Correlated Hybridization in Transition-Metal Complexes

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We apply local orbital basis density functional theory (using SIESTA) coupled with a mapping to the Anderson impurity model to estimate the Coulomb assisted or correlated hybridization between transition-metal d orbitals and ligand sp orbitals for a number of molecular complexes. We find remarkably high values which can have several physical implications including (i) renormalization of effective single-band or multiband Hubbard model parameters for the cuprates and, potentially, elemental iron, and (ii) spin polarizing molecular transistors.

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The properties of transition-metal compounds are often dominated by the $3d$ orbitals because their localized character causes a strong Coulomb repulsion between the electrons. The theoretical progress in the field has been impeded by the extreme difficulties of dealing with even the simplest model Hamiltonian appropriate for these materials, the Hubbard model [1], consisting of a direct electron hopping between orbitals i and j with amplitude t_{ij} and of the Coulomb repulsion U of electrons in the same orbital. U is a matrix element of the Coulomb potential, $U = \langle ii|V(\mathbf{r}-\mathbf{r}')|ii\rangle$. Matrix elements involving different lattice sites i and j are generally smaller than U. One of them is the so-called correlated hybridization $X_{ij} = \langle ii|V(\mathbf{r}-\mathbf{r}')|ij\rangle$ that describes a density dependent hopping. Estimates for X_{ij} (0.5 eV in transition metals [1], 0.8 eV in cuprates [2]) show that the matrix elements of the correlated hybridization are comparable to or even larger than the corresponding amplitudes of direct hopping in real systems. Up to now, effects caused by correlated hybridization have not yet attracted much attention: Hirsch suggested a new mechanism for superconductivity [3], some exactly solvable cases were discussed [4], finite clusters were studied using exact diagonalization [5], metallic ferromagnetism was investigated [6], and correlated hybridization was studied via dynamical mean-field theory in the Falikov-Kimball model [7].

In many compounds, cuprates and manganites are well-known examples, the transition-metal atoms are surrounded by oxygens or other elements with p orbitals so that the $3d$ orbitals are only effectively coupled with each other due to oxygen orbitals. Realistic multiband models including oxygen degrees of freedom, as proposed for the cuprates [8], cannot easily be mapped onto effective single-band models (see [9] and references therein). The effective hopping between transition-metal sites must then be mediated by the hybridization with p orbitals of the oxygens. Despite the somewhat robust interest in correlated hybridization between like orbitals, there have been no *ab initio* studies of the corresponding *correlated hybridization* [10] between the d orbitals and surrounding p orbitals. This may be of considerable interest in molecular transistors based upon transition-metal complexes for which the surrounding ligand atoms provide the linkage to the leads [11].

In this Letter, we estimate matrix elements of the correlated hybridization for several transition metals in different chemical environments from density functional theory (DFT) calculations. To our knowledge, this is the first systematic *ab initio* study of correlated hybridization matrix elements, and we find remarkably high values, although similar spin-dependent hybridization phenomena have been noted in the context of molecular transistors [12]. We demonstrate that these additional hybridization matrix elements could significantly change the parameters in effective single-band models for transition-metal oxides. Furthermore, we demonstrate that the correlated hybridization may possibly provide a means to significant spin polarization of currents through transition-metal based molecular transistors in modest magnetic fields.

We have carried out spin-polarized electronic structure calculations using the fully *ab initio* DFT code SIESTA [13]. It uses Troullier-Martins norm-conserving pseudopotentials [14] in the Kleinman-Bylander form [15] where we included nonlinear partial-core corrections for the transition-metal atoms to take into account exchange and correlation effects in the core region [16]. We used the generalized gradient approximation (GGA) for the exchange-correlation energy functional in the version of Ref. [17]. SIESTA uses a basis set of atomic orbitals where the method by Sankey and Niklewski [18] is employed. We used a double-ζ basis set, and included polarization orbitals for the transition-metal atoms. To determine the minimum energy configuration within DFT all complexes were allowed to relay till the force on each atom was less than 0.03 eV/Å.

