

FIRST PRINCIPAL CALCULATIONS OF EFFECTIVE EXCHANGE INTEGRALS FOR COPPER OXIDES AND ISOELECTRONIC SPECIES

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Abstract. Our theoretical efforts for strongly correlated electron systems such as transition metal oxides have been reviewed in relation to electronic structures of these species. The effective exchange integrals (J) of several transition-metal oxides have been calculated by hybrid DFT methods. The ab initio results for the species are also mapped to the N-band Hubbard model. The two band model for copper oxides has been extended to possible isoelectronic π -d, π -R and σ -R systems, which often exhibit magnetic conductivity and superconductivity. For example, magnetic modifications of conducting polymers, CT complexes and TTF derivatives are examined on the theoretical grounds. Triangular and cubane-type clusters are investigated by general spin orbital (GSO) DFT in relation to spin frustration. The spin orbit interaction is also included to calculate the Dzyaloshinskii-Moriya term.

Key words: Spin-mediated mechanism, J model, Spin fluctuation model, Cooperative mechanism, π -d, π -R and σ -R systems, Material design.

1. Introduction

The instability in chemical bonds¹, leading to electron localization via electron repulsion, is now one of the important and crucial concepts even in material science as well as in chemical reactions. It is closely related to electronic, magnetic and optical properties of strongly correlated electron systems such as p-d, π -d, π -R and σ -R conjugated systems. Theoretical investigations of these systems are indeed essential for elucidation of interrelationship between magnetism and high-T_c superconductivity in general, since both characteristics have been commonly observed experimentally. About 20 years ago, our ab initio calculations indicated that the CuOCu unit exhibits very strong effective exchange interaction ($|J| \gg 0$)². But we could not imagine that such finding might be related to the high-T_c superconductivity, because our main interest is to elucidate electronic structure and reactivity of transition metal oxides. After the discovery of high-T_c cuprates by Bednorz and Müller³, we immediately proposed a spin-mediated J-model ($T_c = cJ(k_B)$)⁴. It is noteworthy that our J model has been presented on the basis of ab initio calculations before the Zhang-Rice t-J model⁵. On the other hand, the spin fluctuation (SF) model has been employed to rationalize metallic and superconducting behaviors of overdoped cuprates⁷. The large $|J|$ value is replaced with strong susceptibility $\chi(\mathbf{q})$ or large SF frequency (ω_{SF}) for overdoped cuprates in spin-mediated model⁸. In this review, we summarize theoretical efforts toward ab initio calculations of J-values and other interaction parameters (t , U , so on) of transition-metal oxides and related species.

2. Theoretical background

2.1. GROUP-THEORETICAL INTERRELATIONSHIP BETWEEN THEORETICAL MODELS

There are several theoretical models for strongly correlated electron systems, which arise from the instability in chemical bonds from the view point of quantum chemistry¹. Our group have investigated several model Hamiltonians for these species as shown in Fig. 1, and have elucidated group-theoretical interrelationships¹ among them on the basis of five different symmetry operations; spatial symmetry (P_n), spin rotation (S), time-reversal (T), gauge transformation (ϕ) and permutation group (S_N).

The classical Heisenberg (spin vector) model is characterized by the magnetic group⁹

$$M = H_n + T(P_n - H_n) \quad (1)$$

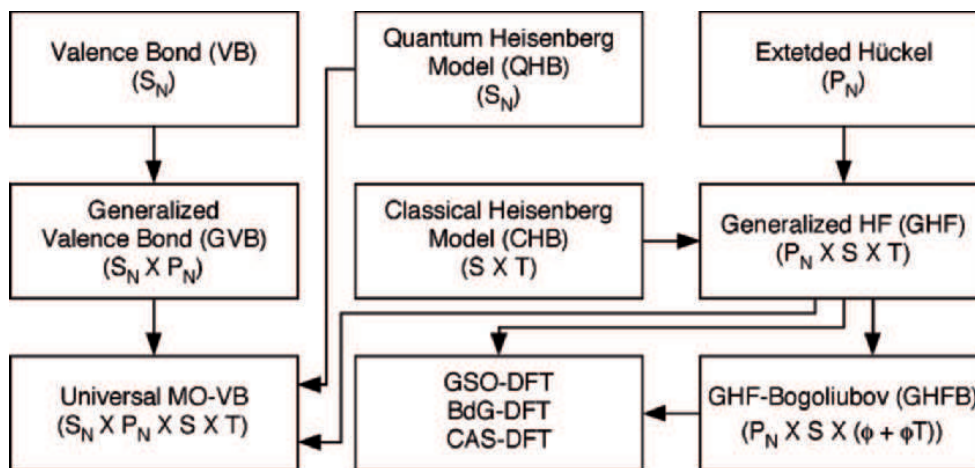


Figure 1. Group-theoretical interrelationships between several theoretical models for strong correlated electron systems (see text).

