**Ab initio** calculation of spin-orbit coupling for NV center in diamond exhibiting dynamic Jahn-Teller effect

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Point defects in solids may realize solid state quantum bits. The spin-orbit coupling in these point defects plays a key role in the magneto-optical properties that determine the conditions of quantum bit operation. However, experimental data and methods do not directly yield this highly important data, particularly, for such complex systems where dynamic Jahn-Teller (DJT) effect damps the spin-orbit interaction. Here, we show for an exemplary quantum bit, nitrogen-vacancy (NV) center in diamond, that **ab initio** supercell density functional theory provides quantitatively accurate prediction for the spin-orbit coupling damped by DJT. We show that DJT is responsible for the multiple intersystem crossing rates of NV center at cryogenic temperatures. Our results pave the way toward optimizing solid state quantum bits for quantum information processing and metrology applications.

Dopants in solids are promising candidates for implementations of quantum bits for quantum computing [1, 2]. In particular, the negatively charged nitrogen-vacancy defect (NV center) in diamond [3] has become a leading contender in solid-state quantum information processing because of its long spin coherence time (up to several milliseconds in ultra-pure diamonds [4]) and ease of optical initialization and readout of spin state,[5] even non-destructively [6, 7]. NV center consists of a nitrogen atom substituting a carbon atom in the diamond lattice adjacent to a vacancy with forming a C₃v symmetry that dictates the selection rules for the magneto-optical processes [Fig. 1(a)]. The geometry and the electronic structure of NV center in diamond have been discussed previously based on highly converged **ab initio** plane wave large supercell calculations [8, 9]. The defect exhibits a fully occupied lower a₁ level and a double degenerate upper e level filled by two parallel-spin electrons in the gap with comprising an S = 1 high-spin ground state [Fig. 1(b)]. The high-spin 3⁢E excited state can be well-described by promoting an electron from the lower defect level to the upper level in the gap [10]. Between excited state and ground state triplets dark singlets appear that can selectively flip ⁢mₜ = ±1 states to mₜ = 0 state in the optical excitation cycle [11–15], i.e., the electron spin can be spin-polarized optically [Fig. 1(c)]. The spin-selective decay is predominantly caused by the intersystem crossing (ISC) between the optically accessible triplet 3⁢E excited state [see Fig. 1(c)] and the singlet ¹⁰⁰A₁ state which is mediated by the spin-orbit coupling between these states and phonons [14, 15]. Generally, the spin-orbit coupling plays a crucial role in the optical spin-polarization and readout of NV quantum bit (qubit) and alike [16–20].

The strength of the spin-orbit coupling in NV center may be detected at low temperature photoluminescence excitation (PLE) measurements of the 3⁢E excited state in high quality diamond samples [21] where the strain does not deteriorate the fine spin level structure of the 3⁢E excited state [14]. By combining the PLE data and group theory analysis, the spin-orbit strength was estimated to be 5.33±0.03 GHz [21, 22] recorded at T < 20 K temperatures. We note that additional splitting and shift of the levels appear due to electron–electron–spin interaction [14] that is not discussed further here. Regarding the spin-orbit mediated ISC process, three different ISC rates have been recently deduced in the experiments [23]. This is surprising because group theory [14] predicts only a single decay channel from the A₁ substate of the 3⁢E triplet. This phenomenon was qualitatively explained by assuming weak coupling of symmetry breaking acoustic e phonons to the A₁, E₁, and A₂ substates that was derived in the frame of perturbation theory of electron-phonon coupling [23, 24]. Nevertheless, this theory does not quantitatively account on the experimental ratio between the ISC rates at cryogenic temperature.

