Nuclear Quantum Effect on Molecular Magnetic Properties for Low Barrier Hydrogen-bonded Systems Based on Multicomponent Density Functional Theory

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We have theoretically analyzed the nuclear quantum effect on the nuclear magnetic shielding (σ) and molecular magnetic susceptibility (χ) of $H_3O_2^-$ and $N_2H_7^+$ systems with a new implementation combined with the multicomponent density functional theory and the gauge-including atomic orbital or continuous set of gauge transformation techniques. Our method easily reproduces the "deshielding" effect of σ on hydrogen atoms and clearly indicates the existence of the H/D isotope effect on χ in $H_3O_2^-$ and $N_2H_7^+$ systems.

The methods for the theoretical prediction of the nuclear magnetic resonance (NMR) parameters of molecules have became useful quantum chemical tools to interpret experimental data.[1] The experimental NMR spectra in combination with theoretical calculation lead to reliable structural assignments of the system.[2] For a given molecular geometry, the magnetic shielding tensor (σ) on the hydrogen, carbon, nitrogen atoms, etc. can be evaluated by ab initio calculations with the gauge-including atomic orbital (GIAO)[3] or the continuous set of gauge transformation (CSGT)[4] techniques. In the accurate theoretical prediction of σ, it is indispensable to take account of not only the electron correlation but also the nuclear quantum fluctuation, because the influence of the nuclear fluctuation on σ is as large as that of the electron correlation.[5–9] Most of the methods to analyze the influence of the nuclear fluctuation, such as the vibrational or rovibrational corrections[6–8] and the path integral Monte Carlo (PIMC) method,[9] are based on the potential energy surface (PES) with the Born–Oppenheimer (BO) approximation. Although these theoretical approaches allow us to evaluate the more reliable absolute magnetic shielding, the nuclear quantum effect on the molecular magnetic properties has not been discussed by the ab initio molecular theory without the BO approximation.

In this study, we focus on the theoretical analysis of the nuclear quantum effect on the magnetic properties, such as the absolute magnetic shielding and magnetic susceptibility (χ), based on the multicomponent density functional theory (MC_DFT)[10] combined with the GIAO and CSGT techniques. In the MC_DFT, the Kohn–Sham orbitals of quantum nuclei are obtained in a similar fashion to the conventional density functional theory, with the electronic and nuclear orbitals being calculated on an equal footing. Our scheme is demonstrated for the low barrier hydrogen-bonded systems of $H_3O_2^-$ and $N_2H_7^+$.

The MC_DFT is described in detail in the literature.[10] In our implementation, the σ and χ are evaluated only with the electronic part of Kohn–Sham orbitals obtained by MC_DFT in order to analyze the magnetic properties arising only from electrons. In the GIAO method in which the σ is represented as the "mixed" second derivative of the energy with respect to the external magnetic field and the nuclear magnetic moment, we neglected the energy components from quantum nuclei. In the CSGT method, we also evaluated σ and χ by the induced first-order current density arising only from electrons. We have implemented these schemes to Gaussian 03.[11]

We use the hybrid exchange-correlation functional of B1LYP which gives a reasonable potential barrier height with respect to the hydrogen-bonded proton (denoted by H*) transfer between X–H*···X and X···H*–X structures (X = O and N), compared to the accurate calculations. The barrier heights of $H_3O_2^-$ with B1LYP/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ are 0.72 and 0.88 kJ mol^{-1}, respectively, and those of $N_2H_7^+$ with B1LYP/aug-cc-pVDZ and CCSD(T)/6-311++G** are 2.73 and 4.04 kJ mol^{-1}, respectively. In the MC_DFT calculation, the aug-cc-pVDZ and [1s1p1d] GTFs were employed as the basis sets of electrons and quantum protons (deuterons), respectively, to obtain the optimized geometries of $H_3O_2^-$ and $N_2H_7^+$ systems. We used the optimized GTF exponents of quantum proton (deuteron) in the Hartree–Fock level.[12] In the optimization procedures the electronic basis centers were fixed on the optimized basis centers of quantum protons (deuterons). The magnetic shielding tensor (σ) and the magnetic susceptibility (χ) for $H_3O_2^-$ and $N_2H_7^+$ were evaluated by the MC_DFT with GIAO and CSGT techniques at each optimized geometry with B3LYP and two basis sets (EPR-III, and aug-cc-pVTZ).

Figure 1a shows the optimized bond lengths of $H_3O_2^-$ with quantum protons (qmH), deuterons (qmD), and classical nuclei (cl). In the case with classical nuclei, the asymmetric O–H*···O or O···H*–O structure becomes the most stable, be-

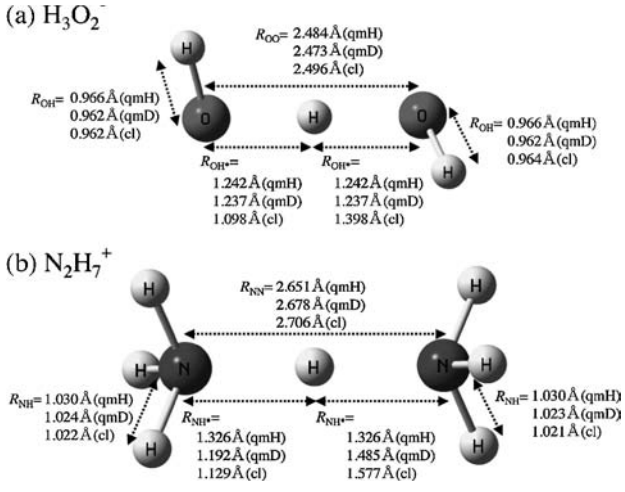

Figure 1. The schematic illustration and optimized bond lengths (Å) of $H_3O_2^-$ and $N_2H_7^+$ species. The bond lengths in the systems with quantum protons, quantum deuterons, and classical nuclei are denoted as qmH, qmD, and cl, respectively.

