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A resonating broken symmetry configuration interaction approach for double-exchange magnetic systems

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Abstract

The correct description for ion–radical systems has recently attracted much attention from density functional theory (DFT) researchers. Although several hybridization schemes using exact (Hartree–Fock) exchange and DFT exchange–correlation functionals have been proposed, it has been reported that such treatments do not work for the description of ion–radical systems. In this study we show that combining the exact exchange term in the Kohn–Sham DFT (or the Hartree–Fock equation) with the following resonating configuration interaction method is effective for the description of double-exchange type molecular magnetic interactions. The results are analyzed in relation to the ‘many-electron self-interaction’ concept that was recently proposed by DFT researchers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Kohn–Sham (KS) density functional theory (DFT) [1] is widely used in quantum chemistry [2, 3] and condensed matter physics [4]. The semilocal approximation for exchange and correlation (XC) effects, such as the local density approximation (LDA) and the general gradient approximation (GGA) functionals, is computationally tractable and has led to enormous growth in computational physics and chemistry for the electronic structure of materials. The semilocal XC functional is usually designed on the basis of a homogeneous electron gas (HEG) system or the periodic analog, such as the sine-or-cosine modulated potential, of the HEG system. However, an HEG system is very different from any molecular and/or magnetic system in which the electrons are partly

bound at the nuclei and occupy orbitals that are more-or-less localized. Then the self-Hartree term is not canceled with other terms, leading to the well-known self-interaction error (SIE) which causes many failures for such systems, e.g. an incorrect (metallic) description for magnetic states such as the antiferromagnetic state of high- T_c copper oxides [5], the localized f electrons of Ce [6], or an underestimation of chemical reaction barriers [3], etc. Molecular magnetic systems are ‘finite’ and ‘magnetic’ systems, and thus semilocal XC treatments are not appropriate. In fact, we reported that the LDA and GGA without any correction for the SIE often lead to an overestimation of magnetic interactions [7].

Most of these behaviors are corrected by mixing with the exact (Hartree–Fock) exchange: the most successful scheme can be seen in the B3LYP XC functional [8] that is the

de facto standard XC functional in quantum chemistry. In the field of condensed matter physics, the LDA + U treatment is usually employed for treating strongly correlated systems [9]. Recently, Kusakabe *et al* [10] have proposed a new scheme to determine the on-site repulsion parameter, U , within the multireference (MR) DFT framework [11]. On the other hand, Kotani, Akai, and Gross also have employed the exact exchange with no parameter and suggested its importance for strongly correlated systems [12, 13]. In order to avoid the self-interactions of LDA and GGA, a more straightforward remedy was proposed by Perdew and Zunger (PZ) [14] and the resulting methods, the SIC-LDA and SIC-GGA methods, were believed to be a complete self-interaction correction scheme for any case.

The description of the ion-radical states has recently attracted much attention in the field of *ab initio* theory. This type of state is often seen in various classes of materials such as magnetic-metals [15], the high- T_c superconductors [16], or biological compounds related to electron transfer reactions [17]. The important point is whether the excess electron (or hole) is localized or delocalized. For instance, the behavior of the excess electron determines whether a hole-doped magnetic system exhibits conductivity or not [15]. In the field of inorganic chemistry, Robin and Day utilized the behavior of the excess electron to classify the mixed valence (MV) transition metal (TM) complex [18, 19]. In this case, it is essential to correctly describe the behavior of the excess electron or hole in order to determine the conductivity and the magnetism of the complex.

This topic leads to a serious problem in conventional DFT [20–38]⁸. In analogy to Robin and Day’s three types of MV-TM systems, the chemical bond of A_2^+ (A = any atom or molecule) is tested. During the past decade, many DFT researchers have examined various types of DFT functionals for A_2^+ systems. However, up to now, for all LDA, GGA, and hybrid DFT methods the energy of the delocalized ($A^{0.5+} + A^{0.5+}$) state becomes lower than the sum of energies of A and A^+ for large intersite distances. This suggests that all of these methods suffer from ‘size-inconsistency’ for A_2^+ systems. This failure is not resolved even if the PZ-SIC-DFT is employed [26, 27]; the energy gap between the delocalized state ($A^{0.5+} + A^{0.5+}$) and the dissociation limit (the sum of A and A^+) remains finite for the PZ-SIC-DFT.

