A theoretical study of de-charging excitations of the NV-center in diamond involving a nitrogen donor

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Abstract

The negatively charged nitrogen vacancy centre in diamond is a promising candidate for future nanoscale quantum applications. For its operation it is important to have control of the centres charge state, and to avoid temporary disappearance of the NV-center’s functionality, termed photo-blinking. In this work, we use density functional theory simulations to investigate excitations that result in loss of an electron from NV\(^{-}\) to a nearby nitrogen donor (donor-N\(^{+}\)), leading to NV\(^{0}\) and donor-N\(^{0}\) charge state, and the corresponding deexcitation. Since these processes involve two different localized defect centres in the diamond lattice (the NV-center and the donor-N) they are non-local excitations. We have studied the de-charging both as a one-photon process and through a sequential two-photon process via the NV-center excited state. We propose de-charging directly from the NV-center to the donor-N as a possible mechanism for photo-blinking of the NV-center that involve an additional electron spin resonance active defect, the donor-N\(^{0}\). We have found that the excitation energies are converged when the distance between the two is larger than 10.4 Å. We also compute excitations to the conduction band edge from NV\(^{-}\) (to NV\(^{0}\)) and from donor-N\(^{0}\) (to donor-N\(^{+}\)) using G\(_{0}\)W\(_{0}\) + BSE.

1. Introduction

The NV-center in diamond has gained a lot of attention during the last few decades. This is because it has properties that makes it an excellent candidate for many new and innovative technological applications, such as nanoscale sensor for magnetic [1–4] and electric fields [5, 6], sensor for strain [7] or temperature [8, 9], qubits in room temperature quantum computing [10–13], and as a single photon source [14, 15].

NV-centers can be created by ion implantation to create vacancies in a nitrogen containing diamond, followed by annealing at around 800 °C to diffuse the vacancies towards substitutional nitrogen defects, thereby forming NV-centers. This results in an assembly of defect centres, but schemes are developed to precisely place the NV-center both latterly and depth wise [16–19]. The NV-center introduces three levels in the diamond bandgap named v, e\(_{1}\), and e\(_{2}\) (see figure 1).

It is the negative charge state of the NV-center (NV\(^{-}\)) that has the properties that are interesting for most technological applications. Those properties include luminescence with the zero phonon line (ZPL) at 1.945 eV (637 nm), a spin-polarization loop where one can initialize and flip the spin state with a laser and microwaves, splitting of the spin sublevels with a magnetic field, photostability at room temperature, and very long spin coherence time (2 ms in ultrapure diamond). The NV-center can get its negative charge state by accepting an electron from a nearby substitutinal nitrogen electron-donor (donor-N) in the diamond lattice (one of the e-levels of the NV-center accepts an electron from the \(\omega_{N}\)-level of the donor-N). See the
Figure 1. Schematic picture of the electronic structure of the individual defects \( \text{NV}^- \), \( \text{NV}^0 \) and \( \text{N}^0 \). The major transitions are marked with red arrows: \( \text{NV}^- \) excitation from the \( ^3\text{A}_2 \) GS to the \( ^3\text{E} \) ES with emission at 637 nm; \( \text{NV}^0 \) excitation from \( ^3\text{E} \) GS (in \( \text{C}_3\text{v} \) symmetry) to \( ^3\text{A}_2 \) ES (in \( \text{C}_3\text{v} \) symmetry) with emission at 575 nm; and donor-\( \text{N}^0 \) to donor-\( \text{N}^+ \). The labels \( \nu \) and \( \epsilon_1 ,\epsilon_2 \) for the NV-center, and \( \omega \) for the donor-N denote the levels introduced into the diamond band gap by these two different defect centres. VBM and CBM denote the valence band maximum and conduction band minimum in diamond, respectively.

Electronic states and the individual defect levels for neutral and negatively charged NV-center and a substitutional nitrogen in figure 1 [20–24]. This results in the formal \( \text{NV}^-/\text{donor-\( \text{N}^+ \) } \) charge state, as demonstrated in [22] and used fruitfully in [20, 21, 23] to compute a charged defect in a neutral supercell and slab. Thus, the explicit incorporation of the donor (acceptor) can be used to circumvent the complications arising with charged slabs and their counter charge. Also experimentally it is worth considering deliberate inclusion of a donor-N per NV-center, especially for ICT and single molecule sensor applications. NV-centers with a devoted donor-N could possibly be fabricated by \( \text{N}_2 \) implantation into diamond [25, 26].

