Quantum Monte Carlo Study of the Optical and Diffusive Properties of the Vacancy Defect in Diamond

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Fixed-node diffusion quantum Monte Carlo (DMC) calculations of the ground and excited state energetics of the neutral vacancy defect in diamond are reported. The multiplet structure of the defect is modeled using guiding wave functions of the Slater-Jastrow type with symmetrized multideterminant Slater parts. For the ground state we obtain the ^1E state in agreement with experiment. The calculated energy of the lowest dipole allowed transition is consistent with the experimentally observed GR1 band, which has long been identified with the neutral vacancy in diamond, although no previous first-principles *ab initio* calculation of this transition exists. The calculated multiplet splitting of over 2 eV indicates the importance of a proper treatment of electron exchange and correlation in this system. DMC calculations of the formation and migration energy of the vacancy defect are presented.

The vacancy in diamond has been studied theoretically and experimentally for over 40 years. This defect is extremely important technologically, it being a dominant defect associated with radiation damage. It is also very interesting scientifically, with a wide variety of physical phenomena interacting in a way that is richer than its counterpart in silicon. A theoretical picture of the defect must account for many-electron correlation [1,2], for the coupling of the defect to the surrounding bulk, and also for Jahn-Teller distortion [3], with each of these effects being important [4].

The best-known optical transition, GR1 at 1.673 eV [5], long associated with the neutral vacancy, cannot be expressed as a transition between one-electron states, and, consequently, a demonstration that the vacancy gives rise to an optical transition at this energy has eluded first-principles approaches. Indeed, present approaches using density functional theory (DFT) are not able to unambiguously determine the ground state electronic structure of this defect center [6,7]. One aim of this work is to rectify this deficiency using accurate quantum Monte Carlo (QMC) methods.

A second motivation for this work is to demonstrate *a priori* the importance of many-electron effects in the treatment of this defect center in diamond. Two contrasting descriptions of the electronic structure of a vacancy exist. The one-electron picture emphasizes a large lattice distortion and is generally applied to the vacancy in silicon [8]. The alternative picture emphasizes many-electron effects and has generally been applied to the vacancy in diamond [1].

A further interesting feature is that we apply QMC simulations to a problem in condensed matter physics in which the strong electron-electron correlation results in DFT approaches being qualitatively incorrect. This contrasts with many of the previous applications of QMC in which only small (but still significant) quantitative improvements have been obtained to DFT. These QMC calculations yielded results in agreement with experiment for quantities such as the cohesive energy and optical gaps in solids [9,10], clusters [11,12], and molecules [13]. Also, in attempting to calculate the multiplet structure of a defect, we are required to calculate the energies of localized electronically excited states in a solid. This novel application is an interesting test of the applicability of QMC methods.

A final motivation stems from the potential importance of vacancies in mediating diffusion. Theoretical work based on the local density approximation (LDA) has suggested that self-diffusion in diamond is dominated by vacancies [14], which contrasts strongly with the case of silicon, where both vacancy and interstitial mediated self-diffusion are important. Since an understanding of self-diffusion in diamond is important for the goal of growing single crystal diamond thin films on nondiamond substrates, accurate calculations of the diffusive properties of the vacancy defect would be very useful. The accuracy of LDA calculations of the diffusive properties in these systems has been called into question recently by fixed-node diffusion Monte Carlo (DMC) calculations in silicon, which found formation energies for self-interstitial defects to be 1 to 2 eV larger than LDA results [15].

Such energy differences have a large effect on the self-diffusion constant D, since it depends exponentially on the defect formation energy E_f and the migration energy barrier E_m that must be overcome, i.e., $D = D_0 \exp[-(E_f + E_m)/kT]$. Measuring these energies accurately in a solid is very difficult. The vacancy formation energy has yet to be measured experimentally. The migration energy has been determined [16] by annealing diamond and measuring the decay of the GR1 optical absorption signal believed to be associated with the diamond vacancy. Uniaxial stress perturbations show that the GR1 transition is between a ground state, which is orbitally doubly degenerate with symmetry E, and an orbitally triply degenerate excited state of T symmetry [17]. Both the ground and excited states undergo Jahn-Teller relaxations, but the effects are dynamic during absorption and in this experiment the vacancy therefore appears to maintain the T_d point group of an atomic site in diamond [18]. There are further transitions at higher energies labeled GR2, GR3, etc., which are also related to the neutral vacancy although we will not consider them here.