where H_n denotes the subgroup of P_n . The spin vector model has been applied to triangular and tetrahedral magnetic clusters as shown in Fig. 2. The corresponding generalized Hartree-Fock (GHF) solutions for the clusters are constructed by using the group-theoretical operation: $P_n \times S \times T$.

However, the GHF solutions are not the eigen functions of \hat{S}^2 and \hat{S}_z operators, leading to the extended Hartree-Fock (EHF) and spin optimized (SO) SCF general spin orbitals (GSO) methods, which are characterized by $S_N \times P_n \times S \times T$ ^{1,10}. The GSO SO-SCF wavefunctions for the D_{3h} and T_d clusters are equivalent to the corresponding full CI wave functions in the case of the Hubbard model. The spin structures of multi-center radicals in Fig. 2 can be regarded as pictorial expression of spin correlation function defined by $\langle \mathbf{S}(1) \cdot \mathbf{S}(2) \rho_2(1,2) \rangle$, where $\rho_2(1,2)$ is the second-order density matrix of GHF, EHF and SO SCF solutions^{1,11}. This implies that the spin structures by GSO HF express spin correlations instead of spin populations¹¹. The spin correlation function is related to the dynamical magnetic susceptibility χ in the k -space⁷. The quantum effects for multi-center radicals can be expressed by the spin-symmetry recovery from broken-symmetry (BS) GHF, which entails the multi-configuration description by EHF and SO SCF in conformity with the quantum resonance effects, particularly for $S=1/2$ spins¹⁰. The number density projection is

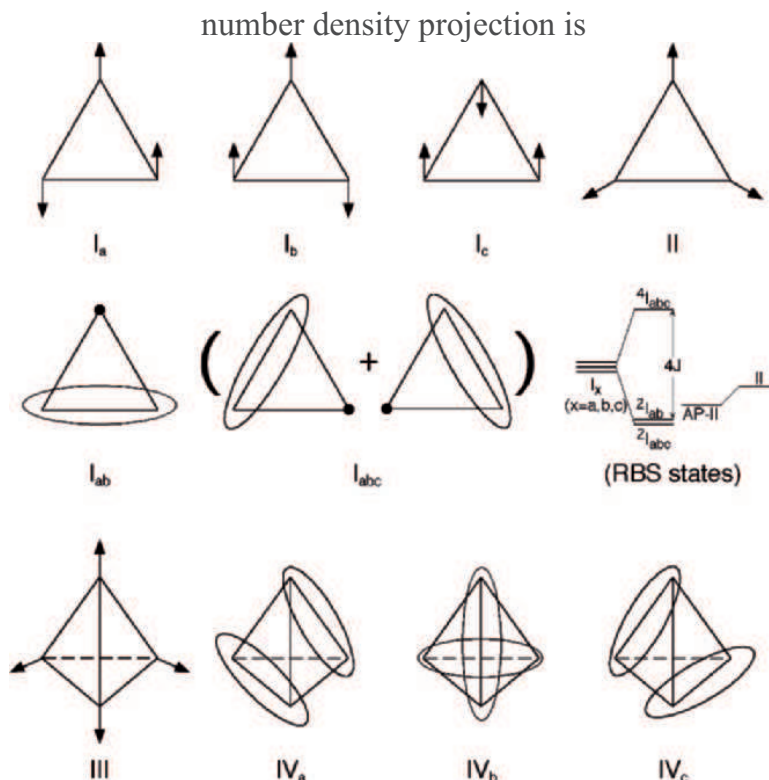


Figure 2. Spin vector (classical) models (II, III) for triangular and tetrahedral radical species. Spin fluctuation models for D_{3h} clusters (I_{a-c}). The resonating BS (RBS) states are expected by I_{ab} , I_{abc} and IV_{a-c} .

required for GHF-Bogoliubov solution of superconducting state of finite clusters¹.