The results of the SIESTA calculations are used to determine effective hybridization matrix elements. For that purpose we map the final DFT Hamiltonian $\mathcal{H}_{\rm DFT}$ obtained from SIESTA onto an effective two-band model,

$$\tilde{\mathcal{H}} = \sum_{i,\sigma} \tilde{\varepsilon}^{d}_{i\sigma} d^{\dagger}_{i\sigma} d_{i\sigma} + \sum_{\alpha,\sigma} \tilde{\varepsilon}^{p}_{\alpha\sigma} p^{\dagger}_{\alpha\sigma} p_{\alpha\sigma} + \sum_{i,\alpha,\sigma} \tilde{V}_{i\alpha\sigma}(d^{\dagger}_{i\sigma} p_{\alpha\sigma} + \text{H.c.}), \quad (1)$$

where the $3d$ orbitals of the transition-metal atoms are separated from the rest. The $d^{\dagger}_{i\sigma}$ ($p^{\dagger}_{\alpha\sigma}$) are fermionic creation operators of $3d$ (ligand) electrons with spin σ at orbital i (α). To determine the one-particle energies, $\tilde{\varepsilon}^{d}_{i\sigma}$ and $\tilde{\varepsilon}^{p}_{\alpha\sigma}$, and the hybridization matrix elements, $\tilde{V}_{i\alpha\sigma}$, we apply unitary transformations to $\mathcal{H}_{\text{DFT}}$. Because the atomic basis states used by SIESTA are not orthogonal the transformation of $\mathcal{H}_{\text{DFT}}$ is performed in three steps: (i) The block of the $3d$ orbitals (single ζ only) is diagonalized. (ii) The $3d$ contributions to the ligand basis states are removed. (iii) The ligand block is diagonalized. After theses steps we obtain an effective Hamiltonian $\tilde{\mathcal{H}}$ of the desired form (1) where $\tilde{\mathcal{H}}$ has the same eigenvalues as $\mathcal{H}_{\text{DFT}}$ because $\tilde{\mathcal{H}}$ is derived by unitary transformation from $\mathcal{H}_{\text{DFT}}$.

Because we performed spin-dependent DFT calculations $\mathcal{H}_{\text{DFT}}$ consists of two completely separated spin sectors. Therefore, the parameters of $\tilde{\mathcal{H}}$ depend on the spin direction, and we find a remarkable spin dependence of the hybridization matrix elements if the transition-metal atoms are in high-spin states (see Table I).

To discuss the spin dependence of the hybridization matrix elements in detail we calculate the hybridization broadening function, $\Gamma_{i\sigma}(\omega) = \sum_{\alpha} |\tilde{V}_{i\alpha\sigma}|^2 \delta(\omega - \tilde{\varepsilon}^{p}_{\alpha\sigma})$, for all impurity states i. As one can see from Fig. 1, the hybridization matrix elements of the minority spin direction are always larger than the values of the majority spin direction.

A detailed analysis shows that this spin dependence can only derive from correlated hybridization. To illustrate the point, let us now consider a Hamiltonian,

$$\mathcal{H} = \sum_{i,\sigma} \varepsilon^{d}_{i} d^{\dagger}_{i\sigma} d_{i\sigma} + \sum_{\alpha,\sigma} \varepsilon^{p}_{\alpha} p^{\dagger}_{\alpha\sigma} p_{\alpha\sigma} + \sum_{i,\alpha,\sigma} [V_{i\alpha} + A_{i\alpha} d^{\dagger}_{i-\sigma} d_{i-\sigma}](d^{\dagger}_{i\sigma} p_{\alpha\sigma} + \text{H.c.}), \quad (2)$$

with correlated hybridization matrix elements $A_{i\alpha}$. $\mathcal{H}$ can be easily transformed to the form of Eq. (1) if a factorization approximation is used where the correlated hybridization leads to spin-dependent one-particle energies $\tilde{\varepsilon}^{d}_{i\sigma}$ and hybridization matrix elements $\tilde{V}_{i\alpha\sigma}$. This consideration can also be used to determine the matrix elements $A_{i\alpha}$ of the correlated hybridization, one obtains

$$A_{i\alpha} = \frac{\tilde{V}_{i\alpha\downarrow} - \tilde{V}_{i\alpha\uparrow}}{\langle d^{\dagger}_{i\uparrow} d_{i\uparrow}\rangle - \langle d^{\dagger}_{i\downarrow} d_{i\downarrow}\rangle}. \quad (3)$$

