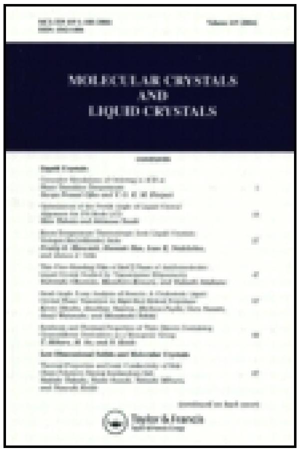

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Theoretical Studies of one Dimensional Tetranuclear Transition Metal Systems and their Clusters

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THEORETICAL STUDIES OF ONE DIMENSIONAL TETRANUCLEAR TRANSITION METAL SYSTEMS AND THEIR CLUSTERS

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Abstract As a continuation of previous UHF calculations, the complete active space (CAS) configuration interaction (CI) calculations by use of their natural orbitals (UNO) were carried out for the linear tetranuclear systems, *i.e.*, $M_1Cr(II)Cr(II)M_1$ (M_1 = Ni(II) or Ni(0)), to elucidate the nature of the d-d conjugated bonds. The energy levels for the ground and excited high-spin states of these species were also calculated by UNO CASCI to estimate the effective exchange integrals in the Heisenberg model.

INTRODUCTION

The d-d conjugated systems are interesting targets from the theoretical viewpoints, *e.g.* magnetism, optical nonlineality, and magnetooptics. However, synthetic efforts toward such linear multimetal complexes have been limited. Recently, Mashima *et al.* first synthesized the linear tetranuclear transition metal complexes, M'-M≡M-M' (M' = Pd or Pt and M = Mo(II)).[1, 2] The *ab initio* unrestricted Hartree-Fock (UHF) calculations of the simplified models of these species were carried out to elucidate the nature of the d-d conjugated bonds.[3] These MO theoretical calculations revealed the d-d conjugation scheme. The UHF wavefunctions for the ground singlet state of unstable species often involve the spin-contamination and such effects were corrected by our approximate spin projection procedure. For the more refined treatments, the multiconfiguration approaches such as the configuration interactions (CI) are desirable.

In a series of the theoretical investigation of tetranuclear transition metal systems, we report here the complete active space (CAS) CI calculations[4] by use of the UHF natural orbitals (UNO). The occupation numbers of UNO by UNO CASCI were obtained for theoretical elucidation of the d-d conjugated bonds in the linear tetranuclear systems. The energy splittings among the ground, excited triplet, and quintet states were also calculated to examine the reliability of the approximate spin projected UHF treatments in combination with the Heisenberg model.

THEORETICAL BACKGROUNDS

(A) d-d Conjugation Bonds

Let us first consider what kinds of bonding patterns are theoretically feasible in the tetranuclear transition metal-metal conjugated systems. The d^4-d^4 system such as Mo(II)-Mo(II) has one σ–bond, two π–bonds and one δ–bond. Figure 1 shows possible linear tetranuclear transition-metal complexes constructed of the M≣M (M = Cr(II) or Mo(II)) and two axial transition metals M_I.

In type **I**, the quadruple bonds M≣M are slightly modified by coordination of axial metals M' but the MM' interactions are not so strong to form the single bond. There are four different cleaving modes of the quadruple bond to form the single M-M' bond with different symmetries. This group is called type **II**. On the other hand, six different cleaving modes are conceivably provided for three double bonds like cumulenes, where the quadruple bond of the MM moiety is formally reduced to the double bond. These d-d conjugated species with different orbital symmetries are grouped into type **III**. Two triple M≡M' bonds provide four different species that are denoted as type **IV**.

(B) Complete Active Space (CAS)

Selection of active orbitals is a key factor for CAS CI descriptions of the linear tetranuclear systems in Figure 1. UHF natural orbital (UNO) analysis was successively applied to determine how many UNOs are necessary for the MO-theoretical descriptions of the binuclear and tetranuclear systems. It was shown that the eight active UNOs and eight active electrons {8, 8} are necessary for CAS of the binuclear systems and the type **I** of tetranuclear compounds such as Ni(II)···Cr(II)≣Cr(II)···Ni(II). On the other hand, the d-d conjugated σ-bond of Ni(I)-Cr(II)≡Cr(II)-Ni(I) delocalized over the whole molecule and the four valence UNOs were necessary for their MO-descriptions. The occupation numbers n_i of all these UNOs fall into the range $0 < n_i < 2$, showing

