Charged dopants in neutral supercells through substitutional donor (acceptor): nitrogen donor charging of the nitrogen-vacancy center in diamond

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Abstract

Charged defects are traditionally computed by adding (subtracting) electrons for negative (positive) impurities. When using periodic boundary conditions this results in artificially charged supercells that also require a compensating background charge of the opposite sign, which makes slab supercells problematic because of an arbitrary dependence on the vacuum thickness. In this work, we test the method of using neutral supercells through the use of a substitutional electron donor (acceptor) to describe charged systems. We use density functional theory (DFT) to compare the effects of charging the well-studied NV-center in diamond by a substitutional donor nitrogen. We investigate the influence of the donor-N on the NV-center properties as a function of the distance between them, and find that they converge toward those obtained when adding an electron. We analyze the spin density and conclude that the donor-N has a zero magnetic moment, and thus, will not be seen in electron spin resonance. We validate our DFT energies through comparison to GW simulations. Charging the NV-center with a substitutional donor-N enables accurate calculations of slabs, without the ambiguity of using charged supercells. Implantation of donor-N atoms opens up the possibility to engineer NV-centers with the desired charge state for future ICT and sensor applications.

1. Introduction

The study of impurities in materials is an important topic for all technological developments, and many impurities are naturally charged, or exist in different charge states at different conditions. Computation of charged defects is thus of widespread interest [1–8]. In diamond, there exist many charged defects, with one, two or more electrons subtracted or added (..., 2+, 1+, 1−, 2−, ...). Some examples are V3− (negatively charged vacancy), NV− (H2-center), BV2− (boron vacancy), V+ (positively charged vacancy), NVN+ (H3-center), O+ (positively charged oxygen). When computing properties of such defects it is common to charge them by adding/subtracting electron(s) to the system. When using periodic boundary conditions for bulk systems, the charged supercell needs to be compensated with a charge of the opposite sign, either as a background or in the supercell’s boundaries. Apart from the inherent problem of having smeared charges in the model, the charge compensation schemes are difficult to implement for the computation of charged defects in slabs, where it introduces an arbitrary dependence on the thickness of the vacuum. To solve this problem, we charge the defect using atomic substitution doping: replacing an atom in the lattice with an electron donor or acceptor. In this way, a neutral supercell is obtained, which can be used for both bulk and slab calculations. To charge the defect with an electron donor or acceptor is also a more physically correct solution compared to charging by adding/subtracting an electron (and treating the counter charge by an external potential). Because all defects that are charged without applying any external field are getting their charge from an internal source, of which a
substitutional defect is most plausible. It is advisable to use a donor/acceptor that is likely to be present in the material naturally. If nothing is known about the donor/acceptor we suggest using a neighbor in the same row of the periodic table, to minimize strain effects.

As a computational method, describing charged dopants using substitutional donors/acceptors to achieve neutral supercells can be generalized to other host materials. To create electron donors or acceptors in an elemental semiconductor, one needs to replace an atom in the lattice with an atom from the column to the right in the periodic table (one more valence electron) or the left (one less valence electron), respectively. The creation of donors and acceptors in compound semiconductors works in a similar way to elemental semiconductors. The difference is what atom one decides to replace to get the desired charge state. An example would be GaAs: if one replaces Ga with Si, the Si atom act as donor. If one instead replaces As with Si, the Si atom will act as acceptor. To investigate the method of charging defects with electron donors/acceptors, we use the nitrogen-vacancy center in diamond.

The electronic, optical and spin properties of the NV-center are well documented [9–30]. However, its charging and how it affects those properties are not well understood. In standard computations it is charged by adding an extra electron to the system without regard to what’s the electron donor. We have pioneered the alternative, to place an additional substitutional nitrogen atom (donor-N) in the vicinity of the NV-center, acting as an electron donor [9]. Also the effect of using a donor-N on the C3v-axis on the NV-center energy levels have been studied [10]. In this work, we further explore at an \textit{ab initio} level how the distance between the NV-center and an electron donor-N affects a range of NV properties. We investigate the effect of a symmetry breaking donor-N at different distances and angles. We also investigate how the donor-N influences the electronic structure of the NV-center, and if it has any residual magnetic moment that might effect the manipulation of the NV-center, by studying its spin density. The NV can sometimes lose its charge state during optical excitation [11–14], but the photostability may be improved by post-annealing treatments [15, 16]. We propose a possible explanation for this behavior through spurious excitations to NV0 and donor-N0.

