

# Optical excitation of spin-triplet states of two-electron donors in silicon

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Received May 5, 2023

Revised June 29, 2023

Accepted July 6, 2023

In this paper, we propose a method for resonant optical excitation of ortho states of two-electron donors in silicon, direct transitions to which from the ground state are extremely suppressed in case of a weak spin-orbit coupling. Excitation is proposed to be carried out using the points of anti-crossing of ortho and para states under conditions of uniaxial stress of the crystal. In these points the states cannot be unambiguously assigned to any group of states with a certain spin, as a result of which the optical transition becomes allowed. The structure of the energy levels of two-electron impurities is such that the excitation of such state almost unambiguously leads to the population of the underlying ortho-type state, which is expected to be very long-lived in the case of weak spin-orbit coupling. In the present work, theoretical estimates of the cross sections for optical transitions in the vicinity of the level anticrossing point as a function of strain for strong and weak spin-orbit coupling are made.

**Keywords:** doubly charged donors, para and ortho states, optical transitions, spin-orbit interaction.

DOI: 10.61011/SC.2023.05.57148.18k

## 1. Introduction

Neutral two-electron donor centers in silicon (Mg and group VI donors) have two groups of states (spin-singlet (para) and spin-triplet (ortho) states), which, in the absence of spin-orbit interaction, are not optically coupled with each other. This allows considering them as a convenient basis for creating a qubit, that, in contrast to the proposals to use singly ionized group VI donors as a qubit [1], have a large energy gap between the levels, which may have a positive effect on temperature stability of the potential qubit.

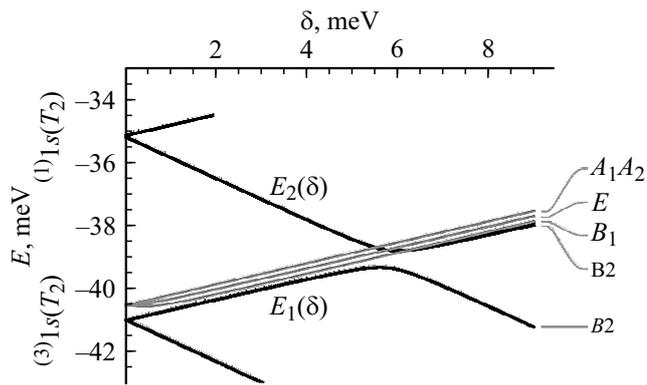
In the case of weak spin-orbit coupling or its absence (S and Mg donors), the controlled optical excitation of orthogroup states is extremely difficult, and resonant excitation is impossible. In donors with strong spin-orbit coupling (Se, Te), direct resonant excitation is possible but the reverse side of this is the short lifetime of the excited orthostate. Excitation through ionization of donors with subsequent capture of an electron by another donor center leads to the random formation of a certain number of donors in orthostates. However, this method is uncontrollable, and the inability to directionally excite orthostates does not allow controlling the potential qubit.

In this study, a method is proposed for non-resonant but controlled optical excitation, which theoretically makes it possible to excite the orthostates of donor centers with an efficiency of almost 100%. The essence of the method is to use the anticrossing point of spin-triplet  ${}^31s(B_2)$  and spin-singlet  ${}^11s(B_2)$  levels in a uniaxially deformed silicon crystal, where, even with an insignificant spin-orbit coupling, the spin is not definite (Fig. 1) and optical transitions are possible. The lower energy area there is

only one of the components of the valley triplet, split off by the deformation: the  ${}^31s(E)$  orthostate (the lower state with  $E$  symmetry in Fig. 1), not involved in the spin orbital interaction with the parastate, and the relaxation transition into it ensures the excitation of the donor into the spin-triplet state. Thus, in the case of exciting an impurity from the ground state with a spin equal to zero ( $S = 0$ ) to the  $1s$  state in the vicinity of the anticrossing point, for example, with an optical  $\pi$ - pulse, the subsequent relaxation process ensures the population of the state with  $S = 1$ . The probability of transition to another state is very low in this case. It should be noted that the strength of the spin-orbit coupling with this method of excitation affects only the range of deformations where transitions to anticrossing levels are possible, which, if its value is low, can also be very small, but the always present inhomogeneity of the deformation in the case of uniaxial compression reduces the requirements for accuracy of the applied pressure and will always provide a certain percentage of such transitions.

