NITROGEN-VACANCY CENTERS IN DIAMOND

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Introduction

Nitrogen-vacancy (NV) color centers in diamond are at the center of a revolution in physics and technology. Because they are responsible for some of the coloration in diamond, NV centers have been studied for several decades; however, their scientific applications only began to draw attention at around the turn of the 21st century. First of all, the spin-triplet ground state of the negatively charged NV center is a nice realization of a solid-state quantum bit (qubit). Second, the quantum state of the centers can be initialized and read out using light, making this system a favorite for workers in the quantum-information field. Other applications of the NV centers include their use as single-photon sources, fluorescent markers in biology, and most recently, as sensors for magnetic-field, electric-field, temperature, and rotation (i.e., gyroscopic) measurements. In magnetometry, actively pursued since around 2008, NV centers offer an unprecedented combination of spatial resolution and sensitivity.

While the physics of the NV centers is reminiscent of that of atoms or small molecules, they are a condensed-matter system, and there may be a certain barrier for those coming from the Atomic, Molecular, and Optical Physics background in understanding them. In this tutorial, we provide an introduction that may be helpful for such newcomers, discussing the crystal structure of diamond, the physical and electronic structure of the NV centers, and describing the NV-center ground-state energy levels and their interaction with an applied magnetic field. Interactive applets allow the user to explore the diamond crystal structure and calculate the energy levels and the frequencies and intensities of the microwave transitions between the ground-state spin sublevels for an arbitrary magnitude and orientation of a bias magnetic field. More advanced or mathematically intensive material is separated from the main text and can be skipped on the first reading.

Crystal structure of diamond

Each carbon atom in a pure diamond sits at the center of a tetrahedron defined by its four nearest neighbors. In units of the cubic cell size, defined below, the positions of the five carbon atoms in one of these groups, which we will denote as **o** (for "origin"), **a**, **b**, **c**, and **d**, can be represented as

```
In[1]:= atoms = {o, a, b, c, d} = {{0, 0, 0}, {1/2, 1/2, 0}, {0, 1/2, 1/2}, {1/2, 0, 1/2}, {1/4, 1/4, 1/4}};
```

Figure 1 is an interactive illustration of the diamond crystal structure. Select **preset 1** to see one of the tetrahedrons. The graphic can be rotated by clicking and dragging with the mouse. Carbon atoms are gray and the covalent bonds between the center atom and its nearest neighbors are shown in yellow.

The complete crystal structure can be formed by placing copies of this tetrahedron at each point on a lattice. The lattice can be defined using three *primitive vectors* **a**, **b**, and **c**, which are determined by the edges of the tetrahedron (**preset 2**). The coordinates of each lattice point are given by $n_1\,\mathbf{a} + n_2\,\mathbf{b} + n_3\,\mathbf{c}$, where n_1, n_2, and n_3 are integers. **Preset 3** shows one additional copy of the tetrahedron translated to the lattice point **a**, while **preset 4** adds copies at **b**, **c**, **a** + **b**, **b** + **c**, **c** + **a**, **a** + **b** − **c**, **a** − **b** + **c**, and −**a** + **b** + **c**. Note that copies of only two of the

atoms from the tetrahedron—the center atom at **d** and one of the corner atoms, say at **o**—are required to fill out the complete crystal (**preset 5**); the other atoms produce overlaps. These two atoms are called the *basis*.

A *cell* is a volume that will fill all of space under suitable translations by the primitive vectors; a *primitive cell* is a cell with the minimum possible volume. **Preset 6** shows a primitive cell. Each primitive cell can be thought of as containing only the two atoms making up the basis. All of the other atoms on the surface of the cell belong to the neighboring primitive cells (**preset 7**).

