

## COMPUTATIONAL STUDY ON THE ELECTRONIC $g$ -TENSORS OF NANODIAMONDS

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### Introduction

Nanodiamonds (NDs) belong to a family of carbon-based nanomaterials that recently gained a lot of attention in such biomedical areas as tissue engineering, labelling, quantum sensing, and drug delivery<sup>1</sup>. Concerning the latter, a combination with the bioimaging capabilities could make NDs a very promising platform for the clinical theranostic applications<sup>2</sup>, thereby allowing a more effective exploitation of these nanoparticles.

In order to fully utilize the bioimaging potential of NDs using such techniques as magnetic resonance imaging based on Overhauser effect<sup>3</sup> (OMRI), which in turn requires a paramagnetic reservoir to be present in the system, one has to be aware of their magnetic properties. In this work, density functional theory calculations were carried out seeking to find out the influence of the shape and surface functionalization of NDs on their electronic  $g$ -tensor values.

### Materials and Methods

Substitutional nitrogen atoms (P1 centers) and dangling bonds (DBs) at the surface – the most common paramagnetic defects observed in NDs – were considered as a paramagnetic reservoir needed for OMRI and therefore introduced into NDs of octahedral, tetrahedral, and cubic shape. Regarding the surface functionalization schemes, hydrogenation and fluorination were chosen. All presented  $g$ -tensor calculations were performed with the ORCA quantum chemistry package<sup>4,5</sup> within the effective nuclear charge framework<sup>6-8</sup> using B3LYP hybrid functional<sup>9,10</sup> and cc-pVTZ basis set<sup>11</sup>.

### Results and Discussion

The  $g$ -shifts obtained for DBs and P1 centers introduced into different NDs are given in Table 1.

**Table 1. The  $g$ -shifts  $\Delta g_{ii}$  and their isotropic values  $\Delta \bar{g}$  (in ppm) of DBs and P1 centers in various NDs.**

Defect & nanodiamond	$\Delta g_{xx}$	$\Delta g_{yy}$	$\Delta g_{zz}$	$\Delta \bar{g}$
DB of octahedral C <sub>35</sub> H <sub>36</sub>	-55	482	766	398
DB of octahedral C <sub>35</sub> F <sub>36</sub>	-329	961	1443	692
DB of cubic C <sub>54</sub> H <sub>48</sub>	-78	574	858	451
DB of tetrahedral C <sub>51</sub> H <sub>52</sub>	-26	366	736	359
P1 center of octahedral C <sub>35</sub> H <sub>36</sub>	-159	315	338	165
P1 center of octahedral C <sub>35</sub> F <sub>36</sub>	-262	993	2077	936
P1 center of cubic C <sub>54</sub> H <sub>48</sub>	-150	278	398	175
P1 center of tetrahedral C <sub>51</sub> H <sub>52</sub>	-128	395	442	236

The  $g$ -shifts are evaluated by subtracting the free electron  $g$ -factor ( $g_e = 2.0023193$ ) from the positive square roots of the eigenvalues of  $\mathbf{g}^T \cdot \mathbf{g}$ , where  $\mathbf{g}$  denotes  $g$ -tensor. The provided values represent the average income of all the possible geometric positions of paramagnetic defects of the same type in a particular ND. By comparing the listed data, one can note that NDs of different shape demonstrate a noticeably distinct behaviour, as the isotropic  $g$ -shifts for DBs and P1 centers vary by  $\sim 90$  and  $\sim 70$  parts per million (ppm), respectively. However, fluorinated ND exhibits much more pronounced deviations from the hydrogenated ND of the same shape, since  $\Delta\bar{g}$  for DBs and P1 centers differ by  $\sim 300$  and  $770$  ppm, correspondingly. Such a result points to the huge impact the fluorine atoms have on the magnetic properties of NDs.

### Conclusions

The obtained results can be highly useful for the experimental studies of NDs, since they can help to analyze and interpret complicated electron paramagnetic resonance spectra.

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