During laser illumination, the NV-center can be made to cycle between the neutral and the negative charge state, and the cycling behaviour depends on the laser wavelength, the laser power/intensity, and if one uses a ‘donor-N rich’ (e.g. type 1b, with 40–212 ppm nitrogen) [24, 27] or ‘donor-N poor’ (e.g. type IIa, with less than 5 ppb nitrogen) diamond [28–35]. In donor-N rich diamond the negative charge state, \( \text{NV}^- \), is the prevailing one, presumably due to the presence of nearby donor-Ns. While in donor-N poor diamond the \( \text{NV}^0 \) state (with ZPL of 575 nm, 2.156 eV) is the most common, although it is higher in energy than the negative state, in this case due to the lack of nearby donor-Ns to get an electron from. In such donor-N poor samples the \( \text{NV}^0 \) to \( \text{NV}^- \) charge switching cycle is broken for longer wavelengths (575–637 nm, 1.94–2.15 eV). For donor-N rich diamond, the local environment around the NV-center contains several donor-Ns [24, 27] and the charge switching cycle is never broken at these wavelengths, but instead there will only be emission from \( \text{NV}^- \) above its ZPL 1.945 eV (637 nm). For short wavelengths (2.33 eV (532 nm) and shorter) there will be emission also (in addition to emission from \( \text{NV}^- \) from \( \text{NV}^0 \) (ZPL of 575 nm, 2.156 eV) in donor-N rich diamond. The surrounding donor-Ns have been shown to be actively involved in the charge cycling process, with electrons directly tunnelling between them and the NV-center, with a rate that depends on the distance between the NV-center and the donor-N for distances estimated to be closer than 5 nm [24]. Thus, the NV-center charge state and operation is intertwined with its closeness to another defect, namely the donor-N (a two centre interaction). In our previous study [20] we conclude that at distances closer than 7.5 Å the NV-centers computed properties are more severely affected by the donor-N, and experimentally an estimate of 12 Å has been suggested to ensure a stable negative charging of the NV-center [24]. In this study we investigate these two centres synergy in detail by considering their experimentally known interactions. It has been reported that in donor-poor diamond, a so called dark state can be reached at certain laser energies, which is also termed photo-blinking, that can seriously interfere with normal operation of the NV-center [28–35]. However, this phenomenon does not appear in donor-rich diamond [24, 27]. It has been speculated that the relative closeness between the NV-center and donor-N in donor-rich diamond is the cause for this through the tunnelling mechanism mentioned above. The dark state in the photo-blinking has been associated with the \( \text{NV}^0 \) (and \( \text{NV}^+ \)) charge states, and in donor-poor diamond the electron from \( \text{NV}^- \) charge state is lost through the conduction band (CB) to a distant donor-N, which can occur via both one-photon and a sequential two-photon processes from the \( \text{NV}^- \) ground state (GS) or excited state (ES), respectively. Thus, the NV-center is in a metastable state from which it can only escape through donor-\( \text{N}^0 \) excitations (to donor-\( \text{N}^+ \)) when the inter-distance is too large for tunnelling. In this work we study these one- and sequential two-photon processes, as well as the direct tunnelling excitations between \( \text{NV}^- \) and donor-\( \text{N}^+ \), that are suggested to occur in donor-rich diamond.
Figure 2. Atomic structure of the NV-center and donor-N (left-hand side). Brown, blue and red spheres represent carbon atoms, the nitrogen atom and the vacancy, respectively (as can be seen in the legend in the upper middle of the picture). The NV-center ($v$ and $e_1$, $e_2$) and donor-N ($\omega_N$) defect levels introduced into the diamond band gap (right-hand side). VBM and CBM denote the valence band maximum and conduction band minimum in diamond, respectively. The two-center excitation is when an electron is excited from one of the $e$-levels of the NV-center to the $\omega_N$-level of the donor-N.

It is also worth mentioning that photo-blinking of the NV-center can occur in other situations separate from the ones discussed above. One example is when the diamond surface is hydrogen terminated, resulting in previously stable NV$^-$ centres getting converted to NV$^0$ and, subsequently, into an unknown nonfluorescent state [36]. Another example is an experimental study that involved a gold–diamond Schottky junction, where a suppressing effect was observed in the emission of NV$^-$, but emission from NV$^0$ was not observed to increase as expected [37].

There are no theoretical studies of the electronic excitations directly between the NV-center and a donor-N. In this work, we fill that gap by computing such excitations, thereby adding to the interpretation of the experimental studies. We, thus, investigate when an NV-center/donor-N pair switches charge state simultaneously between NV$^-$ and NV$^0$, and donor-N$^+$ and donor-N$^0$. We consider these direct non-local two-center excitations (i.e. when an electron is excited from one of the $e$-levels of the NV-center to the $\omega_N$-level of a nearby donor-N, see figure 2) either as a one or a sequential two-photon process involving the NV-center GS or ES, respectively. Such processes are different from indirect excitations involving the diamond CB. The indirect excitations have been studied by Beha et al, who studied the photoluminescence excitation spectra of NV$^-$ in donor-N poor diamond (i.e. type IIA) while continuously varying the excitation wavelength of the laser, and found a peak at 521 nm (2.38 eV) that mediates efficient conversion to NV$^0$, which they assigned to an electronic transition of NV$^-$ out of its ES to a level in the CB in the diamond host lattice [31]. Indirect excitations through the CB has also been discussed in the context of theoretical energy levels and bands [32]. In this work we have performed density functional theory (DFT) simulations of the direct two-center excitations between the NV$^-$/donor-N$^+$ and NV$^0$/donor-N$^0$ charge states both as a one- and a sequential two-photon process. We have also computed excitations to the CB leading to ionization of a donor-N$^0$ and de-charging of NV$^-$ using G$_0$W$_0$ + BSE.