Drawing the lattice points explicitly (**preset 8**), we see that the lattice can be divided into cubes, known as *cubic cells*, with one lattice point at each corner of the cube, and one point at the center of each face (**preset 9**). This type of lattice is known as *face-centered cubic* (fcc). There are eight atoms belonging to each cubic cell (**preset 10**).
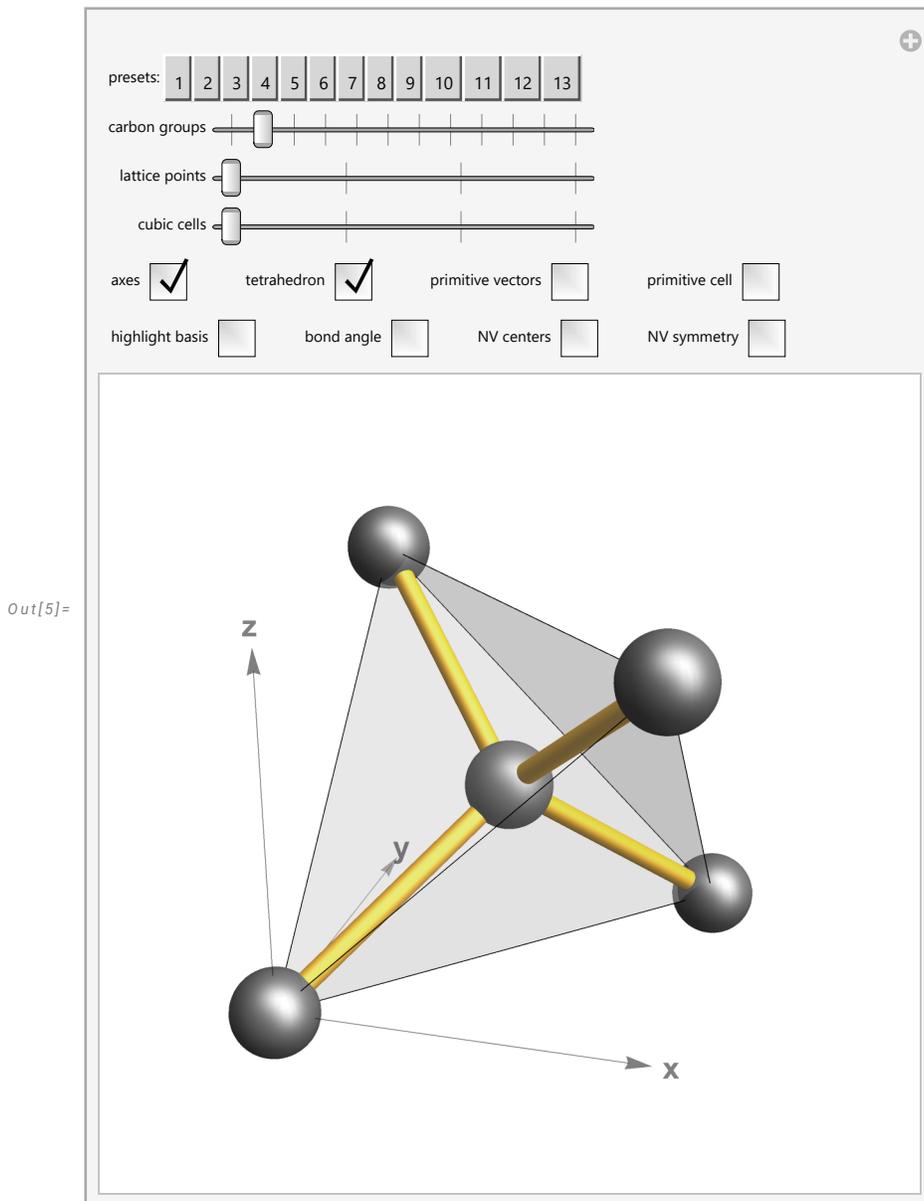
Out[5]=

Figure 1. Crystal structure of diamond.

Nitrogen-vacancy centers

A nitrogen-vacancy center is a defect in the diamond crystal structure, in which a carbon atom is replaced by a nitrogen atom and a neighboring carbon atom is missing, leaving a vacancy (**Figure 1**, **preset 11**; nitrogen atoms are shown in blue, vacancies in white). The angle θ between any two nearest neighbor atoms, for example the angle between the atoms at positions **b** and **o** relative to the vacancy at position **d** (**preset 12**), can be found using the expression for the dot product $\boldsymbol{v} \cdot \boldsymbol{w} = |\boldsymbol{v}| \, |\boldsymbol{w}| \cos \theta$. Solving for θ and substituting $\boldsymbol{v} = \boldsymbol{b} - \boldsymbol{d}$ and $\boldsymbol{w} = \boldsymbol{o} - \boldsymbol{d}$, we find