The simplest model of the electronic structure of a vacancy is a one-electron molecular defect picture in which symmetry adapted combinations of the four dangling bond states have a_1 and t_2 symmetry. These levels are singly and triply degenerate, respectively. Four electrons are placed in these, giving a $a_1^2 t_2^2$ configuration for the neutral defect. This system is unstable to Jahn-Teller distortion and a spontaneous loss of symmetry occurs in which the t_2 states split into a doubly occupied a_1 and empty e state, resulting in a structure with D_{2d} symmetry. For the negatively charged defect, the distortion is to C_{2v} symmetry. Qualitatively similar behavior is seen in atomistic calculations of various degrees of sophistication and expense (see, for example, [6,19–21]), ranging from empirical approaches to DFT calculations in which the one-electron states have been calculated in an approach in which many-body effects have been incorporated in an average sense.

An alternative model concentrates on many-body interactions between electrons in the a_1 and t_2 states. In the original treatment [1], the matrix elements of the Coulomb interaction were treated as fitting parameters and it was found that configuration interaction effects had a large influence on the energy levels. If this is the case, the most popular contemporary approach based on the Kohn-Sham equations of DFT will not be able to give any insight beyond the qualitative positioning of the one-electron states. The same reasoning precludes GW self-energy calculations [22] as these will lead only to a shift in the positions of the one-electron states.

One approximate method for obtaining multiplet energies from DFT calculations has been suggested [23]. The assumption is that the energy of a DFT calculation in which the Kohn-Sham levels are occupied in a given configuration will be a linear combination of the multiplet

energies for which the configuration adopted forms part of the multideterminant wave function. This works reasonably well for the negatively charged vacancy in diamond, in which the energy of the ND1 optical band can be calculated with some accuracy [6], although for the neutral vacancy two multiplet states cannot be calculated [6,7], including what is believed to be the excited state of the GR1 band.

QMC techniques allow for a unified and accurate treatment of both the diffusive and the optical properties of the vacancy defect. The goal of this approach is the direct solution of the many-body Hamiltonian for a system of interacting electrons in the external potential from the ions. To model the diamond vacancy, we considered a periodically repeated simulation cell containing 53 atoms and 212 valence electrons. The core electrons are treated using a norm-conserving nonlocal pseudopotential. The positions of the ions were obtained from an LDA calculation in which each of the t_2 states were fractionally occupied. The nearest neighbor atoms of the vacancy were found to relax outwards by 0.1 Å, while the relaxation of the next nearest neighbors was negligible. Using a generalized gradient approximation (GGA) functional [24], we obtained atomic relaxations and structures in close agreement with our LDA results. The outward relaxation is understandable from a chemical point of view as it leads to the atoms surrounding the vacancy moving more into the plane of their three nearest neighbors, which introduces sp^2 bonding character. Because of the hardness of the pseudopotential required to model carbon atoms accurately, the orbitals were expanded in a Gaussian basis set, which gave an energy equivalent to using a plane wave basis set with an energy cutoff of 125 Ry.

Our guiding wave functions were of the Slater-Jastrow type with the single particle orbitals obtained from an LDA calculation. To calculate the multiplet structure of the electronic states of the vacancy, we used symmetrized multideterminants with the configuration in which the a_1 states were fully occupied and the t_2 states were doubly occupied. For example, for the $^1A_1$ state this linear combination of determinants was taken to be

$$\Psi = (D_\uparrow^x D_\downarrow^x + D_\uparrow^y D_\downarrow^y$$
$$+ D_\uparrow^z D_\downarrow^z) \exp\left[\sum_i^N \chi(\mathbf{r}_i) - \sum_{i<j}^N u(r_{ij})\right], \quad (1)$$

with x, y, and z labeling which of the three t_2 orbitals each determinant contains and N denoting the number of electrons. This restriction to the $a_2^2 t_2^2$ configuration means we can calculate the energies of the ^1E, $^1A_1$, $^3T_1$, and $^1T_2$ multiplets. Another observed state of the vacancy $^5A_2$ [25] is therefore beyond the scope of this calculation.