The GSO HF and GSO density functional theory (DFT) have been applied to elucidate electronic and magnetic properties of triangular and cubane-type clusters of manganese oxides and iron-sulfur compounds¹²⁻¹⁴. Some of these species indeed exhibit noncollinear spin structures (see Fig. 2) which entail antiferromagnetic (singlet-type) spin couplings between spins of Mn (or Fe) ions. The cluster models of triangular lattice of CoO_2 ¹⁵ and κ -(BEDF-TTF)($Cu_2(CN)_3$)¹⁶ have also been investigated in relation to the spin fluctuation effect of the 1/2 spin and the unconventional superconductivity via spin fluctuation.

The valence-bond (VB), generalized VB (GVB)¹⁷ and resonating VB (RVB)¹⁸ approaches have been applied to multi-center polyradicals in Fig. 2. The RVB approach is inevitable for the spin-frustrated systems (I_{a-c} in Fig. 2). Thus the multi-configuration pictures are common in both GSO SO SCF and RVB approaches for electron and spin correlated polyradicals. If the spin-orbit (SO) and related magnetic interactions play important roles, GSO-approaches involving SO terms are rather practical for ab initio computations of those terms. Ab initio calculations of the Dzyaloshinskii-

Moriya (DM) term for spin-frustrated systems by SO GHF, SO GDFT and SO-GHF CASCI is such an example¹⁹. The GSO-HF Bogoliubov (GHFB) solutions are required for superconductors with electronic origin as shown in Fig. 1^{1,20}.

The resonance of BS solutions often takes place because of quantum effect. The resonating BS (RBS) solutions for triangular [3,3] system can be easily constructed by the superposition of the BS solutions in Fig. 2²¹

$${}^2I_{ab} = (I_a - I_b)/\sqrt{N} \quad (2a)$$

$${}^2I_{abc} = (I_{ac} + I_{bc})/\sqrt{N'} = (I_a + I_b - 2I_c)/\sqrt{N'} \quad (2b)$$

where N and N' denote the normalization constants: note that the BS solutions are non-orthogonal. The RBS solutions become equivalent to GSO SOSCF (Full CI) in the case of simple [3,3] system. The RBS solutions are, however, applicable to more larger systems if the DFT parametrizations are utilized²¹, giving rise to an alternative approach to the RVB¹⁸ and GVB¹⁷ methods. The RBS methods are indeed utilized for π -d, π -R and σ -R conjugated systems.

2.2. APPROXIMATE AND EXACT SOLUTIONS OF HUBBARD MODELS FOR POLYRADICAL SPECIES

About 30 years ago, our group initiated theoretical studies on electron localizations via electron correlations in molecular systems^{22,23}. The Hubbard model has often been used for polyradical species to elucidate important roles of electron and spin correlation effects¹

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + U_{eff} \quad n_i \uparrow n_j \downarrow \quad (3)$$

where t_{ij} and U_{eff} denote the transfer and on-site repulsion integrals, respectively. The so-called Mott transition via electron repulsion (U_{eff}) has occurred even in small clusters for the mean-field GSO HF and related theories. The GSO EHF and GSO SO-SCF equations of the multi-center polyradicals in Fig. 2 have also been solved on the basis of the Hubbard model¹⁰, where the binding parameter is defined by

$$x = -t/U_{eff} = \beta/U_{eff}. \quad (4)$$

Electronic and spin correlation effects become very important in the weak bonding region : $0 \leq x \leq 1/2$, where $x=1/2$ is a quasi Mott transition point for the finite system¹.

In the localized electron region ($x < 1/2$), the Hubbard model can be reduced to the Heisenberg spin Hamiltonian model

$$H = - \sum_{a,b} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b \quad (5)$$

where J_{ab} is the effective exchange integral. For example, the J_{ab} values for the triangular spin systems by the symmetry-projected GHF method are given by

$$J_{ab} = \frac{1}{2 + \cos^2 \omega} - 3x \cos \omega - \frac{1}{3} (\sin \omega + \sin^2 \omega) + \frac{2}{3} \quad (6)$$

where ω is the orbital mixing (order) parameter ($0 \leq \cos \omega \leq 1$). The J_{ab} value by the symmetry-projected GHF¹⁰ becomes almost identical to those of GSO EHF and GSO SO-SCF in the strong electron correlation region: $0 \leq x \leq 1/2$. The situation is also recognized for four-center four-electron [4, 4] systems²⁴ in Fig.2, showing the utility of the broken-symmetry approach.

