Effect of DFT Exchange Correlation Functionals and Basis Set Quality on the Calculations of the Magnetic Coupling Parameter J.

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It termed out that some of the combinations functionals/basis set gave satisfactory results for both anion.

A regression analysis were done to correlate the coupling constant with certain theoretical parameters chosen carefully for the above combinations. Because the electronic transitions are sensitive to small geometry variations of the same anion , we have used different approaches to calculate the first two transitions (mainly d-d).

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Abstract- The J magnetic coupling parameters were calculated theoretically by the aid of ORCA software. Seven exchange-correlation functionals combined with seven different basis set including low quality and high quality types. The calculations were done for two different geometries of the same dimer anion Cu_2Cl_6. The first geometry is a square planar, the second is distorted tetrahedral. The differences is due to the accompanied cation. For testing the approach the calculations have extended to the other dimers using only two combinations of the above that seems to give good results. The values of the computed J for all cases were compared to experiments.

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I. Introduction

The study of the anion Cu_2Cl_6 is a subject of interest. Many compounds of the formula ([cation]$^+$ [$CuCl_3$])$_2$) were synthesized and X-ray or/and magnetic data were determined [1-6]. Although we deal with the same anion, different properties are exhibited when we alter the associate cation. Here we have studied six dimmers these are (where the geometry around each copper is given):

1. (Dibenzotetrathiafulvalenium)$_2^{++}$ Cu2Cl6^{--} square planar [1]
2. (Ph4P)$_2^{++}$ Cu2Cl6^{--} distorted tetrahedreal [2]
3. melaminiumH2^{++} Cu2Cl6^{--} square planar [3]
4. (Ph4As)$_2^{++}$ Cu2Cl6^{--} distorted tetrahedral [4]
5. (Ph4Sb)$_2^{++}$ Cu2Cl6^{--} distorted tetrahedral [5]
6. (propyl-triphenyl P)$_2^{++}$ Cu2Cl6^{--} square planar [6]

Calculations of the J parameter of some of these compounds were previously done using one combination B3LYP/pVDZ, using G94 software. The authors claimed to get good correlation.[7]

For calculating J theoretically The total energy of the wave function of spin (3,1), a triplet wave function was calculated. Second the total energy of wave function with (3,0) with broken symmetry was also calculated. According to the work of Bencini and Gatteschi[8], a combination of the two energies in one equation led to:

$$[E_{high\ spin} - E_{broken\ symmetry}]/(S_{max}(S_{max}+1)) = -J \qquad (1)$$

This means that if J is negative the system is anti-ferromagnetic, while positive value implies ferromagnetic interaction.

All our calculations are provided by the ORCA program [9-11].

The angle X(bridging)-Cu-Y (terminal) sometimes is correlated with J.[7]

Instead a relation connecting calculated J with five parameters chosen carefully by us resulting in good correlations.

II. Method of Calculations

We utilize seven functionals in our calculations these are: the hybrid types B3LYP, O3LYP, PW6B95, TPSS0, and the range-separated types cam-B3LYP, LC-BLYP and wB97X-D3. These are combined with seven basis set which are : def2-SVP, 6-311+G*, TZVPP, def2-TZVPP, ma-def2-QZVPP, def2-QZVPP and aug-PC-2 resulting in a total of 49 computations for each of the two anions dimers **1,2**. These computations were aimed to calculate J parameters according to equation (1).

The geometries determined by X-ray were used in the calculations without further optimization. The calculations involved only the anion Cu2Cl6^{2-}, because this part is expected to contribute exclusively to the magnetic properties.

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Figure 1 Shows the two possible geometries of Cu2Cl6 $^{2-}$