Because of the expectation values of the occupation number operators are restricted, $0 \leq \langle d^{\dagger}_{i\sigma} d_{i\sigma}\rangle \leq 1$, the difference between the both spin directions of the effective hybridization matrix elements (as listed in Table I) has to be interpreted as a lower bound for the full matrix element of the correlated hybridization. Thus, we conclude from Table I that the correlated hybridization matrix elements $A_{i\alpha}$ are comparable in magnitude to the regular tight-binding hopping amplitudes $V_{i\alpha}$. Although the commonly used approximations of DFT such as local density approximation or CGA are known to fail in accurately describing strongly correlated transition-metal systems (notably the cuprates and metallic plutonium), there is a notable tradition of successfully using DFT to provide estimates of parameters for many-body Hamiltonians, as in calculations of the hybridization for successfully estimating Kondo scales in a series of cerium heavy fermion systems [19]. This is the spirit of our approach; while we do not include the feedback modification of the density to the DFT, that has successfully been done only in one instance [20].

In the following we want to show that the large values obtained for the correlated hybridization matrix elements could indeed lead to intriguing physical effects. For this purpose we consider in the following with the cuprates and a molecular device two physical systems where the local coordination environment of the transition-metal atoms is precisely the same as in the clusters studied above. At first, we consider a three-band model as proposed for the cup-

TABLE I. Maximal difference between the spin directions of the effective hybridization matrix elements $\tilde{V}_{i\alpha\sigma}$ for several transition-metal complexes in the range ±10 eV about the chemical potential where the overlap between the ligand states of the two spin directions is at least 0.95. $A_{\max}$ is defined in Eq. (4) and the last column gives the orbital symmetry of the maximally different effective hybridization matrix elements referenced to tetrahedral or octahedral symmetry.

Compound	$\max(\lvert\tilde{V}_{i\alpha\uparrow} - \tilde{V}_{i\alpha\downarrow}\rvert)$	$A_{\max}$	Orbital
$[Fe(SH)_4]^{2-}$, perfect structure	0.361 eV	0.791	t_{2g}
$[Fe(SH)_4]^{2-}$, relaxed structure	0.481 eV	0.354	t_{2g}
$[Cu(H_2O)_6]^{2+}$	0.871 eV	0.875	e_g
$[Mn(H_2O)_6]^{2+}$	2.416 eV	2.000	t_{2g}
$[Ni(H_2O)_6]^{2+}$	1.584 eV	1.482	e_g
Co(3, 5-DBSQ)$_2$(phen)	1.021 eV	4.700	t_{2g}
Co(3, 5-DBSQ)(3, 5 DBCat)(phen)	0.271 eV	0.542	t_{2g}
Mn(NO$_2$-phen)(3, 6-DBSQ)$_2$	0.743 eV	0.664	t_{2g}
Mn(II)(Bupy)$_2$(3, 6-DBCat)$_2$	0.479 eV	0.555	t_{2g}
Mn(III)(Bupy)$_2$(3, 6-DBCat)$_2$	0.987 eV	0.717	e_g
Mn(IV)(Bupy)$_2$(3, 6-DBCat)$_2$	0.894 eV	1.132	t_{2g}

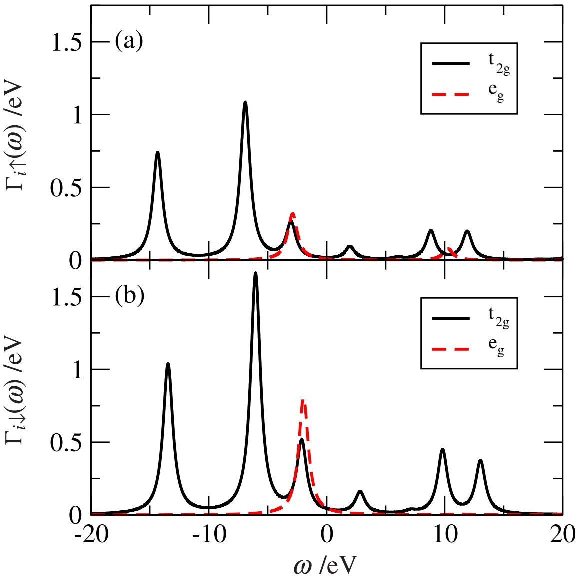

FIG. 1 (color online). Spin-dependent hybridization functions for $[\mathrm{Fe(SH)_4}]^{2-}$, perfect structure, where the line spectra have been broadened with Gaussian functions of width 0.5 eV. The results for the majority [minority] spin direction is shown in panel (a) [panel (b)].