\section{Methods}

All the calculations were carried out with the Vienna \textit{ab initio} Simulation Package (VASP5.3.5) [31, 32], within the density functional theory (DFT) framework, using projector augmented wave potentials [33, 34]. The supercell method with periodic boundary conditions was employed. The lattice parameter for a diamond primitive cell (2 atoms) was optimized (using a plane-wave cutoff energy of 840 eV and a 12 × 12 × 12 gamma-centered k-point grid) and was used to construct the supercells, in which the NV-center and the donor-N were placed in different configurations that were subsequently geometry optimized, until the forces were below 0.001 eV Å\(^{-1}\). The method of Methfessel–Paxton was used for smearing.

The well-known Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional of the generalized gradient approximation (GGA) was used [35, 36]. Also, calculations with the hybrid functional HSE06 (Heyd–Scuseria–Ernzerhof, screening length of 0.2 Å\(^{-1}\), and 25% Hartee–Fock exact exchange) have been carried out for comparison, as it has been shown to give more accurate transition and band gap energies than PBE [37–43]. Furthermore, calculations with the AM05 [44–46], PBEsol [47] and PBE0 (25% Hartee–Fock exact exchange) [48] functionals have been carried out for further comparisons. The charge densities were Fourier-transformed using plane waves with an energy cut-off of 420 eV. We compare the DFT energies with those obtained with the \(\text{G}_{0}\text{W}_{0}\) perturbation theory based correction [49–52].

Charge and spin densities were visualized using VMD1 [53] and Virtual NanoLab (version 2014.3, QuantumWise A/S, respectively).

\section{Results and discussion}

\subsection{The NV\textsuperscript{\textminus} center}

The nitrogen-vacancy (NV) center, composed of a vacancy adjacent to a substitutional nitrogen atom (see figure 1), is one of the numerous color centers found in diamond. The NV-center has \(C_{3v}\) symmetry and the \(C_{3v}\)-axis passes through both the substitutional nitrogen atom and the vacancy.

The negatively charged variant (NV\textsuperscript{–}) have gained considerable interest in later years due to its electronic and optical properties that are well suited for different technological applications [15, 17–19]. The usefulness relies on the ability to optically excite electrons between well-defined gap-states. Some of the important properties of NV\textsuperscript{–} are: (a) photostable at room temperature, (b) long spin-lattice lifetime, and (c) spin-flipping from \(S_z = 1\) to \(S_z = 0\) during optical excitation and decay. Because of this spin–flip property, the spin state can be manipulated using excitation by optical absorption [17, 19–21]. These properties enable applications such as: (a) qubits in a quantum computer at room temperature (photostable at room temperature), (b) high resolution...
magnetometry (sensitive magnetometer), (c) single photon source, (d) quantum key distribution, (e) biomarking and tracking (because diamond is bio-compatible) and (f) nanosensor to detect magnetic and electric fields, temperature, or chemical changes on a surface \[15, 18–20\]. Furthermore, at low temperatures, the optical transitions of the NV-center become very narrow and can be coherently manipulated. This can be used to further explore interesting applications such as spin–photon entanglement generation \[22\] and optical control of spin states \[17, 23\].

Recent studies on small cluster models of the NV-center in diamond reveal that it is stable also in nanometer-sized diamond clusters \[24, 25\]. Also, configuration interaction (CI) \[24\] as well as DFT \[26\] calculations have shown that the \(^1\text{A}_1\) level lies above the \(^3\text{E}\) level. The preferential occupation of the ground state have been experimentally (EPR) determined to be the \(S_z = 0\) spin level \[27\]. This might seem like a contradiction, as group theory suggests a preferential occupation of the \(S_z = \pm 1\) spin levels when relaxation from \(^3\text{E}\) to the ground state occurs. However, when taking into account electron–phonon interactions, this disagreement is resolved \[28–30\].

We compare the properties of NV\(^{−}\) when using the suggested charging through a substitutional donor–N to that of the traditional approach of adding an extra electron (plus the required compensating counter charge) for the color-center’s geometry, energetics, charge density and spin density.