The J_{ab} value for the triangle (or tetrahedral) multi-center radicals is calculated by first principle (FP) methods in Fig. 1.

$$J_{ab}(FP) = \frac{{}^{LS}E_Y - {}^{HS}E_Y}{{}^{HS}\langle \hat{S}^2 \rangle_Y - {}^{LS}\langle \hat{S}^2 \rangle_Y} \quad (7)$$

where ${}^X E_Y$ and ${}^X \langle \hat{S}^2 \rangle_Y$ denote, respectively, the total energy and total spin angular momentum of the spin state X (X = the lowest spin (LS) and/or the highest spin (HS) state) by a computational method Y^{2,25-27}. In our scheme, both \hat{S}^2 and \hat{S}_z -symmetry adapted (SA) GSO EHF and GSO SO-SCF are used to calculate isotropic J_{ab} values in the Heisenberg model. On the other hand, the \hat{S}^2 and \hat{S}_z -symmetry-projection of broken-symmetry (BS) GHF solution has been carried out in combination with the energy splittings of the Heisenberg model, leading to the same equation in eq. (6), where ${}^X E_Y$ and by GHF (together with GHF MP and GHF CCSD) and GDFT can be used²⁵⁻²⁷.

Recent developments of ab initio hybrid density function theory (HDFT) enable us to determine t and U_{eff} parameters in eq. (3) and J_{ab} values in eq. (6) for p-d, π -d, π -R and σ -R conjugated systems^{28,29}. UB3LYP calculations of finite clusters have been carried out to determine t , U_{eff} and J parameters for organic superconductors such as κ -(BEDT-TTF)₂(X) and κ -(BETS)₂X. For the purpose, the singlet-triplet (ST) energy gap by FP calculation is mapped to that of Hubbard model as

$$\Delta(ST)/2 = J_{ab}(FP) = J_{ab}(Hubbard) = \frac{1}{2} U_{eff} + \sqrt{4t^2 + U_{eff}^2} \quad (8a)$$

$$= -t \left(2t/U_{eff} \right) = J_{ab}(Heisenberg) \quad (U \gg t) \quad (8b)$$

$$= -t \left[1 - \left(U_{eff}/2t \right) + \left(U_{eff}/2t \right)^2 \right] \quad (\text{band model}) \quad (U < t) \quad (7c)$$

It is noteworthy that $J_{ab}(FP)$ and $J_{ab}(Hubbard)$ are parameters responsible for magnetic excitations in the whole interaction region: (7a)–(7c).

3. Molecular design of isoelectronic p-d, π -d, π -R and σ -R systems

3.1. N-BAND HUBBARD MODELS VIA AB INITIO CALCULATIONS

The ab initio broken-symmetry (BS) molecular orbital (MO)^{4,31} and MCSCF³² calculations of copper oxides have shown that cuprates exist in the intermediate electron correlation regime with finite on-site Coulomb repulsion ($U_{eff} = 5\sim 6$ eV). The ab initio computational results have been mapped into N-band Hubbard models³¹. For example, two-site (two-band) model considering both copper and oxygen sites is such an example.

This d-p (p-d) model Hamiltonians for metal-oxide clusters M_nO_m ($M = \text{Fe, Co, } \dots, \text{Cu}$) have been diagonalized to elucidate charge and spin populations, and effective exchange integrals (J) in these systems. It was found that holes induced in CuO clusters are populated mainly on oxygen sites³¹. Interestingly, the $1/N$ expansion of this d-p model by Nagoya group³³ has provided reasonable explanations of the phase diagrams and pseudo gaps in cuprates.

On the other hand, Zhang and Rice⁵ have derived the so-called t-J Hamiltonian model from the p-d model, assuming that hole (electron) doped on the oxygen site forms the singlet pair with the unpaired electron on the Cu(II) site. The exact diagonalization of the t-J model has indicated that the *const.* in the J-model ($T_c = cJ$) is about 0.1³⁴. The slave-boson approximation to the t-J model has revealed possible phase diagrams for cuprates³⁵, which have been modified to obtain one of reasonable explanations of our J model^{1,8}.