Deep understanding of the nature of 3⁢E excited state might resolve this issue. **Ab initio** simulations [25] and experiments [26–28] imply that the 3⁢E excited state exhibits dynamic Jahn-Teller (DJT) effect where the vibronic levels split in 10 meV region [25]. This is more than three orders of magnitude larger than the observed spin-orbit coupling, thus spin-orbit coupling can be considered as a perturbation with respect to the DJT effect. In DJT systems, the phonons and orbitals are strongly coupled that goes beyond perturbation theory of electron-phonon coupling. That may lead to the damping or even quenching of spin-orbit coupling [29] where the damping parameter, i.e., the Ham reduction factor depends on the strength of electron-phonon coupling. For this reason, the strength of the intrinsic spin-orbit coupling in NV center is still an open question. In addition, the presumably strong electron-phonon coupling in 3⁢E state may have implications in the ISC process of NV center.

Here we show by **ab initio** supercell density functional theory (DFT) calculations that the intrinsic spin-orbit coupling together with the damping caused by DJT can be accurately predicted for NV center in diamond. We show that strong electron-phonon coupling in the triplet excited state is an important aspect of the theory of non-radiative decay in NV center, and this novel theory accurately reproduces the ratio between the experimental ISC rates.

We apply supercell plane wave spin-polarized density functional theory (DFT) method to model the defect with the usual Born-Oppenheimer approximation. The Born-Oppenheimer approximation
The spin-orbit coupling (SOC) was calculated within non-collinear approach as implemented in VASP 5.4.1 (see ref. 39). In our particular cases, the \( C_{3v} \) axis of the defect set the quantization axis of the spin that fixed in the calculation. As SOC is a tiny perturbation to the system we also fixed the coordinates in SOC calculations as obtained from the spin-polarized DFT calculations. Direct comparison to the experimental data can be extracted from the \( z \) component of SOC which coincides with the quantization axis of the spin, thus it is the diagonal term in the matrix elements representing the different components of SOC. The spin-orbit scattering rate, however, can be calculated from the \( \lambda \) components that are off-diagonal terms in the SOC Hamiltonian. SOC was calculated in the high symmetry configurations of NV\((-\) center. In this case, a single electron should occupy the double degenerate Kohn-Sham \( e \) state in the spin minority channel. After applying SOC this double degenerate Kohn-Sham state will split to \( e_x \) and \( e_y \) states. By using \( \Delta \text{SCF} \) procedure it is feasible either to occupy the \( e_x \) or \( e_y \) state, and the calculated total energy difference is the strength of SOC. We find that the half of this total energy difference is equal within \( 10^{-7} \) eV to the split of \( e_x \) and \( e_y \) Kohn-Sham levels when these two states are occupied by half-half electrons. Thus, the strength of SOC can be calculated by the half-half occupation of the \( e \) states with following the SOC splitting of these \( e \) states. It is crucial to use \( \Gamma \)-point approximation in the integration of the Brillouin-zone in this procedure because the degenerate \( e \) orbitals slightly split in other \( k \)-points by reducing the symmetry of the orbitals that makes the readout of the SOC parameters ambiguous. We further note that \( \langle \mathbf{3}E|H_{SO}|\mathbf{3}E(\mathbf{A}_1)\rangle = \frac{1}{2}\langle e_+|H_{SO}|e_+ \rangle \) and \( \langle \mathbf{3}E|H_{SO}|\mathbf{1}A_1\rangle = \frac{1}{\sqrt{2}}\langle e_+|H_{SO}|e_+ \rangle \) for NV\((-\) defect where the latter is valid with the two basic assumptions described below in the discussion of ISC rates. Here the arrows represent the corresponding spin states and \( |e_\pm \rangle = \frac{1}{\sqrt{2}}[|e_x \rangle \pm i|e_y \rangle] \). We note that we calculated SOC for the considered defects by Perdew-Burke-Ernzerhof (PBE) DFT functional [40] too for test purposes that is a significantly faster method than the HSE06 DFT method. In that case we used PBE optimized lattice constants and defect geometries.

