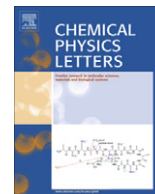




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Zero-field splitting of compact trimethylenemethane analogue radicals with density functional theory

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ABSTRACT

This work presents the computation of spin–spin coupling that arise between interactions of spin-centers which eventually leads to zero-field splitting in organic molecules. With DFT implementation spin–spin Hamiltonian is subjected to recently observed compact trimethylenemethane analogue di-radicals – nitroxide-substituted nitronyl nitroxide and iminonitroxide, which exhibits large positive exchange interactions with ZFS at the room temperature. We obtain the parameters defining the ZFS that have an excellent agreement with the experiment, consistent with the perception that spin–orbit coupling contribution to the ZFS is negligible in organic molecule. \mathbf{g} -tensor shift also calculated with restricted DFT-linear response formalism (RDFT-LR) and compared with realistic observations.

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1. Introduction

Zero-field splitting (ZFS) – arising out of internal field, gives an insight into the spin distribution of active electrons in different molecular centers. With open-shell or high manifold species they are characterized by two independent parameters D and E which essentially determines the placement of different sub-levels in the absence of external field. In recent years considerable interest in these parameters, both in experiment and in theory, were driven by desire to manipulate the spins centers for a successful design of molecular magnets. In organic species almost negligible contributions from spin–orbit interaction leaves spin–spin coupling (SSC) to determine the magnitude of these parameters, unlike in transition metals the strong spin–orbit coupling (SOC) dominates as the metal electrons occupy higher angular momentum orbitals and hence SSC term is generally discarded. However it has been shown by Neese spin–spin also important as they offer non-negligible contribution even in d orbitals elements. ($\sim 1\text{--}2\text{ cm}^{-1}$) [4].

Although the relativistic contributions were known for long time, complete *ab initio* calculations to qualitatively describe the split with SSC and SOC Hamiltonian appears in the literature only in recent times [5,6,8,9,14,15]. There were different implementation of respective theoretical approach both in wave-functions and density based techniques to compute these parameters. Multi-configurational approach offers good description of excited states and hence proper treatment of SO Hamiltonian between the states gives very well agreeable results with experiments [3,4]. Though there has been reports with density based calculations, generalization to any multinuclear complex is still development. On other

hand in organic molecules spin–spin coupling alone explains the split very well and it has been qualitatively explained in recent literature [8–10]. Marian et al. recently reported implementation of SS interaction as a quasidegenerate perturbations with multireference CI treatment [16] and resolution of identity approximation for spin–spin implementation by Neese also emphasize the significance of SS interactions. Here with newly discovered stable nitroxide and iminonitroxide di-radicals this work with DFT implementation of SSC demonstrate its dominance in ZFS.

Trimethylenemethane (TMM) was first characterized by Dowd and it's the first non-kekulé molecule to be subjected to the Electron Spin Resonance (ESR or EPR) [2]. Later Anders Lund experimentally observed the D parameter for TMM with ESR. Since then, TMM and it's derivative has been a subject of interest in many field of chemistry including organic magnetism [17]. Using TMM as a building block there has been many reports to construct high spin poly-radicals [18,19]. In the recent report we compared the parameters of TMM with isoelectronic oxyallyl using MCSCF approach [11]. This work present the DFT implementation of SSC interactions of the triplet ground state of the di-radicals which was synthesized very recently by Okada et al. in which they report compact TMM analogue di-radicals nitroxide-substituted nitronyl nitroxides and iminonitroxide, which shows large positive exchange interactions at room temperature and in air [1]. The structure of these di-radicals is shown in Figure 1. Unlike ZFS there has been lots of literature on *ab initio* calculations of \mathbf{g} -tensors [7,12,20–25]. Each of those following different tactics with an implementation for accurately calculating the corrections to the $\Delta\mathbf{g}$. This work employs the restricted density-functional linear response theory (RDFT-LR) formalism for \mathbf{g} -tensor evaluations. By employing RDFT this formalism inherently rules out the spin-contamination.

