Proposed ultrafast optical control and broadband optical quantum memory with neutral nitrogen-vacancy centers in diamond

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Optical spin manipulation relies on spin-orbit coupling, a relativistic effect. In the nitrogen vacancy center in diamond, composed of low atomic-number elements, this effect is weak. This places a limit on the speed of optical control over the spin ground states of the negatively charged nitrogen vacancy center, as well as on the bandwidth of optical pulses that these states can store. This limit does not apply to the orbital level systems. Here we propose the orbital ground states of the neutral nitrogen-vacancy center in diamond as a solid state platform for ultrafast optically-controlled quantum information processing, as well as broadband, low noise light storage.

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The promise of enhanced technologies based on quantum information processing (QIP) has stimulated a continuing search for suitable quantum bits (qubits). A key requirement is a two-level quantum system that can be manipulated many times without significant error, which entails either finding very low-noise systems, or the ability to perform manipulations rapidly, before errors accumulate. Over the past decade, a global research effort has focused on the negatively-charged nitrogen-vacancy (NV−) center in diamond, which exhibits an optically controllable ground state electronic spin manifold that serves as an extremely low-noise qubit, with a room-temperature coherence time of microseconds [1], and, in isotopically-pure diamonds, even milliseconds [2].

The spin state of the NV− can be prepared and read-out optically, but its control has been limited to direct transitions induced by microwave pulses [1]. This limits the maximal rate at which control operations can be applied to tens of MHz.

Optical control (OC) schemes [3], utilizing two-photon transitions between the qubit states, assisted by auxiliary excited states, may enable faster control. However, as we discuss below, for a spin qubit, such schemes are fundamentally limited in speed by the spin-orbit (SO) interaction strength (∼5 GHz in NV− [4]) that couples the spin state with the electric dipole moment.

OC schemes may also enable the use of the NV− as a quantum optical memory (QOM) [5], transforming photons into matterial excitations, and back. QOMs based on two-photon spin transitions have been proposed and demonstrated in various materials using either resonant or non-resonant interactions. While the resonant schemes, based on electromagnetically-induced transparency, have bandwidths of ∼1 MHz [6, 7], the off-resonant schemes, based on Raman scattering, provide much larger bandwidths, e.g. ∼1 GHz [8, 9], and even ∼1 THz [10]. Here too, however, when the material level system is a spin system, the SO interaction sets a limit on the bandwidth of the optical pulses it can store.

In this Letter, we first formulate a sufficient condition for the large-detuning Raman coupling to vanish identically. We then show that the case of the NV− falls under this condition, leaving significant coupling only for detunings smaller than the SO coupling. Then, the level structure of the neutral NV center (NV0) is explored. It is shown that the orbital parts of its states form a simple Δ-system with direct dipole couplings, and that the large-detuning Raman coupling does not vanish. This system is therefore suitable for off-resonant, broadband QOM schemes, as well as off-resonant single-qubit OC schemes [11]. It is further shown that when electric field or stress are applied, the two optical transitions of the Δ-system become cross-linearly polarized. These selection rules allow for the optical preparation and detection of the ground orbital state using polarized excitation. They also allow for the use of resonant, ultrafast, polarization-based OC schemes [12, 13] on single NV0s, and for a considerable suppression of read-out noise [9] in broadband QOMs based on ensembles of NV0s. Finally, we show how NV0s in common diamond samples could be readily used for these applications.

We begin by pointing out a general property of the Raman coupling coefficient (RCC). Defined using second-order perturbation theory valid for a detuning much larger than the spontaneous decay rate, it reads,

\[ C_{ij}^{αβ} = \sum_k \frac{D_{fk}^β D_{ki}^α}{\Delta_k} \approx \sum_k \frac{D_{fk}^β D_{ki}^α}{\Delta} = \sum_k \frac{D_{fk}^β D_{ki}^α s_k}{\Delta^2}, \]

