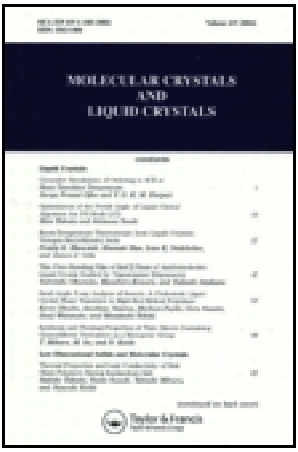

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Theoretical Studies of Spin Populations on Nitronyl Nitroxide, Phenyl Nitronyl Nitroxide and P-NPNN

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THEORETICAL STUDIES OF SPIN POPULATIONS ON NITRONYL NITROXIDE, PHENYL NITRONYL NITROXIDE AND P-NPNN

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Abstract Spin densities for nitronylnitroxide, phenyl nitronyl nitroxide(PNNO) and p-NPNN in the β-phase crystal were calculated by UHF, APUHF and UKS B(S)-LYP methods. Ab initio UHF overestimated a negative spin densitiy induced on the α-carbon atom of nitronylnitroxide group by spin polarization effect, whereas the approximately spin-projected UHF(APUHF)/6-31G* method provided a reasonable negative spin density on the α-carbon atom and almost equal distributions of the spin densities on nitrogen and oxygen atoms in PNNO and p-NPNN, in accord with the recent experiments. The spin populations on the benzene ring in these species by APUHF/6-31G* and APUHF/INDO, and UKS B-LYP/6-31G* methods were similar to the experimental values, indicating the important role of the spin polarization effect.

INTRODUCTION

Schweizer and his collaborators[1-4] have made extensive neutron-diffraction experiments for several nitroxides such as tanol suberate, tanol, phenyl nitronylnitroxide (PNNO) in order to elucidate spin density populations. It was found that the positive spin densities are distributed more predominantly on nitrogen than on oxygen in nitronylnitroxide group. They performed the unrestricted Hartree-Fock (UHF)[4], UHF Møller-Plesset perturbation (UMP2), UHF configuration interaction (CI) and unrestricted Kohn-Sham (UKS) local density functional (LDF)[5,6] calculations of PNNO and have found that relative distributions of the spin densities between nitrogen and oxygen by UHF and LDF are contradictory to the experiments.[4] However, they concluded that the UKS LDF method is the most suitable for computations of spin densities induced on phenyl group of PNNO and para-nitrophenyl nitronylnitroxide (p-NPNN), and a negative spin density induced on the α-carbon atom of nitronylnitroxide by the spin polarization (SP) effect.

Previously [7-9], we compared three different computational methods, namely UHF-, UKS- and complete active space (CAS) self-consistent-field (SCF)-based methods in order to obtain effective exchange integrals (J_{ab}) between open-shell species. The UHF-based methods followed by an approximate spin projection can reproduce J_{ab}-values for radical clusters by spin-restricted CASSCF-based methods if correlation corrections for them are sufficiently performed. On the other hand, UKS-based methods tend to stabilize low-spin (LS) states, and the J_{ab}-values are often negative (antiferromagnetic) in contradiction to UHF- and CASSCF-based methods. Therefore, these computational methods may exhibit different tendencies concerning spin density populations. Here, spin densities for nitronylnitroxide (NN), PNNO and p-NPNN are examined in order to elucidate characteristics of UHF- and UKS-based methods, which have been used for computations of J_{ab}-values for radical clusters. It will be shown that an approximately spin-projected UHF (APUHF) method provides reasonable spin populations for these species as in the case of computations of effective exchange integrals.[7-12]