2. Methods

The computations in this work were carried out with the Vienna \textit{ab initio} simulation package (VASP 5.4.4) [38, 39], within the DFT framework, using projector augmented wave potentials [40, 41]. Periodic boundary conditions were employed through the supercell method. The lattice parameter for a diamond primitive unit cell was optimized, using a plane-wave cut-off energy of 840 eV and a $12 \times 12 \times 12$ gamma-centered $k$-point grid. This lattice parameter was subsequently used to construct a 512 atom supercell, in which an NV-center and an electron donor-N were placed on the C$_3$-axis in an NV-N.
configuration (see reference [20]) with N−N distance of 12.23 Å. The 512 atom supercell was subsequently geometry optimized, using a plane-wave cut-off energy of 420 eV, and only the gamma-point, until the forces were below 0.001 eV Å−1. The method of Methfessel–Paxton was used for smearing. The different states were calculated using the ΔSCF method using constrained occupations at T = 0 K. It is well known that the probability of tunnelling transitions depend greatly on the distance between the NV-center and the donor-N [24]. But the transition energies are unchanged (converged) for distances greater than 10 Å (see supplementary information (https://stacks.iop.org/NJP/22/123042/mmedia)), and it should be pointed out that the 2nd step in the two-photon processes depend greatly on the photon flux, as well as the excitation energy.

The Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional of the generalized gradient approximation [42, 43] has been used for geometry optimizations, and the hybrid-functional HSE06 [44, 45] was employed to compute the electronic structure more accurately. HSE06 in diamond is nearly free of the electron self-interaction and provides more accurate transition and band gap energies than PBE [46, 47]. We investigate the geometry, charge density, spin density, Kohn–Sham eigenvalues and transition energies. Charge and spin densities were visualized using VESTA [48].

For comparison, we have also performed G0W0 + BSE computations on the separate defects donor-N0, NV0 and NV− (charged through adding an electron to the supercell) in 64 atom supercells created in the same way as the 512 atom supercell. We have used this method to compute the excitations to the CB that result in ionization of a donor-N0 (to donor-N+) and de-chargeing of NV− (to NV0).

3. Results and discussion

We have computed the de-charge of NV− to NV0 through a non-local, two-center, excitation from the NV− HOMO level (e-level) to a nearby donor-N+ LUMO level (ωN-level) (see figures 1–3), leading to the NV0/donor-N0 charge state. These excitations could occur from the NV− GS, corresponding to a one-photon process (see figure 3), as well as from the NV− ES, corresponding to a sequential two-photon process (see figure 5). We have used the Franck–Condon approximation (ΔSCF, constrained occupancies) to calculate both vertical and adiabatic excitations and deexcitations.

We focus on the NV−N configuration, where the NV-center and the donor-N are placed on the C3-axis of the supercell with a N−N distance of 12.23 Å, as we found this to be a well converged system after testing other configurations (see supplementary information for details). The converged distance for computation of these ESs is 2.9 Å longer than what was found previously for the states localized on the NV-center, see reference [20].

3.1. One-photon process—excitation from GS of NV− to donor-N+

We have calculated the transition energies for a one-photon process (see figure 3) as one electron gets excited from the spin-up e2-level of the NV-center in its GS, to the spin-up (triplet) or spin-down (singlet) ωN-level of the donor-N. For this non-local (two-center) excitation/deexcitation process, the interesting transitions to look at are the two vertical transitions A → B and C → D. Inspection of table 1 reveals that the absorption energies (A → B) are 2.306 eV (537 nm) (HSE06), for both the spin-up to spin-up (triplet), and spin-up to spin-down (singlet) excitations. We were only able to calculate the corresponding deexcitation energy (C → D) with PBE for the spin-up to spin-up case, which is 0.190 eV. For HSE06 we could only calculate the infinite separation limit between NV0 and donor-N0 using separate supercells, for which we get the C → D transition to be very close to 0.0 eV. We have, thus, found that the NV− to donor-N+ excitation energy is similar regardless of the spin of the final NV0/donor-N0 state. Since 532 nm (2.33 eV) is a common laser wavelength used to excite the NV-center from the $^3A_2$ GS to the $^3E$ ES (experimental ZPL at 1.945 eV or 637 nm for NV−) de-charge to NV0 could also occur at this energy. There are experimental studies of report cases of temporary disappearance of the NV-center’s functionality, termed photo-blinking [49–51]. Thus, a possible explanation for photo-blinking might therefore be excitation from NV− into the ωN-level of a donor-N+ sporadically occurring (since it is a two-center excitation depending on tunnelling), instead of excitation from the v-level to the e-level within the NV-center (a localized one-center excitation to the $^3E$ ES of NV−). For the adiabatic excitation/deexcitation, with structural relaxation for both the NV-center and the donor-N (C → A), we get an energy of 1.027 eV (PBE), for the spin-up to spin-up case. It has been discussed [24] that if the closest donor-N0 is very distant from the NV-center, it might work as an electron trap, not easily donating the electron back to the NV-center. We suggest that for optimum technical performance of the NV-center it should have a dedicated donor-N at a suitable distance (ca. 15–30 Å away), which could be created through dedicated implantation.

