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Small cluster model of the NV centre in diamond

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Abstract

The singlet $^1E$ and $^1A_1$ energy levels of the Nitrogen-Vacancy centre’s ground state configuration each need two Slater determinants in theoretical models, posing difficulties for Density-Functional Theory (DFT) and Hartree-Fock approaches. Configuration Interaction (CI) can handle such states, but not the $C_{284}H_{144}N$ and $C_{163}H_{100}N$ clusters of our recent DFT study as CI computer time and memory scale worse than DFT with system size. Using smaller clusters to model bulk diamond introduces size errors. We examine the smaller diamond cluster $C_{42}H_{42}N$ using DFT to quantify the size error: if not too large it opens the way to CI calculations of these states.

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1. Introduction

The Nitrogen-Vacancy (NV) centre in diamond has received much experimental study due to its applications in quantum information. Optical readout of its electronic ground state triplet has been demonstrated [1] and using a neighbouring $C_{13}$ atom the two-qubit controlled-rotation (CROT) had been implemented [2]. It has also been used as a single-photon source [3,4].

The electronic structure of the NV centre has been described in several papers [5-10]. Starting with linear combinations of the four dangling sp\textsuperscript{3} bonds on the three carbon atoms ($a,b,c$) and the nitrogen atom ($d$) one finds single particle levels $u,v,x,y$. DFT calculations give the energy ordering $u<v<x=y$: both $u$ and $v$ are of symmetry $a_1$ in the group $C_3v$ and arise from symmetric and anti-symmetric combinations of the nitrogen $d$ and the carbon $a+b+c$, leaving degenerate $x$ and $y$ as basis functions for an $e$ irrep [8]. For the negatively charged defect NV\textsuperscript{-} we fill these orbitals with 6 electrons.

The ground state of the defect has occupation $u^2v^1e^3$ and is a spin triplet with symmetry $^3A_2$ (capitals denote irreps of many-body wavefunctions). The $m_S=+1,-1$ states are single Slater determinant wavefunctions: e.g. $m_S=+1$ is $|u\bar{u}v\bar{v}e\bar{e}\rangle$. Here and after all levels below $u$ are assumed completely filled and bars indicate down spin. Laser irradiation can induce a transition to the triplet excited state of the configuration $u^2v^1e^2$ of symmetry $^1E$. Again the
$m_S = +1, -1 \ X$ and $Y$ states are single Slater determinant wavefunctions: $X = | uuvxy \rangle$ and $Y = | uuvx \rangle$ for $m_S = +1$.

Single Slater determinants are naturally modeled by DFT leading to recent calculations of this transition energy [7-10].

Belonging to the $u^2v^2e^2$ configuration of the ground state there are also $^1E$ and $^1A_1$ energy levels, which have small matrix elements with the triplet states through the spin-orbit interaction. Under laser irradiation population could build up in these singlets, altering the centre’s fluorescence properties. However, these states are difficult to treat computationally as they each need two Slater determinants in the simplest theoretical model.

The essence of the latter difficulty can be seen in atomic helium, where the first excited configuration $1s^22s^1$ has triplet and singlet levels. If we multiply out the singlet wavefunction on the left-hand-side of the next equation we see on the right that it is a superposition of two Slater determinants

$$\left[1s(r_1)2s(r_2) + 2s(r_1)1s(r_2)\right] \times \left(\uparrow \downarrow - \downarrow \uparrow\right) = \left|1s\ 2s\right\rangle - \left|1s\ 2s\right\rangle.$$  

Such states are called “open-shell” singlets as the $1s$ and $2s$ levels are not completely filled. Thus, as the singlet requires two Slater determinants the calculation of its energy is not straightforward.

