The foundations of the defect-molecule model of the N–V center in diamond

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Abstract

The negatively charged nitrogen-vacancy center in diamond is highly suited to many quantum information processing applications. Although the center has been comprehensively observed experimentally, there still remains contention regarding some of the key aspects of the current theoretical model of the center. In this article, the explicit development of the defect-molecule model of the center and the implications of the accumulated \textit{ab initio} results are discussed. The aspects of the model that require further \textit{ab initio} investigation are clearly identified and a possible Hartree-Fock extension is motivated.

Key words: Nitrogen-vacancy, Color center, Electronic structure

1. Introduction

The negatively charged nitrogen-vacancy (N–V\textsuperscript{−}) center in diamond is highly suited to a number of quantum information processing (QIP) applications [1, 2, 3]. The center has been empirically demonstrated to possess many of the desirable properties of a solid state spin qubit, including long-lived spin coherence [4], spin coupling [5] and optical spin polarization and readout [6]. The other key features of the center are a strong zero phonon line (ZPL) at 1.945 eV [7], a paramagnetic [8] and Stark [9] affected ground state triplet, a strain and Stark affected excited state triplet [10] and intermediate singlet states [11]. Recent experimental studies have also provided new information about the center’s excited state structure and its temperature dependence [12, 13, 14].

Seemingly at odds with the center’s well documented empirical properties, there still remains contention regarding some of the key aspects of the current theoretical model, which has been otherwise highly successful in describing many of the observed properties of the center. The
model [15, 16, 17] is developed using the framework of the ‘defect-molecule’ model of deep-level defects in semiconductors, which has been applied to similar defect centers in diamond [18, 19, 20] and silicon [21]. The essential character of the defect-molecule model is the ‘decoupling’ of the defect system from the host lattice and the application of semi-empirical molecular methods. The model has provided a good qualitative framework of the center’s electronic structure and spin properties, but has had difficulty in determining the energetic positioning and ordering of the key intermediate singlet states without empirical input. The recent studies of the temperature dependence of the center’s properties, which demand a clear picture of the center’s interaction with the host lattice, are expected to also highlight some of the weaknesses of the current model. Therefore, it appears that a thorough assessment of the fundamental development of the current model is necessary before the theoretical understanding of the N−V− center can advance.

The increasing number of ab initio studies of the center [22, 23, 24, 25, 26, 27, 28] provide the means to conduct such an assessment. However, given their current constraints, the ab initio methods will not alone be able to provide the complete and flexible model of the center’s electronic structure and dynamics that is desired for the QIP applications of the center. The ab initio methods are particularly suited to investigating the ground state of the crystal-defect system and, in doing so, locate the one-electron states introduced by the defect with respect to the host crystal’s band edges, evaluate the one-electron orbitals, account for correlation and exchange effects and also provide the lattice relaxation about the defect. The ab initio methods allow quantities such as hyperfine coupling constants [23, 25] and the ZPL optical polarization anisotropy [28] to be evaluated. A recent study has also produced the electronic and lattice relaxations associated with the excited triplet state [25]. Thus, the ab initio methods provide a detailed picture of the defect-lattice interactions and the defect one-electron states, but are limited in their scope to produce the center’s full electronic structure and spin properties.

In this article, we will discuss the explicit development of the defect-molecule model of the N−V− center and the implications of the accumulated ab initio results concerning the fundamental assumptions and approximations involved in the development. In doing so, aspects of the model that require further ab initio investigation will be clearly identified and the merit of a possible Hartree-Fock extension of the current model will be discussed.

2. Development of the defect-molecule model

Let us first place the defect-molecule model in context with the solid state theory of the complete lattice-defect system, by considering the following procedure [20]: (i) the defect electronic states are first constructed using a basis of highly localized molecular orbitals (MOs); (ii) the defect and lattice electronic states interact and relax into the electronic states of the entire lattice-defect system; and, (iii) the electronic relaxation is complemented by a lattice relaxation, resulting in the final states of the entire system.