(1)

where \( D_{ki}^α \) (\( D_{kf}^β \)) is the transition dipole moment between ground state \( i \) (\( f \)) and excited state \( k \) in polarization \( α (β) \), \( \Delta_k \) is the detuning of the carrier frequencies of the two coupling optical fields from single-photon resonances with the \( i \leftrightarrow k \) and \( f \leftrightarrow k \) transitions, \( \Delta \) is \( Δ_k \), averaged over all excited states, and \( s_k = Δ_k − Δ \). For \( |Δ| \gg |s_k| \), the most significant term is the second-last term in Eq. (1), proportional to \( 1/Δ \). This term, the first-order Raman coupling (FORC), is proportional to a scalar product of two different rows of the dipole transition matrices \( D^α \) and \( D^β \). The FORC will vanish...
identically in cases where this product is zero for every two different rows (ground states) for all polarizations, while the same-row products assume the same value for two different rows (ground states) for all polarizations, identically in cases where this product is zero for every two statements apply: (a) From linearity, \( D^{\alpha} D_{\beta} = a_{\alpha\beta} I \), \( \) for any polarizations \( \alpha' \) and \( \beta' \). (b) From unitarity, for any \( \tilde{D}^{\alpha(\beta)} = U D^{\alpha(\beta)} V^\dagger \), where \( U (V) \) is a unitary matrix operating in the ground (excited) state manifold, \( \tilde{D}^{\alpha} D_{\beta} = a_{\alpha\beta} I \). This means that if Eq. (2) holds in some state and polarization bases, and therefore the FORC vanishes in that case, the FORC will vanish for any other state and polarization bases, as long as ground and excited states are not mixed.

One important set of cases in which Eq. (2) holds and the FORC vanishes identically, involves ground states with different spins and the same orbital function, and excited states that can be unitarily transformed into SO products. This is because the transition dipole moment is proportional to a unit matrix in the spin subspace. The excited states that should be included are those that are closest to resonance with the coupling light, and are separated from one another by less than the detuning. The FORC may therefore not vanish if the SO interaction, which mixes SO products, is larger than the detuning. One prominent example is the D-lines of Alkali atoms, which stem from transitions between a ground \( s \) manifold and two excited \( p \) manifolds separated by the SO interaction. There, FORC between ground states with different spins vanishes for detunings larger than the SO interaction (\( \sim 15 \) THz in Cs), and exists only when each \( p \) manifold is considered separately. Another example where the FORC vanishes in this way is the charged exciton in a quantum dot, where all the states can be transformed into SO products. Indeed, off-resonant OC could be demonstrated only when the transverse magnetic field used for SO coupling was high enough to force the level splitting to be on the order of the detuning [11].

We now turn to the NV−. As shown in Fig. 1(a), the ground state manifold can be spanned by three SO products, \( \{A_{2,0}, A_{2,1}, A_{2,-1}\} \), all sharing the same orbital part. The excited states can also be spanned by SO products, \( \{E_x, 0, E_{x,-1}, E_y, 0, E_{y,1}, E_{y,-1}\} \). This is sufficient for the FORC between any two ground states to identically vanish for detunings larger than the excited states’ splittings, set by the SO interaction: \( \sim 5 \) GHz [11]. Mathematically, since the transition dipole matrices can be written as [3],

\[
D^x \propto (I_3 \ 0_3) \quad D^y \propto (0_3 \ I_3) \quad D^z = (0_3 \ 0_3),
\]  

where \( I_n \ (0_n) \) is an \( n \times n \) unit (zero) matrix, \( \tilde{z} \) points from the Nitrogen atom to the vacancy, and \( \hat{x} \) lies in a reflection plane, Eq. (2) holds, with \( a_{\alpha\beta} \propto \delta_{\alpha\beta}(1 - \delta_{\alpha z}) \).

Accordingly, all schemes of QOM or OC devised so far for the NV− considered excitation frequencies that are either on [3, 14, 15] or very close to [16] resonance with one of the excited states with respect to the others. Their bandwidth is thus inherently narrower than the excited states’ splittings – the SO interaction.

This constraint may be circumvented if a level system involving ground states of different orbitals and the same spin is to be used. Here, the use of the neutral nitrogen vacancy center is proposed. Note that while the NV0 is usually considered to be unsuitable for QIP, this is due mostly to the lack of a spin preparation mechanism [3], and therefore should not necessarily apply for QIP based on electronic orbitals. The ground state manifold, \( ^2E \) of the NV0, can conveniently be spanned by four SO products, composed of two spin states, and two orbitals, \( E_x \) and \( E_y \) [17]. As shown below, under transverse electric field or uniaxial stress, these states are also the eigenstates of NV0. Fig. 1(b) presents the electronic configurations of the ground and first optically accessible exited states of the NV0 in this basis, and the allowed dipole transitions between them.

