J. Phys. Chem. A **2009,** *113,* 6751–6755

Calculation of Exchange Coupling Constants of Transition Metal Complexes with DFT

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Received: January 26, 2009; Revised Manuscript Received: April 17, 2009

A broken-symmetry method for the calculation of exchange coupling constants from DFT calculations, using the Heisenberg−Dirac−van Vleck spin Hamiltonian, has been validated for a dinuclear copper(II) complex. Hybrid functionals in combination with a large basis set on the metal centers and their first coordination sphere, and a smaller basis set on the ligand backbone are shown to be efficient and acceptable with respect to the computational cost and precision in comparison with experimental data. This method was thoroughly tested with a series of oligonuclear transition metal complexes with Cr^{III}, Cu^{II}, Fe^{III}, Mn^{II}, Mn^{III}, Mn^{IV}, Ni^{II}, and V^{IV} as magnetic centers. The computed values of J are within approximately 50 cm^{-1} of the experimental values for most of the examples; with combined basis sets, there generally is a similar accuracy to that obtained with a large basis set for the entire spin cluster but with significantly reduced computational expense. When the experimentally observed structural data are refined prior to the calculation of the exchange coupling constants, the computed values of J are in most cases in slightly better agreement with the experimental data than those obtained from single point calculations based on the X-ray data.

Introduction

In oligonuclear transition metal complexes with unpaired electrons at each of the metal centers, the unpaired electron spins couple antiferromagnetically or ferromagnetically, and this leads to systems with interesting magnetic behavior. The spin quantum number S on the metal centers then is no longer valid and a new quantum number to describe the coupled spin system is required. In the simple case of a dinuclear complex with one unpaired electron on each of the magnetic centers (e.g., Cu^{II}_2) the difference between the antiferromagnetic ($S = 0$) and ferromagnetic ($S = 1$) electronic states is described by the exchange coupling constant J. A negative value of J describes an antiferromagnetic ground state; complexes with a ferromagnetic ground state have positive values of J.[1] The magnetic properties of dinuclear transition metal complexes may be described with the Heisenberg−Dirac−van Vleck spin Hamiltonian.[2−5]

Exchange-coupled transition metal complexes frequently occur in the active centers of metalloproteins and their small molecule model complexes as well as in technical catalysts and also have a wide range of applications in materials sciences, e.g., as possible building blocks in new magnetic storage devices or as components in quantum computers. That is, they are of interest in many areas of fundamental science, e.g. also in quantum physics.[6,7] In molecular systems such as those involved in catalysis and bioinorganic chemistry, a thorough understanding of the electronic structures of the transition metal centers is of importance. In the area of magnetic materials, the quantitative understanding of the exchange coupling is of specific interest. Most of the physics and theory of single-molecule magnets (SMM) and other interesting magnetic materials are well understood.[6−8] In order to be able to design and prepare efficient new SMMs, an accurate prediction of the exchange coupling constant to describe the electronic and magnetic properties is of importance.[9] Initially, DFT-based calculations of exchange coupling constants were based on the Xα method.[10] This was followed by the development of the broken-symmetry approach,[11] and DFT now is widely used for computing exchange coupling constants. More expensive quantum-chemical methods such as CASSCF or CI approaches are only rarely used because, for more than very small model systems they still are computationally too expensive.[12] Semiempirical methods have been used for the qualitative description of magnetic interactions, but DFT is accepted to be required for a quantitative description.[13] Here, we therefore present a systematic search for and validation of a fast and reliable method for the DFT-based calculation of exchange coupling constants of a large range of transition metal complexes.

Computational Details. We use a Heisenberg−Dirac−van Vleck spin Hamiltonian[2−5] for the description of the magnetic properties of dinuclear transition metal complexes. The exchange interaction between the two magnetic centers is derived from the spin coupling Hamiltonian given in eq 1, where J_{12} is the spin coupling constant and S_1 and S_2 are the spin operators for the two respective metal centers.[13,14]

$$H = 2J_{12}S_1S_2 \tag{1}$$

We use the broken-symmetry approach of eq 2 for the DFT-based calculation of the exchange coupling constants.[11,15−20] The calculations cover a wide range of transition metal complexes, and eq 2 is known to be well adapted for complexes with weak as well as compounds with strong orbital overlap.