Anion (**2**)   distorted tetrahedral.   Anion (**1**) square planar
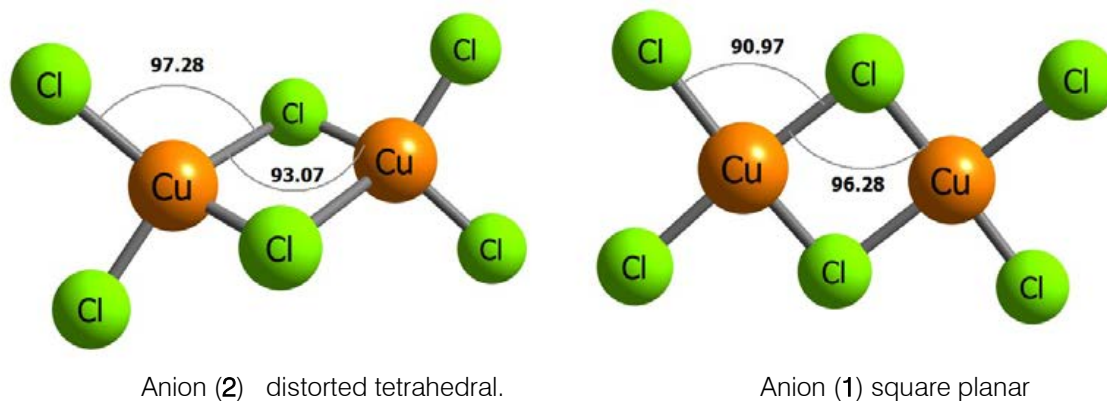
Fig. 1: The anion geometrical structures after X-ray determination[1, 2]

III.   DISCUSSION

a)   Calculation of magnetic coupling parameter (J)

We notice from experimental finding that the square planar configuration is mostly anti-ferromagnetic, while the tetrahedral one is mostly ferromagnetic. In our opinion this is dependent on the Cu-Cu distance. It is shorter in the square planar types which felicitate the interaction of the electrons.

Tables 1. and 2. display the calculated J parameters after equation (1) for the 49 combinations of dimers **1** and **2.**

Table 1: Magnetic coupling parameter of compound **1**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2-QZVPP	Def2-QZVPP	Aug-PC-2
B3LYP	-38.6	-25.3	-30.8	-27.7	-23.7	-22.9	-22.6
O3LYP	-46.4	-29.0	-38.0	-34.7	-28.1	-28.6	-29.5
PW6B95	-24.9	-25.6	-16.3	-13.7	-9.7	-10.0	-10.7
TPSS0	-20.5	-21.0	-12.5	-9.6	-6.1	-6.3	-7.3
cam-B3LYP	-20.8	-20.6	-13.6	-11.0	-7.0	-7.3	-8.0
LC-BLYP	-27.9	-34.2	-21.9	-19.3	-14.5	-14.9	-15.6
wB97X- D3	-18.4	-6.4	-9.2	-6.9	-9.7	-3.7	-4.0

Experimental = -41.8 cm-1.[13]

Table 2: Magnetic coupling parameter for compound **2**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	Ma-def2-QZVPP	Def2-QZVPP	Aug-PC-2
B3LYP	33.3	34.5	31.8	31.5	31.1	31.0	31.6
O3LYP	44.2	48.0	44.2	44.1	44.1	43.9	44.6
PW6B95	30.9	31.2	29.0	28.5	28.0	27.9	28.4
TPSS0	27.5	27.3	25.3	24.8	24.1	24.0	24.5
Cam-B3LYP	28.7	29.0	26.8	26.3	25.9	25.8	26.2
LC-BLYP	30.2	32.5	30.0	19.7	29.5	29.4	29.8
wB97X-D3	26.5	27.9	26.1	25.6	25.1	25.1	25.1

Experimental =+26.5 cm-1.[13]

The values shaded by yellow color in tables 1 & 2 are those near the experimental finding. If you examine the two tables you can find that (a) both calculations predict the right sign of J. (b)   The most correlated combinations of J values for dimer **1** is not necessary those for dimer **2.** According to the two tables the combinations: O3LYP/def2-TZVPP and TPSS0/def2-TZVPP seems reasonable to be used in calculations of the rest of the dimers (table 3). (c) Small differences in the structure (e.g. compounds **2,4,5**) resulting in remarkable differences in J. Which means that J is sensitive to small variations in the geometry.

It is worth to mention here that some of the dimers may be weakly interacting with other dimers in the lattice forming some kind of a linear polymer with weak Second coupling (J') [6].