First, we consider the spin-orbit splitting \( \lambda_2 \). Batalov and co-workers deduced a value of 5.3 GHz for this spin-orbit coupling (SOC) from PLE measurements [21] observed at 6 K temperature. We study this interaction by our \textit{ab initio} method. The convergent SOC was achieved with scaling supercell size up to 1000-atom in the hybrid functional calculations and apply an exponential fit to the calculated results (see Ref. 34). The calculated \( \lambda_2 \) for the \( \mathbf{3}E \) state of NV\((-\) is 15.8 GHz which is about 3\( \times \) larger than the measured one. However, the \( \mathbf{3}E \) excited state is principally Jahn-Teller unstable in the high \( C_{3v} \) symmetry that can lead to partial or full quenching of the spin-orbit coupling [29].

We conclude that the spin-orbit coupling should be stud-
ied beyond Born-Oppenheimer approximation. $^3E$ state is orbitally degenerate where a symmetry breaking $e$ phonon or quasi-local vibration mode can drive out the system from the high symmetry that may couple the components of the double degenerate $E$ electron wavefunctions. This is a so-called $E \otimes e$ mixing related terms. The electrons are represented by the Pauli matrices $\sigma$. $F$ and $G$ can be directly derived from the calculated APES which results in the Jahn-Teller energy ($E_{JT}$) and the barrier energy $\delta_{JT}$ between the global minima (see Fig. 2) as follows: $E_{JT} = \frac{F^2}{2\hbar \omega_e}$, $G = \delta_{JT} \hbar \omega_e/2E_{JT}$. The $\hbar \omega_e$ energy can be derived from the parabola fitting to the calculated APES. Finally, all the parameters can be readout from APES (see Table I) that allows to solve Eq. (1) numerically that provides the electron-phonon coupling coefficients [34]. The exact solution can be expanded into series as $|\Psi_{\pm}\rangle = \sum_{nm} [c_{nm} |E_{\pm}\rangle \otimes |n, m\rangle + d_{nm} |E_{\mp}\rangle \otimes |n, m\rangle]$, where we limit the expansion up to four oscillator quanta ($n + m \leq 4$) which is numerically convergent within 0.2%. The $p$ reduction factor that reduce the spin-orbit interaction can be then calculated from these coupling coefficients as $p = \sum_{nm} [c_{nm}^2 - d_{nm}^2]$ which represents the mixture of the $E^+$ component with the $E^-$ component of the $^3E$ state that results in the quenching of the effective angular momentum. We note that by taking only the linear term either numerically or approximately [41] results in 10% lower value for the damping factor (see details in Ref. 34).

The calculated quenching factor is large that can strongly modify the intrinsic (purely orbital) value. The final result is 4.8 GHz that agrees within 10% with the experimental result (see Table I). Despite the remaining discrepancy between the calculated and measured SOC, the improvement is giant in SOC when DJT effect is considered that demonstrates the complex physics of this system. We emphasize that this result was obtained from first principles calculations in the micro-electronvolt energy region of SOC.

We turn to the investigation of the ISC process which depends on the perpendicular component of the spin-orbit coupling, $\lambda_{\perp}$ [14, 15]. The ISC rate between the triplet $^3E$ and $^1A_1$ may be calculated [23] as

$$\Gamma_{A_1} = 4\pi \hbar \lambda_{\perp}^2 F(\Delta),$$

where $\lambda_{\perp}$ is given in rad/s unit and $F$ is the energy dependent density of states multiplied by the overlap of the vibrational states of $^3E$ and $^1A_1$ electronic states, and $\Delta$ is the energy gap between $^3E$ and $^1A_1$ states. Here, we follow the convention in Ref. 23 for the definition of $\lambda_{\perp}$. We note that Eq. 2 implicitly assumes that the electronic states of $^3E$ and $^1A_1$ participating in the ISC process do not change their character during the motion of nuclei, i.e., the $\lambda_{\perp}$ remains fixed independently from the coordinates of the atoms. This assumption is an analog to the Condon approximation on the optical excitation of polyatomic systems that we call basic assumption (i). This theory can explain the ISC process from $A_1$ state.