### 3.2. Geometry

The experimental lattice constant value of diamond is 3.567 Å \[54\]. Our calculated lattice constant values of diamond using PBE, PBEsol, AM05 and HSE06 are 3.572, 3.556, 3.553 and 3.547 Å, respectively, which agree well with the PBE and HSE06 values reported by Gali and co-workers of 3.567 and 3.545 Å, respectively \[38\]. It can be seen that all the functionals (except PBE) underestimates the lattice constant, which is very common for many systems \[41\]. We have used the value for the lattice constant arrived at with PBE (3.572 Å). We carried out calculations on various sizes of supercells containing the NV\(^{−}\) center charged through adding an electron to investigate how the distance between two neighboring centers (the density of NV\(^{−}\) per volume) affect the transition energies. Charge compensation in VASP is described in \[55\]. Four sizes of supercells were considered: 64 atoms (2 × 2 × 2 unit cells, side-length 7.145 Å, 4 × 4 × 4 k-point grid), 216 atoms (3 × 3 × 3 unit cells, side-length 10.717 Å, 2 × 2 × 2 k-point grid), 512 atoms (4 × 4 × 4 unit cells, side-length 14.290 Å, gamma point), and 1000 atoms (5 × 5 × 5 unit cells, side-length 17.862 Å, gamma point), respectively. We find very similar geometries in these different model-sizes (see table 1).

To study how the distance between the donor–N and the NV-center affect the transition energies, calculations were performed with varying N–N distances and orientations with regard to the \(C_3\)-axis within a 512 atom (4 × 4 × 4) supercell (see figure 2). In this investigation the following configurations were considered:

1. NV–N configuration–donor–N placed on the vacancy side of NV, on the \(C_3\)-axis.
2. N–NV configuration–donor–N placed on the nitrogen side of NV, on the \(C_3\)-axis.
3. NV\(^{−}\)N configuration–donor–N placed on an axis perpendicular to the \(C_3\)-axis.
4. NV\(\theta\)N configuration-donor–N placed on an axis at angle \(\theta\) to the \(C_3\)-axis.

Furthermore, the donor–N was placed adjacent to the NV-center in the 512 atom supercell, with the following distances to the NV nitrogen: 6.334, 7.882 and 12.229 Å in the NV-N configuration; 4.499, 6.045, 10.680 Å in the N-NV configuration; and 2.496, 5.045, 7.577, 10.106 Å in the NV\(\perp\)N configuration. For the NV\(\theta\)N configurations we placed the donor-N at similar N–K distances, larger than 7.5 Å, for all the configurations to minimize the interaction with the NV-center, as will be shown below. In this study, we have selected configurations with angles 9.8°, 17.8° and 56.1°, and the calculated distance between the NV nitrogen and the donor-N in those configurations are 8.523, 8.278 and 7.660 Å, respectively. Considering the geometry of the donor-N systems: the angle between the N–C bonds and the \(C_3\)-axis vary from 105.57° (for the shortest N–K distance in the NV-N configuration) to 105.20° (for the shortest N–K distance in the NV\(\perp\)N configuration). Looking at the N–C bond lengths, they vary from 1.489 Å (for the shortest N–N distance in the NV\(\perp\)N configuration) to 1.473 Å (for the shortest N–N distance in the N-NV configuration). And, finally looking at the C–C distance between the carbon atoms surrounding the vacancy, they vary between 2.666 Å (for the longest N–N distance in the NV\(\perp\)N configuration), to 2.672 Å (for the shortest N–N distance in the NV\(\perp\)N configuration).

3.3. Energetics

The NV\(\,\)exhibits an intense luminescence with a zero-phonon line (ZPL) at 1.945 eV (637 nm) [18, 19]. It corresponds to de-excitation from the excited triplet state \(^3\!E\) to the triplet ground state \(^3\!A_2\). These states are formed by different occupations of the NV-center levels in the diamond fundamental gap. In a one-electron sense, these introduce into the fundamental gap an orbital singlet of symmetry \(a_1\), often referred to as \(\nu\), occupied
by two electrons, lying below an orbital doublet \( e_1, e_2 \) also occupied by two electrons but with parallel spin. It is the optical transition between the occupied spin-down \( \nu \) level and unoccupied spin-down \( \nu \) level \( e_1, e_2 \) that is responsible for the ZPL [56]. We obtained the \( ^3A_2 \) ground state of the NV\(^-\) center by spin-polarized calculations as the lowest energy state, with all the density functionals. To obtain the \( ^3E \) excited state, we promoted an electron from the \( \nu \) level to one of the \( e_1, e_2 \) NV levels in the diamond band gap (see figure 3(b)), and held the electron occupation fixed in the subsequent relaxations. We optimized the geometry of both the ground state \( (q_g) \) and the excited state \( (q_e) \) (see figure 3(a)). The transitions \( A \rightarrow B \) and \( C \rightarrow D \) are readily calculated by fixing the geometry at \( q_g \) and \( q_e \) respectively, while varying the electronic configurations. To take into account the nuclei movements during electronic transitions in a lattice, we have employed the Franck–Condon approximation (see figure 3(a)).

