Spin tunneling in the diamond color center coupled to the $P1$ center

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The spin-1 carried by the nitrogen-vacancy (NV^-) color center of a diamond is a promising candidate as a quantum bit (qubit) for the realization of a solid-state quantum computer. The interaction with the $P1$ center, which is a single substitutional nitrogen atom with spin-$\frac{1}{2}$, converts the NV^- qubit to a multilevel system. The 18-level energy diagram of the NV^--$P1$ coupled defect pair exhibits several level anticrossings and the spin functions change sign at different values of the applied magnetic field. Beyond each resonance, the two electronic spins of the coupled triplet-doublet system flip individually or in concert, offering possibilities to implement quantum logic gates. Interlevel transitions are also possible. The transition probabilities can be predicted rigorously in the framework of the Landau-Zener theory. The spin flip occurs by quantum tunneling. It is also possible to introduce geometric phases, which can be useful for the realization of phase gates.

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Introduction. Various solid-state systems have already been proposed for implementing a quantum computer with electronic or nuclear spins such as quantum bits (qubits) and logic gates.[1] Their main advantage is scalability and their main drawback is the coupling of the qubits to other degrees of freedom of the solid-state system. We show here that this difficulty can be overcome in the case of nitrogen-vacancy (NV^-) color centers of diamonds, which are very promising candidates for a spin-based solid-state quantum computer. The NV^- color centers have several remarkable properties which are fundamental in quantum-information processing (QIP).[2]

The negatively charged NV^- defect has an ^3A ground state with a spin-1. It can interact with other spin impurities and in particular the $P1$ center, which is a single substitutional nitrogen atom with a spin-$\frac{1}{2}$. The addition of the hyperfine interaction (HF), due to the coupling of the electronic and nuclear spins of the $P1$ center, converts the NV^- qubit to a multilevel system. Under the influence of an external magnetic field, the spin functions undergo π phase shifts, or equivalently change sign, while the 18-level energy diagram exhibits several level crossings (LC) and anticrossings (LAC). Beyond a resonance, the two electronic spins carried by the coupled defect pair can flip independently or in concert, offering possibilities to implement quantum logic gates. Interlevel transitions without spin flip are also possible. The spin flips are achieved by a kind of quantum tunneling, similar to that observed in single molecule magnets with a large spin ($S \geqslant 10$) such as Mn_{12} (Ref. 3) and Fe_8 (Ref. 4). To our best knowledge, it is the first time that such quantum tunneling is observed in a low-spin system ($S = \frac{3}{2}$).

We have organized the manuscript as follows. First, we apply the effective spin Hamiltonian formalism to obtain the Zeeman energy diagram and the spin functions of the coupled triplet-doublet system. Second, we show the link between this formalism and the static aspect of the Landau-Zener (LZ) theory[5,6] of a magnetically driven two-level system. The latter is then applied for studying the LAC observed at about 520 G and for which some experimental results exist.[7,8] Third, exact transition probabilities of the initially prepared spin system are obtained and discussed in the framework of the time-dependent LZ theory.

Effective spin Hamiltonian. For a coupled triplet-doublet system, the effective spin Hamiltonian can be written as follows:[9,10]

$$\mathcal{H}_1 = D\left[\left(S_z^{NV}\right)^2 - \tfrac{1}{3}(S^{NV})^2\right] + S^{NV} J S^N, \qquad (1)$$

where $S^{NV(N)}$ are the electron spin operators. The eigenvalues of their z component is noted as $m_S^{NV(N)}$. $D = 2.88$ GHz is the zero-field splitting of the triplet, that is, the gap between the energy level $m_S^{NV} = 0$ and the twofold degenerate level $m_S^{NV} = \pm 1$. The fine-structure tensor J describes the interaction between the triplet and the doublet. Its nonzero elements are:[9]