I	M1 · · · · M	M ≣ M	M · · · · · M1
		$(\sigma)^2(\pi)^2(\pi_\perp)^2(\delta)^2$	

II	M1 —— M	M ≣ M	M —— M1
(a)	$(\sigma)^2$	$(\pi)^2(\pi_\perp)^2(\delta)^2$	$(\sigma)^2$
(b)	$(\pi)^2$	$(\sigma)^2(\pi_\perp)^2(\delta)^2$	$(\pi)^2$
(c)	$(\pi_\perp)^2$	$(\sigma)^2(\pi)^2(\delta)^2$	$(\pi_\perp)^2$
(d)	$(\delta)^2$	$(\sigma)^2(\pi)^2(\pi_\perp)^2$	$(\delta)^2$

III	M1 = M	M = M	M = M1
(a)	$(\sigma)^2(\pi)^2$	$(\pi_\perp)^2(\delta)^2$	$(\sigma)^2(\pi)^2$
(b)	$(\sigma)^2(\pi_\perp)^2$	$(\pi)^2(\delta)^2$	$(\sigma)^2(\pi_\perp)^2$
(c)	$(\sigma)^2(\delta)^2$	$(\pi)^2(\pi_\perp)^2$	$(\sigma)^2(\delta)^2$
(d)	$(\pi)^2(\pi_\perp)^2$	$(\sigma)^2(\delta)^2$	$(\pi)^2(\pi_\perp)^2$
(e)	$(\pi)^2(\delta)^2$	$(\sigma)^2(\pi_\perp)^2$	$(\pi)^2(\delta)^2$
(f)	$(\pi_\perp)^2(\delta)^2$	$(\sigma)^2(\pi)^2$	$(\pi_\perp)^2(\delta)^2$

IV	M1 ≡ M	M —— M	M ≡ M1
(a)	$(\pi)^2(\pi_\perp)^2(\delta)^2$	$(\sigma)^2$	$(\pi)^2(\pi_\perp)^2(\delta)^2$
(b)	$(\sigma)^2(\pi_\perp)^2(\delta)^2$	$(\pi)^2$	$(\sigma)^2(\pi_\perp)^2(\delta)^2$
(c)	$(\sigma)^2(\pi)^2(\delta)^2$	$(\pi_\perp)^2$	$(\sigma)^2(\pi)^2(\delta)^2$
(d)	$(\sigma)^2(\pi)^2(\pi_\perp)^2$	$(\delta)^2$	$(\sigma)^2(\pi)^2(\pi_\perp)^2$

FIGURE 1 Theoretically possible linear tetranuclear transition-metal complexes.

that four σ-UNOs and four σ-electrons {4, 4} are necessary for the complete active space (CAS) for the σ-bonds. For each bicentric π, $\pi_\perp$ and δ type bonds two (bonding and antibonding) UNOs are necessary. Thus ten active orbitals and ten electrons {10, 10} are necessary for the Ni(I)-Cr(II)≡Cr(II)-Ni(I) system. The situation is the same for other d-d conjugated systems in the type **II**. Since the four active orbitals and four active electrons {4, 4} are necessary for each four-centered d-d conjugated bond, the twelve active orbitals and twelve electrons {12, 12} are necessary as CAS for the type

TABLE I The complete active space (CAS) for the tetranuclear systems (see Figure 1).

type		σ	π	$\pi_{\perp}$	δ	total ative orbitals
I		2	2	2	2	8
II	a	4	2	2	2	10
	b	2	4	2	2	10
	c	2	2	4	2	10
	d	2	2	2	4	10
III	a	4	4	2	2	12
	b	4	2	4	2	12
	c	4	2	2	4	12
	d	2	4	4	2	12
	e	2	4	2	4	12
	f	2	2	4	4	12
IV	a	2	4	4	4	14
	b	4	2	4	4	14
	c	4	4	2	4	14
	d	4	4	4	2	14

III compounds. Similarly the fourteen active orbitals and fourteen electrons {14, 14} should be considered as CAS for the type **IV**. Table I summarizes the number of each active UNO for CASCI descriptions of the d-d conjugated bonds in the types **I-IV**.