We used localized spherically symmetric functions for the single-body part of the Jastrow term (denoted by χ), each consisting of a polynomial containing 16 parameters. For the perfect crystal we used the same χ function for

each atom. The atoms in the vacancy structure are not all equivalent, and it was found beneficial to allow the χ functions on inequivalent atoms to differ. The parallel- and antiparallel-spin two-body part of the Jastrow term were constrained to obey the cusp conditions [26] and each contained eight parameters [27]. The values of the parameters were optimized by minimizing the variance of the energy [28,29]. At the variational Monte Carlo (VMC) level this wave function retrieves in excess of 89% of the fixed-node DMC correlation energy in diamond. The "Coulomb finite size effects" [30] were found to be small, and we corrected for the residual "single-particle" finite size effects using the results of LDA calculations.

Figure 1 shows the results of DMC calculations of the energies of the states. Our VMC results are consistent with these more accurate DMC calculations. We obtain the orbitally doubly degenerate ^1E state as the ground state, in agreement with experiment. The transition energy between the ^1E state and the $^1T_2$ excited state was calculated to be 1.51(34) eV in DMC. The experimental value of 1.673 eV for the GR1 band lies within the statistical error bars of our DMC value. This transition is the lowest energy electronic excitation from the ground state which is spin and orbitally dipole allowed. In an independent electron picture, such as an LDA calculation, with a fixed ground state charge density, these four states would all have the same energy. The large multiplet splitting of over 2 eV shows the importance of a proper treatment of exchange and correlation in this system.

Semiempirical defect molecule calculations have predicted that the $^3T_1$ state lies within a few tenths of an eV above the ground state. Since this spin-polarized state has not been observed in high temperature electron paramag-

netic resonance measurements, it must lie at least 0.2 eV above the ground state [31], which is consistent with our DMC results. A molecular defect model of the vacancy [4] with parameters chosen to fit the experimentally observed values of the GR1 and ND1 transition energies (the latter occurring in the negatively charged vacancy) yields energies for the states $^3T_1$, $^1T_2$, and $^1A_1$ above the ^1E of 0.2, 1.7, and 1.6 eV, respectively. These numbers are consistent with our DMC results within the statistical error bars, except for the $^1A_1$ state which we compute to be 2.69 eV above the ^1E state in DMC. It should be noted that earlier modeling [31] suggested a much lower energy for this $^1A_1$ state and another model [32] based on the Coulson-Kearsley model produced a different ordering of the triplet states. This older work is clearly not consistent with the results presented here.

Typically, the magnitude of the vacancy formation energy in a covalent semiconductor correlates with the size of the cohesive energy since both depend on the strength of the covalent bonds. Therefore, an approach which yields an accurate measure of the cohesive energy should give a reliable prediction of the vacancy formation energy. We computed the cohesive energy of diamond within DMC by performing calculations for the atomic ground state and for the perfect solid using a 54-atom simulation cell. For the energy of the solid we added a correction for the zero-point energy of 0.18 eV per atom, a correction for independent finite size effects (k-point sampling) of -0.28 eV per atom obtained from LDA calculations, and a Coulomb finite size correction which we estimated to be 0.222 eV by performing a DMC total energy calculation with a 250-atom simulation cell in diamond-structure silicon and scaling the result by the ratio of the lattice constants of diamond and silicon. The resulting DMC cohesive energy of 7.346(6) eV per atom is in good agreement with the experimental value of 7.371(5) eV per atom [33]. In contrast, an LDA pseudopotential calculation yields a cohesive energy of 8.61 eV [34].

