Comparison of basis sets for DFT calculation of guanine nucleobase

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Deoxyribonucleic acid (DNA) consists of two polynucleotide chains twisted around each other in the form of a double helix. DNA is formed using sequences of four nitrogenous bases (guanine, adenine, cytosine and thymine). Several reports showed that μSR is an experimental technique that can be used to study the properties of organic systems.[1–3] The interpretation and analysis of the μSR results are often complemented and enhanced through computational studies.[4–7]

Two possible muon stopping sites have been reported for each nitrogenous base.[4] In guanine nucleobase, muon is likely to attach itself to the carbon atom (C8). The DFT cluster framework using hybrid functional was used in this study.[8–11] In this study, B3LYP were used in combination with 6 different standard set of Gaussian basis function; (1) 6-31+G, (2) 6-31+G(d), (3) 6-31+G(d,p), (4) 6-31++G, (5) 6-31++G(d), (6) 6-31++G(d,p). The question of how the functional and the basis set is chosen will affect the optimized geometry and electronic structure calculated is therefore becoming the motivation of this study.

Figure 1 shows the total energy of the optimized structure calculated using different basis sets. 6-31+G and 6-31++G produce an optimized structure with the highest energy compared to the other basis sets. The difference in energies between the basis set that uses a diffuse function to all atoms and diffuse function to all atoms except hydrogen is only 0.01 eV. A huge difference in total energy is observed when polarization function is used in the basis set. Total energy produces by using a basis set that includes polarization function
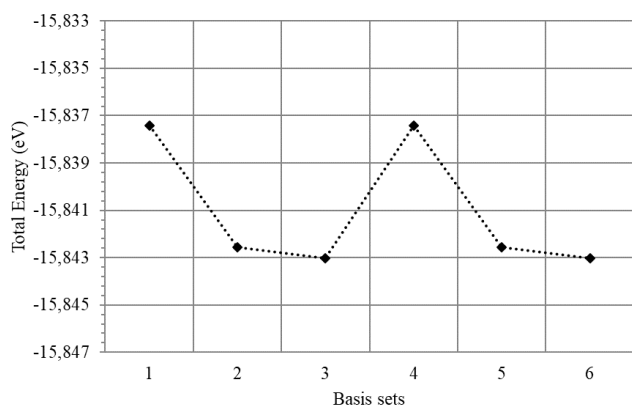
is reduced by approximately ~5 eV. Polarization function gives more room for the atom to get away from each other to minimize the electron-electron repulsion thus reduces the total energy of the system.

The estimated isotropic interaction values calculated using different basis sets were summarized in Fig. 2. 6-31++G basis set produces the lowest isotropic interaction value. This is due to the diffuse function used in the atomic orbital calculation for all atoms including muon. The diffuse function allows the electron to move far away from the nucleus which may affect the isotropic interaction value. As the electron moves far away from the nucleus the isotropic interaction decreases. In particular, among all basis sets, high hyperfine frequency was produced when using 6-31+G(d,p). This value is 13.18% lower than the experimental value obtained by Hubbard $et\ al.$[4] and it is the closest to the experimental value.
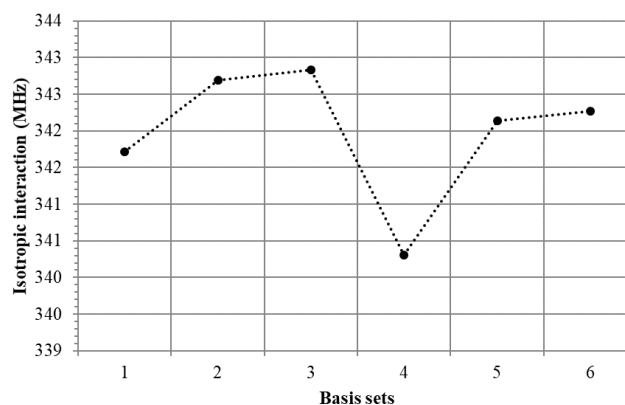

Fig. 2. Isotropic interaction values obtained using different basis sets.

The DFT cluster method was applied to study the effects of different basis sets on the electronic structure and properties of guanine nucleobase. The basis set with polarization function should be utilized for applications where the total energy is crucial and the diffuse function can be excluded to all atoms in a calculation that considers the isotropic interaction between the muon and atoms at the trapping location. By considering both total energy and muon hyperfine interaction, 6-31+G(d,p) basis set is the best one to use for guanine nucleobase molecules.

Fig. 1. The total energy of the optimized structure using different basis sets.

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