(C) Relation to the Experiments

Mashima *et al.* synthesized the type **I** and **II** tetranuclear systems. For example, they really synthesized the multiply-bonded linear tetranuclear transition metal complexes: $Mo_2Pd_2Cl_2(pyphos)_4$ (**1**)[1] and $Mo_2Pd_2Cl_4(pyphos)_4$ (**2**)[2]. Complex **1** is composed of a straight linear Cl-Pd(I)-Mo(II)≡Mo(II)-Pd(I)-Cl skeleton surrounded with four pyphos ligands, while **2** comprises a straight linear Pd(II)···Mo(II)≡Mo(II)···Pd(II) skeleton supported by four pyphos ligands and four chloride ions. It was found that the distance of Mo(II)-Pd(I) is shorter than that of Mo(II)-Pd(II) by more than 0.2 Å and the distance of Mo(II)≡Mo(II) in Pd(I)-Mo(II)≡Mo(II)-Pd(I) is longer than that of Mo(II)≡Mo(II) in Pd(II)···Mo(II)≡Mo(II)···Pd(II). This result clearly indicates that the σ-bond is formed between Mo(II) and Pd(I). Therefore **1** and **2** can be regarded as the types **II** and **I**, respectively. Synthesis of the compounds of types **III** and **IV** is future target.

AB INITIO CALCULATIONS

(A) Ab initio UHF Calculations

In order to elucidate the nature of conjugated d-d bonds, the *ab-initio* UHF calculations were already performed for the model systems without ligands, *i.e.*, Ni(II)-Cr(II)-Cr(II)-Ni(II) (**3**), Ni(I)-Cr(II)-Cr(II)-Ni(I) (**4**) and Ni(0)-Cr(II)-Cr(II)-Ni(0) (**5**). We determined the natural orbitals and their occupation numbers to analyze the conjugated d-d bonds. We also examined variations of the occupation numbers and the effective exchange integrals for **3** and **5** with changing the Cr(II)-Cr(II) intermetallic bond distance (R), where the distance of Cr(II)-Ni was fixed to be 2.00 Å. For the *ab initio* UHF calculations we used the minimal basis set [5333/533/5][5] (this is called BS) and triple zeta basis set [533(21)/53(21)/(41)+ diffuse d(α = 0.0912)] (BSI). The same basis sets are used for the present CASCI calculations.

(B) Valence Bond Pictures

The MO-theoretical pictures of **3** and **4** were obtained by depicting the UNOs. We briefly discuss the valence-bond (VB) pictures of **3**-**5**. Tables II-IV summarize the net charges and the spin densities on the Ni and Cr ions for **3**-**5** calculated by the UHF method. From these Tables, the followings are noticed.

(1) The net charges on the Cr(II) and Ni(II) ions in **3** are about 2.0, showing no significant charge transfer between these ions. Therefore **3** is really described as Ni(II)Cr(II)Cr(II)Ni(II). The spin densities on the Ni(II) ions are almost zero and those on the left and right Cr(II) ions are about 4.0 and -4.0, respectively. This indicates that the quadruple Cr(II)$\equiv$Cr(II) bond in **3** is largely spin-polarized and the antiferromagnetic spin coupling exists as illustrated in Figure 2A. This is consistent with the MO-theoretical picture based on the UNO. Since the interaction between Ni(II) and Cr(II) is almost negligible, **3** is regarded as the type **I** compound.

(2) The net charges on the Cr(II) and Ni(I) ions in **4** are about 2.0 and 1.0, respectively and **4** is described as Ni(I)Cr(II)Cr(II)Ni(I). The magnitudes of the spin densities on the Cr(II) and Ni(I) ions are, respectively, 4.0 and 1.0. This indicates that the antiferromagnetic spin coupling occurs as illustrated in Figure 2B. This VB structure clearly shows that both the spin and electron correlation effects are crucial, although the UHF calculations overestimate the spin polarization effect. Compound **4** belongs to the type **II**.

