



Density Functional Calculations of EPR Parameter g Tensors of Some Transition Metal Complexes

KEYWORDS

Density Functional Theory, EPR Parameter g Tensor, Transition Metal Complexes.

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ABSTRACT

We have calculated EPR spectral parameter g tensors of $[\text{Ni}(\text{CO})_3\text{H}]$, $[\text{Co}(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_5]^+$ transition metal complex using different functionals of density functional theory (DFT). For these calculations VWN,UDFT with $\Delta\text{gso}/\text{oz}(2e)$, VWN,SOS-with $\Delta\text{gso}/\text{oz}(2e)$, VWN,UDFT without $\Delta\text{gso}/\text{oz}(2e)$, VWN ,SOS- DFPT ,without $\Delta\text{gso}/\text{oz}(2e)$, BP86 ,UDFT without $\Delta\text{gso}/\text{oz}(2e)$, BP86 ,SOS- without $\Delta\text{gso}/\text{oz}(2e)$, functional have been used and the results obtained have been compared with experimental values. The results obtained from the density functional methods have been found in close agreement with the result obtained from the experiments. The performance of the functional BP86, UDFT without $\Delta\text{gso}/\text{oz}(2e)$, BP86, SOS- without $\Delta\text{gso}/\text{oz}(2e)$, have been found better for $[\text{Ni}(\text{CO})_3\text{H}]$, VWN, UDFT with $\Delta\text{gso}/\text{oz}(2e)$, BP86, UDFT without $\Delta\text{gso}/\text{oz}(2e)$ for $[\text{Co}(\text{CO})_4]$ and BP86, SOS without $\Delta\text{gso}/\text{oz}(2e)$, VWN,SOS,DFPT,without $\Delta\text{gso}/\text{oz}(2e)$ for $[\text{Fe}(\text{CO})_5]^+$. We have inferred that results obtained by DFT calculated g tensor values using hybrid density functional are in close agreement with experimentally observed values and may be used for efficient calculation of EPR parameter g tensor of transition metal complexes.

1.0:-Introduction

The electronic g-tensor is a characteristic part of any EPR spectrum and can provide information on the identity as well as electronic and molecular structure of the paramagnetic species present. The fundamental physical laws that determine the g tensor are well understood. However, serious computational difficulties had largely prevented a rigorous first-principles prediction of this quantity. Thus, in contrast to the treatment of EPR hyperfine coupling constants that already do have an appreciable history of first principles theoretical treatments, quantitative calculations of electronic g tensors by empirical quantum chemistry have become possible very recently. The first accurate calculations at the HF and multireference configuration interaction (MRCI) levels of theory are due to Lushington et al [9, 10]. Vahtras and coworkers [11] have employed HF and multiconfigurational self-consistent-field (MCSCF) linear response functions. Recently, two different DFT implementations of g-tensor calculations within the Amsterdam density-functional code have been reported by Lenthe et al [16]. Density Functional Theory (DFT) is due to its success in treating transition metal complexes, in stark contrast to the failure of the Hartree Fock method. This technique presently the most successful approach to compute electronic structure of matter and hence for calculation of EPR parameters such as g-tensors and hyperfine coupling constants A of transition metal complexes [4, 5, 6, 7, 8, 12, 13, 14, 15]. The theoretical calculation of EPR parameter hyperfine coupling constants have been conducted by some scientists [1,2,3] and found good agreement with the experimentally observed values. Kaupp Martin et al [8] have reported the first implementation of the calculation of electronic g-tensors by density functional methods with hybrid functionals. Spin-orbit coupling is treated by the atomic mean field approximation, g-tensors for a set of small main group radicals and for a series of ten 3d and two 4d transition metal complexes have been compared using the local density approximation (VWN functional), the generalized gradient approximation (BP86 functional), as well as B3-type (B3PW91) and BH-type (BHPW91) hy-

brid functionals. For main group radicals, the effect of exact-exchange mixing is small. In contrast, significant differences between the various functionals arise for transition metal complexes as has been shown previously, local and in particular gradient-corrected functionals tend to underestimate the "paramagnetic" contributions to the g-tensors in these cases and thereby recover only about 40-50% of the range of experimental g-tensor components. This is improved to ca. 60% by the B3PW91 functional, which also gives slightly reduced standard deviations. The range increases to almost 100% using the half-and-half functional BHPW91. A recently developed density functional (DFT) approach for the calculation of electronic g-tensors has been applied to semiquinone radical anions in the different protein environments of photosynthetic reaction centers by Sylwia et al [15] and found good agreements with experimentally observed values. In present investigation we have reported DFT implementation of electronic g tensors using different density functional VWN, UDFT,with $\Delta\text{gso}/\text{oz}(2e)$,VWN, SOS- with $\Delta\text{gso}/\text{oz}(2e)$,VWN UDFT,without $\Delta\text{gso}/\text{oz}(2e)$,VWN,SOS,DFPT,without $\Delta\text{gso}/\text{oz}(2e)$,BP86,UDFT,without $\Delta\text{gso}/\text{oz}$