THEORETICAL BACKGROUND

As is well known, UHF-based methods suffer from spin contamination effects, although these are practically applicable to larger organic radicals. In principle, the full CI (FCI) wavefunction involves no spin contamination even if the UHF solution is employed as a starting wavefunction. Therefore, the spin contamination effect should become less predominant if UHF-based correlated wavefunctions are close to the FCI wavefunction. For example, the UHF coupled-cluster (UCC) wavefunction is given by an exponential form of excitation operators as

$$\Psi_{UCC} = \exp\{T_i\}\ \Phi_{UHF} \qquad (1)$$

where T_i is the i-tuple excitation operator; for example, single (S), double (D), triple (T) and quadruple (Q) excitation operators. The UCC wavefunction should be very close to FCI if the exponential part in Eq. (1) is taken to involve sufficient higher excitation operators. In fact, spin contamination errors on spin densities are not serious for simple nitroxide radicals at the UCC SD or SD(T) level as shown previously[13,14]. The same is true in the case of UHF quadratic CI (QCI) SD since it is close to UCC SD.[13]

However, spin contamination effects are often significant even for UCC SD or UHF QCI SD in the case of conjugated radicals[7-14], indicating the necessity of spin projections of these wavefunctions. In fact, previous computations of high spin(HS) and low spin(LS) energy gaps manifested the necessity of spin projections for UHF-based wavefunctions.[7-14] However, spin projections for spin densities are not so easy in the case of post UHF wavefunctions. Here, the spin projection is performed only for doublet UHF solution, which is necessary for present calculations.

The UHF MOs for a singlet pair i for doublet radical are usually spin-polarized by the SP effect as[15,16]

$$\psi_i^{\pm} = \cos\theta_i \ \phi_i \pm \sin\theta_i \ \phi_i^{*} \qquad (2)$$

where ϕ_i and ϕ_i^{*} are the bonding and antibonding UHF natural orbitals (UNO), respectively. The spin-projected UHF wavefunction[15,16] is generally given by

$$\begin{aligned}\Phi_i = \mathbf{A}\, N\, \Pi\, [\, |\phi_i \overline{\phi_i}\, \phi_0| + \sin 2\theta_i / 3(1+\cos 2\theta_i)\{\, |\phi_i^{*} \overline{\phi_i}\, \phi_0| - |\phi_i \overline{\phi_i}^{*} \phi_0| \\ - 2\, |\phi_i^{*} \overline{\phi_i}\, \phi_0|\,\} - (1 - \cos 2\theta_i)/(1+\cos 2\theta_i)\, |\phi_i^{*} \overline{\phi_i}^{*} \phi_0|\,] \qquad (3)\end{aligned}$$

where **A** and N are the antisymmetrizer and normalizing factor, respectively, and ϕ_0 is SOMO. The second term in Eq. (3) describes the so-called spin polarization (SP) effect for doublet species. The spin density for each spin polarized pair is expressed by

$$\begin{aligned}\rho_i = (4+5T_i^{2})/3(2+T_i^{2})\ \phi_0^{2} + (1-T_i^{2})/3(2+T_i^{2})\ \{\phi_i^{2} + \phi_i^{*2}\} \\ + 2(1-T_i^{2})^{1/2}/(2+T_i^{2})\ \phi_i \phi_i^{*} \qquad (4)\end{aligned}$$

The negative spin density arises from the last cross term in Eq. (4). It is decomposed into the Mulliken spin populations on atoms.

As shown later, only the spin-polarized HOMO (ϕ_i =HOMO, ϕ_i^{*} = LUMO) is considered in Eq. (3) because of its largest spin polarization, and all other pairs are regarded as closed-shells (T_i =1, i=HOMO). All the spin-unrestricted computations were carried out by using the GAUSSIAN/DFT program package[17] on the IBM RISC computers. On the other hand, the APUHF and related calculations were performed using the program developed in our laboratory.