Mori-Sanchez, Cohen, and Yang (MCY) have suggested the concept of ‘many-electron self-interaction’ [32, 35] (see footnote 8), which is a generalized version of the one-electron self-interaction of the PZ-SIC-DFT. Their discussion is based on the relation proposed by Perdew, Parr, Levy, and Balduz (PPLB) [38], which states that the exact energy functional for a fractional number of electrons, $N + \omega$ ($0 \leq \omega \leq 1$), depends linearly on the number of electrons as

$$E_{\text{PPLB}}(N + \omega) = (1 - \omega)E_{\text{PPLB}}(N) + \omega E_{\text{PPLB}}(N + 1). \quad (1)$$

MCY have analyzed the dependence of various XC functionals on electron number, showing that the inequality

⁸ We follow the distinction between many-electron interaction error and one-electron self-interaction error as defined in [32].

$2E(N + 0.5) < E(N) + E(N + 1)$ holds for the usual semilocal XC functionals as well as hybrid XC functionals including B3LYP. This feature results in the fact that the energy of the delocalized ($A^{0.5+} + A^{0.5+}$) state becomes lower than the sum of energies of M and M^+ for large intersite distances.

From the viewpoint of the interactions between two magnetic sources, this discussion is very important. Consider the system M_2^+ , consisting of two magnetic sites having spins $S + 1/2$ and S [39]. In this system, a lone itinerant electron has a lower energy if the localized spins are all aligned due to the delocalization effect of this excess electron, leading to the stability of the high-spin state. This is known as the double-exchange effect [39]. This implies that, at any finite intersite distance, the energy profile must satisfy the relation

$$E(M^{0.5+} + M^{0.5+}) < E(M + M^+) = E(M^+ + M). \quad (2)$$

As the intersite distance becomes large, the transfer of the itinerant spin reduces. Then at the dissociation limit of the M_2^+ system equation (2) must reduce to

$$E(M + M^+) = E(M^{n+} + M^{(1-n)+}) = E(M^+ + M) \quad (3)$$

for any n ($0 < n < 1$), which is equivalent to the PPLB relation for the exact DFT. Although which type of XC treatment would satisfy equations (2) and (3) is an important issue, there is no right answer up to now.

In this paper we would like to suggest a possible answer to this problem. This is based on the resonating (Res) configuration interaction (CI) approach using broken symmetry (BS) solutions, which has been previously proposed [40, 41]. In this study, we employ the spin-unrestricted Hartree-Fock (UHF) exchange to yield two complementary symmetry-broken solutions. Using these UHF solutions as bases, we solve the resonating CI equation. In order to demonstrate the validity of this scheme, we examined simple double-exchange systems.

2. Method

In this section we shall briefly outline our method in the context of the present applications for the double-exchange system M_2^+ . There are two essential points in our approach. The first point is the use of the exact HF exchange to yield two bases for the following resonating CI computation. It is reported that the PPLB energy profile for the UHF exchange is given by (compare with equation (1))

$$E_{\text{UHF}}(N + \omega) > (1 - \omega)E_{\text{UHF}}(N) + \omega E_{\text{UHF}}(N + 1). \quad (4)$$

This implies that the HF energy favors the localized state as

$$E(M^{0.5+} + M^{0.5+}) > E(M + M^+) = E(M^+ + M). \quad (5)$$

In other words, the excess electron is expected to localize on the left and right sides in the two UHF solutions as denoted by $|L\rangle$ and $|R\rangle$ in figure 1(a).

Now we proceed to recover the resonating effect. The second essential point is that we do not implement the orbital relaxation step in the Res-CI theory, which is critically

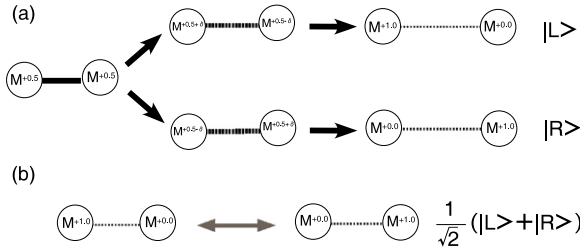


Figure 1. (a) Two localized solutions $|L\rangle$ and $|R\rangle$ for the Mn_2^+ system. (b) The superposition of $|L\rangle$ and $|R\rangle$ for the Mn_2^+ system.