(2e), BP86 ,SOS- without $\Delta\text{gso}/\text{oz}(2e)$ and results obtained are compared with experimentally observed values to know the performance of functional for accurate theoretical calculations of g tensor of $[\text{Ni}(\text{CO})_3\text{H}]$, $[\text{Co}(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_5]^+$ Transition Metal Complexes.

2.0:-Data observation and analysis-

The EPR parameter g tensor of transition metal complexes considered for the DFT calculation in this work, obtained by the application of different density functionals VWN, UDFT,with $\Delta\text{gso}/\text{oz}(2e)$,VWN,SOS-with $\Delta\text{gso}/\text{oz}(2e)$,VWN, UDFT, without $\Delta\text{gso}/\text{oz}(2e)$ VWN, SOS- DFPT,without $\Delta\text{gso}/\text{oz}(2e)$ BP86,UDFT,without $\Delta\text{gso}/\text{oz}(2e)$, BP86 ,SOS- without $\Delta\text{gso}/\text{oz}(2e)$ and experiments are also shown in Figure 1, 2,3,4,5 and 6. From the Figures 1, 2, 3,4,5,6 ,the results obtained by different density functional may be compared with experimental results.

[Ni(CO)3H] Δg Parrellel

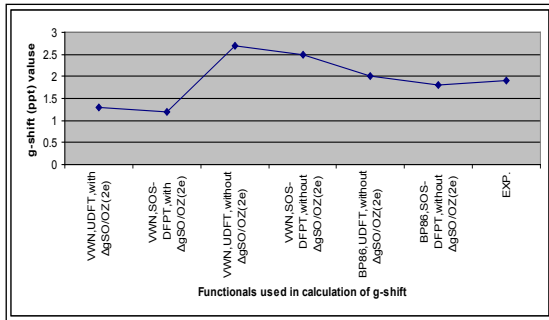


Figure 1 Shows comparison of computed and experimental g-Shift results[Δg parallel values] of [Ni(CO)3H] complex obtained from the calculation using different functionals VWN, UDFT, with Δgso/oz(2e),VWN, SOS- with Δgso/oz(2e),VWN UDFT, without Δgso/oz(2e),VWN, SOS- DFPT, without Δgso/oz(2e),BP86,UDFT,without Δgso/oz(2e) BP86 ,SOS- without Δgso/oz(2e), Exp.

[Ni(CO)3H] Δg Perpendicular

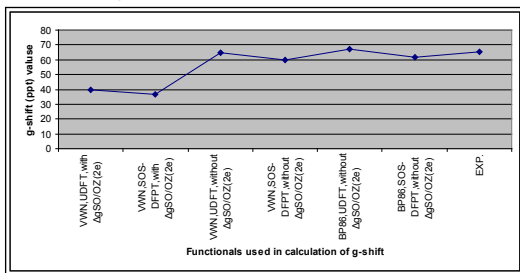


Figure 2 Shows comparison of computed and experimental g-Shift results[Δg perpendicular] of [Ni(CO)3H] complex obtained from the calculation using different functionals VWN, UDFT, with Δgso/oz(2e), VWN, SOS- with Δgso/oz(2e), VWN UDFT, without Δgso/oz(2e), VWN SOS- DFPT, without Δgso/oz(2e), BP86, UDFT, without Δgso/oz(2e), BP86, SOS- without Δgso/oz(2e), Exp.

[Co(CO)4] Δg Parrellel

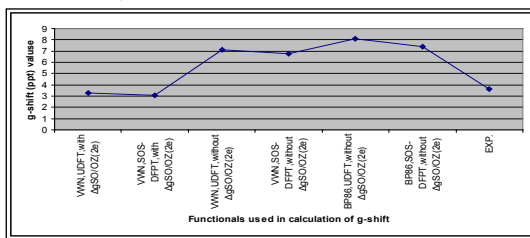


Figure 3 Shows comparison of computed and experimental g-Shift results[Δg parallel values] of [Co(CO)4] complex obtained from the calculation using different functionals VWN, UDFT, with Δgso/oz(2e), VWN, SOS- with Δgso/oz(2e),VWN ,UDFT, without Δgso/oz(2e), VWN, SOS- DFPT ,without Δgso/oz(2e), BP86, UDFT without Δgso/oz(2e), BP86, SOS- without Δgso/oz(2e), Exp.