The excitation to the NV0/donor-N0 state results in significant changes of the geometry of both defects through Jahn–Teller distortion (NV-center). Thus, geometry relaxation of the B-state (resulting in the
Figure 3. The one-photon process. The NV-center (v and e) and donor-N (ωN) defect levels in the diamond band gap, as defined in figure 2. VBM and CBM denote the valence band maximum and conduction band minimum in diamond, respectively. The electronic vertical excitations and accompanying structural relaxations are illustrated with red and blue arrows, respectively. The label 'SR' is short hand for 'structural relaxation'. The one-photon process consists of a non-local (two-center) excitation of an electron from the e-level of the negatively charged NV-center (in the GS) to the ωN-level of the positively charged donor-N (A → B), followed by a structural relaxation (B → C). This results in a state consisting of a neutral NV-center and a neutral donor-N. The deexcitation proceeds through emission from the ωN-level of the donor-N to the e-level of the NV-center (C → D). This is followed by a structural relaxation resulting in the original system with a negatively charged NV-center and a positively charged donor-N (D → A).

Table 1. Calculated transition energies (e-level to ωN-level, one-photon process in figure 3) for the NV-center and the donor-N in the NV-N configuration in the 512-atom supercell using the HSE06 functional (PBE functional in parentheses). The excitation from the e-level to ωN-level can either be calculated as a spin-up to spin-up excitation (α → α) or as a spin-up to spin-down excitation (α → β). All energies are given in eV.

| Excitation | C → A | A → B | B → C | C → D | D → A |
|------------|-------|-------|-------|-------|-------|
| α → α      | 1.064(1.027) | 2.306(1.844) | 1.242(0.817) | ≈0.0 a(0.190) | 1.068(0.837) |
| α → β      | 2.306(1.844) |       |       |       |       |

*The HSE06 energy in the C-state was approximated by the infinite separation limit between NV0 and donor-N0 using separate supercells.

C-state) of the excitation-deexcitation process results in breaking the C3v symmetry of the NV-center, and it becomes C2-symmetric (see table S1). This is as expected as we have a system containing a neutral NV-center and a neutral donor-N (NV0/donor-N0). NV0 is known to have C3 symmetry from earlier work [52–55]. The geometry around the donor-N is also changing (see table S2) due to the change in charge state, with three of the bonds to 3 of the neighbouring carbon atoms shortening to 1.48 Å, while the bond to one of the carbon atoms (C10 in figure 2) is instead elongated to 2.03 Å (see also table S2).

We find that the HSE06 Kohn–Sham eigenvalues (see figure 4) for both the v- and e-levels (in both spin channels) of the NV-center changes in energy considerably after vertical excitation (A → B) from the spin-up e-level to the spin-up ωN-level (see figure 3). Also, the e-levels split apart. After ionic relaxation (B → C) the eigenvalues have changed only marginally (see PBE computed figure S1 in SI. Convergence for the C-state was not possible with HSE06), except for the spin-up ωN level, that has decreased by 1.36 eV (PBE). In the spin-down channel, the e-levels move a bit closer to each other, while they move apart in the spin-up level (PBE). Although the symmetry has changed (from a1- and e-symmetry states in C3v (A-state) to a- and b-symmetry states in C2 (C-state)) the label 'e-levels' is kept for consistency. Likewise, the e-levels in both spin-channels are split in the D-state, while they are degenerate in the A-state (both for PBE and HSE06), due to the change in symmetry. For the NV0/donor-N0 charge state (the B- and C-states) the
Figure 4. One-photon process. Bottom view: the NV-center and donor-N Kohn–Sham energy levels (512 atom supercell) in the diamond bandgap with the HSE06 functional, for different charge states. The A, B, C (not shown), and D states represent excitation (deexcitation) from the NV⁻/donor-N⁺ GS to a NV⁰/donor-N⁰ ES in the Franck–Condon approximation when promoting an electron from the NV spin-up (α) e-level to the donor-N spin up (α) ω_N-level (see the one-photon process in figure 3). The C-state is not shown because of HSE06 convergence issues. However, all the states for PBE are shown in figure S1 in supplemental material. The blue horizontal lines are the diamond conduction and valence band edges. The red horizontal lines are the levels associated with the NV-center (v- and e-levels) and the electron donor-N (ω_N). The α and β are the spin-up and spin-down channels, respectively. Top view: associated spin- and charge-densities in the (100)-plane. Positive and negative values of the spin densities are represented with red and green lobes, respectively. Charge densities are represented with yellow lobes. Brown and blue spheres represent carbon and nitrogen atoms, respectively. The red sphere represents the vacancy. The NV-center is in the upper-left corner, while the donor-N is in the lower right corner. Isovalue = 0.05 Å⁻³.