The energy minima for the ground state and the excited state in the calculations are shown as \( E_g (=^3A_2) \) and \( E_e (=^3E) \), respectively, in figure 3(a). The zero-point energy (ZPE, \( n = 0 \) and \( m = 0 \)) will raise these energies by a value of order a few tens meV. Davies and Hamer deduced a ZPE value of about 35 meV [57]. The difference between the ZPE values of \( E_g \) and \( E_e \) is very small, of the order of a few meV. The energy difference between the energy minima of \( ^3A_2 \) and \( ^3E \) therefore gives a very good estimate of the ZPL (\( A \leftrightarrow C \) transition; see figure 3(a)). We note that the error associated with the ZPE cannot be avoided in the calculated \( A \rightarrow B \) and \( C \rightarrow D \) transitions, which means that the values for these transitions are less accurate than for the ZPL.

### 3.3.1. NV-center charged through addition of electron—negatively charged supercell

We reinvestigate the NV-center charged through addition of an electron for comparison and to gain insight into the role of the concentration of NV-centers in diamond, which we change by varying the size of the supercell. Looking at table 2 it can be seen that the ZPL energy converges to a value closer to experiment for both PBE and HSE06 as the distance between NV\(^-\) centers increases. However, the PBE ZPL gets smaller when the distance between NV\(^-\) centers gets smaller while the corresponding HSE06 values show a small increase (see also figure S1 available online at stacks.iop.org/NJP/20/023002/mmedia). It is known from previous work that the HSE06 functional improves not just the band gap of diamond but also the internal defect transition energies compared to the PBE functional [17, 18, 49–53]. For the largest, 1000 atom supercell (largest NV\(^-\) distance), the PBE values are off by about 13%, and never closer than 4% (the AS energy) to the experimental values. While the HSE06 values are off by about 1%, and never further away than 7% (the AS energy). For the 64 atom supercell (smallest NV\(^-\) distance, maximum perturbance of the NV-center), the HSE06 values are off by about 3–4%, and never further away than 7% (the S energy). We note that the AS energy actually gets closer to the experimental value as the distance between NV-centers is decreased, which is due to error cancellation. Furthermore, calculations for

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**Figure 3.** (a) Energy diagram illustrating the Franck–Condon approximation for the excitation and de-excitation process of a defect. The bottom of the quasiparabolic potential energy curves \( E_g, E_e \) are the minimum energies of the defect in the ground and excited states, respectively, and \( q_g, q_e \) the corresponding coordinates. The ZPE is the zero-point energy, the horizontal black lines (in the potential energy wells) represent the phonon energies, with the phonon ground state \( n = 0 \), for the ground state of the defect, and \( m = 0 \), for the excited state of the defect, respectively. The high-energy phonon states can be occupied by inducing transition \( A \rightarrow B \) (vertical absorption, green arrow), and \( C \rightarrow D \) (vertical emission, red arrow). The \( A \leftrightarrow D \) transition corresponds to the zero-phonon line (ZPL, blue arrow), which indicates the adiabatic absorption and emission. (b) Schematic diagram showing the occupancies in the \( \nu \) and \( e \) levels for the \( ^3A_2 \) ground state and the \( ^3E \) excited state (electron excited to the \( e \) state in the picture, while \( e_2 \) still only have a spin-up electron).
the 1000 atom supercell illustrate that both AM05 and PBEsol functionals give transition energies that are marginally smaller than for PBE.