We have tried to connect the calculated   J constants over the different combinations with some

chosen DFT output variables. We found that calculated J values are dependent (with good statistical correlations) on the HOMO energy, LUMO energy, natural copper charge (CM), natural chlorine charge (CL) (the one at the bridging position), natural spin population on copper center (M*), natural spin population on bridging chlorine (L*) and finally on the exchange correlation energy dependent on the type of functional used (E(XC). Charges and spin population have been calculated using GENBO5 software [12]

We have found that there is poor correlation between calculated J values and the above parameters if we use all the 49 combinations mentioned above together, instead we found that if we take each seven combinations belonging to the same basis set at a time, as shown in table 3, the correlation is very good.

The J values were found to be strongly dependent on only five parameters.

Each basis set has it own five parameters.

Table 3: Indicates which five parameters that give best correlation for dimer **1**

HOMO	LUMO	C_M	C_L	M*	L*	E(XC)
6-311+G*				3+4+5+6+7		
				R=0.99986 S= 0.69		
TZVPP				2+3+4+6+7		
				R=0.99999 S= 0.25		
Def2-TZVPP				1+2+3+4+6		
				R=0.99999 S=0.22		
Def2-QZVPP				1+2+3+4+7		
				R=0.999999 S=0.034		
ma-def2-QZVPP				2+3+4+5+7		
				R=0.999999 S= 0.036		
Aug-P-C2				2+3+5+6+7		
				R=0.9998 S=0.93		
Def2-SVP				2+4+5+6+7		
				R=0.99995 S=0.49		

R=correlation coefficient, S=standard error.

Another dependence was visualized by drawing a contour diagrams of dimers **1** & **2**, of calculated J over the different combinations reflected in the basis set dimension (Number of contracted functions) against exchange-correlation energy of the DFT functional. (Figures 2&3).

Table 4: J values for compounds 1-6 using only two combinations

Dimer	O3LYP/ def2-TZVPP	TPSS0/ def2-TZVPP	Experimental[13]
1	-34.7	-9.6	-41.8
2	+44.1	+24.8	+26.5 cm^{-1}
3	-7.0	-7.0	- 19.0 [3]
4	+47.9	+28.7	+19.5[14]
5	+46.9	+29.1	+43.9
6	+6.4	+19.2	+46.5

Countor Plot of -J for compound (1)

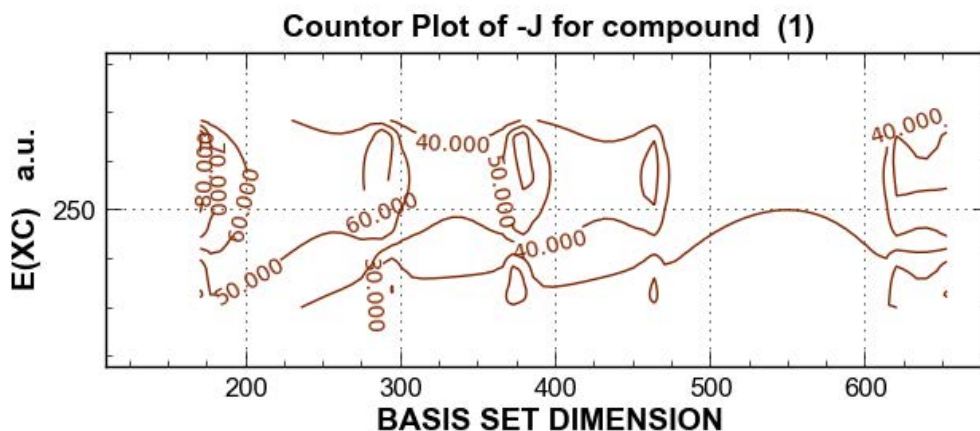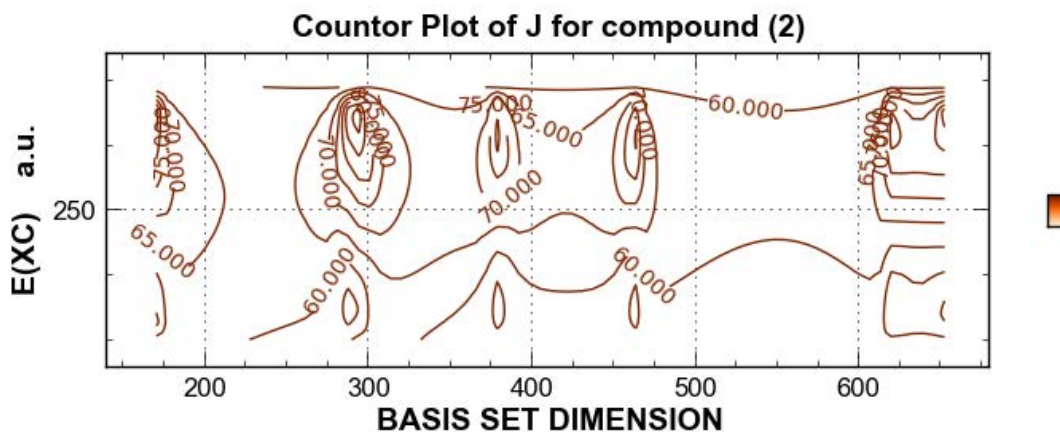*Fig. 2*