3.2. EQUIVALENCE TRANSFORMATION OF CUO (CUO₂) TO ISOELECTRONIC P-D, π -R AND σ -R SYSTEMS

From the view point of material science, molecular design of new materials is one of important and interesting problems. Concerning with the high-T_c superconductivity, we have proposed new p-d, π -R and σ -R conjugated systems which are considered to be isoelectronic to the CuO bond of cuprates on the basis of the two band (p-d) model^{8,31}. The doubly occupied p-orbital of O²⁻ in CuO can be replaced by π -orbital of organic donors such as TTF derivatives. While the open-shell dx²-y² orbital of Cu(II) may be substituted with the open-shell d-orbital of transition metal complexes. These chemical modifications enable us to propose various π -d conjugated systems. Similarly, we may have π -R conjugated systems by replacing the open-shell d-orbital of π -d systems with that of organic radical species (R) such as nitroxide. On the other hand, the π -orbital of π -R conjugated systems can be regarded as a σ -orbital of σ -R conjugates systems. All these p-d, π -R, π -R and σ -R conjugated systems in Fig. 3 are strongly correlated electron systems because of existence of unpaired electrons on d or R sites before carrier doping.

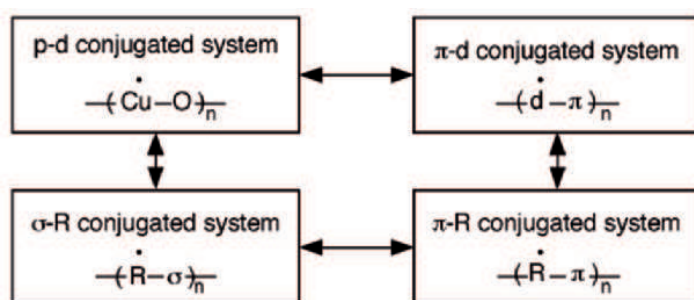


Figure 3. Molecular design of p-d, π -R and σ -R systems which are isoelectronic to CuO bonds on the basis of the two-band models.

Ab initio calculations have been performed to elucidate theoretical possibilities of magnetic modifications of molecular-based materials by introduction of spin sources. Fig. 4 illustrates such theoretical proposals, where the conducting parts are constructed with (1) conducting polymers²⁴, (2) charge-transfer (CT) complexes³⁶, (3) organic metals such as TTF-derivatives (BEDT-TTF, BETS, etc)^{31,37}, (4) nonmagnetic metal clusters³⁸ or DNA wires^{39,40}. On the other hand, stable organic radicals such as nitroxides and transition metal complexes (MX₄) are employed as spin sources³¹.

First principle computational results of cluster models of these species are mapped into the Anderson model used in heavy fermion systems as

$$H = \sum_{i,\sigma} \varepsilon_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{j,\sigma} E_j d_{j\sigma}^\dagger d_{j\sigma} + U_{eff} \sum_j n_{j\uparrow} n_{j\downarrow} + V \sum_{k\sigma} \left(d_{j\sigma}^\dagger c_{i\sigma} + c_{i\sigma}^\dagger d_{j\sigma} \right) \quad (9)$$

where V denotes the coupling constant between delocalized electron i and localized spin j . The natural orbital analysis of the first-order density matrix by the computations has elucidated the spin polarization path of conduction electron via localized spins³⁶⁻⁴⁰.

Past 15 years, many experiments have been carried out to realize π -d, π -R and related systems⁴⁰⁻⁴⁴. Now, many interesting molecular-based materials have been discovered experimentally: (a) high-spin ion-radicals, (b) antiferromagnetic metal (AFM), (c) d-wave superconductor (SC), (d) coexistence of AFM and d-wave SC, so on. These exotic materials have already been extensively examined on the theoretical grounds in relation to the theoretical proposals³⁶⁻⁴⁰ in Fig. 4. Exact diagonalization of the derived model Hamiltonian of the species provides a guarantee of future achievements.

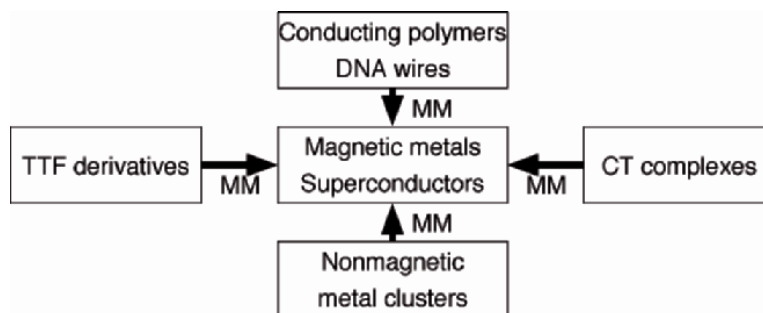


Figure 4. Theoretical proposals of magnetic modification (MM) of molecule-based materials.

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