## 2. Theoretical part and results

First of all, it should be noted that problem solved in this study, i.e. the problem of optical transitions to  $1s$  split-off states of the valley triplet in the vicinity of the anticrossing point of parastates and orthostates, is not a new one and was solved by authors of [2,3]. However, the published materials do not contain information on the structure of the wave function, which is necessary to assess the dependence of the optical transition cross section on the deformation of the crystal. Therefore, in this study, this wave function is calculated on the basis of the values of matrix elements of



**Figure 1.** Levels of the  $1s(T_2)$  state of Se donors in Si depending on the intervalley splitting caused by deformation along the  $\{100\}$  axis. Letters on the right indicate symmetry of the state.

the spin-orbit interaction operator, estimates of which are given in [2,3].

The wave function at the anti-crossing point  $1s(T_2)$  of parastates and orthostates under conditions of deformation and spin-orbit interaction (see the level diagram in Fig. 1) was built up using experimentally measured spin-orbit coupling parameters for various donors [2,3], as well as the known fact that the spin-orbit interaction couples only two levels with the same symmetry (in the case under consideration, this is the  $B_2$  symmetry) of the split state  $1s(T_2)$ . The latter fact allowed the consideration to be limited to  $2 \times 2$  perturbation matrix (spin-orbit interaction). Diagonalization of the matrix gives the spectrum of states and wave functions of anticrossing levels.

In this study, the following model representations [4] were used to describe wave functions of the states of two-electron centers. The wave function of the excited state is based on the idea that the orbitals of two electrons are significantly different, which leads to the fact that one of the electrons (the inner one) is localized close to the center and „feels“ only the potential of the atomic core with a charge of +2, and the second electron (the external one) moves in the field of the atomic core, screened by the first internal electron, i.e. in a Coulomb potential with a charge of +1. Thus, the wave function is built up from hydrogen-like functions, taking into account the permutation symmetry of electrons. In the absence of spin-orbit interaction, wave functions of the ground state and excited parastate (spin singlet) and orthostate (spin triplet) can be written in the following form [4]:

$$\Psi_{g.s.}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)s_1(\uparrow)s_2(\downarrow),$$

$$\Psi^{\text{para}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\varphi_{1s}^+(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) + \varphi_{1s}^+(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)) \times (s_1(\uparrow)s_2(\downarrow) - s_1(\downarrow)s_2(\uparrow)),$$

$$\begin{aligned} \Psi_1^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} (\varphi_{1s}^+(\mathbf{r}_1)\varphi_3(\mathbf{r}_2) - \varphi_{1s}^+(\mathbf{r}_2)\varphi_3(\mathbf{r}_1)) \\ &\quad \times (s_1(\uparrow)s_2(\uparrow)), \\ \Psi_2^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} (\varphi_{1s}^+(\mathbf{r}_1)\varphi_3(\mathbf{r}_2) - \varphi_{1s}^+(\mathbf{r}_2)\varphi_3(\mathbf{r}_1)) \\ &\quad \times (s_1(\downarrow)s_2(\downarrow)), \\ \Psi_3^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} (\varphi_{1s}^+(\mathbf{r}_1)\varphi_3(\mathbf{r}_2) - \varphi_{1s}^+(\mathbf{r}_2)\varphi_3(\mathbf{r}_1)) \\ &\quad \times (s_1(\uparrow)s_2(\downarrow) + s_1(\downarrow)s_2(\uparrow)), \end{aligned} \quad (1)$$

where  $\mathbf{r}_1, \mathbf{r}_2$  are coordinates of the first and the second electrons,  $\varphi_{1s}^+(\mathbf{r}_{1,2})$  is wave function of the ground state of a singly ionized donor,  $\varphi_1(r_{1,2})$  and  $\varphi_{2,3}(r_{1,2})$  are one-electron wave functions in the ground state (with subscript 1) and excited state (with subscripts 2 and 3),  $s_1$  and  $IFx24xE$  are spin functions of the first and the second electrons, the spin direction is indicated in brackets. The possible slight difference in  $\varphi_3$  functions for different states of the spin triplet can be neglected in the case considered in this study.