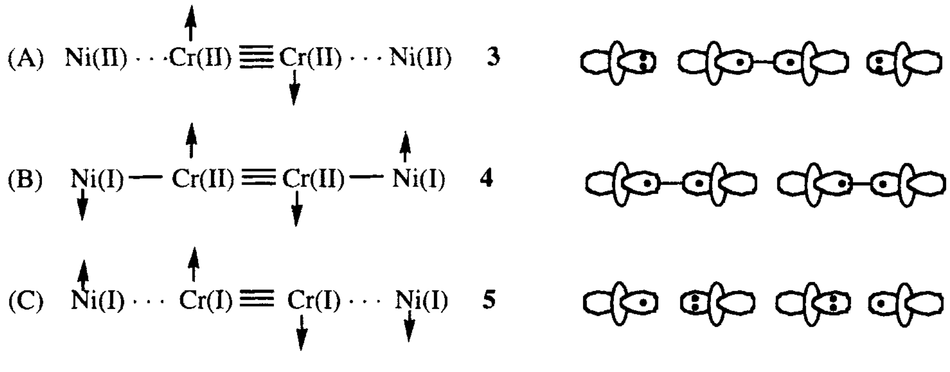

FIGURE 2 Calculated valence bond (VB) structures for the tetranuclear systems.

TABLES II The net charges and spin densities on the Cr and Ni ions in the Ni(II)^{a}Cr(II)^{a}Cr(II)^{b}Ni(II)^b(**3**) system by the UHF/BSI calculation.

	charge density		spin density	
R	Ni(II)^a	Cr(II)^a	Ni(II)^a	Cr(II)^a
2.000	2.200	1.800	.061	3.842
2.015	2.201	1.799	.061	3.843
2.389	2.192	1.808	.052	3.869
2.500	2.180	1.820	.049	3.888
3.000	2.123	1.877	.045	3.942
3.500	2.093	1.907	.049	3.944

TABLE III The net charges and spin densities on the Cr and Ni ions in the Ni(I)^{a}Cr(II)^{a}Cr(II)^{b}Ni(I)^b(**4**) system by the UHF/BSI calculation.

	charge density		spin density	
R	Ni(I)^a	Cr(II)^a	Ni(I)^a	Cr(II)^a
2.000	0.890	2.110	-0.896	3.882
2.389	0.843	2.157	-0.841	3.903
2.500	0.828	2.172	-0.825	3.888
3.000	0.764	2.236	-0.757	3.791
3.500	0.701	2.299	-0.692	3.701

TABLE IV The net charges and spin densities on the Cr and Ni ions in the Ni(0)^{a}Cr(II)^{a}Cr(II)^{b}Ni(0)^b (**5**) system by the UHF/BSI calculation.

	charge density		spin density	
R	Ni(0)^a	Cr(II)^a	Ni(0)^a	Cr(II)^a
2.000	0.990	1.010	0.965	2.952
2.400	0.967	1.034	0.955	3.023
3.000	0.948	1.052	0.958	3.038
3.500	0.943	1.057	0.961	3.038

(3) The net charges on the Cr(II) and Ni(0) ions in **5** are about 1.0, indicating the one-electron transfer from Ni(0) to Cr(II). Therefore, **5** is described as Ni(I)Cr(I)Cr(I)Ni(I). The magnitudes of the spin densities on the Cr(I) and Ni(I) ions are, respectively, 3.0 and 1.0, indicating that dσ-lone pair is formed on the Cr(I) ion and the spin density on Cr ion is reduced. The spin densities on the Cr(I) and Ni(I) ions are parallel, showing the spin delocalization as depicted in Figure 2C, in contrast to the SP case in **4**. The compound **5** is different from the types in Figure 1.

UNO CASCI CALCULATIONS

(A) Occupation numbers by UNO CASCI

The UHF natural orbital (UNO) analysis showed that the CAS {8, 8} and {10, 10} are indeed necessary for **3** and **4**, respectively, in conformity to the general discussion in the preceding section and theoretical prediction in Table I. On the other hand, the two σ-bonding orbitals for **5** are closed-shell type and therefore the CAS for **5** is reduced from {10, 12} to {8, 8}.

For computational economy, we have performed the UNO CASCI {8, 8} calculations for **3** and **5**. The occupation numbers of UNOs are summarized in Tables V and VI, indicating the followings conclusions:

(1) The occupation numbers for the bonding UNOs of **3** decrease in the order: σ > π > δ. This tendency is the same as that for the binuclear Cr(II) system without axial transition metal (M').

(2) The occupation numbers of the antibonding σ* UNO of **3** are larger than 0.5 even at the interatomic distance R = 2.0 Å. The CASCI clearly supports the theoretical pictures concluded for the unstable d-d bonds from the UHF calculations.