NV-center’s eigenvalues should be similar to a neutral NV⁰, which we have computed alone in the same size supercell (see figure S2 in SI). The B- and C-state energy levels relating to the NV-center (v- and e-levels) are indeed comparable to the isolated NV⁰, confirming that these truly correspond to the NV⁰/donor-N⁰ charge state. There is a smaller split of the e-levels in the B-state when using the PBE functional, which is known to give less accurate excitation and eigenvalues than the HSE06 functional. Comparison with the isolated neutral NV-center calculation shows that the same behaviour is present also in this case, again confirming that we have a NV⁰/donor-N⁰ system. Excitation of an electron from the spin-up e-level to the spin-down ω_N-level gives very similar results for the B-state (with the occupied spin-up ω_N-level being a little higher in energy than the unoccupied spin-down ω_N-level instead).
Figure 5. The sequential two-photon process. The NV-center (v and e) and donor-N (ωN) defect levels in the diamond band gap, as defined in figure 2. VBM and CBM denote the valence band maximum and conduction band minimum in diamond, respectively. The electronic vertical excitations and accompanying structural relaxations are illustrated with red and blue arrows, respectively. The label ‘SR’ is short hand for ‘structural relaxation’. The two-photon process involves: firstly, a local excitation of a spin-down electron from the v-level of the negatively charged NV-center (in the GS) to the e-level of the NV-center, giving the common ZPL ES of the negatively charged NV-center (A → A∗), followed by structural relaxation (A∗ → Aa∗). The next step is a non-local excitation from the e-level of the negatively charged NV-center (in ES) to the ωN-level of the donor-N (Aa∗ → B∗ (can only be calculated as a pentuplet)), followed by a structural relaxation (B∗ → C∗). This results in a system consisting of a neutral NV-center (in ES) and a neutral donor-N. The deexcitation proceeds through an emission from the ωN-level of the donor-N to the v-level of the NV-center (C∗ → D). Finally, a structural relaxation will return the system to the starting state: a negatively charged NV-center (in GS) and a positively charged donor-N (D → A). The subscripts na (non-adiabatic) and a (adiabatic) differentiates between electronic states before and after structure relaxation when necessary.

We have in addition studied if the Kohn–Sham eigenstates are changing in character through their band decomposed charge densities (see figure 4 and figures S1, S2 in SI). In the B-state, the HSE06 computed v-level changes slightly due to the Jahn–Teller effect in NV0. Comparing these with the levels of an isolated neutral NV-center, we see that their v-levels look very similar, which is expected for the NV0/donor-N0 charge state. The reduced symmetry also causes changes to the e-level (not degenerate in the lower C2v-symmetry) of NV0. These changes in the eigenstates are less pronounced when the PBE functional is used. For the A-state there’s some slight difference in the v-level compared with HSE06. For the ES NV0/donor-N0 the lower symmetry of the v- and e1-levels are more pronounced, while the e2-level only looks slightly different compared with the HSE06 result. The band densities for state B and C compare favourably with NV0 without donor-N also for PBE, as they look very similar (but rotated). If we instead excite an electron from the spin-up e2-level into the spin-down ωN-level we get very similar eigenstates for the B-state (except rotated for PBE) as the aforementioned case.

Further, we have made an in detail study of the computed spin densities (see figure 4 and figures S1, S2 in SI) in the different states involved in the excitation to NV0/donor-N0, since these can be measured using electron spin resonance (ESR). The NV-center has spin density in both the negative and neutral charge state, while the donor nitrogen only in the neutral charge state [20, 21]. Thus, the excited B- and C-states have spin density in addition to on the NV-center also on the donor-N site (donor-N0) (see the spin density in the C-state computed with PBE in figure S1). The spin density on a neutral substitutional nitrogen is due to its five valence electrons, which leaves one unpaired and localized. Thus, the donor-N could be seen in ESR after such an excitation. Otherwise, there is no considerable change in the shape of the spin density around the NV-center between NV− and NV0. Comparison with the spin density of a neutral NV-center shows that they look similar, as expected. Excitation of an electron from the spin-up e2-level into the spin-down ωN-level (B-state) also results in spin-density around the donor-N site but with opposite spin.
### Table 2. Calculated transition energies (sequential two-photon process in figure 5) for the NV-center and the donor-N in the NV-N configuration in the 512-atom supercell using the HSE06 functional (PBE functional in parentheses). The values in the bottom row are when a structural relaxation is performed in the A' state (giving the adiabatic A' state, and subsequently the non-adiabatic Aaa state after releasing the promoted electron) before excitation to B'. All energies are given in eV.

| Excitation | $A \rightarrow A'$ | $A' \rightarrow A_{aa}$ | $A_{aa} \rightarrow A$ | $A_{aa} \rightarrow A$ |
|------------|-------------------|-----------------------|-------------------|------------------|
| 1st        | 2.188(1.883)      | 0.264(0.206)          | 1.705(1.482)      | 1.924(1.676)     | 0.219(0.194)     |
|            | $A_{aa} \rightarrow B'$ | $B' \rightarrow C'$ | $C' \rightarrow D$ | $D \rightarrow A$ |
| 2nd        | 0.814(0.725)      | 1.240(0.794)          | 0.037(0.603)      | 1.460(1.006)     |