Hamiltonian of the system is taken in the following form:

$$H = H_0 + H_{s.o.}, \quad (2)$$

where  $H_0$  is the unperturbed Hamiltonian describing the states of the two-electron center under conditions of uniaxial compression of the crystal,  $H_{s.o.}$  is the spin-orbit interaction operator acting as a perturbation.  $\Psi^{\text{para}}(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Psi^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2)$  functions determined by formulae (1) are eigenfunctions of the  $H_0$  operator. With a uniaxial compressive deformation of the crystal the  $\varphi_1(r_{1,2})$  and  $\varphi_{2,3}(r_{1,2})$  functions are certain combinations of single-valley wave functions. In the case considered in this study,  $\varphi_1(r_{1,2})$  is a six-valley function, i.e. a sum of wave functions of  $1s$  states<sup>1</sup>, each of which is related with one valley, with  $(c_i)$  coefficients the same as for the  $1s(A_1)$  state of a hydrogen-like donor center in silicon [5], i.e. it can be written as follows:

$$\varphi_1(r_{1,2}) = \sum_i c_i F_i \xi_i, \quad (3)$$

where  $F_i$  is envelope of the ground state wave function of  $1s$  type,  $\xi_i$  is Bloch function of the conduction band bottom of the  $i$ -th valley, the summation is carried out over all six valleys of silicon. The  $\varphi_2(r_{1,2})$  function is a  $1s$  state formed by the contribution of two opposite valleys lying on the axis along the pressure applied to the crystal [5]:

$$\varphi_2(r_{1,2}) = \frac{1}{\sqrt{2}} (G_1 \xi_1 - G_2 \xi_2), \quad (4)$$

where  $G_{1,2}$  are envelopes of the wave function of the split-off component of the  $1s$ -type valley triplet in the first and

<sup>1</sup> Hereinafter, the indicated type of the  $1s$  state corresponds to the classification of the envelope wave function of a hydrogen-like center in the effective mass method.

the second valleys, lying on the axis along the axis of the pressure applied to the crystal. It should be noted that such a valley combination of the  $\varphi_2(r_{1,2})$  function ensures that it ceases to be even, and optical transitions from the ground state (which is an even state) become possible in principle, however, they are not observed in all donors. The  $\varphi_3(r_{1,2})$  function is a  $1s$  state consisting of the contributions from four valleys lying on axes perpendicular to the direction of pressure. Due to the degeneracy of the state, the coefficients that determine the valley contributions can be chosen as follows [3]:

$$\varphi_3(r_{1,2}) = \frac{1}{2} ((G_3\xi_3 - G_4\xi_4) \pm i(G_5\xi_5 - G_6\xi_6)), \quad (5)$$

where  $G_{3,4,5,6}$  are envelopes of wave functions of the split-off component of the  $1s$ -type valley triplet in four valleys lying along the axes perpendicular to the axis of the pressure applied to the crystal. This valley configuration of the wave functions ensures the presence of a non-zero projection of the orbital momentum.

The presence of a perturbation leads to mixing of parastates and orthostates, so that the wave function in the vicinity of the anticrossing point of split-off levels should be derived in the form of the following superposition:

$$\Psi = \alpha \cdot \Psi^{\text{para}}(\mathbf{r}_1, \mathbf{r}_2) + \beta \cdot \frac{1}{\sqrt{3}} (\Psi_1^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2) + \Psi_2^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2) + \Psi_3^{\text{ortho}}(\mathbf{r}_1, \mathbf{r}_2)), \quad (6)$$

where  $\alpha$  and  $\beta$  are expansion coefficients. With the assumption made that the consideration can be limited to  $2 \times 2$  perturbation matrix, the equation for finding the energy eigenvalues taking into account the spin-orbit interaction will have the following form:

$$\det \begin{pmatrix} V_{11} + E_2 - \frac{2}{3}\delta - E & V_{12} \\ V_{21} & V_{22} + E_1 + \frac{1}{3}\delta - E \end{pmatrix} = 0, \quad (7)$$

where  $E_{1,2}$  are energies of the levels of parastates ( $^11s(T_2)$ ) and orthostates ( $^31s(T_2)$ ) split by the exchange interaction at a zero deformation,  $\delta$  is the intervalley splitting caused by the uniaxial compressive deformation in the  $\{100\}$  crystallographic direction (a pressure of 1 kbar corresponds approximately to an intervalley splitting of 8.5 meV),  $E$  are the required level energies taking into account the spin-orbit interaction,  $V_{11}$ ,  $V_{12}$ ,  $V_{21}$ ,  $V_{22}$  are matrix elements of the spin-orbit interaction operator, which are represented through a single parameter  $\xi$  in [2,3]. The  $\xi$  parameter is measured experimentally through the level splitting. The matrix elements that determine the splitting of the ( $^31s(T_2)$ ) orthostate are as follows:

$$V_{21} = V_{12} = \frac{\xi}{\sqrt{2}}, \quad V_{11} = -\frac{\xi}{2},$$

and the matrix element  $V_{22}$  is obviously equal to zero, because the ( $^11s(T_2)$ ) parastate has a zero spin. Values of