In table 3 we compare the one electron eigenvalues obtained with the functionals PBE and HSE06, and the G0W0 method (plane-wave energy cutoff of 400 eV). The trend for the α-spin v→e transition (corresponding to the levels in an electron transitions for the ZPL) is the same for the PBE and HSE06 functionals: the energy decreases by about 0.01 eV when increasing the supercell size from 64 atoms to 216 atoms. However, for the G0W0 method, the trend is the opposite: energy increases with about 0.01 eV when increasing the supercell size from 64 to 216 atoms. It is noted that the trend for the α-spin channel is the same for all the methods/functionals, while the trend for the β-spin channel is same for PBE and HSE06 but different for G0W0. For both the spin-channels and all the methods/functionals, the band gap is decreasing between 0.5 and 1 eV when increasing the supercell size from 64 atoms to 216 atoms. This is attributed to band folding. Also, for both spin-channels and all methods/functionals, the v→e gap decreases around 0.5 eV when increasing the supercell size from 64 atoms to 216 atoms. The same can be said about the e-CBM gap. These energies are in good agreement with previous G0W0 calculations [58]. Comparing our results with the trend for the ZPL in table 3 (and figure S1), we see that the PBE and HSE06 β-spin v→e gap corresponds to the HSE06 ZPL trend, while the G0W0 trend corresponds to the PBE ZPL trend. Looking at the trend for the α-spin v→e gap, we see that the energy increases with about 0.1 eV (10 times more than for the β-spin channel) for all methods/functionals, when increasing the supercell size from 64 atoms to 216 atoms.

Compared to the vertical adsorption in the 64 atom supercell using PBE (1.955 eV) and HSE06 (2.300 eV) the latter compares more favorably with the first optical transition from G0W0+BSE (2.394 eV).

### Table 2

Calculated transition energies for the \( \text{NV}^- \) system. All energies are given in eV, and the closest separation between \( \text{NV}^- \) centers are given in Å. S and AS are the Stokes and anti-Stokes shift and A, B, C and D are defined in figure 3(a). \( ^{3}\text{E} \) state computed with occupation of the \( e_\text{t} \) state.

| Supercell | \( r \) | \( k \)-point | ZPL (C \( \rightarrow \) A) | A \( \rightarrow \) B | S (B \( \rightarrow \) C) | C \( \rightarrow \) D | AS (D \( \rightarrow \) A) |
|-----------|---------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Exp [57]  | —       | —           | 1.945 2.180 0.235 1.760 | 0.185           |
| 1000 HSE06| 17.86   | Γ           | 1.683 1.886 0.203 1.507 | 0.177           |
| 1000 PBE  |         | Γ           | 1.668 1.866 0.198 1.491 | 0.177           |
| 1000 PBEsol|        |             | 1.633 1.833 0.201 1.459 | 0.174           |
| 512 HSE06 | 14.29   | Γ           | 1.967 2.190 0.223 1.773 | 0.194           |
| 512 PBE  |         | Γ           | 1.692 1.891 0.201 1.518 | 0.173           |
| 216 HSE06| 10.72   | 2 \times 2 \times 2 | 1.677 1.879 0.202 1.501 | 0.176           |
| 216 PBE  |         | 2 \times 2 \times 2 | 1.701 1.887 0.186 1.538 | 0.162           |
| 64 HSE06 | 7.14    | 4 \times 4 \times 4 | 2.042 2.300 0.258 1.904 | 0.138           |
| 64 PBE  |         | 4 \times 4 \times 4 | 2.016 2.236 0.220 1.829 | 0.187           |

### Table 3

Calculated energy differences at the gamma point, using the PBE, HSE06 and G0W0 method. The α and the β represent the spin-up and spin-down channels, respectively.

| Supercell | \( k \)-grid | Method/functional | Spin | Band gap | \( v \rightarrow e \) | \( v \rightarrow \text{VBM} \) | \( e \rightarrow \text{CBM} \) |
|-----------|-------------|------------------|------|-----------|----------------------|----------------------|----------------------|
| 216       | Gamma       | PBE               | α    | 4.260     | 1.131 0.861          | 2.266                 |
|           |             |                   | β    | 4.222     | 1.866 1.356          | 1.001                 |
|           |             | HSE06             | α    | 5.498     | 1.128 0.718          | 3.652                 |
|           |             |                   | β    | 5.425     | 2.857 1.655          | 0.914                 |
|           |             | G0W0              | α    | 5.624     | 1.215 0.857          | 3.552                 |
|           |             |                   | β    | 5.576     | 2.823 1.438          | 1.316                 |
| 64        | 4 \times 4 \times 4 | PBE               | α    | 4.869     | 1.040 1.323          | 2.507                 |
|           |             |                   | β    | 4.760     | 1.872 1.606          | 1.281                 |
|           |             | HSE06             | α    | 6.203     | 1.015 1.299          | 3.889                 |
|           |             |                   | β    | 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                 |
### 3.3.2. NV-center charged through donor-N—neutral supercell