$$J_{12} = \frac{E^{BS} - E^{HS}}{\langle S\rangle_{HS}^{\ 2} - \langle S\rangle_{BS}^{\ 2}} \tag{2}$$

The program packages Gaussian 03 ("G03"),[21] Jaguar 6.5 ("Jaguar")[22] and Orca 2.6.04 ("Orca")[23] were used for the calculations. Initial guesses for the high-spin states are trivial

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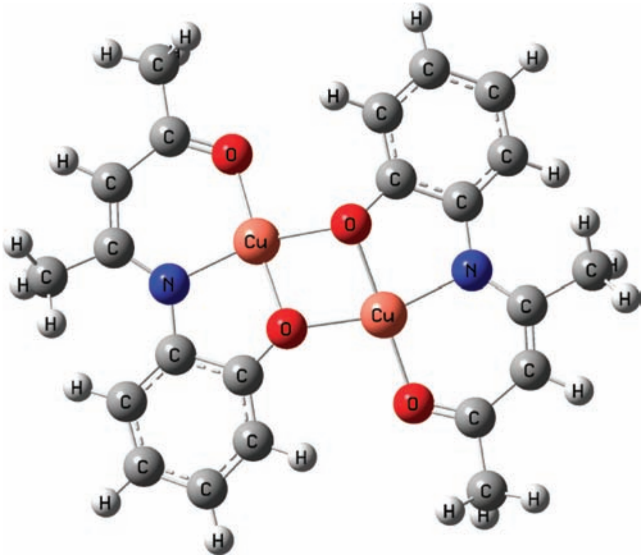

Figure 1. Plot of the experimental structure of the bisphenolate-bridged dicopper(II) complex with $J_{\text{exp}} = -298$ cm^{-1}, used for the benchmark broken-symmetry DFT computation of the exchange coupling (see Table 1).[24,25]

to obtain in all three program packages. For the broken-symmetry states Jaguar was used to create an initial guess for G03 (keyword ip160 = 4). The broken-symmetry states were generated with Gaussview or, more conveniently, the Jaguar atomic section module was used for placing unpaired electrons on the transition metal centers to generate the broken-symmetry input files. In Orca the "BrokenSym"-keyword was used in the %scf section to generate input files for the broken-symmetry states. All calculations were converged to an energy threshold of 10^{-06} (10^{-07} for Orca) and a root mean square in the density of 10^{-08}. Geometry optimizations were performed on the high-spin states with default options for Jaguar as well as for Orca. The iacscf = 4 flag in most of the cases was used in Jaguar to help the optimizer to reach the minimum. Geometries were checked by frequency calculations for minima on the potential energy surface. In parallel computations with Jaguar with MPICH, TZVP is not available. A good alternative, when more than one processor is needed, is LACV3P++**. For parallel calculations with Jaguar, LACV3P++** was therefore used instead of TZVP. Single point calculations were then performed on the optimized structures. All of the benchmark calculations in Jaguar were performed on an Intel Core 2 Quad Q9450 CPU with 8 GB of RAM, using one of the four available cores.

Results and Discussion

1. Validation of the Method. A series of functionals and basis sets were tested with the three programs, using an experimentally well-characterized bisphenolato-bridged dicopper(II) complex with two antiferromagnetically coupled Cu$^{\text{II}}$ centers and an exchange coupling constant of $J = -298$ cm^{-1} (see Figure 1).[24,25] The relatively small complex allowed for an efficient validation of the programs and theoretical methods. The combination of a series of well established functionals (B3LYP,[26−28] B3P86,[29] B3PW91,[30] BLYP,[31−33] BP86,[29,31−33] BPW91,[30] BLYP,[31−33] PBE,[34] SVWN[35,36]) with common basis sets (3-21G,[37−41] DZP[42−44] TZV,[45,46] TZVP,[45,46] 6-31G*[47−56]) were used for benchmark calculations with G03, Jaguar, and Orca, to test the efficiency and level of accuracy in the calculation of the exchange coupling constant of the model complex. These results are given in Table 1.