In[6]:= `ArcCos[` $\dfrac{\text{(b - d) . (o - d)}}{\text{Norm[b - d]} \times \text{Norm[o - d]}}$ `]`

Out[6]= `ArcCos[` $-\dfrac{1}{3}$ `]`

In[7]:= `% / Degree // N`

Out[7]= `109.471`

Thus any two NV pairs will either be oriented parallel to each other, or at a relative angle of approximately $109°$. This is important when considering the effect of a magnetic field on multiple NV centers.

Each carbon atom has four valence electrons, which normally form covalent bonds with the nearest-neighbor carbon atoms. In the case of an NV center, the nitrogen atom has five valence electrons, three of which are taken up by bonds with its neighboring carbon atoms. The dangling bonds from the three carbon atoms adjacent to the vacancy contribute an additional three electrons, for a total of five electrons associated with a neutral NV center, which is designated NV^0. There is also a negatively charged NV^- center, which has captured an additional electron, for a total of six. As we will consider only NV^-, we will take "NV center" to refer to the negatively charged state.

Symmetry of NV centers

The symmetry properties of the NV center are illustrated in **Figure 1**, **preset 13**. It is clear that the axis connecting the N and V is associated with the highest symmetry in this system; because of this, we will find it convenient in the following to reorient the coordinate system so that the z axis lies along the NV axis. The diamond lattice surrounding the NV center is invariant under rotations of $2 \pi n / 3$ about the NV axis, as well as reflections through any of the planes containing the NV axis and one of the C atoms adjacent to the vacancy. The corresponding symmetry group for this case is known as C_{3v}. These symmetries constrain the possible spatial eigenstates of the NV center. The simplest case is when the spatial part of the eigenstate is unchanged under any of the symmetry operations—such states are labeled A_1. States that behave the same except that they acquire a negative sign under reflections are labeled A_2. A third possibility, labeled E, is a pair of degenerate eigenstates that have the same transformation properties as the vectors $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ (assuming $\hat{\mathbf{z}}$ along the NV axis) under the symmetry operations. Note that the electronic spin part of the NV center eigenstate will have its own symmetry properties; the total symmetry behavior is a combination of that of the spatial and spin parts.

Ground-state electronic structure

The ground state of the NV center is a $^3A_2$ state, i.e., an A_2 state with electronic spin $S = 1$. There are three magnetic sublevels, $m = 0, \pm 1$. As discussed above, we will choose the z axis (quantization axis) to be along the NV axis, as opposed to the coordinate system used in Figure 1. Using the fact that spin is an axial vector, it can be shown that the $m = 0$, or $|z\rangle$, sublevel, transforms overall as A_1, while the $m = \pm 1$ sublevels can be written as a

superposition of $|x\rangle$ and $|y\rangle$ states, which transform together as E.

The $m = 0, \pm 1$ sublevels are split by a spin-spin interaction, which raises the energy of $|\pm 1\rangle$ with respect to $|0\rangle$ by $\mathcal{D} \simeq 2.87$ GHz. Ignoring other small effects, the ground-state Hamiltonian can thus be written $\mathcal{H}_0 = \mathcal{D}\,S_z^2$, where the Cartesian components of the spin operator are given by

In[8]:= $\mathcal{S}$ = {**Sx, Sy, Sz**} = $\left\{ \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}, \begin{pmatrix} 0 & -\frac{i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\}$;

The effect of a magnetic field **B** applied at an arbitrary angle to the NV axis is described by the Hamiltonian $\mathcal{H}_B = g_S\,\mu_B\,\mathbf{B.S}$, where $g_S \simeq 2$ is the electron-spin g-factor, and μ_B is the Bohr magneton. The unit vector pointing at an angle β to the z axis is given by