[Co(CO)4] Δg Perpendicular

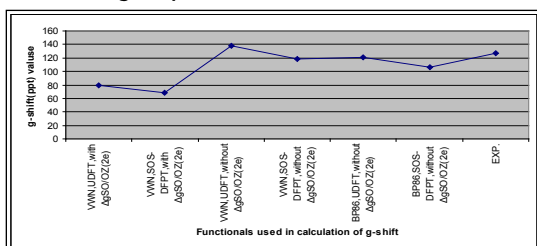


Figure4 Shows comparison of computed and experimental g-Shift results[Δg perpendicular] of [Co(CO)4] complex obtained from the calculation using different functionals VWN, UDFT, with Δgso/oz(2e), VWN, SOS- with Δgso/oz(2e), VWN, UDFT, without Δgso/oz(2e), VWN SOS- DFPT, without Δgso/oz(2e), BP86, UDFT, without Δgso/oz(2e), BP86 SOS- without Δgso/oz(2e), Exp.

[Fe(CO)5] Δg Parrellel

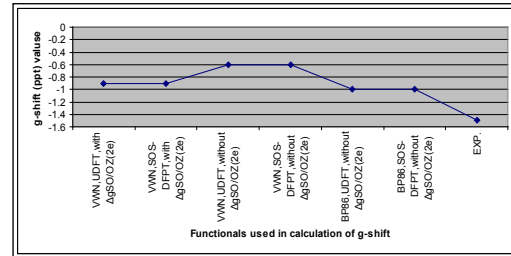


Figure 5 Shows comparison of computed and experimental g-Shift results[Δg Parallel values] of [Fe(CO)5] + complex obtained from the calculation using different functionals VWN, UDFT, with Δgso/oz(2e), VWN, SOS- with Δgso/oz(2e),VWN, UDFT, without Δgso/oz(2e),VWN, SOS- DFPT, without Δgso/oz(2e), BP86, UDFT, without Δgso/oz(2e), BP86, SOS- without Δgso/oz(2e), Exp.

[Fe(CO)5] Δg Perpendicular

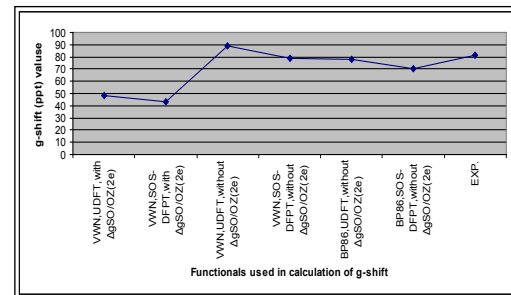


Figure 6 Shows comparison of computed and experimental g-Shift results[Δg perpendicular] of [Fe(CO)5] + complex obtained from the calculation using different functional VWN ,UDFT with Δgso/oz(2e),VWN ,SOS- with Δgso/oz(2e),VWN, UDFT, without Δgso/oz(2e), VWN ,SOS- DFPT ,without Δgso/oz(2e), BP86, UDFT without Δgso/oz(2e), BP86 ,SOS- without Δgso/oz(2e), Exp.

3-Results and Discussions: - From the comparison of g tensor values obtained from different density functionals with experimentally observed values of the complexes considered in this study, the performance of different functional have been found as follows.

[Ni(CO)3H] Δg Parrellel

From the Figure 1 it is concluded that in the case values [Ni(CO)3H] Δg Parrellel , the functional > BP86, UDFT, without Δgso/oz(2e) without in close agreement with experimental values .It is also concluded that results of the VWN, SOS- with Δgso/oz(2e) are very poor and hence not recommended to calculate g tensors constants using these functionals .The performance of different density functionals are as VWN, SOS- with Δgso/oz(2e)> VWN, UDFT, with Δgso/oz(2e)> VWN UDFT, without Δgso/oz(2e)> VWN SOS- DFPT, without Δgso/oz(2e) > BP86 SOS- without Δgso/oz(2e)> BP86, UDFT, without Δgso/oz(2e) > Exp.