TABLE 1: Exchange Coupling Constant *J* of the Dicopper(II) Complex Shown in Figure 1 ($J_{\text{exp}} = -298$ cm^{-1} [24,25]), Calculated (Equation 2) with Different Functionals and Basis Sets

method	J_{G03} (cm^{-1})[a]	J_{Orca} (cm^{-1})	J_{Jaguar} (cm^{-1})	CPU time$_{\text{Jaguar}}$ (h)
B3LYP/TZV	−229	−231	−231	4.60
B3P86/TZV	−238	−227	−241	3.71
B3PW91/TZV	−228	−230	−227	3.44
BLYP/TZV	−838	−838	−854	4.00
BP86/TZV	−861	−834	−880	4.26
BPW91/TZV	−831	−832	−848	4.20
PBE/TZV	−841	−841	−854	4.31
SVWN/TZV	−1156	−1178	−1181	5.07
B3LYP/3-21G	−103	−99	−114	0.56
B3LYP/TZVP	−215	−214	−231	4.60
B3LYP/DZP/TZVP[b]		−218	−246	4.12
B3LYP/6-31G*/TZVP[c]	−237	−216	−239	2.38

[a] Initial guess obtained with Jaguar. [b] TZVP for Cu$^{\text{II}}$, DZP for the remaining atoms. [c] TZVP for Cu$^{\text{II}}$ and the donor atoms, 6-31G* for the remaining atoms.

The results indicate that G03 leads to acceptable results with negligible differences between the hybrid functionals B3LYP, B3P86, and B3PW91. The pure density functionals BLYP, BP86, BPW91, PBE, and SVWN lead to a poor description of the broken-symmetry state and therefore to an exchange coupling constant *J* which does not well reproduce the experimental value. This is in agreement with earlier observations that hybrid functionals such as B3LYP lead to the best results.[57] This is also supported by the calculations with Jaguar and Orca (see Table 1). Very small basis sets such as 3-21G are, as expected, not able to compute accurate values. Very large basis sets such as TZVP are unnecessary for the majority of the ligand system, and smaller basis sets already give a relatively accurate description of exchange-coupled systems. Larger basis sets are needed for the metal centers and the donor atoms. However, with TZVP for large transition metal complex systems the cost of CPU time is enormous. In order to reduce the computational cost for these calculations, a combination of the TZVP basis for the transition metal centers and the first coordination spheres with the smaller 6-31G* basis set for the ligand backbone was used to increase the performance. The resulting values are very similar to those with the TZVP basis set used for the entire complex, and this combination was therefore adopted for the further studies. Figure 2 is a visualization of the data obtained by Jaguar presented in Table 1 (the results with G03 and Orca are qualitatively similar).

The important result is that for the accurate computation of *J* values for reasonably large systems the method with the combined basis set (B3LYP/6-31G* & TZVP) significantly reduces the computational cost, and this method was therefore used for the applications to larger spin clusters (see below). We have also compared this method with the popular split basis set TZVP (for the metal centers)/DZP (for the remaining atoms). The accuracy of these two methods is similar but the computational time is reduced by almost a factor of 2 with the TZVP/6-31G* split basis (see Table 1). An analysis of the performance of the TZVP/DZP and the TZVP/6-31G* methods shows that SCF convergence is achieved in fewer steps with the 6-31G*/TZVP, compared to the TZVP/DZP method. The accuracy of the two methods is very similar, but with larger systems, the performance is at least factor of 2.5 better for TZVP/6-31G*.