Within the 512 atom supercell we compare traditional charging through addition of an electron with the donor-N charging, resulting in a neutral supercell. The calculated transition energies are displayed in table 4 and reveal that the ZPL values obtained from the PBE calculations are consistently underestimated compared to the experimental value by ~250 meV, while the HSE06 values are in better agreement, as we have found also for the NV-center charged through an additional electron (see table 2). We also note that the Stokes–Stokes shift (S) and anti-Stokes–Stokes shift (AS) are close to the experimental values and are in agreement with previous calculated results [38]. We find that when the distance between the NV-center and the donor-N is large the values for the two charging methods are comparable. We have also performed calculations with the distance between the NV-center and the donor-N being too small, resulting in a distorted local structure (the donor-N and the NV-center start to interact with each other, making the total energy decrease).

#### 3.3.2.1. NV-N and N-NV configurations

We find that the ZPL value increases slightly as the N–N distance in the N-NV configuration decreases (see table 4), while the ZPL value decreases marginally when the N–N distance decreases in the NV-N configuration for both PBE and HSE06. However, the ΔZPL absolute value decrease with increasing N–N distance for both configurations (see also figures S2 and S3). The ZPL value obtained with the HSE06 functional ranges from 1.958 to 1.999 eV (0.009 and ~0.032 eV difference to the value obtained when charging the center with an additional electron) for these configurations where the donor-N is placed on the C3-axis. The conclusion from this is that a donor-N placed on the C3-axis is not a major perturbation for the NV-center. This is due in part to how close the donor-N can be placed to the NV-center in these configurations (no closer than 4.499 Å and 6.334 Å for the N-NV and NV-N configuration, respectively), and part to that the C3 symmetry is not broken in these configurations. The trend remains unaltered for the energies of both vertical absorption (A → B) and emission (C → D). The changes in the value of both S and AS with distance is also only marginal. Further, close analysis reveals that S and AS for these systems follow the same trend as the ZPL.

#### 3.3.2.2. NV+N configuration

The ZPL and vertical absorption (A → B)/emission (C → D) energies decrease significantly when the N–N distance decreases in the NV+ configuration, and table 4 further reveals that so does both S and AS. The values also do not completely converge to those obtained when charging the center with an additional electron even for the largest N–N distance (10.106 Å), which has a ΔZPL of 89/44 meV for PBE/HSE06. This observation can be attributed to the symmetry breaking. As expected when the distance between the two nitrogen atoms (i.e. N atom of NV and donor-N atom) increase, this effect is found to be reduced. But it is always more pronounced than for the NV-N and the N-NV configurations at comparable N–N distances.

The influence of the N–N distance on the ZPL energy for different donor-N configurations are displayed in supplementary figures S2 and S3. It can be seen that the ZPL value for the NV-N configuration decreases gradually with increasing N–N distance, while it increases for the other two configurations NV-N and NV+N. However, the ZPL of the systems with a donor-N always converges to the ZPL of the system with an additional electron as the distance to the donor-N increases. It is, though, noteworthy to mention that it does so more slowly for the NV+N configuration. For N–N distances smaller than 5 Å the difference in ZPL is in the order of a

### Table 4. Calculated transition energies for the NV− system: N-NV, NV-N, and NV+N configurations (512 atom supercell). All energies are given in eV, and the N–N distances are given in Å. ΔZPL is the energy difference between the zero-phonon-line obtained when charging the center through an additional electron and charging it with a donor-N. The values in and out of parenthesis are calculated using HSE06 and PBE, respectively. S and AS are the Stokes and anti-Stokes shift. A, B, C and D are defined in figure 3(a).

![Table 4](image)
As can be seen in table 5 the symmetry breaking for different angles, between the 3.3.2.3 NV experimentally by the shift in ZPL. Perhaps NV-centers with a devoted donor-N could be fabricated by N2 implantation into diamond at desired donor-N implantation could be used to get negatively charged NV-centers for ICT and sensor applications. This trend is clear for both HSE06 and PBE. Therefore, the AS energy increases by a total of 13.2% and 19.2% for the PBE and HSE06 functionals, respectively. (ii) The S energy increases by a total of 13.2% and 19.2% for the PBE and HSE06 functionals, respectively. (iii) The C → D transition energy decreases by a total of 3.2% and 4.8% for the PBE and HSE06 functionals, respectively.