NITRONYL NITROXIDE

There are two chemically important problems for nitronylnitroxide derivatives. One is the magnitude of a negative spin density induced on the α-C atom by the SP effect. The other is the almost eqaul spin distributions on nitrogen and oxygen atoms revealed by the experiments.[4] A nitronylnitroxide **1** (2-hydro 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxy 3-oxide) was first examined as shown in fig. 1, where the geometry of **1** (X=H, F and Cl) was taken from the X-ray structure of 2-phenyl derivative of **1**, namely phenyl nitronylnitroxide (PNNO) **2**.[4] The several basis sets were used for ab initio calculations of spin densities for **1a** (X=H), whereas the 6-

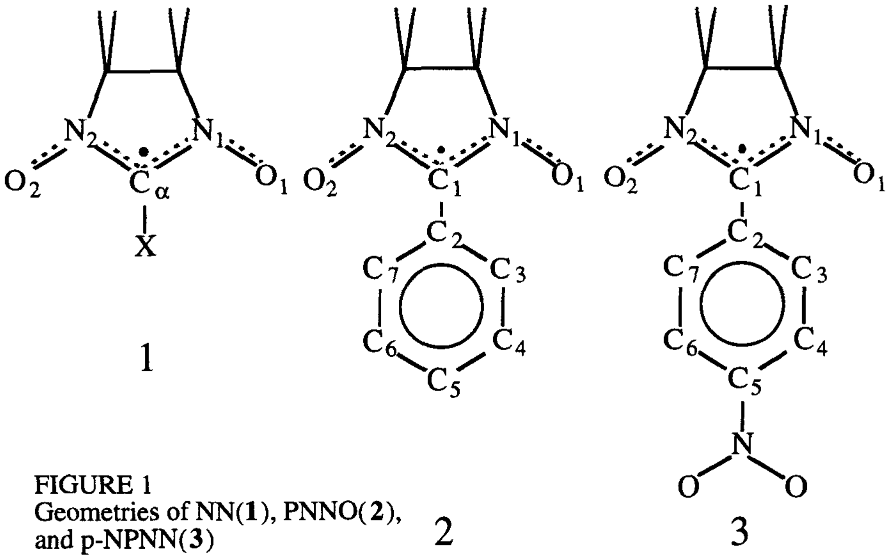

FIGURE 1
Geometries of NN(**1**), PNNO(**2**), and p-NPNN(**3**)

TABLE I Spin densities calculated for **1a** (X=H) by the UHF, APUHF and B-LYP methods with several basis sets

Basis set		N_1	N_2	O_1	O_2	C_α
STO-3G	UHF	0.154	0.147	0.801	0.783	-0.938
	APUHF	0.104	0.099	0.514	0.488	-0.212
	B-LYP	0.168	0.141	0.444	0.401	-0.158
4-31G	UHF	0.471	0.465	0.522	0.496	-0.953
	APUHF	0.232	0.219	0.346	0.316	-0.146
	B-LYP	0.238	0.204	0.358	0.322	-0.136
6-31G*	UHF	0.484	0.475	0.461	0.432	-0.852
	APUHF	0.262	0.243	0.311	0.277	-0.127
	B-LYP	0.247	0.211	0.342	0.306	-0.125
6-31G**	UHF	0.484	0.475	0.461	0.432	-0.849
	APUHF	0.262	0.243	0.310	0.277	-0.127
	B-LYP	0.247	0.211	0.342	0.306	-0.124

31G** basis set was used for **1** (X=F and Cl). Table I and II summarize the calculated results for **1a** (X=H), and **1b** (X=F) and **1c** (X=Cl), respectively.

From Table I, a large negative spin density (-0.85 ~ -0.95) appeared on the α-carbon atom of **1a** under the ab initio UHF approximation. The magnitude of negative

TABLE II Spin densities calculated for **1** (X=F, Cl) by the UHF, APUHF and B-LYP/6-31G** methods