2. Application to Larger Spin Clusters. The method described above (B3LYP/6-31G* & TZVP) was used to

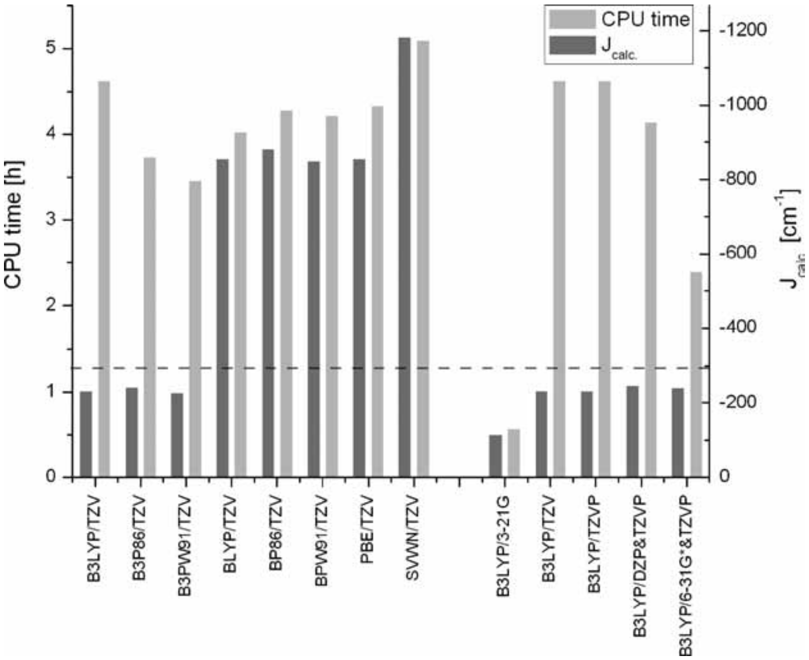

Figure 2. CPU time required for the computation of J [QuadCore Q9450 (one processor), 8GB RAM; light gray] and accuracy compared with the experimental value of J (dashed line, $J = -298$ cm^{-1}).[24,25] of the bisphenolato-bridged dicopper(II) complex shown in Figure 1, as a function of the method used (see Table 1; calculations performed with Jaguar).

TABLE 2: Comparison of Experimental and Computed Exchange Coupling Constants J of a Series of Transition Metal Complexes with Cr^{III}, Mn^{II}, Mn^{III}, Fe^{III}, and Cu^{II} Centers (See *Supporting Information* for the Detailed Structures; The Numbers in Parentheses in the Table Refer to the Corresponding Figures)

compound	J_{jaguar} (cm^{-1})	J_{exp} (cm^{-1})	note	references
TPP[HO-Cr(cyclam)-NC-Cr(CN)$_5$] (**1**)	−33.1	−29.8	Cr−Cr	65
Na[HO-Cr(cyclam)-NC-Cr(CN)$_5$] (**2**)	−41.4	−35.5	Cr−Cr	
trans-Cr[MnL^1]$_2$Cl (**3**)	−12.5	−12.8	Mn−Cr	61
	5.0	0.9	Mn−Mn	
trans-Fe[MnL^1]$_2$Cl (**4**)	9.6	8.0	Mn−Fe	61
	−7.7	−0.5	Mn−Mn	
trans-Fe[MnL^1]$_2$PF$_6$ (**5**)	6.8	4.2	Mn−Fe	
	−8.3	−0.3	Mn−Mn	
[Tp$_2$(Me$_3$tacn)$_3$Cu$_3$Fe$_2$(CN)$_6$]$^{4+}$ (**6**) [CuFeZn$_3$]	9.1	8.5	*a*	58
[CuCuZn$_3$]	−8.8	0	*a*	
[FeFeZn$_3$]	9.9	0	*a*	

[a] In this pentanuclear complex (trigonal bipyramidal, see Supporting Information; single-molecular magnetic material) three of the five paramagnetic centers were substituted by diamagnetic Zn^{2+} ions for an efficient calculation of the coupling constant between the remaining two paramagnetic ions.

compute the exchange coupling constant J of a variety of oligonuclear transition metal complexes with Cu^{II}, Fe^{III}, Cr^{III}, V^{IV}, Mn^{II}, Mn^{III}, Mn^{IV}, Ni^{II}, and/or Co^{III} as magnetic centers. As shown above, G03, Jaguar and Orca are well suited for these calculations and lead to very similar results. For convenience we generally used Jaguar and Orca (see computational details), and these results are presented in Table 2. In all cases the J values are reproduced with acceptable accuracy. Of special interest is the pentanuclear spin cluster Fe$_2$Cu$_3$ (6). Here, the experimental data were only fitted with an Fe−Cu coupling, neglecting the Fe−Fe and the Cu−Cu magnetic exchange.[58] Our calculations indicate that there is a significant exchange coupling between all magnetic centers (see Table 2). In these calculations, we have substituted three of the five metal ions (Cu^{II} or Fe^{III}) with diamagnetic Zn^{II} centers to reduce the number of calculations required for the exchange coupling constants (11 spin states for 10 J values would be necessary to explicitely consider all exchange coupling pathways). From the data in Table 2 it follows, that the Cu^{II} centers are coupled antiferromagnetically while the Cu^{II}/Fe^{III} pairs as well as the Fe^{III}/Fe^{III} pairs are coupled ferromagnetically. This may result in the overall ferromagnetic behavior observed in the experiment.