$$J_{yy} = \xi\left(1 - \frac{3y^2}{r^2}\right),\ J_{zz} = \xi\left(1 - \frac{3z^2}{r^2}\right),\ J_{yz} = -\xi\frac{3yz}{r^2}, \qquad (2)$$

with $\xi = J_{xx} = g^2\beta^2/r^3$ and $J_{zy} = J_{yz}$. g is the isotropic electronic g factor, β the Bohr magneton, and r the distance between the two defects. y and z are the Cartesian coordinates of the $P1$ center. The NV^- defect is lying along the z axis, which is parallel to the $\langle 111\rangle$ crystallographical direction of the diamond structure. The origin is halfway from the vacancy and the nitrogen atom.

The six-dimensional energy matrix is obtained by rewriting Eq. (1) in the basis $\{|m_S^{NV} m_S^N\rangle\}$, which is the tensor product of the triplet basis $\{|m_S^{NV}\rangle\}$ and the doublet basis $\{|m_S^N\rangle\}$. The effect of the J coupling is to lift the twofold degeneracy of the energy level $m_S^{NV} = \pm 1$ (see Fig. 1). The separation depends on the relative position of the two defects but does not exceed 328 MHz ($r \geqslant 5.4$ Å). This gap will modify somewhat the positions and the number of the LACs in the Zeeman diagram. The relative position of the two defects will be probably different from one sample to another (see Ref. 7). With a $P1$ defect placed at a distance $r = 12.12$ Å from the NV^{-1} defect, the known LACs are well positioned.[7,10,11] The second polar coordinate, measured from the z axis, is equal to 106°. Clearly, if the origin of the coordinate framework is placed at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ with respect to the cubic crystallographic axes, the nitrogen atom will be at (0, 0, 0), the vacancy at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, and the $P1$ defect at $(2,2,\overline{2})$. This configuration introduces a gap of 33 MHz between the levels $m_S^{NV} = -1$ and $m_S^{NV} = 1$.

With the nuclear Zeeman energy and the quadrupole interaction dropped, the Hamiltonian of the HF interaction is given by

$$\mathcal{H}_2 = S^N A I^N + g\beta H S, \tag{3}$$

where I^N is the nuclear spin operator of the $P1$ center. The second term on the right-hand side is the electronic Zeeman energy. $S = (S^N + S^{NV})$ is the total electronic spin operator and H the magnetic field. In the case of axial symmetry, the tensor A has only two independent components:[12] $A_\perp = A_{xx} = A_{yy} = 81.3$ MHz and $A_\parallel = A_{zz} = 114.0$ MHz. The effective hyperfine coupling parameter differs slightly from $A_\parallel$.[11] The energy levels and the spin functions are obtained with the total Hamiltonian $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$ and the basis $\{|m_S^{NV} m_S^N m_I\rangle\}$. m_I is the eigenvalue of I_z^N. The 18-dimensional energy matrix is partitioned into three blocks which differ only by the value of m_I. Each block has been diagonalized iteratively. For $H = 0$, the energy diagram is composed of nine levels which are twofold degenerated (see Fig. 1). The external magnetic field, applied parallel to the z axis, lifts the Kramers degeneracy since the energy levels with $M_S = m_S^N + m_S^{NV} > 0$ increase while those with $M_S < 0$ decrease. Energy levels of the states with the same value of m_I can approach each other but do not cross. LC and LAC occur at five regions numbered 1 to 5 in Fig. 1 (see details in Fig. 2). Their position in the energy diagram and their number depend somewhat on the relative position of the two defects and the misalignment of H with the z axis, i.e., a component of H perpendicular to the z axis will modify the off-diagonal elements of the energy matrix. Beyond a resonance, where two energy levels approach a minimum distance, the two electronic spins flip individually or in concert. For each value of m_I, the spin functions are mixtures of the six basis states $\{|m_S^{NV} m_S^N m_I\rangle\}$. LC and LAC are encountered in various areas of physics and chemistry. For example, in atomic spectroscopy, these effects allow a simple and precise determination of atomic structures and radiative lifetimes.[13] Recently, they have been detected in the nanomagnets Mn_{12} (Ref. 3) and Fe_8 (Ref. 4) and are expected to play an important role in QIP.