It is clear that in applying the above procedure, adiabatic dependence between the lattice electrons and ions and the defect electrons and ions is implicitly assumed. A consequence of such adiabatic relaxations is the expectation that the highly localized states of the defect-molecule will diffuse into the surrounding lattice. The one-electron defect states which are close or within the host crystal’s conduction and valence bands become significantly dispersed as a result of the relaxations and form ‘resonant’ states of the defect [20]. Therefore, only deep-level defect electronic states will retain some highly localized character and thus be suitably described by the defect-molecule model.
Defining the system of the N−V−center to be the 6 ‘defect electrons’ (the 5 unpaired electrons of the atoms surrounding the vacancy and the additional electron assumed trapped from elsewhere in the lattice) and the 4 ‘defect ions’ (the nuclei and K-shell electrons of the vacancy’s nearest neighbor nitrogen and carbon atoms), the defect-molecule equations can be written down by assuming an adiabatic dependence of the defect electronic, $\Phi_n$, and ionic, $\chi_n$, states on some set of generalized lattice coordinates, $Q$, and by invoking the Born-Oppenheimer approximation to separate the defect electronic and ionic problems:

$$\hat{H}_{en}(r; Q)\Phi_n(r; Q) = E_n(r; Q)\Phi_n(r; Q)$$ (1)

$$\left(\hat{T}_{en}(R) + E_{en}(R; Q)\right)\chi_n(R; Q) = E_{en}(Q)\chi_n(R; Q)$$ (2)

where $r$ denotes the spatial and spin coordinates of the defect electrons, $R$ denotes the spatial and spin coordinates of the defect ions, $\hat{H}_{en}(r; R, Q) = \sum_i \hat{h}_i(r; R, Q) + \sum_{i>j} \hat{V}_{ee}(r_i, r_j)$ is the electronic Hamiltonian, $E_{en}(R; Q) = E_{en}(R) + \hat{V}_{NN}(R) + \hat{V}_{LM}(R; Q)$ is the electronic energy that forms the effective potential of the ionic problem, $\hat{V}_{ee}(r_i, r_j) = T_e(r_i) + V_{ee}(r_i, r_j) + \hat{V}_{le}(r_i; Q)$ is the one-electron kinetic energy and potentials, $V_{ee}$ is the electron-electron potential, $V_{ne}$ is the defect ion-electron potential, $\hat{V}_{NN}$ is the ion-ion potential, and $\hat{V}_{le}(r_i, Q) = \hat{V}_{lle}(r_i; Q) + \hat{V}_{lm}(r_i; Q)$ is the adiabatic effective potential of the host lattice. Note that in the zero-order Born-Oppenheimer approximation, the total defect state corresponding to the energy, $E_n(Q)$, is the direct product

$$\Psi_n(r; R, Q) = \Phi_n(r; R, Q)\chi_n(R; Q)$$ (3)

In defining (1) and (2), several severe approximations have been made, including: all the electron exchange and correlation interactions between the defect and lattice electrons have been discarded; the adiabatic dependence of the defect on the lattice coordinates enforces a weak and non-dynamic interaction; and, the dynamic interactions between the defect electronic and ionic states have also been discarded. In the current model [15, 16, 17], only the electronic problem (1) is considered using assumed $C_{3v}$ symmetric ground state ionic and lattice coordinates, and the self-consistent character of (1) and (2) is ignored. Clearly, the model is then constrained to the low-temperature/ small phonon-coupling limit and the possibly important and subtle effects of the ionic solutions are potentially missed. These effects may include the Jahn-Teller splittings of the excited electronic states and vibronically allowed transitions induced via non-symmetric ionic and lattice relaxations [29]. More obvious effects, such as the Stokes and anti-Stokes shift of the ZPL, have already been demonstrated through ab initio means [25, 27].

In order to apply the desired molecular methods, the one-electron approximation is applied to reduce (1) to a problem involving just the coordinates of one electron. In doing so, the many-electron state, $\Phi_n$, is approximated in the zeroth-order by a single Slater determinant, $\Phi_n^{(0)}$, of one-electron states, $\phi_n^\mu$. Applying the Hartree-Fock method, (1) reduces to the self-consistent set of one-electron equations of the general form [30]

$$\left(\hat{h}_\mu(r_1) + \sum_\beta \hat{J}_\beta^n(r_1) - \hat{K}_\beta^n(r_1)\right)\phi_n^\mu(r_1) = e_n^\mu \phi_n^\mu(r_1)$$ (4)

where the ground state defect ion and lattice coordinates have been adopted, the sum is over the occupied one-electron states for the given configuration, $n$, and the direct and exchange interactions between the one-electron states are explicitly included in the respective operators [30]

$$\hat{J}_\beta^n(r_1)\phi_n^\mu(r_1) = \int \phi_n^{\mu*}(r_2)\hat{V}_{en}(r_1, r_2)\phi_n^\mu(r_2)dr_2 \phi_n^\mu(r_1)$$ (5)
\[ \hat{K}^{\beta}_{\nu}(r_1) \phi^{\alpha}_{\nu}(r_1) = \left[ \int \phi^{\beta}_{\nu}(r_2) V_{ee}(r_1, r_2) \phi^{\alpha}_{\nu}(r_2) dr_2 \right] \phi^{\alpha}_{\nu}(r_1) \] (6)