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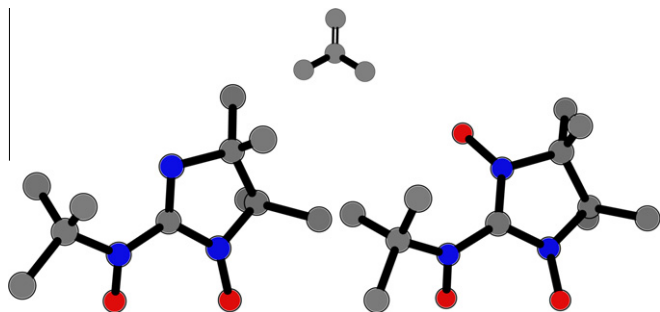


Figure 1. TMM, structure of radical I (iminonitroxide) and II (nitroxide-substituted nitronyl nitroxides) without hydrogen (N in blue, O in red and C in grey). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Theoretical methods

It's well known that spin–spin Hamiltonian that results due to interactions between the electronic magnetic moment is given by

$$\hat{H}_{ss} = \frac{\alpha^2}{2} \sum_{ij} \left[\frac{\vec{S}_i \cdot \vec{S}_j}{r_{ij}^3} - \frac{3(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \quad (1)$$

where α is the fine structure constant, the above equation can be also be recognized as classical dipole–dipole interactions type.

One can elegantly reduce Eq. (1) in a parameter form in an appropriate co-ordinate system, which diagonalize the Hamiltonian in terms of D and E

$$\hat{H}_{ZFS} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (2)$$

Note that, here we neglect the contributions from spin–orbit Hamiltonian as it has negligible effect in organic molecules

While in implementation Eq. (1,2) computed in terms of ZFS tensor D_{ij}

$$D_{ij} = \sum_{\mu\nu\rho\sigma} d_{ij,\mu\nu\rho\sigma} q_{\mu\nu\rho\sigma} \quad (3)$$

where $q_{\mu\nu\rho\sigma}$ gives zeroth component of the quintet combination of two-electron spin operators and so called two-electron density matrix, $d_{ij,\mu\nu\rho\sigma}$ is the integral of i and j 'th Cartesian component of two-electron field gradient operator over μ, ν, ρ, σ indexed orbitals.

Considering only the non-zero values of quintet density, Eq. (3) reduce to

$$D_{ij} = \frac{1}{2} \sum_{\mu\nu\rho\sigma} d_{ij,\mu\nu\rho\sigma} (P_{\mu\nu}P_{\rho\sigma} - P_{\mu\sigma}P_{\rho\nu}) \quad (4)$$

where P is the active density matrix in atomic orbitals given in terms of molecular orbital co-efficients C_{ij} , i.e.,

$$P_{ij} = \sum_k C_{ik}C_{kj} \quad (5)$$

For triplet reference state the task is to compute the expectation value of Eq. (1) over the properly described or variationally treated ground state. Here the reference states are triplet ground state of the radicals obtained from density functional.

$$H_{ij} = \langle {}^3\Psi_0 | H_{ss} | {}^3\Psi_0 \rangle \quad (6)$$

which is simplified in terms of ZFS tensor expression Eq. 4, hence by using the following relations we arrive at magnitude of D and E

$$D = \frac{3}{2} D_{zz} \quad (7)$$

$$E = \pm \frac{1}{2} (D_{xx} - D_{yy}) \quad (8)$$

The positive sign of transverse anisotropy E (D is axial anisotropy) depends on the condition $D > 0$.

Here a very brief theoretical description has been outlined about the g -tensor evaluation through RDFT-LR formalism, which inherently avoids spin-contamination as they are based on non-UDFT. In this report the relevant terms employed for the g -tensor given by the equation

$$g = g_e I + \Delta g_{RMC} + \Delta g_{GC(1e)} + \Delta g_{GC(2e)} + \Delta g_{OZ/SO(1e)} + \Delta g_{OZ/SO(2e)} \quad (9)$$

where g_e is free electron g -factor and Δg is decomposed into mass-velocity, one and two-electron gauge corrections, one and two-electron spin–orbit corrections term which couples through Zeeman effect. The first three Δg terms are evaluated with perturbation theory, where as latter two-electron spin–orbit terms are implemented through atomic mean-field approximations [22,26]. We refer detailed discussion of linear response (LR) formalism, g -tensor with LR approach and for a review of EPR to the following reference [13,25,27].