Let's examine the LACs which occur at about 520 G. Some experimental results have been published recently.[7,8] Figure 3 shows that corresponding to $m_I = 0$. The tunnel splitting, $2\,|\Delta| = \varepsilon_+ - \varepsilon_-$, is equal to 57 MHz. ε_+ and ε_- are the noncrossing levels. Beyond the transition region, the two electronic spins flip in concert. The corresponding spin functions reduce to $|\psi_\pm\rangle = c_{1\pm}|\Downarrow\downarrow m_I\rangle \pm c_{2\pm}|0\uparrow m_I\rangle$. We found that the four coefficients $c_{I\pm}$ are purely imaginary. Their moduli vary rapidly only in the transition region (see Fig. 3) and their arguments $\phi_\pm$, equal to $\frac{\pi}{2}$ or $-\frac{\pi}{2}$, undergo π jumps at different values of H; i.e., the spin functions change sign. In his review of the literature on the π phase shift, Berry[14] reported the connection between the sign change and the degeneracy of the cyclicly transported state. We conclude that we are dealing with a new case of change of sign of eigenvectors.

Static aspect of the LZ theory. The above-mentioned results can be reanalyzed in the framework of the LZ theory. Consider the two-level system $|+\rangle$ and $|-\rangle$ governed by the Hamiltonian

$$\mathcal{H}_{LZ} = \varepsilon_1\,|+\rangle\langle+| + \varepsilon_2\,|-\rangle\langle-| + \Delta(|+\rangle\langle-| + |-\rangle\langle+|), \tag{4}$$

with $|+\rangle = |\Downarrow\downarrow m_I\rangle$ and $|-\rangle = |0\uparrow m_I\rangle$. The off-diagonal element Δ is the coupling between the two states. It is related to the components of the fine-structure tensor J