By applying the one-electron approximation, defect electron correlations (other than exchange) have been neglected. In order to partially regain the correlations, configuration interactions between the zero-order many-electron states, \( \Phi^{(0)}_n \), must be considered. In the current model [15, 16, 17], configuration interaction is treated through a perturbative technique. However, the zero-order states used in the perturbative treatment are constructed from one-electron states that are not solutions to (4), but are rather approximate solutions to just \( \hat{h}_e \). This implies that the best zero-order approximations of the defect many-electron states are not being used in the consideration of configuration interaction and that the current model is constrained to small exchange and correlation interactions. Applications of the defect-molecule model to other defects [18, 21] have indicated that these many-body effects are important in determining the correct ordering of electronic energy levels. Consequently, these aspects of the current treatment may be the cause of the ambiguous energy orderings of the current model.

The approximate solutions of \( \hat{h}_e \) used in the current model [15, 16, 17], are direct products of MOs and spin-up/down angular momentum states. The four MOs of the current model are constructed by applying the LCAO method and symmetry considerations to a basis of tetrahedrally coordinated \( sp^3 \) orbitals, where the orbitals are directed towards the vacancy from each of the defect ions. The MOs represent good approximate solutions of the orbital components of \( \hat{h}_e \), but do not include the effects of one-electron spin-dependent interactions, such as spin-orbit and nuclear-electron spin interactions. These spin-dependent interactions as well as exchange, will couple the one-electron states and will potentially have significant implications for the construction of the many-electron states.

The above development of the defect-molecule model of the N\( -V^- \) center highlights the fundamental assumptions and approximations that require some form of assessment, so that the limitations of the model can be determined. It is also clear that in order to obtain the maximum amount of information from the defect-molecule framework, an extension that explicitly treats the spin-dependent, direct and exchange interactions of (4) is required. Such a Hartree-Fock extension will provide the best zero-order many-electron states for the consideration of configuration interaction and avoid the current constraints. As will be discussed in the next section, the ab initio studies conducted to date, provide some of the assessment of the model and further motivate the Hartree-Fock extension.

3. Implications of the \textit{ab initio} studies

The ab initio studies reported to date have applied density functional theory (DFT) methods to molecular cluster [22, 24, 26] and periodic defect (supercell) [23, 25, 27, 28] models of the center. The molecular cluster models treat the center and a chosen number of surrounding lattice atoms as essentially a large molecule, whereas the periodic defect models define periodic boundary conditions on a unit cell containing the center and lattice atoms, thereby effectively forming a diffuse lattice of defects [31]. Clearly both models are expected to converge to the ideal of an isolated center within an infinite lattice, as the number of lattice atoms surrounding the center increases in each [31].

The advantage of the molecular cluster model is that it produces defect electronic states which are directly comparable to the ideal case and the defect-molecule model [29]. However,
the model’s disadvantages include ambiguity in defining suitable boundary conditions and difficulty in determining the energetic positioning of the defect electronic states relative to the band structure of the host crystal [29]. The advantages of the periodic defect model are instead, clearly defined boundary conditions and energetic locations of the defect electronic states [31]. Its disadvantage being the inherent transformation of the isolated defect electronic states into defect bands, therefore, introducing ambiguity in their comparison with the ideal case and the defect-molecule model [31]. Thus, a complete understanding of the center and the assessment of the defect-molecule model requires the input of both models in order to mitigate the disadvantages of each.