Most notably, the \( A_1 \) excited-state orbital is optically connected to both \( E_x \) and \( E_y \) ground-state orbitals, creating a \( \Lambda \)-system. This enables non-vanishing FORC between the two orbital ground states. To illustrate this, consider the matrices of the transition dipole components between the ground states, \( \{E_x \uparrow, E_x \downarrow, E_y \uparrow, E_y \downarrow\} \), and the excited states, \( \{A_1 \uparrow, A_1 \downarrow\} \) [Fig. 1(b)],

\[
D^x = \frac{d_{ge}}{\sqrt{2}} \begin{pmatrix} I_2 & 0_2 \end{pmatrix}, \quad D^y = \frac{d_{ge}}{\sqrt{2}} \begin{pmatrix} 0_2 & I_2 \end{pmatrix}, \quad D^z = \begin{pmatrix} 0_2 & 0_2 \end{pmatrix}.
\]  

![FIG. 1. (a) [(b)] Electronic configurations (left) and schematic level structure (right) of the NV− [NV0] under electric field along the \( \hat{x} \) direction in the NV coordinate system (see text). VB (CB) denotes the valence (conduction) band. An upward- (downward-) pointing arrow represents an electron with spin \( \uparrow \) (\( \downarrow \)). The ellipses in (a) represent spin triplet configurations. Only one of the three states is presented. The ellipse in (b) represents a superposition of both electrons occupying the \( E_x \) state or the \( E_y \) state, with a relative phase of 0. Only the spin \( \uparrow \) states are presented. The double-headed arrows on the right represent allowed optical transitions. The transition dipole direction is specified next to each arrow.](image-url)
The value of $d_{yz}$ estimated from the lifetime of the NV$^0$ ($\sim 20$ ns) is about 6 GHz $\cdot \mu$m/V. Here the row-product matrix $D^x D^y$ is non-diagonal: there are pairs of different ground states (different orbitals, same spin) for which the row-product is non-zero, and for those states, the FORC will not vanish. Furthermore, in this basis, ground states are coupled to the excited state in orthogonal linear polarizations. Such selection rules allow for the control of the coupling, and therefore the manipulation of the ground states’ superposition, by the polarization of the light. They therefore enable the use of ultrafast control pulses, whose bandwidth exceeds the energy splitting of the ground states. This also enables the optical preparation and detection of the orbital quantum state of the electrons through direct analogues of standard techniques in atom optics. Optical preparation can be achieved by polarized resonant excitation, coupled to just one of the ground states, and the consequent pumping of population to the uncoupled state. Optical detection can be achieved by polarized resonant excitation, projecting the population of the coupled state onto the excited state, followed by the measurement of the resulting absorption or fluorescence.

It will now be shown that in low-strain samples, under a moderate electric field (or, equivalently, uniaxial stress), the NV$^0$s eigenstates are well approximated by $E_x$, $E_y$, and $A_1$. Neglecting internal strain, the relevant part of the Hamiltonian is composed of the SO interaction and the electric-field-induced energy

$$H = \lambda_z \hat{L}_z \hat{S}_z - \hat{d}_x F_x - \hat{d}_y F_y,$$

where $\lambda_z$ is the longitudinal SO coupling energy, $\hat{d}_x(y)$ is the $\hat{x}$ ($\hat{y}$) component of the electric dipole operator, and $F_{x(y)}$ is the $\hat{x}$ ($\hat{y}$) component of the electric field vector. The $A_1$ state has no orbital angular momentum $\hat{z}$-component, and therefore no internal SO structure. It also does not have an intrinsic dipole moment, and therefore, to first-order, it will not be affected by the electric field. For the ground states, the Hamiltonian can be written in the basis $\{E_x \uparrow, E_x \downarrow, E_y \uparrow, E_y \downarrow\}$ as,

$$H = \frac{\lambda_z}{2} \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} + d_g \begin{pmatrix} -F_x & 0 & F_y & 0 \\ 0 & -F_x & 0 & F_y \\ F_y & 0 & F_x & 0 \\ 0 & F_y & 0 & F_x \end{pmatrix},$$