Table I lists our computed vacancy formation and migration energies using LDA and DMC. We have included the estimated 0.36 eV Jahn-Teller relaxation energy for the vacancy in our computed values [6]. Each of our DMC values includes a correction for finite size effects obtained from LDA calculations using a simulation cell twice as large as that used in our DMC calculations.

$^1A_1$ ———— 2.69 +− 0.33

$^1T_2$ ———— 1.51 +− 0.34

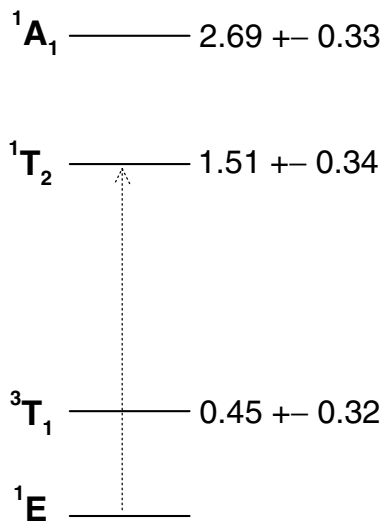**$^3T_1$** ———— 0.45 +− 0.32

^1E ————

FIG. 1. The computed DMC energies in eV with statistical errors of the four lowest symmetry states of the neutral diamond vacancy, obtained with the single particle a_1 states being occupied. The dotted arrow indicates the lowest spin and orbitally dipole allowed transition from the ground state.

TABLE I. Formation and migration energies for the neutral diamond vacancy in eV calculated with the LDA and DMC methods, with DMC statistical error bars shown. The experimental value [16] of the migration energy with error bar is included.

	LDA	DMC	Experiment
Formation energy	6.98	5.96(34)	...
Migration energy	2.83	4.40(36)	2.3(3)

Our LDA formation energy is in very close agreement with an LDA value of 6.97 eV previously published in the literature [20]. Our DMC formation energy indicates that it is approximately 1 eV more favorable to form a neutral vacancy in diamond than predicted by the LDA. An approach that had been used in the past [14] to find the migration energy within the LDA assumed that the diffusion path involves an atom moving in a straight line from a site neighboring the vacancy to the vacancy site while the surrounding atoms relax at each step. The saddle point was assumed to lie midway between the substitutional sites. Inspection reveals that this has D_{3d} symmetry with the e state containing two out of a possible four electrons, which is unstable to Jahn-Teller distortions. Including atomic relaxations within LDA we found a lower energy diffusion path in which the saddle point moves off axis by 0.4 Å in the plane perpendicular to the line joining two atoms, splitting the e state and breaking the degeneracy. Since a diffusion path with an even lower energy could exist, the DMC migration energy given in Table I is expected to be an upper bound on the true value. There is an additional effect which may mean that our bound on the migration energy is high; the degeneracy of the electronic states at the saddle point of the straight line path indicates that the energy might be lowered by considering a multideterminant wave function. We believe, however, that computing the atomic structure within QMC (which is currently computationally unfeasible) will not change our results much, since LDA and GGA both give very similar structures.

QMC provides a unified and accurate treatment of both the ground and excited state energetics of the vacancy defect in diamond. The calculated energy of the lowest dipole allowed transition is consistent with the experimentally observed GR1 band, which has long been identified with the neutral vacancy in diamond, although there had been no previous first-principles calculation of this transition energy. The calculated multiplet splitting of over 2 eV indicates the importance of a proper treatment of electron exchange and correlation.

We offer a prediction of the vacancy formation energy, which has yet to be measured. Our value shows a small but significant reduction in the value calculated within DFT, again illustrating the importance of a more accurate quantitative treatment of many-electron effects. Our calculation of the energy of the GR1 band also suggests that the energies of optical transitions associated with defects in solids can be obtained using the QMC approach using multideterminant forms of excited state trial wave functions. QMC techniques are therefore applicable to a wide range of real materials and hold great promise as an accurate computational method to enhance our understanding of the nature of defects in solids.

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