Values of the exchange interaction energy ( $E_2 - E_1$ ) and the  $\xi$  parameter, which determines the spin-orbit splitting, for group VI donors. For S donors, optical transitions from the ground state to the ( $^31s(T_2)$ ) orthostate are not observed experimentally

	Si:Te [3]	Si:Se [2]	Si:S <sup>2</sup>
$E_2 - E_1$ , meV	9	6	6
$\xi$ , meV	1.5	0.4	0.07

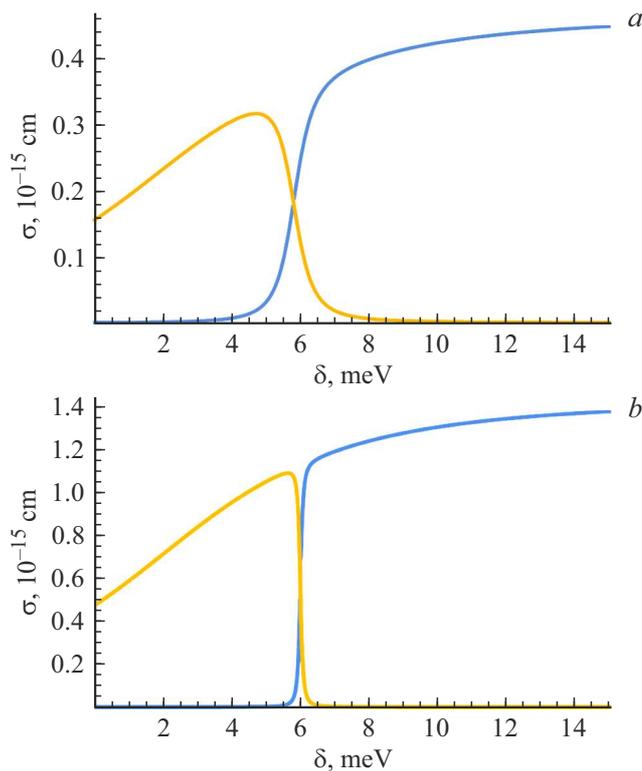
the  $\xi$  parameter for various group VI donors are shown in the table.

The dependences of level energy on deformation shown in Fig. 1 are the result of solving (thick line) equation (7) for Si:Se. Let us denote the lower component of anti-crossing levels with ( $B_2$ ) symmetry as  $E_1(\delta)$  and the upper component as  $E_2(\delta)$ , coefficients  $\alpha$  and  $\beta$  for the lower component as  $\alpha_1$  and  $\beta_1$ , and those for the upper component as  $\alpha_2$  and  $\beta_2$ , respectively. Then the  $\alpha_1, \beta_1, \alpha_2, \beta_2$  coefficients can be represented as follows:

$$\begin{aligned} \alpha_1 &= \frac{\frac{\xi}{\sqrt{2}}}{\sqrt{\frac{\xi^2}{2} + (E_1 + \frac{\delta}{3} - E_1(\delta))^2}}, \\ \beta_1 &= \frac{E_1 + \frac{\delta}{3} - E_1(\delta)}{\sqrt{\frac{\xi^2}{2} + (E_1 + \frac{\delta}{3} - E_1(\delta))^2}}, \\ \alpha_2 &= \frac{\frac{\xi}{2} - E_2 + \frac{2}{3}\delta + E_2(\delta)}{\sqrt{\frac{\xi^2}{2} + (\frac{\xi}{2} - E_2 + \frac{2}{3}\delta + E_2(\delta))^2}}, \\ \beta_2 &= \frac{\frac{\xi}{\sqrt{2}}}{\sqrt{\frac{\xi^2}{2} + (\frac{\xi}{2} - E_2 + \frac{2}{3}\delta + E_2(\delta))^2}}. \end{aligned} \quad (8)$$