3. Computational details

In this report local density approximation (LDA) and hybrid Becke3–Lee–Yang–Parr (B3LYP), pure numerical Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) functional were employed. All the calculations were performed with Dunning's core-valence, correlation consistent cc-pVDZ basis set. With un-restricted Kohn–sham (KS) formalism we optimize for the triplet ground state of the radical using X-ray geometry as the initial guess structure in GAMESS-US suite of programs [28,29]. Using the UDFT geometry with spin-restricted open-shell linear response (RDFT-LR) this work compute the g -tensor of the diradicals. In which the density functionals describing the triplet ground state were fed into spin–spin coupling computation. For qualitative description and comparison, the calculations were also done at the single point geometry from the experimental configurations.

All the ZFS and g -tensor calculations were done using local version of DALTON quantum chemistry program [30]. The figure was generated using Gabedit visualization program [35].

4. Results and discussions

The results are summarized in Table 1 for the ZFS parameters. The computed D and E have an excellent agreement with very recently reported experimental discoveries of the radicals from Okada and co-authors [1], in which they report for the first time, synthesis of compact stable TMM-analogues which shows large positive exchange interactions $J/K > 300$ K in air and at room temperature. As this letter tries to address the ZFS computation with DFT, here we focus only on the additional terms (ZFS + g -tensor)

Table 1
Zero-field splitting parameter.

| Functionals | Radical I | | Radical II | |
|--------------------|-----------|---------|------------|---------|
| | D^a | E^a | D^a | E^a |
| Expt. ^b | 0.0639 | 0.0050 | 0.0250 | 0.0016 |
| B3LYP ^c | −0.0681 | −0.0061 | −0.0379 | −0.0101 |
| PBE ^c | −0.0638 | −0.0058 | −0.0351 | −0.0099 |
| LDA ^c | −0.0631 | −0.0054 | −0.0345 | −0.0096 |
| B3LYP | −0.0659 | −0.0088 | −0.0387 | −0.0111 |
| PBE | −0.0588 | −0.0097 | −0.0346 | −0.0103 |
| LDA | −0.0573 | −0.0110 | −0.0350 | −0.0103 |

^a In cm^{-1} .

^b In $|D/hc|$ and $|E/hc|$.

^c At the experimental configurations.

Table 2
g-Tensor and shifts with restricted density functional theory linear response formalism (RDFT-LR) using cc-pVDZ.

| Functionals | Component | Radical I | | | | Radical II | | | |
|-------------|-----------|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|
| | | (i) ^a | | (ii) ^b | | (i) ^a | | (ii) ^b | |
| | | g-tensor ^c | Δg^d | g-tensor ^c | Δg^d | g-tensor ^c | Δg^d | g-tensor ^c | Δg^d |
| B3LYP | rx | 0.00567 | 3350 | 0.00560 | 3280 | 0.00586 | 3540 | 0.00722 | 4902 |
| | yy | 0.00232 | –4 | 0.00283 | 506 | 0.00331 | 991 | 0.00455 | 2235 |
| | zz | 0.00887 | 6552 | 0.00856 | 6242 | 0.00815 | 5833 | 0.00571 | 3395 |
| | avg | 0.00562 | | 0.00566 | | 0.00577 | | 0.00583 | |
| PBE | xx | 0.00550 | 3175 | 0.00540 | 3083 | 0.00579 | 3468 | 0.00693 | 4609 |
| | yy | 0.00215 | –168 | 0.00275 | 429 | 0.00316 | 842 | 0.00445 | 2132 |
| | zz | 0.00823 | 5905 | 0.00783 | 5509 | 0.00793 | 5615 | 0.00573 | 3412 |
| | avg | 0.00529 | | 0.00533 | | 0.00563 | | 0.00570 | |
| LDA | xx | 0.00568 | 3361 | 0.00556 | 3237 | 0.00592 | 3600 | 0.00731 | 4990 |
| | yy | 0.00196 | –364 | 0.00284 | 518 | 0.00278 | 461 | 0.00460 | 2301 |
| | zz | 0.00893 | 6611 | 0.00833 | 3256 | 0.00843 | 6114 | 0.00592 | 3596 |
| | avg | 0.00552 | | 0.00558 | | 0.00571 | | 0.00595 | |
| Expt. | xx | 0.0032 | | | | 0.0070 | | | |
| | yy | 0.0048 | | | | 0.0023 | | | |
| | zz | 0.0032 | | | | 0.0041 | | | |
| | avg | 0.0037 | | | | 0.0045 | | | |

^a Optimized geometry with various functionals.

^b With respect to experimental geometry.

^c +2.0000.