Configuration Interaction (C.I.) is a wavefunction-based quantum chemical method of great generality. It expands the many-body wavefunction $\Psi$ in a basis set of Slater determinants $\Psi_i$

$$\Psi = \sum_{i=1}^{N_{SD}} c_i \Psi_i, \quad N_{SD} = \binom{2m}{n}$$

and calculates many-body energy levels and wavefunctions by diagonalising the many-body Hamiltonian in this basis. It naturally handles open-shell states. However, it does not scale well with system size: the number $N_{SD}$ of Slater determinants one can construct by filling $2m$ molecular spin-orbitals with $n$ electrons is the binomial coefficient given above.

In this paper we study the small cluster $C_{42}H_{42}N^-$ as a model for the NV centre in bulk diamond. The pay-off is the ability to do C.I. – the cost is that small clusters may not be good models of bulk diamond. We quantify these size errors by comparing bond distances and single-particle energy levels in $C_{42}H_{42}N^-$ and the larger clusters $C_{163}H_{100}N^-$ and $C_{284}H_{144}N^-$.  

2. Calculation

To build a model of the NV centre we start with the hydrogen-terminated diamond clusters of Figure 1. The larger clusters have tetrahedral symmetry ($T_d$). For the smallest cluster we chose bond-centered $C_{42}H_{42}$ of $D_{3d}$ symmetry rather than atom-centered $C_{35}H_{36}$ of $T_d$ symmetry because the former has all the second nearest neighbours of $N$ and $V$. We cut the $C_{42}H_{42}$ diamond so as to have no surface carbons terminated by three hydrogens, few terminated by two, no $H-H$ distances shorter than 2 Å and no unnaturally-long $C-C$ bonds on the surface, both before and after relaxation.
Figure 1. The $\text{C}_{44}\text{H}_{42}$, $\text{C}_{165}\text{H}_{100}$ and $\text{C}_{286}\text{H}_{144}$ diamond clusters from which our NV models are built.

Figure 2. The $\text{C}_{44}\text{H}_{42}$ cluster, showing the carbon atoms which become the vacancy and the nitrogen to give $\text{C}_{42}\text{H}_{42}\text{N}^-$. 

Figure 2. The $\text{C}_{44}\text{H}_{42}$ cluster, showing the carbon atoms which become the vacancy and the nitrogen to give $\text{C}_{42}\text{H}_{42}\text{N}^-$. 
To form NV models we remove one central carbon and replace a neighbour with a nitrogen atom giving $C_{3v}$ symmetry, as shown in Figure 2 for $C_{42}H_{42}N^-$. For all clusters we computed the optimized DFT ground state geometries with the Becke-Perdew exchange-correlation functional from the TURBOMOLE suite of programs [11]. For the larger clusters we used the valence double-zeta polarized [VDZ(P)] basis set. For the $C_{42}H_{42}N^-$ cluster we retained polarization functions only on the four neighbours of the vacancy, and used effective core potentials (ECPs) to remove the 1s level for the remaining 39 carbon atoms. This reduces the number of active electrons and two-electron integrals for the CI calculation. The results of our new calculations for bond lengths and single-particle energy levels are shown in Tables 1 and 2 respectively and compared to results from the larger clusters.

### Table 1

| Property       | $N – C_N$ | $N – C_V$ | $C_V – C$ | $\angle C_N – N – C_N$ |
|----------------|-----------|-----------|-----------|-------------------------|
| $C_{42}H_{42}N^-$ | 1.481     | 2.916     | 1.503     | 1.503                   | 1.500 | 105.5 |
| $C_{163}H_{100}N^-$ | 1.476     | 2.776     | 1.510     | 1.510                   | 1.513 | 105.1 |
| $C_{284}H_{144}N^-$ | 1.478     | 2.771     | 1.511     | 1.511                   | 1.513 | 105.1 |

### Table 2

| Orbital | $C_{42}H_{42}N^-$ (up) | $C_{163}H_{100}N^-$ (up) | $C_{284}H_{144}N^-$ (up) | $C_{42}H_{42}N^-$ (down) | $C_{163}H_{100}N^-$ (down) | $C_{284}H_{144}N^-$ (down) |
|---------|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| e=(x, y)| 0                      | 0                        | 1.179                    | 1.245                    | 1.262                    |
| v      | -0.830                 | (0.830)                  | -1.243                   | (1.243)                  | -1.259                   | (1.259)                  |
| u      | -2.490                 | (1.660)                  | -3.029                   | (1.786)                  | -2.989                   | (1.730)                  |