rates [8] where we use standard parameters [21], Cu $3d$ O $2p$ hybridization $t_{pd} = 1.3$ eV, O $2p$ O $2p$ hybridization $t_{pp} = 0.65$ eV, Cu on-site repulsion $U_d = 8.8$ eV, and charge transfer energy $\Delta = 3.5$ eV. Furthermore, we add a correlated hybridization between Cu $3d$ and O $2p$ orbitals to the Hamiltonian with matrix elements $A_{pd} = 0.5$ eV. In accordance to our DFT estimates, A_{pd} has the same sign and phase factors as t_{pd}. The three-band model can be reduced [22] to a $S = \frac{1}{2}$ Heisenberg model on the square lattice of Cu sites where the coupling strength in fourth order perturbation theory is given by $J = 4t_{pd}^4/2\Delta^3 + 4t_{pd}^2(t_{pd} + A_{pd})^2/\Delta^2 U_d$ Thus, the matrix elements $A_{pd} = 0.5$ eV of the correlated hybridization lead to an increase of the Heisenberg exchange from 0.24 to 0.34 eV.

The correlated hybridization also affects the mapping of the three-band model onto an effective single-band model by means of a cell perturbation theory [9,23]. Despite an increase of the magnitudes of the effective hopping matrix elements by about 20%, the on-site Hubbard U is significantly lowered from 2.48 to 1.94 eV. This reduction in U may have some relevance in understanding the need to use smaller Hubbard interactions in models of, e.g., metallic Fe than one obtains from estimates using constrained occupancy DFT [24]: If there is significant correlated hybridization of d levels with s, p levels on a neighboring site then the same mechanism of U reduction upon folding down to the d-band only model from the multiband model will be operable.

Perhaps the most interesting application of our results is to tunable molecular transistors [11,25,26], with the strongest response possible not in the Kondo limit but rather the mixed valent limit. In the presence of a relatively modest field, the correlated hybridization can impart a potentially significant spin polarization of the current through the device without requiring spin polarization of the leads as has been considered both experimentally [27] and theoretically [28]. To illustrate the idea, consider the schematic device of Fig. 2, in which a transition-metal based molecule is attached to ordinary metallic leads, and assume that a spin 1/2 large U model is applicable, as relevant for the low spin Co complexes considered in Ref. [11] (electron hopping) or a Cu complex (hole hopping). The bare lead-to-transition-metal site hybridization V_{Ld} goes as $V_{Ld}^{\sigma} \approx \frac{WV_{\sigma}}{\varepsilon_l - E_F}$, where W is the lead-to-ligand hybridization matrix element, ε_L is the ligand lowest unoccupied molecular orbital (highest occupied molecular orbital) for electrons (holes) to transition from lead to ligand, and $V_{\sigma} = V_0(1 - Am\sigma)$ is the spin-dependent hybridization discussed earlier, with A a dimensionless ratio of the assisted hopping matrix element to the direct one V_0, and m the induced polarization $m = n_{d\uparrow} - n_{d\downarrow}$ of the transition-metal ion in an applied field H. Note that estimates,

$$A_{\max} = 2\frac{\max|\tilde{V}_{i\alpha\downarrow} - \tilde{V}_{i\alpha\uparrow}|}{\tilde{V}_{i\alpha\downarrow} + \tilde{V}_{i\alpha\uparrow}}, \tag{4}$$

for the ratio A can be found in Table I. Importantly, we note that A can be as large as 3–5.