Countor Plot of J for compound (2)

Fig. 3

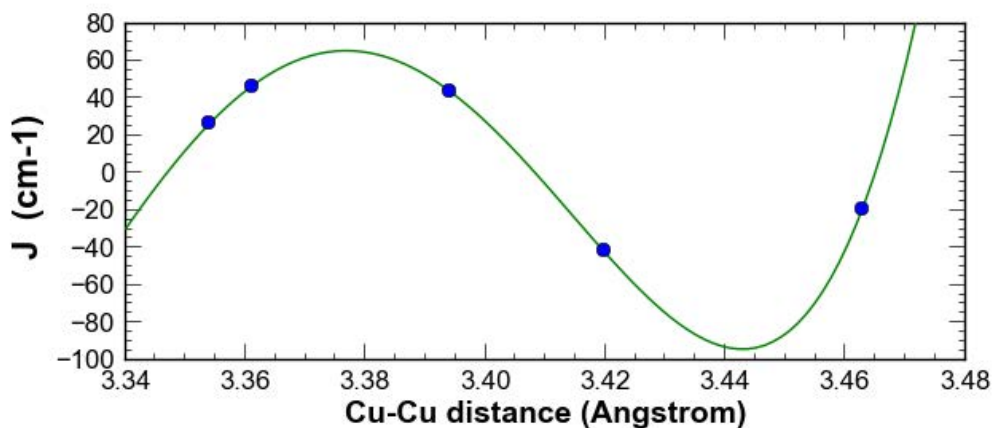*Fig. 4:* Dependence of J on the Cu-Cu distance through a cubic equation

It is well establish the relation of J with the the Cl-Cu-Cl in Cu2Cl6 anion[7].

In this work a relation between J and Cu-Cu distance is also proposed (see figure 4).

One can notice that the larger distances belong to anti-ferromagnetic Systems, while smaller distances are for ferromagnetic systems.

b) Calculations of the first electronic transition energy

Table 5: Transition energy is given in cm^{-1}

	TDDFT/ Cam-B3LYP/ def2-TZVPP	CI(D)/ def2-TZVPP	CASSCF(10,12)/ def2-TZVPP	EE-EOM- CCSD/ TZVP	Experimental Reference 15,16
1	14962	11760	7796	12640	9900
2	9352	7748	6655	5750	8000
3	14138	10639	9140	11844	11760
4	9925	8224	7008	8507	8700
5	10456	8585	7294	8915	9524
6	14271	10733	7020	11804	10000

The first electronic transition of our dimers has been calculated theoretically by four different methods, together with their corresponding experimental values.

The one which approximate closely the experiments is the CI(D) approach, next to it the CASSCF(10,12) method.

IV. CONCLUSION

The use of 49 combinations (compounds **1&2**) of calculation variables (Exchange-correlation functionals/basis set) widen the scope for the search of good correlated set with respect to the magnetic coupling parameters. Many combinations satisfy close

resemble with experiment. At least good prediction of ferro/antiferro coupling properties was achieved very well in our six dimers.

We succeeded to get equations relating the J constants with five theoretical parameters extracted mainly form ORCA program output. Although the correlation between J and the five parameters is very good, unfortunately they are basis set dependent. The J constant was known to be related to the angle employing the bridging atoms in the polymer. We found that it is also related to the Cu-Cu distance in our systems.