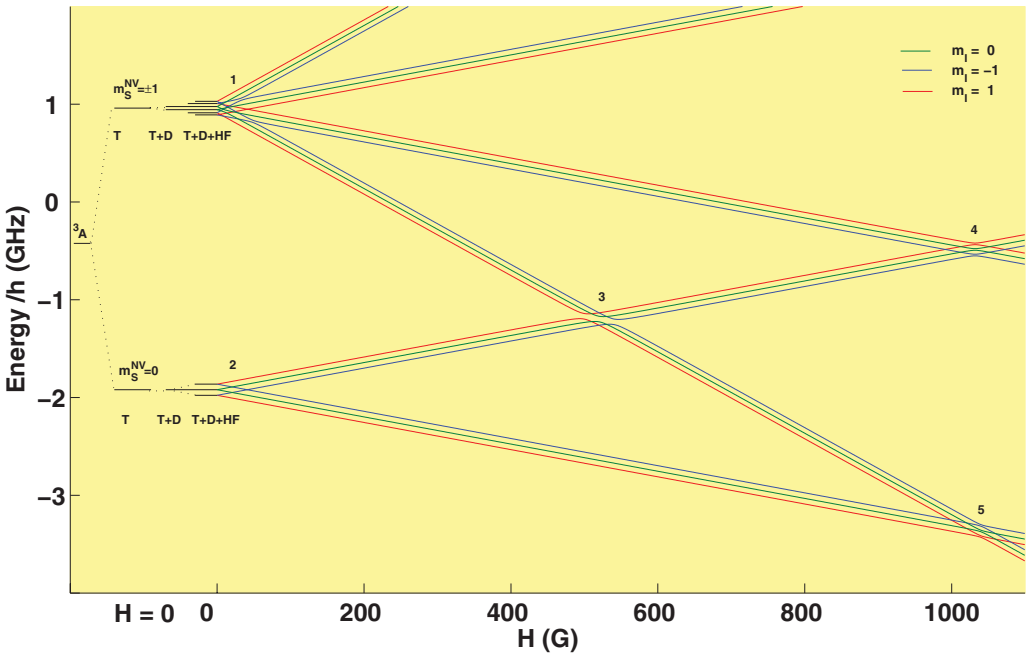

FIG. 1. (Color online) Zeeman energy diagram of the NV^--$P1$ coupled defect pair in a diamond. In the absence of an external magnetic field, the dipolar interaction between the triplet (T) and the doublet (D) lifts the twofold degeneracy of the upper level. The effect of the hyperfine (HF) interaction of the $P1$ center is to triple the number of levels. A magnetic field applied along the z axis lifts the Kramers degeneracy. The 18-level diagram exhibits five regions, numbered 1 to 5, where level crossings and anticrossings occur (see details in Fig. 2).