### 3.2. Sequential two-photon process—excitation from ES of NV$^-$ to donor-N$^+$

We have calculated the transition energies for the two-photon process (see figure 5) as one electron first gets excited from the NV$^-$ GS ($^3A_2$-state) v-level to the e-level giving the NV$^-$ ES ($^3E$-state). From this state we subsequently excite an electron from the e-level to the $\omega_N$-level of the donor-N, giving the NV$^0$ ES and the donor-N$^0$ GS. For this process, the first excitation is the vertical and adiabatic absorptions $A \rightarrow A'$ and $A \rightarrow A_{aa}$ (v- to e-level) to the $^3E$ ES of the NV$^-$ ZPL excitation at 2.188 and 1.924 eV (see table 2), respectively, in good agreement (a small difference is noted due to the orientation and placement of the NV-center in the supercell) with our previously published values [20]. The corresponding vertical deexcitation $A_{aa} \rightarrow A_{aa}$ gives emission at 1.705 eV. The second vertical excitation from $A_{aa} \rightarrow B'$ (e- to $\omega_N$-level) involves tunnelling from the NV-center to the donor-N (two-center excitation), which we find to be 0.814 eV. The vertical deexcitation energy $C' \rightarrow D$ is 0.037 eV. The $D \rightarrow A$ transition, which corresponds to a structural relaxation of the whole system is quite large (1.460 eV), which reflects that the geometry around the neutral charged donor-N is far from that for donor-N$^+$, as described for the one-photon process above. The B* and C* states can only be calculated with the final NV$^0$/donor-N$^0$ state as a pentuplet using $\Delta$SCF. However, we found virtually no difference in energy between the singlet and triplet B state of NV$^0$/donor-N$^0$ state in the one-photon process (cf table 1). The 1st excitation (2.188 eV) is slightly lower than for the one-photon process above (2.306 eV), while the 2nd excitation is very low compared to the laser energies used in these experiments. We have, thus, established that the direct excitation to a donor-N$^+$ via the NV-center ES would normally not interfere with the intended excitations, as was found to be the case for the one-photon process. However, the 2nd excitation resulting in de-charging, could alternatively happen indirectly from the NV$^-$ ES to the diamond CB and is reported below using the $G_0W_0$ + BSE method. In donor-N poor (with less than 5 ppb nitrogen) diamond, an N that traps the electron could be very distant from the NV-center, it might even be placed outside the region of the laser spot, thereby not getting ionized during the laser experiment, making recreation of the NV$^-$ state very difficult. We have also computed the vertical excitation from the NV$^-$ v-level directly to the donor-N $\omega_N$-level to be 2.874 eV ($A \rightarrow B'$ ($B'$ with A structure)), and it is thus too high to interfere with NV$^-$ processing. The vertical emission back to the $^3A_2$ GS (recharging) we have computed to be 0.037 eV ($C' \rightarrow D$).

We find that the HSE06 Kohn–Sham energy eigenvalues of the spin-down (spin-up) v- and e1-levels move closer (further apart) to each other (see figure 6) after vertical excitation of an electron from the spin-down v-level to the spin-down e1-level, and subsequent structure relaxation ($A \rightarrow A_{aa}$). The e-levels in the spin-up and spin-down levels split apart by 0.61 and 0.83 eV, respectively. After the 2nd vertical excitation ($A_{aa} \rightarrow B'$) we see that the v- and e1-levels in the spin-down channel move apart from each other again (with the e-levels becoming almost energy degenerate with a small split of 0.16 eV). In the spin-up channel, the e-levels move down in energy and become almost energy-degenerate (split of 0.13 eV) again. After ionic relaxation ($B' \rightarrow C'$) the v-level in the spin-down channel moves up slightly, while the $\omega_N$-level in the spin-up channel also moves down considerably (2.38 eV) due to the large change in geometry around the donor-N (one N–C bond stretches out to 2.03 Å). The e-levels in both spin-channels get degenerate again. And, finally after emission from the spin-up $\omega_N$-level to the spin-down e1-level ($C' \rightarrow D$) the e-levels in both spin channels split apart (with 0.33 and 1.53 eV in spin-up and spin-down channels, respectively), with the v-level being slightly higher in energy than in the A-state (structure relaxation of the D-state). The $\omega_N$-level in the spin-up channel is still positioned mid gap in the D-state, while it is closer to the CBM in the A-state.

For the NV$^0$/donor-N$^0$ charge state (the B - and C -states) the NV-center’s eigenvalues should be similar to an excited neutral NV$^0$, which we have computed alone in the same size supercell (see figure S3 in SI). We find that this is true, which reinforces that we indeed have a NV$^0$/donor-N$^0$ charge state.