where $\lambda_z \approx 5$ GHz and $d_g \approx 6$ GHz $\cdot \mu$m/V. The energies of the ground and excited states, as functions of an external electric field, applied along the $\hat{x}$ direction ($\hat{z} = [110]$ for an NV aligned along $\hat{z} = [111]$), are presented in Fig. 2(a). At zero field, the SO interaction mixes the $E_x$ and $E_y$ orbitals, while for fields larger than $\lambda_z/d_g \approx 1$ V/µm they become distinct. Fig. 2(b) shows the linear polarization component (Stokes parameter $S_1$) of the optical transitions in the NV$^0$ system, calculated according to Eq. 4 and Eq. 5, as functions of the electric field, applied along the $\hat{x}$ direction. Fig. 2(c) shows the resulting RCC, $C^{xy}_{E_x E_y} \Delta$, calculated according to Eq. 4, for two ground states of different orbitals (and the same spin), in orthogonal linear polarizations [$\hat{x}$ ($\hat{y}$)-polarized pump (Stokes)].

FIG. 2: (a) NV$^0$ energy levels vs. transverse electric field. The NV axis is along [111] ($\hat{z}$). The field is along [112] ($\hat{x}$). (b) Stokes parameter $S_1$ (equals 1 (-1) for $\hat{x}$ ($\hat{y}$) polarization) of the transitions connected to the lower (solid line) and the higher (dashed-dotted line) ground state. (c) Raman coupling in cross-linear polarizations (pump (stokes) $\hat{x}$ ($\hat{y}$) polarized). (d) Vibrionic mixing probability of the higher ground state. (e) Relative probability of $\hat{x}$-polarized light to couple to the higher ground state.

One potential disadvantage of the NV$^0$ level scheme is that the orbital states interact with lattice phonons, possibly leading to short life and coherence times ($\sim 1$ ps) expected at room-temperature. Note, however, that since the excited states of the NV$^-$ also interact with phonons, all OC and QOM schemes proposed or demonstrated for the NV$^-$ operate only at low temperatures. The NV$^-$ excited states show rather long life and coherence times ($\sim 1 \mu$s at 10K). Further note that under the relatively weak fields to be considered here, the mixing probability of the higher-energy NV$^0$ ground state with localized vibronic states due to field-induced dynamic Jahn-Teller distortion is still negligible ($\sim 10^{-4}$). Fig. 2(d) presents a calculation of this probability as a function of the applied external field. It is therefore expected that the NV$^0$ orbital ground states would exhibit long life and coherence times at low temperatures. Indeed, optical transition line-widths as low as a few hundred MHz, comparable to the radiative line-width, have been measured for the NV$^0$ zero-phonon line at 2K. Polarization-enabled optical preparation, detection, and ultra-fast control schemes could then be readily performed, with the application of transverse electric field, on single NV$^0$’s perpendicular to the sample surface. Such NVs could be easily found in diamonds cut...
along the (111) plane.

For quantum memory operation with a single photon as the signal, polarization alone is usually not sufficient for separating the strong control from the weak signal. Energy selective filtering is then used, and the energetic separation between the control and signal fields, i.e., the separation between the two ground-state levels, sets the maximum bandwidth of the memory \[3, 9\].

As shown in Fig. 2(a), energy splittings in excess of 100 GHz are achievable with reasonable electric fields (\(\sim 10 \text{ V/\mu m}\)) \[13], \[22], \[23\] and/or moderate compressive uniaxial stress (\(\sim 100 \text{ MPa}\)) \[17\]. In addition, the NV\(^0\) system may provide a way to suppress the read-out noise encountered in Raman type alkali-metal vapor QOMs. There, noise photons at the signal frequency are extracted from the memory by the read-out pulse even when no signal photons were stored.

This is attributed to a four-wave-mixing (FWM) process induced by the coupling of the read-out pulse to the fully populated ground state \[2\]. In the NV\(^0\) system, due to the polarization selection rules under the application of electric field or stress, this coupling could be considerably suppressed. This is because the control field, which is, e.g., \(x\)-polarized, couples almost exclusively to the lower ground state. This is shown in Fig. 2(e), which presents the probability of an \(x\)-polarized optical field to couple to the higher ground state, as a function of the applied external electric field. For electric field- or stress-induced splitting of 100 GHz, this suppression factor is about 1/3000, practically eliminating the FWM noise \[3\].