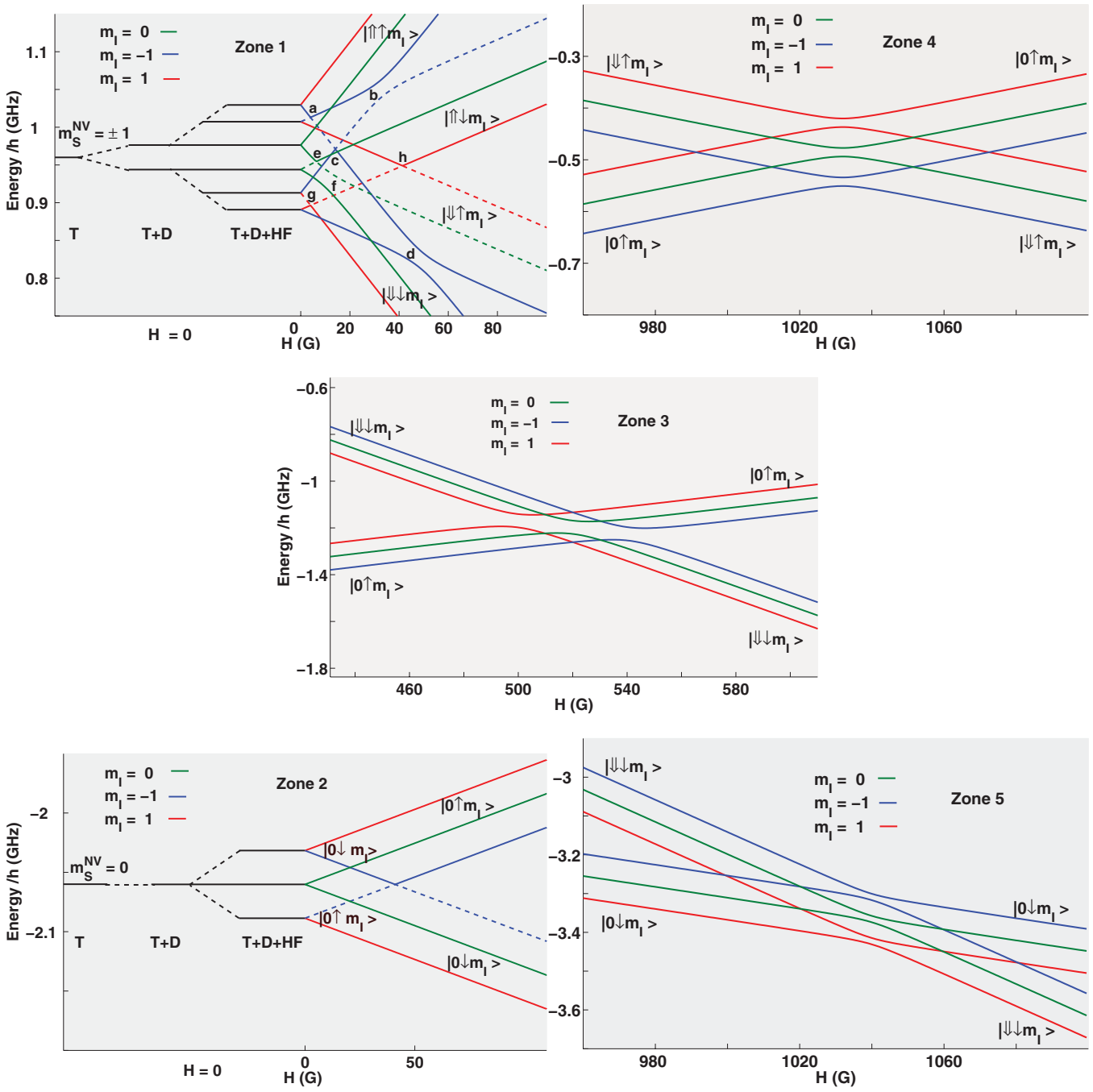

FIG. 2. (Color online) LCs and LACs of the NV^{-}-$P1$ coupled defect pair. For H < 80 G, the tunnel splittings are very small, except those indicated by the letters b and d in zone 1. Dashed lines were required to reveal the existence of some of them (a, c, e, f, g, and h). Spin flips are indicated and can be guessed when they are not, since only two-state vectors are involved. A single upward (downward) arrow stands for the spin state $\frac{1}{2}(-\frac{1}{2})$ and a double upward (downward) arrow stands for the state $1(-1)$.

[see Eq. (2)]. Its numerical value is given above. As shown in Fig. 3, the energy levels $\varepsilon_1 = \langle +|\mathcal{H}|+\rangle$ and $\varepsilon_2 = \langle -|\mathcal{H}|-\rangle$ vary linearly with the magnetic field and should cross at the resonant field H_o in the absence of coupling. Then, the following LZ assumption holds: $(\varepsilon_2 - \varepsilon_1) = \kappa(H - H_o)$, with $\kappa = 2g\beta$ and $H_o = (2D + G_{zz} - 2m_I A_\parallel)/2\kappa$, and where the magnetic field has been substituted to the time. Numerically, κ is equal to 55.56 GHz while H_o is equal to 500 G for $m_I = 1$, 520 G for $m_I = 0$, and 541 G for $m_I = -1$. Slightly different resonant fields have been detected by Hanson *et al.*[7] using photoluminescence spectroscopy. The noncrossing levels are the eigenvalues of $\mathcal{H}_{\rm LZ}$: $\varepsilon_\pm = \varepsilon_c \pm \sqrt{\Delta^2 + \delta^2}$ with $\varepsilon_c = \frac{1}{2}(\varepsilon_1 + \varepsilon_2)$ and $\delta = \frac{1}{2}|\varepsilon_2 - \varepsilon_1|$ (see Fig. 3). The normalized eigenvectors are mixtures of the basis states $|\psi_\pm\rangle = e^{i\varphi_\pm}(a_{1\pm}|+\rangle \pm a_{2\pm}|-\rangle)$ with $i^2 = -1$. Each of the four coefficients $a_{J\pm}$ is a basic trigonometric function of $\vartheta/2$ with $\vartheta = \arctan\frac{\Delta}{\delta}$. $\varphi_\pm$ are arbitrary phases. For example, the eigenvector of the lower energy state is $|\psi_-\rangle = e^{i\varphi_-}(\sin\frac{\vartheta}{2}|+\rangle - \cos\frac{\vartheta}{2}|-\rangle)$ for $H \leqslant H_o$ and $e^{i\varphi_-}(\cos\frac{\vartheta}{2}|+\rangle - \sin\frac{\vartheta}{2}|-\rangle)$ for $H \geqslant H_o$. The