We demonstrate below that by invoking the DJT nature of $^3E$ triplet state, the three ISC rates at cryogenic temperatures...
[23, 24] can be naturally explained. To this end, we express the four \( m_s = \pm 1 \) electron-phonon coupled \( 3E \) wave functions in the Born-Oppenheimer basis of symmetry adapted terms, \( |\tilde{A}_1\rangle, |\tilde{A}_2\rangle, |\tilde{E}_1\rangle, |\tilde{E}_2\rangle \) (see Supplemental Materials). The symmetry adapted basis allows us to determine the phonon-induced or DJT induced mixing of electronic orbitals between the \( m_s = \pm 1 \) states. One can realize that degenerate \( |\tilde{E}_1\rangle \) and \( |\tilde{E}_2\rangle \), and \( |\tilde{A}_2\rangle \) vibronic wave functions contain the \( |A_1\rangle \) electronic orbital which makes the spin-orbit mediated scattering to the \( ^1A_1 \) singlet state feasible. This explains the three different ISC rates even at cryogenic temperature. By taking the vibronic nature of these \( m_s = \pm 1 \) states into account, the corresponding ISC rates can be written as

\[
\Gamma_{A_1} = 4\pi \hbar \lambda_1^2 \sum_{i=1}^{\infty} \left[ c_i^2 F \left( \Delta - n_i \hbar \omega_c \right) \right],
\]

\[
\Gamma_{E_{12}} = 4\pi \hbar \lambda_3^2 \sum_{i=1}^{\infty} \left[ \frac{d_i^2}{2} F \left( \Delta - n_i \hbar \omega_c \right) \right],
\]

\[
\Gamma_{E_2} = 4\pi \hbar \lambda_4^2 \sum_{i=1}^{\infty} \left[ f_i^2 F \left( \Delta - n_i \hbar \omega_c \right) \right],
\]

where \( c_i, d_i \) and \( f_i \) expansion coefficients are calculated \textit{ab initio} by solving the electron-phonon Hamiltonian, and \( n_i \) is the quantum number of the phonons of \( ^1A_1 \) electronic state.

Here, we still applied the basic assumption (i) in the ISC process but we explicitly consider the DJT nature of \( 3E \) state. We found that \( f_i^2 \) is very small (see Supplemental Materials), thus \( \Gamma_{A_1} \) is two orders of magnitude smaller than \( \Gamma_{A_1} \) or \( \Gamma_{E_{12}} \), in agreement with the experiment. The ratio of \( \Gamma_{E_{12}}/\Gamma_{A_1} \) requires the explicit calculation of \( F \) function that depends on \( \Delta \) and the overlap of phonon states of the electronic states. As the value of \( \Delta \) is unknown we use it as a parameter. The theoretical upper limit of \( \Delta \) can be calculated from the ZPL energies of the visible and near-infrared (NIR) optical transitions [44] that results in \( \Delta < 0.75 \text{ eV} \) which ensures that the \( 1E \) singlet level is above that of \( ^3A_2 \) groundstate. Regarding the overlap of phonon states, we apply the Huang-Rhys approximation to calculate this quantity that is within our assumption (i) but further assumes that the parabolic APES of the electronic states so the phonon energies and states are the same in the two electronic states involved in ISC. This Huang-Rhys approximation was already implicitly employed by using \( \omega_c \) in Eqs. 3-5 where the value \( \hbar \omega_c \) can be read in Table I. As the ISC occurs between \( 3E \) and \(^1A_1 \) states, the optimized geometry of these states are required in the calculation of their phonon overlap function that is characterized by its \( S \) Huang-Rhys factor (see Supplementary Materials). However, Kohn-Sham HSE06 DFT cannot explicitly calculate the \(^1A_1 \) state. An upper bound theoretical limit on the \( S \) factor can be taken from the geometry change between the \( ^3A_2 \) groundstate and \( 3E \) excited state where the DJT feature in \( 3E \) geometry should be eliminated. Our calculated

\[ S \]