| Angle  | δN...N | ZPL   | A → B | S     | C → D | AS    |
|--------|---------|-------|-------|-------|-------|-------|
| 0.00°  | 7.882   | 1.677 | 1.874 | 1.974 | 1.506 | 0.171 |
| 9.79°  | 8.523   | 1.675 | 1.876 | 2.021 | 1.489 | 0.186 |
| 17.79° | 8.278   | 1.661 | 1.871 | 2.010 | 1.468 | 0.192 |
| 36.10° | 7.660   | 1.657 | 1.871 | 2.114 | 1.463 | 0.194 |
| 90.00° | 7.577   | 1.651 | 1.874 | 2.223 | 1.458 | 0.193 |

Table 5. Calculated transition energies for the NV⁻ system: NV⁻N configuration (512 atom supercell). All energies are given in eV, and the N–N distances are given in Å and angles in degrees. The values in and out of parenthesis are calculated using HSE06 and, PBE, respectively. S and AS are the Stokes and anti-Stokes shift. A, B, C and D are defined in figure S4. The 3A2 state computed with occupation of the e1 state.

tenth of an eV. Thus, NV-centers with donor-N positioned very closely should be possible to detect experimentally by the shift in ZPL.

3.3.2.3. NV₆N configurations

As can be seen in table 5 the symmetry breaking for different angles, between the C₃-axis and the straight line intersecting the donor-N and the nitrogen in the NV-center, has a similar effect on the transition energies as in the NV⁻ configuration at comparable N–N distances. The effect of varying the angle is small for the ZPL (see also figure S4), but the Stokes and anti-Stokes shift are affected a bit more.

When moving the donor-N from 0° to 90° with respect to the C₃-axis, the following observations can be made: (i) the ZPL energy decreases very marginally by a total of 1.55% and 2.86% for the PBE and HSE06 functionals, respectively. (i) The AS energy increases by a total of 12.9% and 14.6% for the PBE and HSE06 functionals, respectively. (ii) The S energy increases by a total of 13.2% and 19.2% for the PBE and HSE06 functionals, respectively. (iii) The C → D transition energy decreases by a total of 3.2% and 4.8% for the PBE and HSE06 functionals, respectively.

3.3.3. Summary

We show, in accordance with published results on other systems that the PBE, PBEsol, AM05, and HSE06 functionals reproduce the geometrical parameters with only small deviation which clearly highlights the strength of DFT based functionals to reproduce the experimental geometries. The HSE06 values for the ZPL are very close to the experimental value of 1.945 eV by Davies and Hamer [57]. Scrutiny of the other transitions for the 1000 atom supercell in table 2, reveals that the PBE values for the NV⁻ system are off by about 13%, and never closer than 4% (the AS value) to the experimental values. Looking at the corresponding values for HSE06, we see that they are generally off by about 1%, and never further away than 7% (the AS value). Therefore, the results clearly reinforce the strength of the HSE06 method over the PBE. Looking at the AM05 and PBEsol calculations, we see that they are comparable to PBE, and are even a small bit further away from the experimental values.

The value of the transition energy when charging the system with a donor-N, for all the configurations, and charging the system with an additional electron converges when the distance to the donor-N increases (see supplementary figures S2 and S3). This trend is clear for both HSE06 and PBE. Therefore, it is noteworthy to mention that charging the NV-center with a donor-N with N–N distances larger than 7.5 Å is a viable alternative to describe its negative charge state. One can even argue that it is a more realistic way of charging the color center than adding an additional electron, since the electron must come from a donor of some kind. And donor-N implantation could be used to get negatively charged NV-centers for ICT and sensor applications. Perhaps NV-centers with a devoted donor-N could be fabricated by N₂ implantation into diamond at desired sites [59]. However, when the distance between the donor-N and the active center is shorter than 5 Å it severely influences the absorption-emission energies. We note that the 64 atom supercell is too small to describe the NV-center with either charging method. For the 216 supercell the traditional charging by adding an electron gives acceptable results compared to the 512 and 1000 atom supercells (see table 2), and can thus be considered the smallest suitable model. For this model the N–N distance larger than 7.5 Å for charging with donor-N can also be fulfilled. Comparing such calculations with the two charging methods gives similar results and requires similar computational effort.