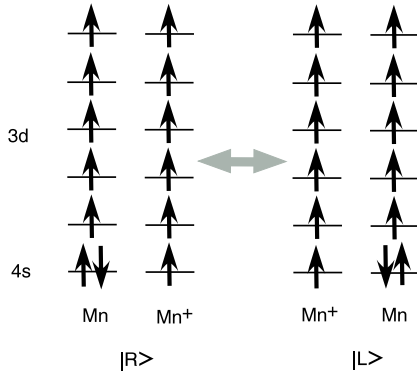


Figure 2. The ground-state state configuration of the Mn_2^+ . The gray double-sided arrow indicates the in-phase superposition of configurations due to itinerancy of the excess electron [39].

different from the Res-Hartree-Fock theory of Fukutome [42]. This is because the orbital relaxation step involves a nonlinear equation as in the case of the UHF, leading to the localized solution again [41]. Employing these $|L\rangle$ and $|R\rangle$ as two bases, we solve the CI equation:

$$\begin{bmatrix} \langle L|\hat{H}|L\rangle & \langle R|\hat{H}|L\rangle \\ \langle L|\hat{H}|R\rangle & \langle R|\hat{H}|R\rangle \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = E_0 \begin{bmatrix} \langle L|L\rangle & \langle R|L\rangle \\ \langle L|R\rangle & \langle R|R\rangle \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}. \quad (6)$$

Here \hat{H} is the *ab initio* Hamiltonian. In general, the ground-state solution takes the form

$$|Res\rangle = C_L|L\rangle + C_R|R\rangle, \quad (7)$$

which covers all delocalized $\{1/\sqrt{2}, 1/\sqrt{2}\}$, localized ($\{1, 0\}$ or $\{0, 1\}$), and intermediate states. For a homonuclear case, the Res-CI solution becomes equivalent to a superposition of $|L\rangle$ and $|R\rangle$, as shown in figure 1(b).

In the following, we use the Gaussian 03 [43] for UHF, and DFT calculations, and the original non-orthogonal CI code for the Res-CI calculation. The basis set employed is Wachters + f [44], which is has triple-zeta plus diffuse and polarization functions quality.

3. Computational results

We shall examine the manganese dimer cation (Mn_2^+) whose the ground-state has been reported to have the highest spin

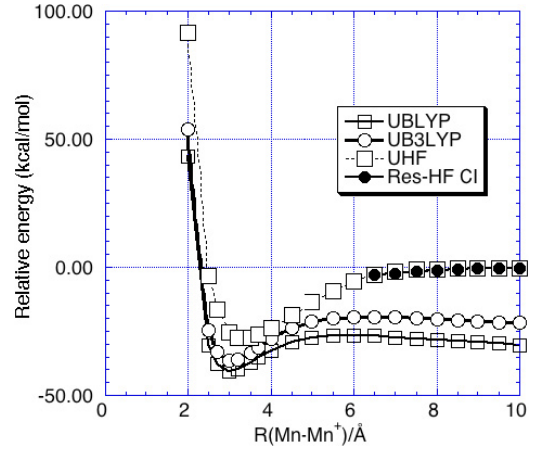


Figure 3. The potential surfaces for the quintet state of Mn_2^+ calculated by the UBLYP, UB3LYP, UHF, and Res-HF CI methods.

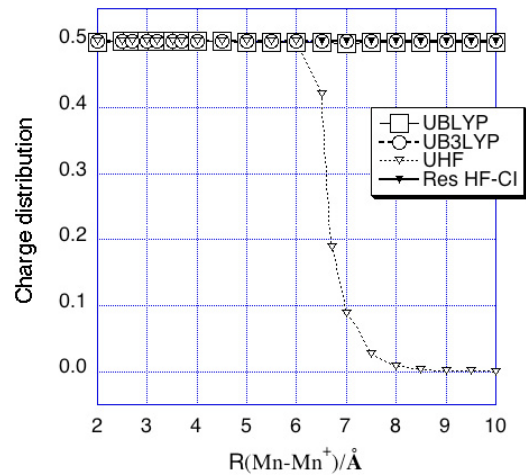


Figure 4. Calculated charge distributions on a relatively cationic site of Mn_2^+ for various intersite distances.

($^{12}\Sigma_g^+$) state [45]. The corresponding electronic configuration is expected to be a simple and representative double-exchange system as shown in figure 2.

We first compute Mn_2^+ using the UHF, UB3LYP (hybrid DFT), and UBLYP (DFT) methods. As expected, the ground state is found with the highest spin for all the methods. However, as presented in figure 3, the potential surfaces of UBLYP and UB3LYP fail for the long distance between Mn and Mn^+ . Obviously these errors are due to the self-interaction error involved with the use of the DFT XC term as in the case of other ion-radical systems [20–38]: in fact, the potential surface is correctly described by using the UHF method.