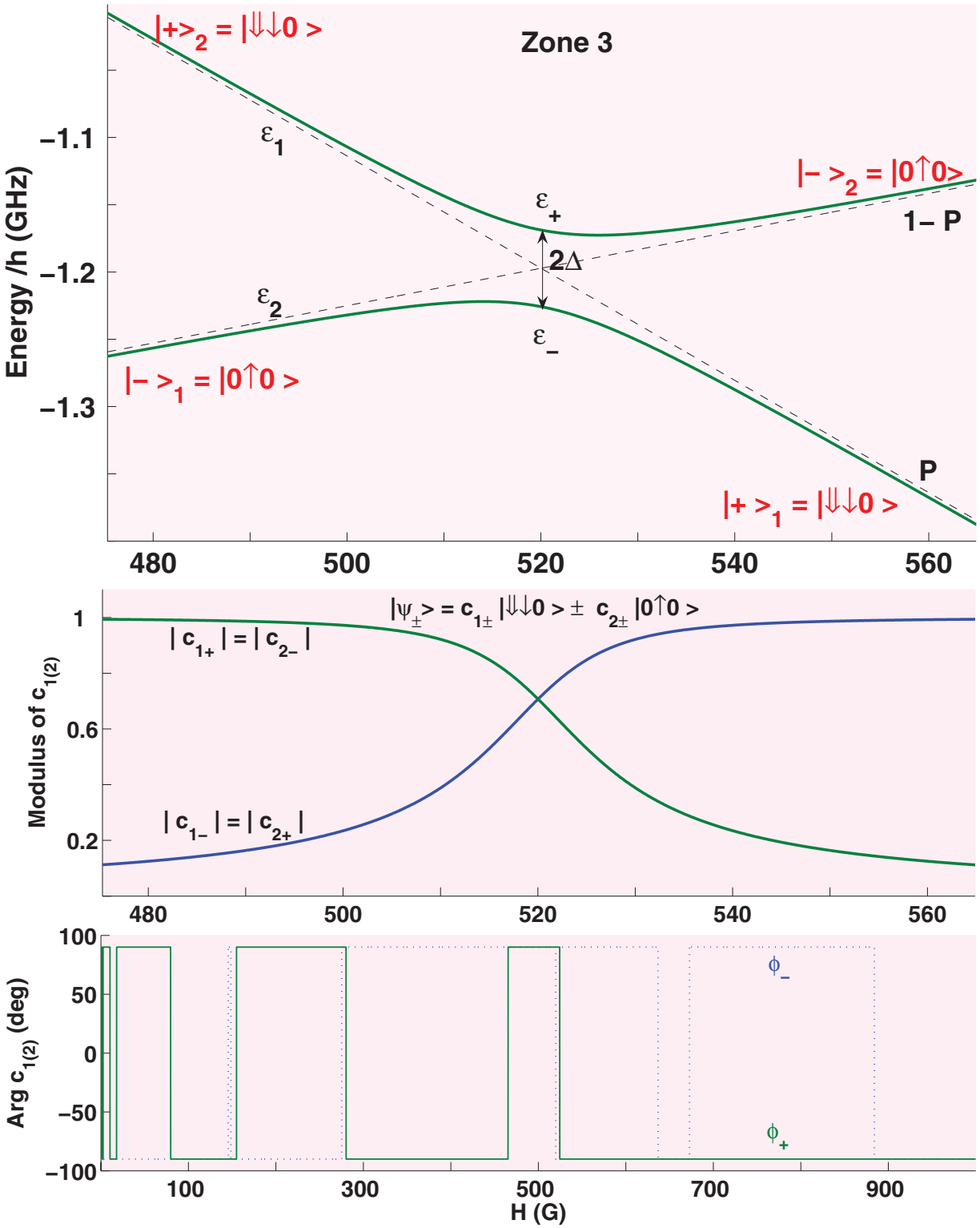

FIG. 3. (Color online) Top: LAC of the NV^--$P1$ coupled defect pair. $\varepsilon_{+(-)}$ are the noncrossing levels and $\varepsilon_{1(2)}$ their asymptotes. 2Δ is the tunnel splitting. P is the probability of occurrence of a spin flip $|-\rangle_1 \Rightarrow |+\rangle_1$ and $(1-P)$ that of an interlevel transition $|-\rangle_1 \Rightarrow |-\rangle_2$ (see text). Middle: Variation of the moduli of the transition amplitudes $c_{J\pm}$ in the vicinity of the resonance. They are purely imaginary. Bottom: π phase jumps of $\phi_\pm = \arg(c_{J\pm})$. The solid green line shows the variation of the angle ϕ_+ and the dotted blue line that of ϕ_-.

comparison with the results obtained with the effective spin Hamiltonian $\mathcal{H}$ leads to set $\varphi_\pm = \phi_\pm$ and $a_{J\pm} = |c_{J\pm}|$. Now, assume that the system is prepared in the lower-energy state $|\psi_-\rangle = |-\rangle_1 = |0 \uparrow m_I\rangle$ at $H \ll H_o$ (see Ref. 7). It transits to the state $|+\rangle_1 = |\Downarrow\downarrow m_I\rangle$ with a probability equal to 1/2 at the resonance ($\vartheta = \pi/2$) and equal to 1 above H_o ($\vartheta = 0$);

that is, the two electronic spins flip in concert. The interlevel transition probability is null. The same analysis can be applied to the other LAC. Below, we find the same results when the spin system is transported infinitely slowly (adiabatically).