In addition to the changes in eigenvalues we have studied if the Kohn–Sham eigenstates change character through their band decomposed charge densities (see figure 6 and figures S3–S7).
Figure 6. Two-photon process. Bottom view: the NV-center and donor-N Kohn–Sham energy levels (512 atom supercell) in the diamond bandgap with the HSE06 functional, for different charge states. The $A, A^*, B, C$ and $D$ states represent excitation (deexcitation) from the NV$^-$/donor-N$^+$ GS to a NV$^0$/donor-N$^0$ ES when promoting an electron first from the NV spin-down ($\alpha$) v-level to the NV spin-down $e_1$-level and further to the donor-N spin up ($\beta$) $\omega_N$-level (see the sequential two-photon process in figure 5). The blue horizontal lines are the conduction and valence band edges. The red horizontal lines are the levels associated with the NV-center ($v, e_1,e_2$) and the electron donor-N ($\omega_N$). The $\alpha$ and $\beta$ are the spin-up and spin-down channels, respectively. Top view: associated spin- and charge-densities from the (100)-plane. Positive and negative values of the spin densities are represented with red and green lobes, respectively. Charge densities are represented with yellow lobes. Brown and blue spheres represent carbon and nitrogen atoms, respectively. The red sphere represents the vacancy. The NV-center is in the upper-left corner, while the donor-N is in the lower right corner. Isovalue $= 0.05$ Å$^{-3}$.

For the NV$^0$/donor-N$^0$ charge state (the $B^*$- and $C^*$-states) the NV-center’s charge-density should be similar to an excited neutral NV$^0$, which we have computed alone in the same size supercell (see figure S3 in SI). While the v-level is quite similar for both PBE and HSE06, the $e_1$ and $e_2$ levels differs for HSE06 (see figures S4–S7 in SI for detailed pictures for the $C^*$-state). However, both functionals gives similar eigenstates/orbitals within the NV$^0$/donor-N$^0$ and NV$^0$ models, and the changes are probably symmetry related.

Further, we have made an in detail study of the computed spin densities (see figure 6 and figure S3) in the different states involved in the sequential two-photon excitation process, since these can be measured using ESR. The NV-center has spin density in both the negative (GS and ES) and neutral (GS and ES) charge state, while the donor-N$^+$ has none (as mentioned earlier). The excited $B^*$- and $C^*$-states have in addition spin density at the donor-N site (donor-N$^0$). This means that the donor-N could be seen in ESR after such an excitation. Again, for the NV$^0$/donor-N$^0$ charge state (the $B^*$- and $C^*$-states) the NV-center’s spin-density should be similar to an excited neutral NV$^0$, which we have computed alone in the same size supercell (see figure S3 in SI). This we found to be true, which reinforces that we indeed have a NV$^0$/donor-N$^0$ charge state. Looking at the D-state, we see that there is a little spin-density around the donor-N, despite it being in the positive charge state. This is because the spin-up $\omega_N$-level hybridizes with the $e_1$-level of the NV-center.
3.3. Comparisons with experiment and G0W0 + BSE computations

From our simulations of the direct transitions from NV−/donor-N+ to NV0/donor-N0, we have found the one-photon process to be most likely to interfere in normal NV-center processing. For donor-N rich (e.g. type 1b with 40–212 ppm nitrogen concentration) diamond we can compare with the NV-center’s experimental absorption spectrum by Manson et al [24], but we find no significant signatures around 538 nm (vertical excitation A → B at 2.306 eV) for the negatively charged state. In their emission spectra for NV− there is a major peak around 647 nm (vertical deexcitation C → D at 1.916 eV), but this could be unrelated. But when they specifically target the NV0 state there are emission peaks around 647 nm, that could correspond to our suggested mechanism of going from the neutral state to the charged (NV−/donor-N+) lowest energy state. However, we find no support of their suggested sequential two-photon process of de-charging via the NV− ES (and the NV0 ES) happens directly to donor-N+, as we find the 2nd absorption to be only 0.814 in the vertical case. The experimentally reported laser energies used are much larger than these. The direct (i.e. not proceeding via diamond CB) one-photon process we report is close to the energies reported to convert NV− to NV0 and we suggest it could be an important mechanism in donor-N rich samples, although it is a process involving two defect centres. Our G0W0 + BSE simulation for NV− reveals that the 3A2 to 3Eg(1A1) transition (A → A∗) has an energy of 2.340 eV, which compares favourably with our HSE06 computed vertical excitation A → A∗ at 2.306 eV (see table 2). Using G0W0 + BSE it is also possible to compute the A∗ de-charging transition to the CB (A → CB), which has an energy of 4.046 eV and higher, and results in NV0 in the GS. The corresponding de-charging in the 3Eg(1A1) ES (A → CB) is computed to 2.249 eV with G0W0 + BSE, and results in NV0 in the ES. This energy of de-charging fits well with what is reported experimentally as a two-photon process at energies around or above 2.3 eV [31, 34, 35]. We can also try to deduce some intervals for this sequential two-photon de-charging via the NV− ES from what is known from experiment. It has been reported that when starting from the NV− state a max-energy of 610 nm (2.03 eV) only excites it to the ES (A → A∗), and there are no NV0 formed [27]. This could be interpreted as the further excitation to the diamond CB (A∗ → CB) has an energy that is larger than 2.03 eV. However, a 532 nm (2.33 eV) laser will produce NV0 and should be above the A∗ → CB transition [24]. This argument was used to explain why the 514 nm (2.41 eV) laser only produces NV0 when the 610 nm (2.03 eV) laser also is turned on [27], since this energy overshoots the (A∗ → CB) minimum transition energy, and the CB is continuous with states. It is, however, unclear to us why not two subsequent excitations with 514 nm could not achieve the same. Could it be because the NV− excitation is overshot too grossly, or due to low photon flux? An electron excited to the CB would be delocalized and could, thus, either emit back to the NV0 or down to a donor-N+. If it goes to a donor-N+ the result is the metastable NV0/donor-N0 state (C), and possible photo-blinking. Otherwise it goes back to the GS (NV−/donor-N+) [36, 37]. In the state C there are two routes back to the GS, of which one is the C → A emission at probably small energies (0.19 eV vertically, and 1.0275 eV adiabatically, as calculated with PBE), which is NV/donor-N distance dependent tunnelling. The other involves excitation of donor-N0 to the CB resulting in donor-N+, which we have computed to start at 1.420 eV using G0W0 + BSE. However, since the CB is delocalized the relaxation to either donor-N− or NV0 is largely determined by chance. But since the A state is the overall GS the targeting of the charging excitation of donor-N0 to get rid of unwanted NV0 (C-state) due to processing should be desirable, and the excitation energy is low enough to not interfere with the NV-center processing.