For an ensemble-based quantum memory, ideally one would like to have an ensemble of [111]-oriented NVs. Though the growth of such diamond samples is under development, and significant advancements towards this goal have been very recently made \[24, 25\], such samples are not readily available yet. Nevertheless, as will now be shown, it is possible to obtain a practically noise-free ensemble quantum memory also with the use of a common (100) sample containing all NV orientations.

Fig. 3(a) presents all the possible orientations of the NV center. The direction of the applied field (optical axis) is denoted by a red, horizontal (black, vertical) arrow. (b) NV\(^0\) energy levels vs. transverse electric field. (c) The allowed transitions’ [100]-[010] Stokes parameter. The solid (dash-dotted) line presents the polarization of the transition coupled to the lower (higher) ground state. (d) Raman coupling in cross-linear polarizations [the higher-(lower-) frequency light-field polarized along [100] ([010])]. (e) Relative probability of the higher energy light to couple to the higher energy ground state, summed over all orientations.

**FIG. 3:** (a) All possible orientations of the NV center. The Nitrogen atom is in the middle. The direction of the applied field (optical axis) is denoted by a red, horizontal (black, vertical) arrow. (b) NV\(^0\) energy levels vs. transverse electric field. (c) The allowed transitions’ [100]-[010] Stokes parameter. The solid (dash-dotted) line presents the polarization of the transition coupled to the lower (higher) ground state. (d) Raman coupling in cross-linear polarizations [the higher-(lower-) frequency light-field polarized along [100] ([010])]. (e) Relative probability of the higher energy light to couple to the higher energy ground state, summed over all orientations.

Therefore contains almost no component along the direction of the applied field, and its Stokes parameter goes to \(-1\). The Raman coupling for a higher- (lower-) frequency control (signal) field polarized along [100] ([010]) is also the same for all orientations, and saturates at \(1/\sqrt{3}\) of the maximal value calculated for the case where both the NV and the optical axis are oriented along the [111] direction [Fig. 2(c)]. Furthermore, as shown in Fig. 3(c), the total relative probability for FWM noise, including all NV orientations, is still suppressed by more than three orders of magnitude. Finally, optical pumping and detection would still be effective: for a [100] polarized pump resonant with the higher-energy transition, all the NVs will be pumped to the higher ground state, and upon [100] polarized excitation, the resulting fluorescence or absorption would be proportional to the population in the lower ground state. The optical pumping, memory read-in, and memory read-out, are schematically illustrated in Fig. 4 for a NV oriented along [111].

The efficiency of the memory can be estimated from the calculated RCC [Fig. 3(d)], given the control pulse energy, wavelength, and detuning, and the NV\(^0\) density \[8, 9\] (where the Rayleigh range is matched to the sample length). For control pulses of 10 nJ and a density of \(10^{17} \text{ cm}^{-3}\), \(\sim 25\%\) total memory efficiency is calculated for a detuning of 300 GHz, much larger than the low-temperature inhomogeneous broadening in low-
FIG. 4: (a) Optical pumping, (b) memory read-in, and (c) memory read-out, for an NV oriented along [111]. The transition dipole direction is stated next to each ground state. The polarization directions of the optical fields are indicated next to the relevant arrows. The right diagram in (c) corresponds to a read-out attempt where no photon was initially stored. The control pulse couples only to one ground state, and no FWM noise photon is emitted.

strain samples 15. The efficiency may be significantly improved by the use of waveguides to increase the interaction volume 26. With a 1µm×1µm×1mm waveguide, the total calculated memory efficiency exceeds 99% even for control pulses of 0.1 nJ.

In conclusion, the use of the orbital ground states of the neutral NV center in diamond as a quantum two-level system is proposed. This system can be prepared and measured optically, and manipulated by ultra-fast optical pulses. It could also serve as an efficient, low-noise, ultra-broadband quantum-optical memory. The main feature that enables these capabilities is the direct coupling of both ground states to a third, excited level, in orthogonal polarizations. While these schemes are not expected, at this stage, to operate at room temperature, they could be readily implemented with existing diamond samples, and may open the way to ultrafast quantum opto-electronics in the solid state.

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