Time-dependent LZ Hamiltonian. The exact transition probabilities are obtained by solving the time-dependent Schrödinger equation: $\mathcal{H}_{LZ}[H(t)]\,|\psi(t)\rangle = i\hbar\frac{d}{dt}\,|\psi(t)\rangle$, with the transported state vector $|\psi(t)\rangle = c_1(t)|+\rangle + c_2(t)|-\rangle$ and $\sum_J |c_J(t)|^2 = 1$. $H(t)$ is the time-varying magnetic field. The tunnel splitting remains constant. Zener[6] gave an elegant solution to this problem of mathematical physics which remains an active area of research. It is applied below with a different phase transformation. The two-dimensional Schrödinger equation is first converted to a Weber differential equation, $(\frac{d^2}{dz^2} + n \pm \frac{1}{2} - \frac{1}{4}z^2)w_J(z) = 0$, by using the following phase change: $w_J(z) = c_J(t)e^{i\omega(t)}$, where $\omega(t)$ is given by the integral $\frac{1}{2\hbar}\int^t[\varepsilon_1(t') + \varepsilon_2(t')]dt'$. The sign $+(-)$ in the Weber equation is associated with $c_{1(2)}$. $z = \sqrt{\alpha}e^{-i\frac{\pi}{4}}t$ can be seen as the complex time and $n = i\gamma = i\frac{\Delta^2}{\hbar^2\alpha}$ is a purely imaginary constant. α is a positive constant related to the rate of change of the magnetic field (see below) and γ is the LZ parameter. The solutions of these differential equations are the parabolic cylinder functions or Weber functions $D_n(\pm z)$ and $D_{-n-1}(\pm iz)$.[15] Following Zener,[6] we assume that the magnetic field varies linearly with the time, $H(t) - H_o = qt$. The zero of the time is shifted to the hypothetical crossing point of the diabatic levels; i.e., $\varepsilon_2(t) - \varepsilon_1(t) = \hbar\alpha t$, with $\alpha = q\kappa > 0$. We are interested in the time evolution of an initial state of the spin system. As above, let us prepare it in the state $|-\rangle_1$, defined by $c_{1-}(-\infty) = 0$ and $|c_{2-}(-\infty)| = 1$. These conditions uniquely determine the solutions:[6]