The binding energy estimated from the UHF potential surface is approximately 28 kcal mol^{-1} , which is similar to the experimental value (31 kcal mol^{-1}) [45]. However, judging from the calculated density distribution shown in figure 4, the UHF solutions reduce either to $|L\rangle$ or to $|R\rangle$, missing the delocalized nature of the double-exchange system shown in figure 2 for long distances. By using these complementary UHF solutions as two bases, Res-HF CI calculations are performed for distances where the bifurcated

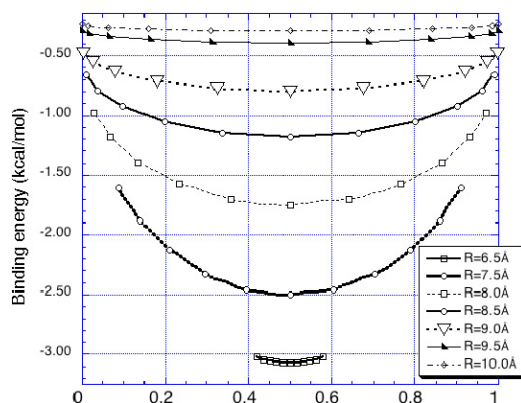


Figure 5. Dependence of the Res-HF CI binding energy on charge distribution for Mn_2^+ .

UHF solutions appear. The potential surface of the Res-HF CI solutions, which is plotted in figure 3, is similar to that of UHF, implying that the resonating correction for the UHF energy is small. However, as shown in figure 4, the Res-CI solutions yield the completely delocalized charge distributions for all intersite distances, because the superposition between the $|L\rangle$ and $|R\rangle$ states is recovered.

Furthermore, we have analyzed the Res-HF CI energies for various $\{C_L, C_R\}$ sets. The total energies versus the charge distribution at the specific site are plotted in figure 5. We observe that the delocalized state ($C_L = C_R = 1/\sqrt{2}$) is stabilized and the energy rises parabolically as the charge localizes. As the intersite distance (R) increases, this energy profile becomes shallow, and it is approximately flat (the deviation becomes smaller than $0.01 \text{ kcal mol}^{-1}$) for $R = 10 \text{ \AA}$. These results indicate that the Res-HF CI solutions satisfy both equations (2) and (3), the conditions of a ‘many-electron self-interaction-free’ theory⁹.

4. Conclusions and future directions

We present the resonating broken symmetry treatment for double-exchange magnetic systems. We confirm that this method provides (i) the correct energy surface and (ii) the correct charge distribution for the simple examples. Both of these are important chemical reactions involving mixed valence states such as metalloenzyme reactions [46]. By analyzing the Res-HF CI solutions, we show that this Res-HF CI treatment satisfies both equations (2) and (3), implying that it is a ‘many-electron self-interaction-free’ (ME-SIF) method. To our knowledge, this is the first time that the *ab initio* ME-SIF calculation has been implemented for double-exchange systems. Here we employed UHF solutions as our basis, but if the XC functional satisfies equation (5) note that we can implement the resonating correction for the DFT treatment of the general mixed valence systems using the

⁹ We also examine several examples such as the CH_2 dimer cation and other cationic transition metal dimers, but these results are not presented here since the results are similar to those of Mn_2^+ and space is limited.

following equation:

$$E_{\text{Res-BS-DFT}} = E_{\text{DFT}} - \frac{1}{S^2 - 1} \times \left(St - \frac{\Delta E}{2} - \sqrt{t^2 - St\Delta E + \left(\frac{\Delta E}{2}\right)^2} \right), \quad (8)$$

where $t \equiv \langle R|\hat{H}|L\rangle$, $S \equiv \langle R|L\rangle$ and $\Delta E \equiv |\langle L|\hat{H}|L\rangle - \langle R|\hat{H}|R\rangle|$, which is estimated for the *ab initio* Hamiltonian, \hat{H} . In these expressions, $|L\rangle$ and $|R\rangle$ states are obtained using DFT calculations. If the XC functional does not satisfy equation (5), this Res-CI type of correction is impossible since both $|L\rangle$ and $|R\rangle$ reduce to the delocalized state. Therefore, we emphasize that it is important for the XC functional to satisfy equation (5), in other words to be always concave for $E_{\text{DFT}}(N + \omega) - E_{\text{PPLB}}(N + \omega)$. We expect that an accurate XC functional satisfying such a condition will be designed, but then the resonating CI correction given by equation (8) will be a powerful tool for ion-radical systems.

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