We, thus, suggest that laser energies should be carefully tuned to avoid unwanted direct excitations between the NV-center and nearby donor-N+ defects at close distance. Here we confirm that energies around 2.3 eV (539 nm) should be avoided as it can lead to de-charging of NV− through a spurious two-center excitation. And we propose that all excitations leading to de-charging of the NV-center (NV− to NV0) involves a donor nitrogen, either directly or indirectly through the diamond CB (or possibly other defects in donor-N poor diamond). We, consequently, propose that a donor-N in the diamond lattice, or another donor defect, is always involved in the conversion from NV− to NV0. For cases with direct excitation from NV− to donor-N+ (rather than via the diamond CB) the mechanism for mapping of the charge state, depending on if mN = ±1, or mN = 0, needs to be slightly reworked [36, 57]. Although the conclusions seem to hold on what mN-value maps to which charge state, since our suggested mechanism to reach NV0 more easily happens starting from the NV− GS, which is attained most frequently for mN = 0. Also the measure of photocurrent when converting NV− to NV0 should in such a case have its origin in a proportional increase in N0 doping centres in the diamond lattice, and excitation of such electrons into the CB. Further, we suggest that for ICT and single-molecule sensor applications based on the NV-center that a donor-N should be placed nearby to form a dedicated pair (NV−/donor-N+). This would ensure the correct charge state since it is the GS, and give the least variations in properties between NV-centers (uniformity). We further note that deexcitation energies also need to be considered when tuning laser energies used for processing, as they can couple through stimulated emission when populated. However, the
non-local two-center deexcitations from donor-N$^0$ to NV$^0$ studied in this work are below 1.95 eV, and should not interfere.

4. Conclusions

In summary, we have found, using first principles theory, that the excitation from NV$^-$ GS into donor-N$^+$ (one-photon process) requires 2.31 eV and lead to a meta-stable NV$^0$ and donor-N$^0$ charge state, both of which are ESR-active and, thus, this transition could be seen experimentally. The uncharged meta-stable state could act as an electron trap and lead to photo-blinking. Such non-local, two-center, excitations are dependent on tunnelling rates and would only occur spuriously. We have found that the excitation energies are converged when the distance between the NV-center and the donor-N is larger than 10.4 Å. By engineering dedicated NV-center/donor-N pairs by design, these transitions could possibly be used for technological applications. But in the ordinary applications using the NV$^-$ state properties we would recommend keeping the laser energy below 2.3 eV to thwart excitations to NV$^0$ and donor-N$^0$ (note that a common wavelength in many experimental studies is 532 nm, corresponding to 2.33 eV). We have also found that the excitation to the neutral state can be achieved through a sequential two-photon process with the 1st step at 2.19 eV (1.92 eV adiabatically) and the 2nd step at 0.81 eV (0.64 eV adiabatically). The 1st excitation corresponds to the normal absorption from the NV$^-$ GS ($3A_2^*$) to its ES ($3E$). The 2nd step is the two-center excitation, and we find its energy to be much lower than the normal processing laser, and this two-photon process should normally not interfere. The vertical emission back to the $3A_2^*$ GS (recharging) we have computed to be 0.037 eV. For indirect de-charging excitations via the diamond CB we have used $G_0W_0 +$ BSE to compute the transition from NV$^-$ to NV$^0$ in the GS (4.046 eV) and the ES (2.249 eV), as well as the corresponding excitation from donor-N$^0$ to donor-N$^+$ (1.420 eV).

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