X		N_1	N_2	O_1	O_2	C_α	X
X=F	UHF	0.451	0.457	0.517	0.482	-1.429	0.617
	APUHF	0.228	0.239	0.300	0.335	-0.140	0.006
	B-LYP	0.211	0.178	0.325	0.285	-0.055	0.034
X=Cl	UHF	0.478	0.472	0.453	0.423	-0.612	-0.152
	APUHF	0.260	0.276	0.282	0.315	-0.114	-0.054
	B-LYP	0.248	0.216	0.337	0.306	-0.086	-0.034

spin density on the α-C atom of **1a** is 0.153 by the ESR experiment.[18] Apparently, the spin projection for UHF-based methods is necessary to obtain reasonable negative spin densities as in the case of previous calculations of high- and low-spin energy gaps. The negative spin densities on the α-C atom are -0.146 and -0.127 for **1a** (X=H) by the APUHF/4-31G and 6-31G*, respectively, being consistent with the experiment.[18] Thus the removal of spin contaminations from UHF solutions is essential for reliable calculations of negative spin densitites induced by the SP effects.[15,16]

The spin density on the α-C atom of **1a** (X=H) is -0.12 ~ -0.16 by the spin-unprojected UKS B-LYP.[19,20] Thus UKS B-LYP/6-31G* is practical and useful in order to elucidate the magnitude of negative spin density on the α-C atom of nitronylnitroxides. The present result is compatible with previous conclusions by Schweizer's group.[1-4]

Let us consider the second problem, namely almost equal populations of spin densities on nitrogen and oxygen of the nitronylnitroxide group revealed by the neutron diffraction experiments for **2**.[4] The positive spin densities are distributed almost equally on the N- and O-atoms of **1a** (X=H) at the UHF/6-31G** level. However, APUHF/6-31G** predicted larger spin populations on oxygens than on nitrogens. The situation is the same for APUHF/6-31G*. APUHF/4-31G and STO-3G predicted a relatively large positive spin density on oxygen.

The UKS B-LYP/6-31G** calculations indicated that spin populations on $O_{1(2)}$ of **1a** (X=H) are quite larger than those of $N_{1(2)}$. The UKS B-LYP/4-31G and STO-3G calculations also predicted much larger positive spin densities on oxygens than on nitrogens.

The UHF/6-31G** calculation showed that the large positive spin density is distributed on the fluorine atom in the case of the fluorine substituted derivative **1b** (X=F), whereas the abnormally large negative spin density appears on the α-C atom, indicating the spin polarization of the C-F bond. On the other hand, the APUHF and UKS B-LYP/6-31G** calculations provided the reasonable magnitudes of spin densities on these atoms as shown in Table II. Judging from the sign of the positive spin density on F, the SP effect is predominant for the C-F bond. On the other hand, these computations elucidated that the negative spin density is populated on the chlorine atom in the case of the chlorinated derivative **1c** (X=Cl), showing that the spin delocalization (SD) effect is predominant for the C-Cl bond. Probably, the situation is the same for much soft carbon-halogen bonds; C-X(X=Br, I). Thus, the spin-appearing mechanisms (SP or SD) are different between the fluorine and other halogen substituted nitronylnitroxides **1**.

PHENYL NITROXYL NITROXIDE

Fig.1 shows phenyl nitronylnitroxide **2** and p-NPNN **3** examined here. The UHF, APUHF and UKS B-LYP calculations with the 6-31G* basis set were carried out for these species whose geometries were taken from the X-ray structures.[4] Tables III and IV summarize the calculated spin densities for **2** and **3**, respectively, together with the experimental values determined by the neutron diffraction method.[21]

The UHF/6-31G* calculations for **2** showed the larger positive spin densities on nitrogen atoms than those on oxygen atoms, whereas UKS B-LYP/6-31G* predicted the reverse tendency. On the other hand, APUHF/6-31G* provided almost equal spin populations on these atoms, in accord with the experiment.[4] This experimental tendency cannot be reprodeced by the LDF calculation by the use of the D-Gauss program package[4], and by UHF/INDO and APUHF/INDO.

The neutron diffraction experiment revealed the smaller positive spin densities on nitrogen atoms than those on oxygen atoms in the case of **3**. The APUHF/6-31G* calculations for p-NPNN itself reproduced the experimental spin densities determined for the crystal of p-NPNN. On the other hand, APUHF/INDO and UKS B-LYP/6-31G* indicated much larger positive spin densities on oxygen atoms of **3**.