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Supplementary Material

Table S1: Calculated HOMO, LUMO, M*, L* for compound **1**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2-QZVPP	Def2-QZVPP	aug-PC-2
B3LYP	.994	1.076	1.065	1.068	1.106	1.068	1.106
	-.601	-.612	-.614	-.611	-.629	-.611	-.629
	.450	.478	.492	.485	.483	.485	.483
	.186	.2118	.204	.210	.211	.210	.211
O3LYP	.955	1.026	1.016	1.012	1.016	1.013	1.052
	-.587	-.593	-.596	-.594	-.590	-.5894	-.608
	.454	.427	.437	.437	.4282	.429	.427
	.202	.232	.224	.225	.233	.2325	.233
PW6B95	1.033	1.116	1.109	1.109	1.114	1.113	1.150
	-.618	-.631	-.635	-.634	-.631	-.631	-.649
	.534	.520	.531	.535	.530	.530	.529
	.171	.1936	.186	.186	.191	.191	.191
TPSS0	1.077	1.139	1.138	1.138	1.140	1.140	1.175
	-.632	-.638	-.644	-.643	-.640	-.640	-.657
	.566	.546	.558	.562	.558	.558	.556
	.162	.1848	.177	.177	.181	.182	.182
Cam-B3LYP	1.041	1.123	1.118	1.116	1.121	1.121	1.156
	-.621	-.633	-.638	-.636	-.633	-.633	-.651
	.537	.520	.532	.536	.530	.531	.529
	.169	.193	.182	.185	.191	.191	.191
LC-BLYP	.987	1.065	1.057	1.054	1.059	1.057	1.094
	-.603	-.612	-.616	-.613	-.610	-.610	-.628
	.496	.468	.480	.481	.473	.473	.472
	.181	.212	.202	.205	.212	.212	.211

wB97X-D3	1.061 -.630 .545 .166	1.133 -.638 .529 .190	1.128 -.643 .539 .182	1.127 -.641 .543 .182	1.130 -.637 .537 .188	1.130 -.638 .538 .188	1.166 -.655 .537 .188

Table S2: Calculated HOMO, LUMO, M*,L * for compound **2**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2 QZVPP	Def2-QZVPP	aug-PC-2
B3LYP	1.033 -.639 .546 .148	1.115 -.654 .526 .172	1.112 -.659 .540 .162	1.109 -.657 .542 .146	1.115 -.654 .539 .168	1.115 -.654 .539 .167	1.149 -.670 .537 .168
O3LYP	.988 -.623 .493 .166	1.0583 -.633 .4658 .194	1.0527 -.637 .479 .184	1.0485. -.636 .479 .185	1.0538 -.632 .473 .191	1.0529 -.632 .474 .191	1.0889 -.648 .472 .192
PW6B95	1.0709 -.654 .582 .135	1.155 -.671 .570 .155	1.153 -.676 .584 .146	1.153 -.676 .588 .145	1.159 -.672 .586 .149	1.1600 -.673 .586 .149	1.194 -.689 .584 .150
TPSS0	1.081 -.659 .589 .130	1.180 -.678 .600 .145	1.182 -.684 .615 .137	1.1823 -.684 .618 .136	1.1868 -.681 .617 .139	1.188 -.681 .617 .139	1.221 -.697 .615 .140
Cam-B3LYP	1.0804 -.659 .589 .130	1.165 -.676 .574 .151	1.164 -.681 .589 .142	1.1630 -.679 .592 .142	1.170 -.677 .591 .146	1.1701 -.677 .591 .146	1.203 -.693 .589 .147
LC-BLYP	1.0200 -.641 .541 .141	1.102 -.656 .514 .169	1.0969 -.661 .529 .158	1.0936 -.659 .529 .160	1.101 -.656 .524 .165	1.1008 -.656 .525 .165	1.135 -.672 .523 .166
wB97X-D3	1.0989 -.667 .595 .128	1.174 -.680 .582 .148	1.172 -.685 .594 .140	1.170 -.684 .597 .140	1.1760 -.680 .596 .144	1.177 -.681 .596 .144	1.211 -.697 .595 .144

Table S3

	B3LYP	O3LYP	PW6B95	TPSS0	Cam-B3LYP	LC-BLYP	wB97X-D3
E(XC)*	-245.3	-268.9	-225.3	-230.4	-235.3	-273.9	-228.8

Exchange-correlation energy a.u.