru-based dye molecule N719

In this section, we present the DFT+QMC results for the dye molecule N719 of which molecular structure is seen in Fig. 2. In these calculations, the inter-orbital Coulomb interactions along with the Hund’s coupling are taken into account.

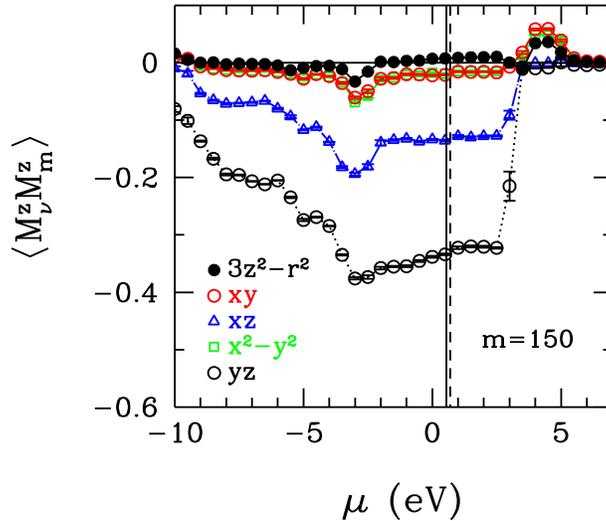


Figure 7: Magnetic correlation function $\langle M_\nu^z M_m^z \rangle$ between the $m = 150$ 'th host state and the Ru($4d_\nu$) orbitals. These results are from the DFT+QMC calculations for the Ru-based dye molecule N719. Here, the intra-orbital and inter-orbital Coulomb interactions were taken into account along with the Hund’s coupling. The Coulomb parameters were taken to be $U = 4$ eV and $J = 0.6$ eV. In addition, the vertical solid and dashed lines denote the HOMO and LUMO found by DFT, respectively.

In this section also we only discuss results on the magnetic correlation function between the Ru($4d_\nu$) orbitals and the host orbitals which has the highest

hybridization. Figure 7 shows $\langle M_\nu^z M_m^z \rangle$ vs μ for the $m = 150$ 'th host state which consists mainly of the N(2p) orbitals neighbouring the Ru atom. Here, we observe that the $m = 150$ 'th host state has strong AF correlation especially with the Ru($4d_\nu$) yz and xz orbitals. These AF correlations vanish at $\mu \approx 3$ eV. Hence, we conclude that an IBS exists at this energy in the dye molecule N719. We think that the IBS found in these calculations might be important for the functioning of the N719 dye molecule.

3. Summary and Conclusions

In our studies, we have chosen the vitamin B₁₂ as an example for metalloenzymes and metalloproteins. For the CNCbl molecule, we have performed HF+QMC and DFT+QMC calculations within an extended multi-orbital Haldane-Anderson model including the intra-orbital and inter-orbital Coulomb interactions. We find that the IBS is a robust feature of the electronic spectrum. For example, it is not smeared by the Hund's coupling. We have also seen that the occupancy of the IBS is critical for determining the magnetic properties.

We have performed similar many-body calculations for the dye molecule N719 which contains a Ru atom, in which case we have also found the existence the IBS. The results we have found for the IBS in CNCbl and the N719 dye molecule are very similar to what is known about the IBS in the DMS materials. Hence, we have seen that the IBS is a crucial electronic feature of these three very different types of materials.

The artificially-synthesized organic molecules containing transition-metals are interesting because they may lead to important future applications. In the light of the results presented in this article, we expect that the IBS may also play a key role in these new molecules which are yet to be synthesized. In particular, it would be interesting to exploit the properties of the IBS in such molecules with possible applications in electronics, chemical and pharmaceutical industries.

Acknowledgments

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