We next assume that the Friedel sum rule [29] can be applied so that the number of electrons (holes) n_d on the transition-metal site is given by $n_d = n_{d\uparrow} + n_{d\downarrow} = \frac{\delta_\uparrow + \delta_\downarrow}{\pi}$ and the polarization m by $m = \frac{1}{\pi}(\delta_\uparrow - \delta_\downarrow)$, where δ_σ is the Fermi energy phase shift for an electron of spin σ to scatter off the transition-metal site. We further take a renormalized resonant level model for the phase shift, with resonance position $\tilde{\varepsilon}_\sigma = \tilde{\varepsilon}_0 - \mu H\sigma$, μ the magnetic moment of the d levels, and resonance width $\tilde{\Gamma}_\sigma = \tilde{\Gamma}_0(1 - 2Am\sigma)$, where only contributions linear in the magnetic

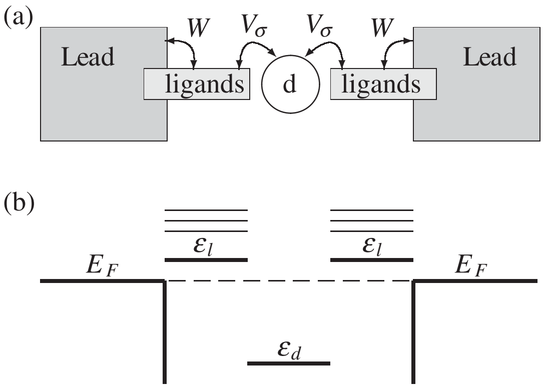

FIG. 2. Panel (a) shows the schematic design of the proposed spin filter device with the definitions of the lead-to-ligand and ligand-to-transition-metal site hybridization matrix elements W and V_σ. The energies of the involved electronic states are sketched in panel (b).

field H are taken into account. Note that in the Kondo regime the zero-field resonance parameters satisfy $\sqrt{\tilde{\varepsilon}_0^2 + \tilde{\Gamma}_0^2} \approx k_B T_K$, with T_K the Kondo temperature of the transistor. In this model, the phase shift is $\delta_\sigma = \frac{\pi}{2} - \tan^{-1}(\frac{\tilde{\varepsilon}_\sigma}{\tilde{\Gamma}_\sigma})$. Assuming zero bias, identical leads, and low temperature, the conductance $\mathcal{G}_\sigma$ within our mean-field treatment of the correlated hybridization in spin channel σ is approximately given by [30], $\mathcal{G}_\sigma \approx \frac{e^2}{\pi\hbar} \sin^2 \delta_\sigma$.

Using the definitions and results of the previous paragraph we thus find

$$\frac{(\mathcal{G}_\uparrow - \mathcal{G}_\downarrow)}{\mathcal{G}(H = 0)} \approx \frac{2\sin(2\delta_0)}{1 + \frac{2A}{\pi}\sin(2\delta_0)} \frac{\mu H}{\tilde{\Gamma}_0} \tag{5}$$

with δ_0 the zero field phase shift.

The A dependent enhancement factor follows from the impurity polarization $m \propto \mathcal{G}_\downarrow - \mathcal{G}_\uparrow$. This effect is overestimated within our mean-field approximation, although it has a clear physical origin: the up-spin resonance narrows significantly in applied field as the down-spin resonance broadens, allowing a feedback effect that enhances the tendency towards magnetization saturation. The effect is most pronounced in the mixed valent regime for $n_d \approx 1.5$, where a critical A value of $\pi/2$ yields divergent m within the approximation. Indeed, a significant enhancement of the zero field local susceptibility was found in a nonperturbative treatment of this model for $U_d = 0$ in the mixed valent regime [10]. It might be possible to tune the resonance into the highly polarizing regime through a combination of gate control (to tune ϵ_d) and contact chemistry (to tune the lead-transition-metal ion hybridization). The enhancement effect can also be significant in the Kondo regime, for which $|1 - n_d| \leq 0.3$ [31] and $|\sin(2\delta_0)| < 0.81$. Examining the A values in our table, we obtain critical $|1 - n_d|$ values of 0.11 and 0.29 for the $\mathrm{Co(II)(3,5-DBSQ)_2(phen)}$ and $[\mathrm{Mn(H_2O)_6}]^{2+}$ complexes, safely within the Kondo regime.

To conclude, we have presented here the first systematic *ab initio* study of correlated hybridization matrix elements for several transition-metal complexes. Based on DFT calculations we have found correlated hybridization matrix elements comparable in magnitude to the regular tight-binding hybridization amplitudes which can lead to significant changes in the parameters of effective models for transition-metal compounds. Finally, we have sketched how the correlated hybridization can be employed to design spin sensitive devices, polarizing the spin current dramatically with potentially modest applied fields and paramagnetic leads.

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