3.4. Charge density

Calculated band decomposed charge density (spin-up + spin-down) contours for the e1-level of N-NV, NV-N and NV⁻N-configuration, along with NV⁻ (charging with additional electron) for the 3A2 state are given in figure 4.
When comparing the contour plots of NV-N or N-NV configuration (figures 4(b) and 4(c)) with NV$^-$ (figure 4(a)) it is clear that the donor-N, when placed on the symmetry axis, has very little effect on the shape of the $e_1$-level of the NV-center, as they show the closest possible $N\cdots N$ distances in those configurations. This is not the case for NV$^\perp$-configuration for which the donor-N significantly influences the $e_1$-level. At longer distances than those shown in figures 4(d)–4(f), the effect is smaller, and we can conclude from figure 4(f) that the effect on the charge density is marginal at distances above 7.5 Å. Charging the NV-center with a donor-N introduces a defect level in the diamond band gap that we term $w_N$. For a converged $N\cdots N$ distance calculation ($r = 12.229$ Å and $\Delta ZPL = 0.005$ eV) the Kohn–Sham $w_N$-level is 0.44 eV below the CBM and 0.15 eV above the empty spin down $e$-level. However, this state is localized at the donor-N and should in normal cases be far away in real-space from the localized states of the NV-center. It is, though, not inconceivable that excitations to $w_N$ could occur.

### 3.5. Spin density

Figure 5 shows the spin density (spin-up–spin-down) of diamond with NV$^-$, for the systems with the closest $N\cdots N$ distances in each of the three configurations (NV-N, N-NV and NV$^\perp$N).

The charge and spin density plots clearly reveal the role of the donor-N on the NV-center. Where the main effect of placement of the donor-N on the $C_3$-axis (NV-N and N-NV configuration) gives less influence than placement of the donor-N in the side configurations (NV$^\perp$N and NV$^\theta$N), which reinforces the conclusions drawn from the changes in the transition energies: From the density plots and the transition energies we conclude that the distance to the donor-N needs to be at least 7.5 Å for a minimal effect on the NV-center (see also supplementary material). We can also conclude from figure 5 that there is no spin density at the site of the donor-N, which means that it will not interfere with the manipulations of the optically active NV-center states even at very close $N\cdots N$ distances. It also means that the donor-N will not be seen in ESR (electron spin resonance). However, since nitrogen atoms have nuclear spin, it will interact with the NV-center when nuclear spins are being used and manipulated. Furthermore, we speculate that when the NV$^-$ looses its charge state during optical excitation an electron is excited to the donor-N giving a NV$^0$ and N$^0$ state instead of NV$^-$ and N$^+$. 

![Figure 4. Band decomposed charge density for the $e$-level in the $^3A_2$ ground state, looking top-down on the $C_3$-axis. Cyan spheres are carbon atoms, and blue spheres are nitrogen atoms (isovalue = $0.05 \text{1 Å}^{-3}$ ($=0.0074$ Bohr))](image)
4. Conclusions

We have investigated a method of charging a charged defect through using an electron donor/acceptor at a substitutional lattice site, and compared it to the method of charging the supercell with an added/subtracted electron. As the test case we used the well-known negatively charged NV-center in diamond, and another nitrogen atom as the electron donor. We have looked at how properties are affected by varying the distance between the electron donor (the nitrogen atom) and the defect (the NV-center). The properties investigated includes: the ZPL, the eigenvalues in the diamond energy-gap, the charge density and the spin-density. Vertical and adiabatic transition energies between the $^3A_2$ ground state and the $^3E$ excited state, for the following configurations were studied: (i) different distances between N$^-$ centers (charged with addition of an electron), (ii) varying distance to a donor-N and (on $C_3$-axis and at 90° to the $C_3$-axis), and (iii) varying the angle to the donor-N with respect to the $C_3$-axis. The salient findings from this study are:

1. No difference in the properties of N$^-$ whether charged by an additional electron or by a donor nitrogen atom at a substitutional site. Thus, charging a color center through a substitutional donor/acceptor atom is a viable alternative to adding/removing electrons from the supercell, and can favorably be used for slab models without the complications attributed with the associated compensation of charge.
2. The transition energies for the systems with a donor nitrogen vary and converge to the results obtained when charging with an additional electron for large N·N distances.
3. As a general conclusion we have found that both the distance to neighboring NV-centers and to donor-N must be larger than 7.5 Å. For shorter separations the NV-centers properties are severely influenced, and close separations could be detected experimentally by the changes in transition energies.
4. Calculated transition energies with the HSE06 hybrid functional are closer to experimentally measured energies than the corresponding transition energies calculated with the PBE, PBEsol and AM05 functionals.
5. The substitutional donor-N has no spin density regardless of the N·N distance, and thus it cannot be seen in ESR.

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