3. Optimization of the Structures. The calculations discussed so far are all based on experimentally determined X-ray structural data, and the standard procedure therefore was to perform single point electronic calculations on the observed structural data. For the design of novel complexes with specific magnetic properties, it obviously is of importance to be able to structurally optimize the compounds. Also, the computed wave function based on an experimental structure is likely to represent a point which is not in a minimum of the potential energy surface, and a preoptimization of the structure might therefore be appropriate. In order to test this assumption, we have also used DFT-optimized structures of 25 complexes to compute the corresponding J values, and these are compared in Table 3 to the experimental data and the values derived from the X-ray structural data.[22,63,64] The values based on the X-ray structures were calculated with both Jaguar and Orca, and similar results were obtained (see Table S1 in Supporting Information). The values that are presented here are from Jaguar using B3LYP

TABLE 3: Comparison of Calculated and Experimental *J* Values of a Series of Oligonuclear Complexes (J_{calc} and J_{opt} are obtained with Equation 1, J_{calc} Is Derived from the Experimental Structure (Jaguar, 6-31G*/LACV3P++) and J_{opt} from the DFT-Refined Structure (High-Spin State, Orca, 6-31G*/TZVP); see *Supporting Information* for Structures of the Complexes, the Numbers in Parentheses in the Table Refer to the Corresponding Figures)**

compound	J_{calc} (cm^{-1})	J_{opt} (cm^{-1})	J_{exp} (cm^{-1})	references
$[Cu_2(MeC(OH)(PO_3)_2)_2]^{4-}$ (**7**)	−103.0	−118.2	−30.9	9, 66
$[(Et_5dien)_2Cu_2(\mu\text{-}C_2O_4)]^{2+}$ (**8**)	−99.0	−112.2	−37.4	66, 67
$[Mn(NH_3)_4Cu(oxpn)]^{2+}$ (**9**)	−40.8	−37.0	−15.7	66, 68
$[(\mu\text{-}OCH_3)VO(maltolato)]_2$ (**10**)	−84.3	−83.4	−107.0	66, 69
$[Fe_2OCl_6]^{2-}$ (**11**)	−148.0	−109.5	−112.0	66, 70
$[MnMn(\mu\text{-}O)_2(\mu\text{-}OAc)DTNE]^{2+}$ (**12**)	−156.3	−117.9	−110.0	66, 71
$[Cu_2(\mu{-}OH)_2(bipym)_2]^{2+}$ (**13**)	95.8	−98.5	57.0	66, 72
$[(Dopn)Cu(OH_2)Cr(OCH_3)L]^{2+}$ (**14**)	12.8	31.5	18.5	66, 73
$[(Dopn)Cu(\mu\text{-}CH_3COO)MnL]^{2+}$ (**15**)	54.2	54.9	54.4	66, 73
$[V_2O_2(\mu{-}OH)_2(^9aneN_3)_2]^{2+}$ (**16**)	−241.8	−52.5	−177.0	74, 75
$[Et_3NH]_2[(VO)_2(BBAC)_2]$ (**17**)	−160.9	−81.6	−167.9	74, 76
$[HB(pz)_3VO(OH)_2]_2$ (**18**)	14.3	29.2	−38.8	74, 77
$[(VO)_2(cit)(Hcit)]^{3-}$ (**19**)	−267.8	−29.0	−212.0	74, 78
$[V_2O_2(\mu{-}OH)(tpen)]^{2+}$ (**20**)	−461.7	−19.1	−150.0	74, 79
$[(VO)_2L(\mu\text{-}SO_4)]$ (**21**)	−132.6	−121.9	−128.0	74, 80
$[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]^{-}$ (**22**)	−245.7	−211.2	−117.0	74, 81
$[(VO)(3\text{-hydroxy-3-methylglutarate})]_2{}^{2-}$ (**23**)	8.9	−2.5	1.5	74, 82
$[(VO(Hsabhea))(VO(acac)(HOMe))(\mu_2\text{-}OMe)]$ (**24**)	18.6	15.4	5.3	74, 82
$[Cu_2(tren)_2CN](ClO_4)_3$ (**25**)	−98.6	−98.3	−79.0	83
$[Cu_2(tren)_2CN](BF_4)_3$ (**26**)	−119.1	−71.9	−80.0	83
$[Cu_2(tren)_2CN](ClO_4)(PF_6)_2$ (**27**)	−77.0	−79.2	−91.5	83
$[Cu_2(tmpa)_2CN](ClO_4)_3$ (**28**)	−70.1	−57.8	−52.0	83
$[Cu_2(tmpa)_2CN](BF_4)_3$ (**29**)	−69.8	−57.9	−50.0	83
$[Cu_2(tmpa)_2CN](BF_4)_{3*}(CH_3CN)_2$ (**30**)	−76.9	−57.9	−49.5	83
$[Ni_2(tetren)_2CN][Cr(CN)_6]$ (**31**)	−15.4	−9.3	−12.5	83
rmsd	75.6	*71.2*		

