Spin-polarized DFT calculations of nitrogen-vacancy color centers in diamond with various XC potentials

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Abstract

The nitrogen-vacancy (NV) color center in diamond is one of the most promising candidates for future solid-state quantum-enhanced sensor and quantum communication applications. The solid-state defect-related qubit with usable coherence time up to room temperature makes this structure extensively investigated in the last decade. Density Functional Theory (DFT) is one of the important tools to investigate the details of the electronic structure of diamond and radiative and non-radiative defect states related to the NV color center. In this study, we implement DFT calculations with several different exchange-correlation functionals (BLYP, XLYP, PBE, PBES, RPBE) used in Spin-Polarized Generalized Gradient Approximation (SGGA) to explain the defect structure of NV centers in diamond better.

Introduction

The nitrogen-vacancy (NV) center is a point defect in diamond has shown great promise for quantum information due to the ease of initializing the qubit and of reading out its state as it is a single-photon emitter [1,2]. The center is a point defect in diamond with C_{3v} symmetry consisting of a substitutional nitrogen–lattice vacancy pair orientated along the [111] direction. The center can be produced by radiation damage and annealing [3], or unintentionally in CVD growth process [4] or with ion implantation and annealing [5] processes. The center is known to exist in negative (NV–) and neutral (NV0) charge states. The identifying features of these charge states are their optical zero phonon lines (ZPLs) at 1.945 eV (637 nm) [3] and 2.156 eV (575 nm) [6], respectively. Figure 1 shows the structure and the related states of NV center, calculated and shown by Thiering and Gali [7].

Methods

Calculations are performed with Quantumwise ATK 2017.2 software. XC-Functionals are used under spin-dependent SGGA approach. Cut-off energy and maximum force applied to the crystal are taken respectively as 300 eV and 0.05 eV/Å. In addition, Monkhorst – Pack 5x5x5 k- point grid parameters have been used. PBE, RPBE, PBES, BLYP and XLYP are used for closed lattice and BLYP, PBE and XLYP are used for open lattice calculations. Supercell contains 64 atoms.

Results





Figure 1. (a) Schematic diagram of the structure NV center. (b) Calculated defects of the system in ground state (c) The corresponding ground state and excited states are shown as well as the optical electron spin polarization cycle (figure from [7]).

In figure 1, the curved arrows shows the Δ SCF procedure for creating the triplet excited state. The *e* states are double degenerate.

The defect exhibits a fully occupied lower a¹ level and a double degenerate upper e level filled by two parallel-spin electrons in the gap with comprising an S= 1 high-spin ground state. The high-spin ³E excited state can be well-described by promoting an electron from the lower defect level to the upper level in the gap. Between excited state and ground state triplets dark singlets appear that can selectively flip $m_s=\pm 1$ states to $m_s=0$ state in the optical excitation cycle. Therefore, the spin-orbit coupling plays an important role in the optical spin-polarization and readout of NV quantum bit (qubit).

The better investigation of the spin dependent states are crucial for further research. There are already many studies done in this field. To make better calculations in future, we need to find a proper XC-functional and a suitable cell with a good number of atoms.



Fig 3. Band structure obtained with XLYP functional. Table 1. Calculation times and results

Different XC-functionals are used to find a more realistic results. We successfully calculated the band structure for a NV center. Things are similar for also NV- centers. With 64 atoms, all states are at the bandgap can be observed as expected scheme $u u v v e_{x,v} e_{x,v}$.







In figure 2, the results one of these studies are shown for PBE, HSE06 and G0W0 XC-functional choices [8].

In this study, we implemented BLYP, PBE, PBES, RPBE, XLYP and BLYP xcfunctionals with GGA to find out best realistic functional to use in bulk diamond density functional theory calculations.

Table 3. Calculated energy differences at the gamma point, using the PBE, HSE06 and G_0W_0 method. The $lpha$ and the eta	
represent the spin-up and spin-down channels, respectively.	

Supercell	<i>k</i> -grid	Method/functional	Spin	Band gap	v–e	v-VBM	e-CBM
216	Gamma	PBE	α	4.260	1.131	0.861	2.266
			eta	4.222	1.866	1.356	1.001
		HSE06	α	5.498	1.128	0.718	3.652
			eta	5.425	2.857	1.655	0.914
		G0W0	α	5.624	1.215	0.857	3.552
			eta	5.576	2.823	1.438	1.316
64	4 imes 4 imes 4	PBE	α	4.869	1.040	1.323	2.507
			eta	4.760	1.872	1.606	1.281
		HSE06	α	6.203	1.015	1.299	3.889
			eta	5.980	2.927	1.838	1.215
		G0W0	α	6.313	1.113	1.394	3.807
			β	6.146	2.812	1.712	1.622

Figure 2. For 216 and 64 atom supercells, spin, bandgap, v-e transition energy and valance band and conduction band energy differences (table from [8].

Fig 5.Density of states for calculations with different XC-functional usage.

Conclusion

All these calculations took a total of 1 month. CPU time = Cost of a calculation. Best ve and Band-to-Band energy values with a "acceptable" cost is needed! XLYP with a closed-lattice is seemed to be best choice for future calculations. This results will be useful to expand the calculations for diamond crystals with different impurities added.

Acknowledgments

S.B.L was supported in part by the Distinguished Young Scientist Award of the Turkish Academy of Sciences (TUBA-GEBIP 2016). E.O. acknowledges partial support from the Turkish Academy of Sciences.

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