The DFT methods reported thus far utilize the Kohn-Sham formulism [32], in which the total electron density of the ground state is determined by first solving a self-consistent set of one-electron equations to determine the one-electron states. As for the Hartree-Fock method discussed in the previous section, the many-electron ground state of the defect is approximated by a single Slater determinant of the one-electron solutions. However, unlike the Hartree-Fock method, the one-electron solutions approximately include the effects of correlations through the inclusion of the exchange-correlation potential in the one-electron equations [32]. This adoption of the one-electron approximation and the typical neglect of spin-dependent interactions in the Kohn-Sham formulism limits the DFT based \textit{ab initio} studies to just the consideration of the orbital properties of the center. A treatment of the spin properties of the center would require the introduction of spin-dependent interactions and the capability of representing the center’s many-electron states by linear combinations of Slater determinants.

The limitations of the current DFT methods suggests that a complete understanding of the center requires the integration of the \textit{ab initio} and defect-molecule models. The similar adoption of the one-electron approximation in both the Kohn-Sham and Hartree-Fock methods motivates the Hartree-Fock extension of the defect-molecule model, since such an extension would provide a more direct comparison between the \textit{ab initio} studies and the defect-molecule model at the one-electron level. This direct comparison would enable a more efficient integration of the two approaches to modeling the center.

Figure 1 contains examples of \textit{ab initio} results which are consistent across the \textit{ab initio} studies [24, 25, 26, 27, 28]. The band structure (Figure 1(b)) was produced by a recently reported periodic defect DFT model [28] and depicts a total of six defect one-electron states introduced deep within the band gap of the host crystal. These include four occupied defect one-electron states below the Fermi line and two virtual unoccupied one-electron states above the Fermi line. The orbital density iso-surface plot (Figure 1(a)) of one of the occupied states [28], clearly indicates that these deep defect states are indeed highly localized to the center and are well represented by linear combinations of \(s^3\) orbitals. On closer examination, it was found that the spin-up/down states of the lowest energy MO predicted by the defect-molecule model have merged deep within the valence band [28]. As expected, these states have been significantly dispersed through the lattice due to interactions with the lattice electronic states and therefore correspond to delocalized ‘resonant’ states of the center. The resonant nature of these states indicate that they do not contribute significantly to the observable properties of the defect [27].

The \textit{ab initio} orbital and band structure results have thus provided a means to confirm the symmetry and energy ordering of the one-electron states of the defect-molecule model. The highly localized nature of the deep defect electronic states determined by the \textit{ab initio} studies also enable a number of conclusions to be made regarding the fundamental assumptions of the defect-molecule model. Firstly, the localized nature indicates that the defect electronic states do indeed interact with a strong local potential attributable to the defect ions and a much weaker
Figure 1: Examples of *ab initio* results: the electron density plots of (a) the highest occupied spin-down MO; and, (b) the associated periodic defect band structure diagram, depicting the conduction and valence bands of the host crystal and the defect induced bands deep inside the band gap (zero energy indicates the Fermi line and state labels are as defined in [16]).
non-local potential corresponding to the lattice. Secondly, the significant energy localization of the defect energy levels in the band gap complements the state localization in implying that the defect electronic states do indeed only weakly interact with the lattice states and the neglect of exchange and correlation interactions between the defect and lattice electrons is justified.

The *ab initio* evaluations of the defect ion and lattice relaxations have determined that the equilibrium configurations corresponding to the ground and excited electronic triplet states are completely symmetric [25]. This indicates that the symmetry and energy splittings of these electronic states are not influenced by the associated ionic state, since only non-symmetric ionic states will introduce Jahn-Teller type splittings and other couplings. The lattice relaxations associated with the intermediate electronic singlet states should be the subject of future *ab initio* studies, since they may provide an insight into the mechanisms of the important inter-system crossings involved in the optical dynamics of the center. Furthermore, an *ab initio* study of the phononic structure of the center and lattice will complement a similar defect-molecule model development in providing an understanding of the phononic interactions between the center and the lattice as well as the temperature dependence of the center’s properties.

4. Conclusion

In this article we have discussed the explicit development of the defect-molecule model of the N−V− center and the implications of the *ab initio* results accumulated to date. In doing so we have identified the strengths and weaknesses of the defect-molecule and *ab initio* approaches and demonstrated that an integrated approach is necessary for a complete understanding of this important center to be achieved. In particular, the limitations of the current defect-molecule model and the methodology of current *ab initio* studies, both strongly motivate a Hartree-Fock extension of the defect-molecule model to enable an efficient integration of the two approaches. Given the points of contention of the current theoretical understanding of the center, the ionic states associated with the intermediate singlet states and the phononic structure of the center-lattice system were identified as the key future areas of the investigation for both approaches.

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References