factor for this optical transition agrees well with the value deduced from the experimental PL spectrum of NV(–) [see Fig. 3(b)] that confirms the accuracy of our \textit{ab initio} approach [45]. By eliminating the DJT feature in the phonon overlap function, we find \( S = 3.11 \) [see Fig. 3(c)]. By assuming that the geometry of the \(^3A_2 \) groundstate and the \(^1A_1 \) singlet is the same because of sharing the same \( e^2 \) electronic configuration, \( S = 3.11 \) can be a theoretical upper bound limit. However, sharing the same \( e^2 \) electronic configuration does not guarantee the same optimized geometries for \(^3A_2 \) and \(^1A_1 \) and \( 1E \) singlets. Indeed, NIR PL and absorption studies found \( S = 0.9 \) for the \(^1A_1 \leftrightarrow 1E \) optical transition in NV(–) [44], thus the geometries of the two singlets differ. We conclude that it is not well supported to assume that the geometries of \(^1A_1 \) and \(^3A_2 \) are exactly the same. Therefore, we roughly approximate the geometry of \(^1A_1 \) state from \( (e_x e_y) \) singlet spin-polarized HSE06 DFT calculation. We find \( S = 2.61 \) with this procedure that reflects a small change in the geometry [see Fig. 3(c)]. The final result on the ratio of \( \Gamma_{E_{12}}/\Gamma_{A_1} \) as a function of \( \Delta \) is plotted in Fig. 3(a). As can be seen the \( S = 3.11 \) curve implies too large \( \Delta \) values going above the theoretical upper limit in a wide region when the experimental ratio is reproduced. On the other hand, \( S = 2.61 \) curve mostly provides reasonable \( \Delta \) values. This implies that \( S \) should be indeed significantly smaller than that of \( S = 3.11 \) derived from the groundstate geometry.

In order to calculate the ISC rates, \( \lambda_{\perp} \) should be determined. Unlike the case of \( \lambda_{\parallel} \), one has to apply an approximation to do this, namely, that the Kohn-Sham wave functions building up the \( 3E \) state and the \(^1A_1 \) multiplet do not
change. This is basic assumption (ii) in the ISC rate calculation which permits to compute $\lambda_\perp$ ab initio by using the $a_1$ and $e_{x,y}$ Kohn-Sham wave functions of the NV($-$) in the $^3E$ excited state [see Fig. 1(b)]. The converged intrinsic value is $\lambda_\perp = 56.3$ GHz which is relatively large, and it is not damped by DJT because $^1A_1$ state is not the part of DJT effect. We note that the nitrogen contribution is minor in $\lambda_\perp$ whereas it is significant in $\lambda_z$ that explains the large anisotropy between $\lambda_z$ and $\lambda_\perp$. With these $\lambda_\perp$, $S$ factors and reasonable $\Delta$ values in Fig. 3(a), we obtain an order of magnitude larger ISC rates than the experimental ones at $\Gamma_{A_1} = 16.0$ MHz and $\Gamma_{E_{1,2}} = 8.3$ MHz [23]. We conclude that $\lambda_\perp$ might be too large. We suspect that the large $\lambda_\perp$ is the consequence of the two basic assumptions, particularly, of assumption (ii). The exact determination of $\Delta$ and $\lambda_\perp$ requires an accurate $ab$ initio calculation of the $^1A_1$ multiplet state as a function of configuration coordinate of NV($-$) center. That would make possible a full $ab$ initio calculation of the ISC rates. Finally, we emphasize here that the ratio of the low-temperature multiple ISC rates is quantitatively reproduced by our DJT theory.

In conclusion, we demonstrated on NV center in diamond that the spin-orbit coupling can be well calculated from $ab$ initio methods in dynamic Jahn-Teller systems. We implemented and applied a method to calculate the damping factor on spin-orbit coupling caused by DJT effect from first principles. Our theory revealed that the strong coupling between electrons and phonons is responsible for the multiple scattering rates at cryogenic temperatures. Our results demonstrate the power of $ab$ initio modeling of this complex system that can be applied to other solid state qubits, in order to predict their key properties (electron-phonon coupling and spin-orbit coupling) that determine their initialization and readout.

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