Due to the fact that the ground state of the donor is a parastate, and optical transitions between pure parastate and orthostate are impossible, the matrix element of the optical transition from the ( $^11s(A_1)$ ) ground state of the donor to the states corresponding to levels  $E_1(\delta)$  and  $E_2(\delta)$  is proportional to the expansion coefficients  $\alpha_1, \alpha_2$ , respectively, i. e. it is proportional to the weight contribution of the ( $^11s(B_2)$ ) parastate into the overall wave function of states associated with these levels. Thus, using the known absorption cross section ( $\sigma$ ) during the transition to the ( $^11s(T_2)$ ) state [7], the dependence can be calculated of the

<sup>2</sup> Optical transitions in Si:S to the ( $^31s(T_2)$ ) spin triplet state are not observed due to the small magnitude of the spin-orbit coupling  $\xi$ . However, the closeness of the energy spectrum of Si:Se and Si:S suggests that the magnitude of the exchange interaction ( $E_2 - E_1$ ) for these donors is almost the same. The  $\xi$  parameter was estimated using the data from spectral measurements in silicon with singly ionized donors Si:S<sup>+</sup> [6], where splitting of the  $1s(T_2)$  level is noticeable due to the spin-orbit interaction as compared to Si:Se<sup>+</sup>. It was assumed that the ratio of spin-orbit splittings in Si:S<sup>+</sup> and Si:Se<sup>+</sup> coincides with the ratio of splittings in Si:S and Si:Se.



**Figure 2.** Cross sections of transitions to both components of anticrossing levels with  $B_2$  symmetry depending on the magnitude of the intervalley splitting caused by the deformation along the [100] axis for donors with a relatively large (Selenium (Se)) (a) and small (Sulfur (S)) (b) spin-orbit coupling.

absorption cross section into  $E_1(\delta)$  and  $E_2(\delta)$  levels on the uniaxial deformation, which will be represented as follows:

$$\sigma_{1,2}(\delta) = \alpha_{1,2}(\delta)c(\delta)\sigma, \quad (9)$$

where the  $c(\delta)$  factor reflects the dependence on the intervalley splitting of the contribution to the wave function of the ground state of the donor  $1s(A_1)$  for valleys along the deformation axis [5]. Fig. 2 shows the calculated dependences of the absorption cross section for the transition to the states associated with the energy levels  $E_1(\delta)$  and  $E_2(\delta)$  in Se and S neutral donors in silicon. Due to the fact that the  $(^1)1s(B_2)$  state is formed by the contributions of only two valleys lying on the axis along the applied pressure, electric dipole optical transitions are possible only when the radiation is polarized along the same axis.<sup>3</sup>

The results for selenium are consistent with experimental data [2]. However, for sulfur donors, due to the small magnitude of the spin-orbit coupling parameter  $\xi$ , conventional spectroscopy shows neither lines associated with transitions to the  $(^3)1s(T_2)$  valley orthotriplet nor splitting

<sup>3</sup> Oddness of the total wave function of the  $(^1)1s(B_2)$  parastate is ensured by the symmetry of the valley contributions to it. Along axes orthogonal to the axis of the valleys that form this state, the wave function is even and optical transitions in the electric dipole approximation from the ground state of the donor are prohibited.

in the vicinity of the anticrossing point of paralevel and ortholevel  $1s$  [2]. The latter is due to the fact that with a small spin-orbit coupling such splitting is also small (of the order of  $\xi$ ), which requires the use of high-resolution spectroscopy. According to the authors of this study, the resolution should be  $< 0.07$  meV.

### 3. Conclusion

The calculations of the spectrum and wave functions  $1s$  of parastate and orthostate carried out in this study taking into account the spin-orbit interaction show the possibility of intracenter optical excitation of orthostates in two-electron donors in uniaxially deformed silicon. Theoretically, with this method it is possible to carry out excitations even at small magnitudes of spin-orbit interaction with its associated splittings not noticeable with conventional absorption spectroscopy. For example, the fact of the existence of optical transitions in the vicinity of the anticrossing point in sulfur donors can be identified by recording the population of the single lowest excited energy level associated with the  $(^3)1s(E)$  orthostate, which is associated with the lower valleys of the conduction band in deformed silicon. Thus, in addition to excitation of a potential qubit realized on a pair of  $1s$  levels of parastate and orthostate, this method can be useful for spectroscopy of orthostates in donors with low spin-orbit coupling, in which their direct observation is impossible.

### Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by Y.Alekseev