with the 6-31G*/LACV3P++** basis set combination. For the values based on the optimized structures only Orca was used, because the structure optimization was more efficient than with Jaguar.

Note that these preoptimizations are "gas phase" calculations, although packing forces in the crystals are known to be able to significantly influence the geometry with respect to an optimized "gas phase" structure; also, relatively small structural variations are known to have a significant impact on the calculated *J* value.[8,59−62] In most cases there is good agreement with the experimental data and the sign of the experimental *J* value is correctly predicted in all examples with one exception, which has a very low *J* value. The calculated rmsd values (eq 3) for the *J* values of all 25 complexes indicate that the calculations based on the preoptimized structures are in general leading to slightly more accurate magnetic data. That is, crystal lattice effects might—in the examples studied here—be of minor importance or lead to enforce specific conformations which were constrained during the preoptimization. The good quality of the prediction of *J* values based on computed structures is of importance because it indicates that the method presented here may also be used for the computation of *J* values of novel and structurally unknown complexes. We assume that an efficient design must involve MM-based modeling procedures which also allow to efficiently model crystal lattices, followed by a preoptimization by DFT.[8]

$$\mathrm{RMSD}(x_{\mathrm{calc}}, x_{\mathrm{exp}}) = \sqrt{\frac{\sum_{i=1}^{n} (x_{\mathrm{calc}}(i) - x_{\mathrm{exp}}(i))^2}{n}} \qquad (3)$$

Conclusions

With various program packages (G03, Jaguar, and Orca) and a number of established DFT functionals and basis sets we have established and validated a reliable and computationally relatively inexpensive method for the calculation of exchange coupling constants *J* of oligonuclear transition metal compounds. Results of acceptable accuracy in comparison with the available experimental data were obtained for a wide range of dinuclear complexes and compounds with higher nuclearity with a variety of transition metal ions. With a combination of the TZVP and 6-31G* basis sets for the chromophore and ligand backbones, respectively, we are able to compute exchange coupling constants *J* of moderately sized compounds within a few hours. The preoptimization of the experimentally observed geometries provides results, which are in general more accurate with respect to the experimental data. This is of importance for the denovo design of complexes with desired magnetic properties. The structural modeling may involve MM or QM/MM calculations of novel spin clusters prior to the calculation of the exchange coupling by the DFT methods described here.[8]

Acknowledgment. Generous financial support by the German Science Foundation (DFG) and the University of Heidelberg is gratefully acknowledged.

Supporting Information Available: Calculated and experimental *J* values of a series of oligonuclear complexes using Jaguar and Orca and structures of complexes studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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(63) A comparison between the TZV and the combined 6-31G*&TZVP basis sets for all structures, is given as Table S1 in Supporting Information; data based on the LACV3P++** basis set,[22,61] implemented in Jaguar, as well as the combination of LACV3P++** and 6-31G* are also included in Table S1 in Supporting Information. These data indicate that the LACV3P++**/6-31G* combined basis set leads to slightly more accurate values in comparison with the experimenta data.

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JP900752P