The negative spin densities on the α-C atom for **2** are -0.08 and -0.146 by APUHF/6-31G* and APUHF/INDO, respectively, whereas it is -0.07 by UKS B-LYP/6-31G*. These methods can reproduce the experimental tendency (-0.121) for **2**.[4] On the other hand, APUHF/6-31G* provides the very similar value to the

TABLE III Spin densities of phenyl nitronylnitroxide (PNNO) **2** by the UHF- and UKS-based methods

Atoms	UHFa)	APUHFa)	UHFb)	APUHFb)	B-LYPa)	D-Gc)	Expc)
N_1	0.502	0.264	0.286	0.203	0.253	0.238	0.278
N_2	0.494	0.247	0.285	0.191	0.200	0.210	0.278
O_1	0.451	0.292	0.556	0.410	0.335	0.319	0.277
O_2	0.424	0.262	0.511	0.354	0.301	0.288	0.247
C_1	-0.842	-0.079	-0.562	-0.146	-0.106	-0.065	-0.121
C_2	0.761	0.035	0.108	0.002	0.015	0.004	0.024
C_3	-0.733	-0.017	-0.107	-0.011	-0.016	-0.009	-0.037
C_4	0.711	0.006	0.068	0.000	0.006	0.002	0.011
C_5	-0.701	-0.029	-0.091	-0.007	-0.014	-0.009	-0.016
C_6	0.681	0.004	-0.064	0.000	0.006	0.002	0.025
C_7	-0.729	-0.021	-0.108	-0.011	-0.015	-0.009	0.000

a) The 6-31G* basis set is used.
b) The INDO parameter is used.
c) Ref. 16 in the text.

TABLE IV Spin densities of p-NPNN **3** in the β-phase crystal by the UHF- and UKS-based methods

Atoms	UHFa)	APUHFa)	UHFb)	APUHFb)	B-LYPa)	Expc)
N_1	0.484	0.251	0.287	0.199	0.223	0.278
N_2	0.484	0.251	0.287	0.199	0.223	0.258
O_1	0.443	0.282	0.526	0.378	0.322	0.283
O_2	0.443	0.282	0.526	0.378	0.322	0.283
C_1	-0.868	-0.090	-0.572	-0.150	-0.111	-0.090
C_2	0.777	0.032	0.077	0.000	0.014	-0.000
C_3	-0.717	-0.013	-0.072	-0.007	-0.010	-0.001
C_4	0.678	0.004	0.040	0.000	0.004	-0.011
C_5	-0.649	-0.022	-0.054	-0.004	-0.009	-0.008
C_6	0.678	0.004	0.040	0.000	0.004	-0.011
C_7	-0.717	-0.013	-0.072	0.007	-0.010	-0.001
N	0.098	-0.000	0.007	-0.000	0.000	0.021

a) The 6-31G* basis set is used.
b) The INDO parameter is used.
c) J. Schweizer, private communacation.

experimental one determined for **3** by the neutron diffraction method.[21]

The spin populations on the benzene ring are of particular importance in relation to ferromagnetic interactions between PNNO derivatives such as p-NPNN.[22] The UHF/6-31G* calculations for **2** and **3** showed that large positive and negative spin densities are distributed alternately over the benzene ring, in compatible with the SP rule.[23] On the other hand, the spin projection procedure for UHF/6-31G* reduced significantly their magnitudes, showing that the spin densities by APUHF/6-31G* are compatible with the experiments.[4] Therefore the removal of spin contamination from UHF is essential even for qualitative discussions of spin densities induced by the SP effect. Interestingly, both signs and magnitudes of spin densities on the benzene ring by UKS B-LYP/6-31G* method without spin projection are qualitatively compatible with the experiments[4] although it is one of the spin-unrestricted approaches.