Ni(CO)3H] Δg perpendicular

From the Figure 2, it is concluded that in the case values [Ni(CO)3H] Δg perpendicular , the functional > VWN UDFT, without Δgso/oz without Δgso/oz(2e) in close agreement with experimental values .It is also concluded that results of the

VWN, SOS- with $\Delta g_{so/oz(2e)}$ are very poor and hence not recommended to calculate g tensors constants using these functionals. The performance of different density functionals are as VWN, SOS- with $\Delta g_{so/oz(2e)}$, VWN, UDFT, with $\Delta g_{so/oz(2e)}$ VWN SOS- DFPT without $\Delta g_{so/oz(2e)}$ BP86 SOS- without $\Delta g_{so/oz(2e)}$ BP86, UDFT, without $\Delta g_{so/oz(2e)}$ VWN UDFT, without $\Delta g_{so/oz(2e)}$ Exp.

[Co(CO)4] Δg Parrellel

From the Figure 3, it is concluded that in the case values [Co(CO)4] Δg Parrellel, the functional VWN, UDFT, with $\Delta g_{so/oz(2e)}$ (without in close agreement with experimental values). It is also concluded that results of the BP86, UDFT, without $\Delta g_{so/oz(2e)}$ are very poor and hence not recommended to calculate g tensors constants using these functionals. The performance of different density functionals are as BP86, UDFT, without $\Delta g_{so/oz(2e)}$ BP86 SOS- without $\Delta g_{so/oz(2e)}$ VWN UDFT, without $\Delta g_{so/oz(2e)}$ VWN SOS- DFPT without $\Delta g_{so/oz(2e)}$ VWN, SOS- with $\Delta g_{so/oz(2e)}$ VWN, UDFT, with $\Delta g_{so/oz(2e)}$ Exp.

[Co (CO) 4] Δg perpendicular

From the Figure 4 it is concluded that in the case values [Co(CO)4] Δg perpendicular the functional BP86, UDFT, without $\Delta g_{so/oz}$ without in close agreement with experimental values. It is also concluded that results of the VWN, SOS- with $\Delta g_{so/oz(2e)}$ are very poor and hence not recommended to calculate g tensors constants using these functionals. The performance of different density functionals are VWN, SOS- with $\Delta g_{so/oz(2e)}$ VWN, UDFT, with $\Delta g_{so/oz(2e)}$ BP86 SOS- without $\Delta g_{so/oz(2e)}$ VWN UDFT, without $\Delta g_{so/oz(2e)}$ VWN SOS- DFPT without $\Delta g_{so/oz(2e)}$ BP86, UDFT, without $\Delta g_{so/oz(2e)}$ Exp.

[Fe(CO)5] + Δg Parrellel

From the Figure 5 it is concluded that in the case values

[Fe(CO)5] + Δg Parrellel the functional BP86 SOS without $\Delta g_{so/oz(2e)}$ in close agreement with experimental values. It is also concluded that results of the VWN UDFT, without $\Delta g_{so/oz(2e)}$ are very poor and hence not recommended to calculate g tensors constants using these functionals. The performance of different density functionals are as VWN, UDFT, without $\Delta g_{so/oz(2e)}$ VWN, SOS- DFPT without $\Delta g_{so/oz(2e)}$ VWN, UDFT, with $\Delta g_{so/oz(2e)}$ VWN, SOS- with $\Delta g_{so/oz(2e)}$ BP86, UDFT, without $\Delta g_{so/oz(2e)}$ BP86, SOS without $\Delta g_{so/oz(2e)}$ Exp.

Fe(CO)5] + Δg Perpendicular

From the Figure 6 above results it is concluded that in the case values [Fe(CO)5] + Δg perpendicular, the functional VWN SOS- DFPT without in close agreement with experimental values. It is also concluded that results of the VWN, SOS- with $\Delta g_{so/oz(2e)}$ are very poor and hence not recommended to calculate g tensors constants using these functionals. The performance of different density functionals are as VWN, SOS- with $\Delta g_{so/oz(2e)}$, VWN, UDFT, with $\Delta g_{so/oz(2e)}$, BP86, SOS- without $\Delta g_{so/oz(2e)}$ VWN, UDFT, without $\Delta g_{so/oz(2e)}$ BP86, UDFT, without $\Delta g_{so/oz(2e)}$ VWN, SOS- DFPT without >Exp.

4- Conclusion: - We have inferred that results obtained by DFT calculated g tensor values using hybrid density functional are in close agreement with experimentally observed. Further although the results of the density functionals have been found in close agreement with the experimental results but the better performance of the functionals have been found different for different metal complexes. We have not identified any such functional, the results of which is excellent for all transition metal complexes considered for study in this work. The theoretical results for EPR parameter g tensor obtained in this investigation suggesting that further development of density functionals is needed.

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