^d In parts per million (10^{-6}).

calculation from the first principle. In fact the above experiment validates the observed exchange interaction with Yamaguchi's formulations for calculating the exchange Hamiltonian.

As it's obvious that experimental least energy geometry gives very well agreement for theoretical prediction of D and E . While both GGA and LDA functionals at the X-ray geometry gives better accuracy, optimized structure with respect to these functionals suffers little accuracy. This can be immediately thought to be from inherent approximations associated with the basis set and functionals, provided if we completely ignore the negligible SOC. Also with UDFT geometry which is prone to the spin-contamination from the higher multiplicity, in this case the contamination of (S^2) is of the order ~ 0.0010 . Compared to di-radical I the computed parameters for di-radical II slightly overestimates from the experiment (~ 1.5 times of expt.).

Examining the molecular orbital co-efficients explain the distribution of the spin-centers, which eventually make the spin-density matrix and so the ZFS. As expected molecules of this type have their spin distributions over oxygen and nitrogen atoms since they have unpaired π orbitals contributing for bond between them. In fact due to stability of nitroxide free radical it has been used as a good choice for spin labels in probing bio-molecular structure, in physics and in chemistry [31,32]. The dominant Mulliken spin densities for di-radical I are as follows for both O $\rho_s \sim 0.5$, three N has $\rho_s \sim 0.3$; for di-radical II spin densities are $\rho_s(N) \sim 0.25-0.32$ and $\rho_s(O) \sim 0.30-0.54$. Spin densities are localized between the nitrogen and oxygen atoms for both the radicals, although the distribution among them is not mutual, indicating relatively dominant spin-centers around oxygen atoms and hence influencing the splitting much. It has been shown before with MCSCF implementation replacing a methyl group in TMM by an oxygen atom (resulting oxyallyl) reverses the spin-splitting due to spin-spin interactions [11], i.e., the sign of D and E is negative for oxyallyl though they have isoelectronic structure with TMM (TMM $D = 0.02 \text{ cm}^{-1}$, $E = 0 \text{ cm}^{-1}$; oxyallyl $D = -0.06 \text{ cm}^{-1}$, $E = -0.003 \text{ cm}^{-1}$). It's worth to note that pure O atom has positive split for the triplet ground state $D_{SO+SS} = 3.96 \text{ cm}^{-1}$, $D_{SS} = 1.44 \text{ cm}^{-1}$ [8]. Here as well, the calculations predict negative sign of ZFS split in these radicals, since fitting from ESR can only determine the magnitude of D and E . The negative sign for D parameter is significant in molecular

magnetism perspective as it thought to be behind anisotropy barrier $|D|S^2$ arising out of double well potential approximation between the energy difference of $\pm S_z$ states for any high spin ground state [33]. However one has to take caution while deriving an analogy between ZFS and magnetic anisotropy barrier [34]. The magnitude of the parameter for radical I is higher than II, this can be reasoned using the Eq. (1) – small distance between the nitroxide centers leads to larger spin-spin interactions.

This work also computes the g-tensor for radical I and II, the results are presented for g-tensor and shift (Δg) with respect to various functionals in Table 2. The shift in g-tensor appears to be very sensitive to the geometries as one can infer from its components from experimental and optimized geometry. Note that these calculations are in gas phase while the observed spectrum is in presence of frozen diethylphthalate. Yet for both the radicals g_{avg} is consistent with respect to the functionals in GGA and in LDA, while they are slightly above the experimental values, with small deviation in radical II. Nonetheless the variations are homogeneous and reasonably agreeable with realistic observation. Perhaps proper treatment of spin polarization effects for the open-shell and careful choice for the compatibility between basis set and functionals might influence the result for the better accuracy [27].

5. Conclusions

Ab-initio computation for ZFS gains much attention in recent years owing to their application in molecular magnetism and spintronics. This work with DFT spin-spin implementation explains the splitting among triplet ground state of recently discovered compact TMM like di-radicals – nitronyl nitroxide and iminonitroxide, which exhibits high stability in air and at room temperature. The obtained results have an excellent agreement with the observed D and E and the calculated results are logical with the fact that SSC dictate the splitting in organic molecules with ignorable SOC contributions. Here we presented the g-tensor and shift as well with RDFT-LR formalism which have reasonable agreement with observed spectrum. Applying the SSC operator for strongly interacting magnetic organic species could be a good choice for validating the theoretical approach. These findings can also be considered

as a support to the experimental observation of new stable di-radical species.

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