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Assignment of ^{13}C hyperfine interactions in the P1-center in diamond

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ABSTRACT

Diamond is an attractive material due to its extreme physical properties, and has recently found a key role in the developing field of quantum bits based upon long spin coherence times at room temperature. In both natural and synthetic diamond, nitrogen is probably the dominant impurity, with the simplest configuration being substitution of a host carbon atom, which has a single unpaired electron. This defect, seen as the P1 paramagnetic resonance center, has been the subject of detailed experimental investigation, revealing the extensive interaction of the electron spin with nearby ^{13}C nuclei. The interaction between the electron and nuclear spins is not only of importance in determining defect structure, but is of technological importance, such as in the main decoherence mechanism for NV centers, so understanding the coupling between ^{13}C and the electron spin is of critical importance. In this paper we assess the assignment of hyperfine interactions to the various carbon sites in the vicinity of the nitrogen atom. We show that although the experimentally derived model is correct in the main, the best fit to the calculated data requires reassignment of at least one of the carbon sites.

1. Introduction

Diamond has a wide band-gap and a large breakdown field [1], high intrinsic carrier-mobility and optical transparency in the infrared region, which makes it interesting for applications such as high-temperature diodes, transistors that work in the microwave range, thermistors and radiation detectors [2,3]. Perhaps of greater significance is the rapid expansion of research into the use of diamond in quantum computing and long-distance quantum communication. Diamond is a scalable material solution in this field, with appropriately long coherence times [4]. The control and exploitation of coupling of the electron spin in which the quantum information is stored to other magnetic elements in the environment is a key challenge in development of quantum bits, with ^{13}C nuclei being the single most significant issue. Individual NV centers, which currently represent the main quantum center in diamond, can be optically spin polarized [5], but ^{13}C nuclear spins are the main factor limiting coherence time [6]. It is therefore imperative that we understand the hyperfine interactions between electron spins and nearby ^{13}C nuclei.

Perhaps the simplest electronic system for which such interactions have been examined extensively is isolated substitutional nitrogen impurities (N_s). The neutral charge state of substitutional nitrogen, N_s^0, is observed in electron paramagnetic resonance (EPR) as P1, with C_{3v} symmetry and an effective spin of $S = 1/2$. N_s^0 consists of a nitrogen atom bonded to three carbon neighbors, with the fourth, more distant, carbon neighbor being the site most associated with the unpaired electron. The unique, broken N–C bond has been calculated [7–10] to be between 24 and 32% longer than a host C–C bond. Chemically one can describe N_s^0 as a fully bonded N atom and a single carbon radical, and the electronic structure reflects this with the lone-pair orbital having an energy a little above the valence band top, and the carbon-radical occupied by one electron being in the upper half of the band gap. This chemical reconstruction drives the donor level deep into the band-gap (1.7 eV–2.2 eV below the conduction band minimum [11,12]). N_s^+ lies on-site, has T_d symmetry, and with no unpaired electrons is EPR-inactive. Similarly, negatively charged [13–15] centers, although resulting in a qualitatively similar structure to N_s^0, are also EPR-inactive. N_s is also observed via infrared absorption spectroscopy, exhibiting a maximum at 1130 cm^{-1} and a local mode at 1344 cm^{-1} [16,17], but it is the paramagnetic properties that form the focus of this study.

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The P1 center has been examined experimentally via EPR [18,20] and ENDOR [19,21]. In addition to the central N and carbon-radical sites, six other ^{13}C sites were resolved via the hyperfine interactions, and with a knowledge of the underlying geometry of the defect, these more distant carbon sites were assigned. However, one must be cautious with these assignments: although they are based upon a proximity argument combined with site symmetry and degeneracy, the low symmetries and uncertainties in the degeneracies mean that these assignments should be viewed as a plausible explanation. Fig. 1 shows the sites in the vicinity of the defect, labeled according to their distance from the defect. Table 1 lists the assignments from the experimental literature, including the labeling scheme used previously [18,19]. Of the seven carbon systems described by hyperfine interactions from experiment, $C_1 - -C_5$ have both the principal values and directions determined, with C_6 and C_7 being recorded only as an isotropic value. For these final two systems, it is unclear whether they represent nearly isotropic interactions or that the anisotropy is not resolved. It is also worth noting the uncertainty in the site degeneracies for C_5, C_6, and C_7 may be result from the relatively small interactions rendering quantification problematic, or perhaps, as we shall discuss later, it may arose from these spectra being due to two or more unresolved group of ^{13}C sites with similar interactions.

In this paper we present the results of first-principles quantum-chemical simulations of the P1-center, and compare the calculated N and ^{13}C hyperfine interactions with those from experiment. We show that although many of the experimental site assignments are probably correct, there is clear evidence to the contrary in others. We also show that it is not only the distance from the center of the defect that controls the magnitude of hyperfine interaction, but critically so does the connection via chemical bonding in the vicinity of the unpaired spin, as noted previously for other paramagnetic defects in diamond [22].