(3) The occupation numbers for the bonding UNOs of **5** decrease in the order: $\pi > \delta > \sigma$. This tendency is quite different from that recognized for **3**.

(4) The occupation numbers of the σ and σ^* UNO are almost 1.0 for **5**. This tendency is independent of the Cr-Cr distance R. The indirect interaction between the unpaired electrons on the dσ-type orbitals (d_{z2}) of the Ni(I) ions through the Cr-Cr moiety is very weak in conformity with the VB structure in Figure 2C.

TABLE V The occupation numbers for **3** by CASCI.

R·Å	σ	π	$\pi_\perp$	δ	δ^*	$\pi_\perp^*$	π	σ^*
2.000	1.453	1.320	1.320	1.061	0.939	0.680	0.680	0.547
2.015	1.441	1.306	1.306	1.057	0.943	0.694	0.694	0.559
2.389	1.233	1.105	1.105	1.014	0.986	0.895	0.895	0.767
2.500	1.192	1.079	1.079	1.010	0.990	0.921	0.921	0.808
3.000	1.074	1.022	1.022	1.002	0.998	0.978	0.978	0.926
3.500	1.025	1.006	1.006	1.000	1.000	0.994	0.994	0.975

TABLE VI The occupation numbers for **5** by CASCI.

R·Å,	π	$\pi_\perp$	δ	σ	σ^*	δ^*	$\pi_\perp^*$	π^*
2.000	1.447	1.477	1.138	1.035	0.965	0.862	0.424	0.424
2.400	1.176	1.176	1.035	1.012	0.988	0.965	0.824	0.824
3.000	1.055	1.055	1.008	1.004	0.996	0.992	0.945	0.945
3.500	1.020	1.020	1.0024	1.0020	0.998	0.9976	0.980	0.980

(B) Calculation of J_{ab} by UNO CASCI and CASSCF

The UNO CASCI calculations show that bondings between Cr and Ni are weak in **3** and **5**. In this situation the ground singlet and excited triplet and quintet states are nearly degenerate in energy. We have already calculated the J_{ab} values for the model compound **3** from the UHF total energies. Here, in order to examine the reliability of the spin multiplet splittings by the UHF plus Heisenberg model, the J_{ab} values for the direct exchange coupling between the Cr(II) ions were calculated from total energies E(Z) by UNO CASCI methods as follows:

$$J_{ab}(1) = (E(S) - E(Q)) / 6 \tag{1}$$

$$J_{ab}(2) = (E(T) - E(Q)) / 4 \tag{2}$$

$$J_{ab}(3) = (E(S) - E(T)) / 2 \tag{3}$$

where S, T and Q(= Z) denote, respectively, the signlet , triplet and quintet states. If these J_{ab} values are nearly equal to one another, *i.e.*, $J \cong J_{ab}(1) \cong J_{ab}(2) \cong J_{ab}(3)$, the spin multiplet splittings should be close to those of the Heisenberg model. Tables VII and VIII summarize the $J_{ab}(1)$, $J_{ab}(2)$ and $J_{ab}(3)$ values obtained for **3** and **5** by CAS CI{8, 8} method. The J_{ab} values by APUHF are also shown in Table VII. From Tables VII and VIII, the followings are noticed:

(1) All the $J_{ab}(n)$ values are negative in sign, being independent of the computational methods employed. The direct exchange interaction between the two Cr(II) ions is antiferromagnetic.

(2) The absolute values of $J_{ab}(1)$, $J_{ab}(2)$ and $J_{ab}(3)$ at each geometry by UNO CASCI are similar to one another, showing that the energy splittings can be described by the Heisenberg model. This indicates that our approximate spin projection scheme is reliable for **3**.

(3) The absolute $J_{ab}(1)$ value for **3** by UNO CASCI at each geometry is always larger than that of AP UHF, where the J_{ab} value is calculated by the energy difference between the HS (s = 4) and LS (s = 0) states. This implies that the correlation correction for the UHF solution by the MØller-Plesset (MP) and/or coupled-cluster (CC) methods is required for quantitative discussion.