$$c_{1-}(t) = \chi D_{-n-1}(-iz)e^{-i\omega(t)}, \tag{5}$$

$$c_{2-}(t) = \gamma^{-\frac{1}{2}}\chi D_{-n}(-iz)e^{i[3\pi/4-\omega(t)]}, \tag{6}$$

with $|\chi| = \sqrt{\gamma}e^{-\frac{1}{4}\pi\gamma}$. At the resonance (t = 0), the probability $P(0) = |c_{1-}(0)|^2$ to find the spin system in the state $|+\rangle_1$ is equal to $\frac{1}{2}(1 - e^{-\pi\gamma})$. For evaluating $P(t \to +\infty)$, the appropriate asymptotic expansion of $D_{-n-1}(-iz)$ is required;[15] i.e., because of the presence of the Stokes phenomenon, each of the asymptotic expansions of a single-valued Weber function is only valid in a limited sector of the complex z plane. As the time becomes positive and tends toward $+\infty$, z moves away from the origin on the anti-Stokes line with $\arg(z) = -\pi/4$. In the far future, the state vector is given by

$$|\psi_-(t)\rangle \simeq e^{-i\omega(t)}(\sqrt{(1 - e^{-2\pi\gamma})}e^{i[\varpi(t)-\frac{3\pi}{4}-\arg(\Gamma)]}\,|+\rangle - e^{-\pi\gamma}e^{-i\varpi(t)}\,|-\rangle), \tag{7}$$

with $\varpi(t) = [\frac{\alpha t^2}{4} + \gamma\ln(\sqrt{\alpha}\,|t\,|) + \frac{\pi}{4}]$ and $\arg(\chi) = 0$. $\Gamma = \Gamma(i\gamma)$ is the γ function. Terms that vary as $1/|t|$ are neglected. For $H \gg H_o$, the asymptotic probability to find the spin system in the state $|+\rangle_1$ is then equal to $(1 - e^{-2\pi\gamma})$. It is clear that the behavior of the spin system depends on the tunnel splitting and the sweep speed of the magnetic field. In the case of an adiabatic evolution ($\gamma^{-1} \sim q \to 0$), the two electronic spins flip in concert ($|-\rangle_1 \Rightarrow |+\rangle_1$) by quantum tunneling, as in molecular nanomagnets; i.e., a discontinuous change in the value of M_S without thermal activation is equivalent to crossing a potential barrier.[16] The same result has been obtained by means of the time-independent Hamiltonians. In the case of a fast sweep ($q \to \infty$), there is no spin flip, but a nonadiabatic transition to the higher energy state ($|-\rangle_1 \Rightarrow |-\rangle_2$) occurs with an asymptotic probability equal to $e^{-2\pi\gamma}$. This is the well-known result of Zener.[6] From a theoretical point of view, these quantum transitions can be regarded as the physical manifestations of the Stokes phenomenon, which is a purely mathematical concept.

It has been well-known in quantum physics, since the work of Berry,[17] that the state vectors of a spin system may acquire phases of geometric character if they are transported around a circuit in the parameter space. It is straightforward to take them into account. The addition of a weak rotating magnetic field in the plane perpendicular to H gives rise to such geometric phases. They have potential applications in QIP, such as fault-tolerant quantum logic gates.[18]

Conclusion. We have investigated the interaction between the NV^- qubit and the spin-$\frac{1}{2}$ carried by the $P1$ center in a diamond. For certain values of an external magnetic field, the two electronic spins flip individually or in concert, offering possibilities to implement quantum logic gates. Also, the state vectors undergo π phase jumps and can gain phases of geometric origin that might be useful for the realization of phase gates. The work provides a theoretical foundation for reinterpreting recent experimental findings on the NV^--$P1$ coupled defect pair and opens new research avenues for the development of a diamond-based quantum computer. Nevertheless, there remains much to do.

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