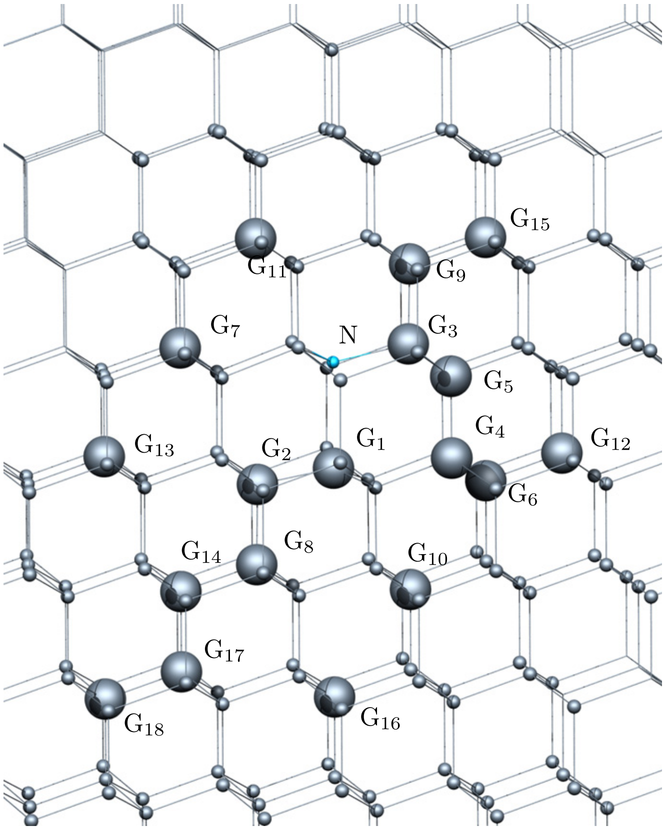

Fig. 1. Schematic of the P1-center in diamond labeling the C sites in the vicinity of the defect. G_1 labels the carbon radical, with $G_2 - -G_{18}$ being sites of increasing distance from the mid-point of the C–N broken bond. Labels indicate sites with a calculated RMS hyperfine value >1 MHz. All other sites for which the hyperfine has been calculated are shown with smaller spheres. The horizontal and vertical are [11$\bar{2}$] and [111], respectively, with a slightly tilted view used to allow all sites to be seen.

Table 1
Assignment of the seven ^{13}C hyperfine interactions resolved for the P1-center in diamond [18,19]. The a–g labeling system adopted previously are shown in parentheses to facilitate comparison. Also listed are the experimentally inferred site symmetries and site degeneracies, *n*.

	Site assignment			
Hyperfine	Ref. [18]	Ref. [19]	*n*	sym
C_1	G_1(a)	G_1(a)	1	C_{3v}
C_2	G_8(d)	G_8(d)	3	C_s
C_3	G_2(c) or G_3(b)	G_2(c)	3	C_s
C_4	G_2(c) or G_3(b)	G_3(b)	3	C_s
C_5	G_4(e) or G_5(g)	G_4(e) or G_5(g)	5.7 ± 0.6	C_1
C_6	G_9(f)		3.6 ± 0.6	–
C_7	G_4(e) or G_5(g)		8.4 ± 1.8	–

2. Computational method

Generalized-gradient-approximation density functional calculations were performed [23], using the AIMPRO code [24,25]. A Gaussian basis was used to expand Kohn-Sham Eigen functions [26] and a plane wave expansion of density and Kohn-Sham potential [27] was used to determine the matrix elements of the Hamiltonian, with a cut-off of 175 Ha, yielding well-converged total energies. Atoms were modeled using norm-conserving, separable pseudo-potentials [28]. The functions used are independent sets of *s*, *p* and *d* orbitals with four widths, amounting to 40 functions per atom.

The structure was optimized using a conjugate gradients scheme, with the optimized structures having forces on atoms of $< 10^{-3}$ au, and the final structural optimization step required to result in a reduction in the total energy of less than 10^{-5} Ha. The lattice constant and bulk modulus of pure bulk diamond have been calculated, with a 0.2% overestimate and 0.5% underestimated determined, respectively. The calculated value of the band-gap at 4.2 eV is close to previous calculations [29].

The P1-center was modeled using periodic boundary conditions, based upon the conventional unit cell of the diamond structure. For the results presented in this paper, a $4 \times 4 \times 4$ combination of 8-atom conventional cells is used, the system therefore containing 512 host sites. The Brillouin zone was sampled using a $2 \times 2 \times 2$ Monkhorst-Pack scheme [30], which yields a total energy converged to better than 1 μeV/atom.

The hyperfine interactions for ^{14}N and ^{13}C were modeled, using a systematic polynomial basis [31]. Briefly, hyperfine calculations combine pseudo-potentials and reconstructed all-electron wave functions in the core region [32,33]. Reconstruction of the ion cores allows us to calculate the hyperfine tensor elements within a frozen-core all-electron wave function approximation, without the computational difficulties associated with a full all-electron calculation [34]. This approach has been shown to be quantitatively accurate for other relevant defects in diamond [35–37], including substitutional-nitrogen pairs [10].

The nitrogen pair cases are particularly relevant to the current study, as the paramagnetic charged forms can be described as perturbed P1-centers. The six EPR centers (W24, N1, W7, M2, N4 and M3) exhibit hyperfine for the two N sites, and in the case of N1 ^{13}C hyperfine has also been experimentally resolved. Our calculated values [10] show very good agreement with both directions and magnitudes across all variations of the N-pair centers examined, both between the N-sites and in the case of N1, for the more distant ^{13}C sites, which are of the same order of the sites in the vicinity of the P1 center. N4 is quantitatively accurate and the theory correctly predicts the dynamical nature of site.