(4) The absolute $J_{ab}(1)$, $J_{ab}(2)$ and $J_{ab}(3)$ values for **5** are different from one another in the region R < 2.3 Å, in contrast to the case of **3**. The energy splittings among the singlet(S), triplet(T) and quintet(Q) states are different from those predicted by the Heisenberg model. Probably the back charge transfer effect from Cr(I) to Ni(I) is the origin of this behavior.

(5) However, the $J_{ab}(n)$ values become simialr if R exceeds 2.5 Å. The multiplet splittings become close to those given by the Heisenberg model because the antiferromagnetic interactions is weak.

TABLE VII $J_{ab}(n)$ (n = 1-3) values of **3** by CASCI (BSI).

R(Å)	$J_{ab}(1)$	$J_{ab}(2)$	$J_{ab}(3)$	J_{ab}(AP UHF)
2.000	-722.2	-720.8	-725.0	-516.2
2.015	-672.0	-670.1	-675.7	-487.2
2.389	-128.4	-128.5	-128.1	-110.0
2.500	-79.95	-80.08	-79.70	-68.68
3.000	-8.73	-8.74	-8.72	-7.55
3.500	-0.89	-0.89	-0.89	-0.73

TABLE VIII $J_{ab}(n)$ (n = 1-3) values of **5** by CASCI (BS).

R(Å)	$J_{ab}(1)$	$J_{ab}(2)$	$J_{ab}(3)$
2.000	-368.1	-436.5	-231.2
2.400	-89.601	-92.22	-84.37
3.000	-8.80	-8.86	-8.89
3.500	-1.23	-1.23	-1.23

In conclusion, the CASCI results showed that the sign of the J_{ab} values by the UHF plus Heisenberg model is reliable for the linear tetranuclear transition metal systems **3** and **5**.

DISCUSSIONS AND CONCLUDING REMARK

(A) UNO CACI for Other Systems

The present UNO CASCI {8, 8} calculations of **3** and **5** showed that the selection of active orbitals for tetranuclear transition metal systems is feasible based on the occupation numbers of UNOs, and the UNO CASCI is effective for computations of the energy splittings between the ground singlet and lower-excited high-spin states of these species. The UNO CASCI method is equally applicable to other tetranuclear systems in Figure 1. However, the larger CAS {m, m} (m = 10 - 14) than {8, 8} is necessary for these species as shown in Table I. The UNO CASCI {m, m} (m = 10 - 14 will be performed elsewhere to elucidate the ground and lower excited states of various species in Table I.

(B) Linear Extended Systems

The tetranuclear systems in Figure 1 and Tables 1 can be used as the building blocks for consisting the linear extended systems as illustrated in Figure 3. Several linkage groups are theoretically conceivable to form the oligomers and polymers which are regarded as the extended d-π systems in general. Although the UNO CASCI calculations are desirable even for the d-π systems with mesoscopic sizes, they are impossible for such large systems at the present computer level. However, concerning with the spin property, the UNO CASCI results are approximately reduced to the Heisenberg-type spin Hamiltionian as shown in the preceding section. The Heisenberg model can be applicable to more larger systems. The synthetic efforts toward these oligomers are in progress.

(C) Macroscopic Quantum Tunneling

Recently several quantum phenomena in the mesoscopic systems have received great interest. One of such properties is the macroscopic quantum tunneling[6,7] of spins shown as illustrated in Figure 4. The extended oligomers shown in Figure 3 will be interesting candidate to study this quantum phenomenon. A merit of chemical synthesis of such mesoscopic systems will be the controls of the oligomer size and the reduction of the intercluster interactions with bulky ligands.

$$\left(M_1 - M \equiv M - M_1 - X \right)_m$$

$$\left(M_1 = M = M = M_1 - X \right)_m$$

$$\left(M_1 \equiv M - M \equiv M_1 - X \right)_m$$

X = Ligands

FIGURE 3 The extended d-π systems consisted of the tetranuclear transition metal species.

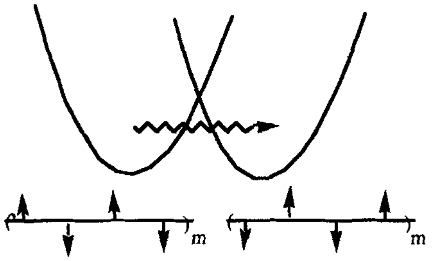

FIGURE 4 Macroscopic quantum tunneling of spin.

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