### 3. Discussion

Counting neighbours by bond hops, the $C_{42}H_{42}N^-$ cluster (Figure 2) contains all 4 first nearest-neighbours (nnbrs) of the vacancy, all 12 of the second nnbrs and 15 of the 36 third nnbrs of bulk diamond. As the nitrogen is placed at a symmetry-equivalent position in the $C_{44}H_{42}$ diamond cluster it has the same numbers of first, second and third nnbrs if the vacancy is counted.

Table 1 shows that the bond distance $N – C_N$ between the nitrogen and its three neighbours is little different in the $C_{42}H_{42}N^-$ cluster compared to the larger $C_{163}H_{100}N^-$ and $C_{284}H_{144}N^-$ clusters. Similar remarks apply to the bond distance $C_V – C$ between any of the three carbons around the vacancy ($C_V$) and their carbon neighbours ($C$), and to the angle $\angle C_N – N – C_N$ between the $C_3$ symmetry axis of the defect and any of the $N – C_N$ bonds [8]. The second-nearest neighbour distance $N – C_V$ between nitrogen and carbon atoms around the vacancy has the largest change of 5%.

Table 2 shows the spin-orbital energies of our spin-unrestricted DFT calculation compared to the larger clusters. Examining the changes to the calculated energies, it is the relative energies that are significant and the $\nu\leftrightarrow\kappa$ gap changes by around 0.1 eV on going from the larger clusters to the smaller cluster, while the $\nu\leftrightarrow\nu$ gap changes significantly by $-0.4$ eV (spin up) and $-0.6$ eV (spin down). By comparing to $C_{42}H_{42}N^-$ clusters where polarization
functions were used on all carbons and no ECPs were used (not reported) we see that these changes are not responsible for the shift in the $\nu \leftrightarrow \epsilon$ gap: it is largely due to the decrease in cluster size.

The shift in the $\nu \leftrightarrow \epsilon$ gap does indicate that the $^3A_2 \leftrightarrow ^3E$ major transition in $C_{42}H_{42}N^-$ will be predicted by DFT to be smaller than in bulk diamond. We, however, have designed $C_{42}H_{42}N^-$ to obtain information about the excitation energy to the singlet $^1E$ and $^1A_1$ states which are of the same $u^3\nu^3\epsilon^2$ configuration as the $^3A_2$ ground state: as electrons are not being promoted from $\nu$ to $\epsilon$ this $\nu \leftrightarrow \epsilon$ gap enters similarly in the total energies of $^3A_2$, $^1E$ and $^1A_1$ and so tends to cancel in the excitation energy. Therefore we argue that $C_{42}H_{42}N^-$ will have reasonably good quantitative accuracy as a model for these singlet states in bulk diamond.

4. Conclusion

Bond lengths and single-particle energy levels have been calculated within DFT for the small cluster $C_{42}H_{42}N^-$. Comparing to larger clusters, the bond distances and angles and the $\nu \leftrightarrow \epsilon$ gap are little changed. The only substantial change is the $\nu \leftrightarrow \epsilon$ gap which decreases by $-0.4–0.6$ eV implying that DFT excitation energies to the $^3E$ and $^1E$ states of the higher configuration $u^3\nu^3\epsilon^2$ should be significantly smaller in $C_{42}H_{42}N^-$ than in bulk diamond. However the vertical excitation energies to the lowest $^1E$ and $^1A_1$ states should be adequate models of the same energies in bulk diamond, as the single-particle energies of $u, \nu$ and $\epsilon$ will tend to cancel out in states of the same configuration. This opens the way to future C.I. calculations of these difficult singlet levels.

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