cause the H* atom in $H_3O_2^-$ has the double-well potential along the proton-transfer coordinate. On the other hand, in the case of $H_3O_2^-$ with quantum protons (deuterons), the effective PES with respect to the H*(D*) coordinate changes to the single well, so that the H*(D*) is located at the central position of two oxygen atoms as O···H*(D*)···O which corresponds to the transition state by the conventional DFT methods. These results clearly show that H*(D*) is able to pass over the potential barrier height due to the zero-point vibration energy (ZPE). Actually the harmonic ZPE of $H_3O_2^-$ with classical protons (82.4 kJ mol^{-1}) is considerably greater than the barrier height. In addition, we found the geometric isotope effect in the OO distance (R_{OO}); that is, $H_3O_2^-$ has the slightly longer R_{OO} compared to the case of $D_3O_2^-$. Similar results were also reported by the ab initio path-integral simulation[13] and quantum Monte Carlo calculation.[14]

Figure 1b also shows the optimal structure of $N_2H_7^+$ species, where the H* atom in $N_2H_7^+$ are known to have a double-well potential along the proton-transfer coordinate. In the case with quantum protons, the symmetric N···H*···N structure becomes the most stable, because of the single-well shape of the effective PES. On the other hand, the optimal structure of the D-species is the asymmetric structure of N–D*···N or N···D*–N as well as the $N_2H_7^+$ with classical nuclei, because the ZPE of deuteron is smaller than that of proton. Similar geometric isotope effect (GIE) was also reported by the ab initio path-integral simulation.[15]

Table 1 shows the absolute isotropic magnetic shielding ($\tilde{\sigma} = 1/3\,\mathrm{Tr}[\sigma]$) on each hydrogen atom obtained by the GIAO method and the absolute isotropic magnetic susceptibility ($\tilde{\chi} = 1/3\,\mathrm{Tr}[\chi]$) of each species by the CSGT method. In the $H_3O_2^-$ with classical nuclei, we found three different values of $\tilde{\sigma}$ on hydrogen atoms, because all hydrogen atoms take the nonequivalent electronic environment due to the asymmetric structure of $H_3O_2^-$. In the case with quantum protons or deuterons, since the electronic environment of outer hydrogen atoms is equivalent to each other due to the symmetric form of $H_3O_2^-$, two different $\tilde{\sigma}$'s on outer hydrogen atoms become identical. We have also found large differences (3.6–3.8 ppm) between $\tilde{\sigma}$'s on H* atoms ($\tilde{\sigma}_{H^*}$) in $H_3O_2^-$ with classical and quantum protons, which reflects difference in each optimal nuclear and electronic structures. In addition, the slight shift of $\tilde{\sigma}$ between $H_3O_2^-$ with quantum protons and deuterons (0.3–0.4 ppm) clearly indicates the existence of the "deshielding" effect arising from the spatial delocalization from the deuteron to proton. Such deshielding effect is also indicated for other molecules by the Hartree–Fock calculation of MC_MO,[16] zero-point vibrational correction,[8] and the PIMC simulation.[9] Furthermore, we found that the $\tilde{\chi}$ of H-species is greater than that of D-species. This difference clearly indicates the H/D isotope effect in the absolute isotropic magnetic susceptibility. It is thought that the relatively weak attraction between electrons and protons occurs the enhancement of $\tilde{\chi}$, because the weakly bound electrons by nuclei are more easily perturbed by the external magnetic field.

Table 1. The absolute isotropic magnetic shielding ($\tilde{\sigma}$ in ppm) on each hydrogen atom and the absolute isotropic magnetic susceptibility ($\tilde{\chi}$ in cgs-ppm) of $H_3O_2^-$ and $N_2H_7^+$

			$\tilde{\sigma}_{H^*}$	$\tilde{\sigma}_{H}$	$\tilde{\chi}$
$H_3O_2^-$	EPR-III	qmH	11.41	33.97	−30.92
		qmD	11.80	34.37	−30.75
		cl	15.26	33.99/35.30	−30.64
	aug-cc-pVTZ	qmH	11.32	34.21	−30.89
		qmD	11.67	34.52	−30.69
		cl	14.95	33.75/35.09	−30.60
$N_2H_7^+$	EPR-III	qmH	7.05	28.17	−30.10
		qmD	9.32	28.08/29.21	−29.93
		cl	13.10	28.17/29.95	−29.35
	aug-cc-pVTZ	qmH	9.74	27.54	−30.70
		qmD	11.60	27.69/28.62	−30.51
		cl	12.82	28.03/29.80	−29.90

In the $N_2H_7^+$ we found two different values of $\tilde{\sigma}$ on outer hydrogen atoms even in the D-species, because only quantum H-species takes the symmetric structure. We also found large differences (3.1–6.1 ppm) between $\tilde{\sigma}_{H^*}$'s in $N_2H_7^+$ with classical and quantum protons, which reflects differences in each optimal nuclear and electronic structures. The relatively large shift of $\tilde{\sigma}_{H^*}$ in quantum H- and D-species (1.9–2.3 ppm) compared to the case of $H_3O_2^-$ and the enhancement of $\tilde{\chi}$ between the quantum H- and D-species arise from both the GIE and magnetic isotope effect.

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