The spin populations on the benzene ring of **3** by these methods are quite close to those of **2**, indicating that an introduction of nitro group into the para-position of the benzene ring has no significant effect on the topological pattern[23] for spin populations induced by the SP effect. However, the neutron diffraction experiments revealed that all the induced spins on the benzene ring are negative in sign, in accord with the intermolecular SP effect,[23] whereas the positive spin density is induced on the nitrogen atom of the nitro group because of the close contact with the nitroxide group of the nearest neighbour p-NPNN. The APUHF/6-31G* and UKS B-LYP/6-31G* calculations of p-NPNN itself could not reproduce this positive spin density on the nitrogen atom, indicating the necessity of its cluster calculations. In fact, these spin populations are consistent with the SP mechanism of the benzene ring in the clusters of p-NPNN as illustrated in fig.5 in ref. 23. This in turn indicates that the indirect mechanism via nitrophenyl group plays a crucial role for the ferromagnetism of the β-phase crystal of p-NPNN.

The magnitudes of induced spin densities on the benzene ring of **2** and **3** by UHF/INDO are reduced to about one ninth of corresponding UHF/6-31G* values, although they are still larger than the experiments.[4] On the other hand, the APUHF/INDO values are similar to the experiments[4], showing the utility of the method for qualitative calculations of spin densities for larger organic radicals and their clusters. Previously, APUHF/INDO were successfully applied to qualitative computations of J_{ab} values for clusters of **2** and **3**[22,23], and m-MPYNN cation.[12]

The McConell model[24] predicts that the local contact between the nitrogen with small positive spin density in nitro group and nitroxide group of the nearest neighbor should give rise to the antiferromagnetic intermolecular interaction between p-NPNN. In fact, the previous APUHF/INDO calculation[11] showed that the J_{ab}-value is -0.81

cm^{-1} if the planar conformation is assumed for the nitrophenyl group. On the other hand, it manifested that the rotation of the nitro group gives rise to the positive J_{ab}-value (1.51 cm^{-1}), in accord with the selection rule V proposed in ref. 25. Thus, the pseudo perpendicular conformation of nitro group in p-NPNN plays an important role for the intraplane ferromagnetic interactions in the β-phase crystal of p-NPNN[22], indicating the importance of the second-order potential exchange interaction.[16] The spin density populations on PNNO and p-NPNN are useful indices for understanding of the electronic mechanism of their ferromagnetic interactions.

CONCLUSION

The numerical results for **1-3** indicated that spin projections of both ab initio and semiempirical UHF[7-16, 22,23] are necessary and effective for improvement of calculated spin populations. The APUHF/6-31G* method provides qualitatively correct populations of spin densities on nitrogen and oxygen atoms and a reasonable negative spin density on the α-carbon atom of nitronylnitroxide groups. Spin populations on the benzene ring for parent compound (PNNO) **2** by APUHF/6-31G* and INDO are parallel to those of the experiment.[4,21] This is the reason why the APUHF/INDO calculations have provided qualitatively reasobale effective exchange integrals (J_{ab}) between phenyl nitronylnitroxide derivatives such as p-NPNN[22,23]. Thus, APUHF is useful for qualitative explanations of experimental results obtained for β- and γ-phase crystals of nitronylnitroxide derivatives.

The UKS B(S)-LYP methods without spin projection provide resonable negative spin densities on the α-carbon atom of nitronylnitroxide groups and reproduced qualitatively spin populations on the benzene ring for phenyl nitronylnitroxide by the neutron diffraction experiment.[4,21] On the other hand, UKS B-LYP/6-31G* can not reproduce almost equal spin populations on nitrogen and oxygen atoms of nitronylnitroxide group. However, these methods are practically useful for qualitative studies on spin density populations for π-conjugated radicals.

In conclusion, APUHF/6-31G* and INDO methods are handy and practical for qualitative studies of spin populations on nitroxide and nitronylnitroxide derivatives and J_{ab} values for clusters of these species. However, quantitative calculations of spin density populations on these species are a difficult task. Fot this purpose, the spin-restricted calculations followed by the extensive correlation corrections (for example CAS CI or CASPT2[8]) of spin densities are necessary. They will be performed elsewhere.

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