In[9]:= **nvec** = {**Cos[ϕ]** $\times$ **Sin[β], Sin[β]** $\times$ **Sin[ϕ], Cos[β]**};

where ϕ is the azimuthal angle. The total Hamiltonian is then given by

In[10]:=

    (**$\mathcal{H}$tot** = $\mathcal{D}$ **Sz.Sz** + Ω **nvec.$\mathcal{S}$** /. $\phi \to 0$ // **FullSimplify**) // **MatrixForm**

Out[10]//MatrixForm=

$$\begin{pmatrix} \mathcal{D} + \Omega\,\mathsf{Cos}[\beta] & \frac{\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & 0 \\ \frac{\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & 0 & \frac{\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} \\ 0 & \frac{\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & \mathcal{D} - \Omega\,\mathsf{Cos}[\beta] \end{pmatrix}$$

where Ω is the Larmor frequency $g_S\,\mu_B\,B$, and we have set $\phi = 0$, as the rotational symmetry of the system implies that all physical results must be independent of ϕ.

In some cases, the effects of strain can lead to an additional term $\mathcal{E}\left(S_x^2 - S_y^2\right)$ in the Hamiltonian, where $\mathcal{E}$ is the strain parameter. The total Hamiltonian then becomes

In[11]:=

    (**$\mathcal{H}$totStrain** = $\mathcal{D}$ **Sz.Sz** + Ω **nvec.$\mathcal{S}$** + $\mathcal{E}$ (**Sx.Sx** – **Sy.Sy**) // **FullSimplify**) // **MatrixForm**

Out[11]//MatrixForm=

$$\begin{pmatrix} \mathcal{D} + \Omega\,\mathsf{Cos}[\beta] & \frac{e^{-i\phi}\,\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & \mathcal{E} \\ \frac{e^{i\phi}\,\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & 0 & \frac{e^{-i\phi}\,\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} \\ \mathcal{E} & \frac{e^{i\phi}\,\Omega\,\mathsf{Sin}[\beta]}{\sqrt{2}} & \mathcal{D} - \Omega\,\mathsf{Cos}[\beta] \end{pmatrix}$$

where we now retain the ϕ dependence since the results depend on ϕ in the presence of strain.

The energy-level diagram for the ground state with a magnetic field directed along the NV axis (and no strain) is shown in **Figure 2**.
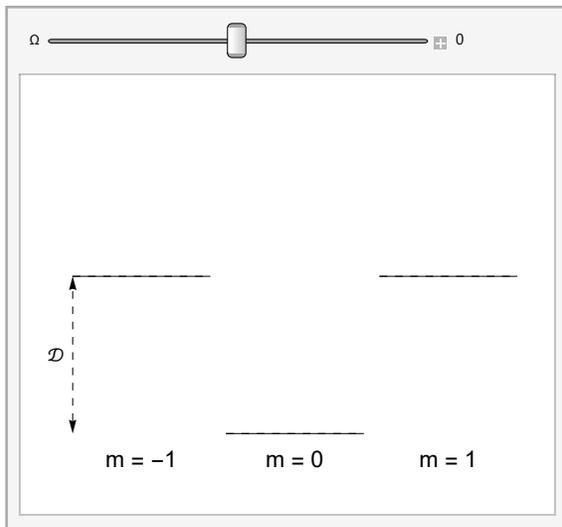
Out[12]=

Figure 2. Ground-state energy-level diagram for an NV center, with magnetic field applied along the NV axis.

For a magnetic field applied at a nonzero angle to the NV axis, or in the presence of strain, the eigenenergies can be found by diagonalizing the Hamiltonian. This can be done in *Mathematica* using the `Eigenvalues` function, but we can obtain more useful expressions for the eigenvalues λ and gain more insight by performing some additional manipulations and then directly solving the characteristic equation $|\mathcal{H}_{tot} - I\lambda| = 0$.

To follow the derivation of the eigenenergies, click the cell below; otherwise, proceed on to the discussion and plots of the results.

Derivation of eigenenergies

The eigenenergies are plotted as a function of Ω for a selectable value of β in **Figure 3.** The eigenenergies for $\beta = 0$ (dashed lines) correspond to the indicated Zeeman sublevels; for $\beta \neq 0$, the energy eigenstates are no longer eigenstates of S_z, but depend on Ω as well as β.
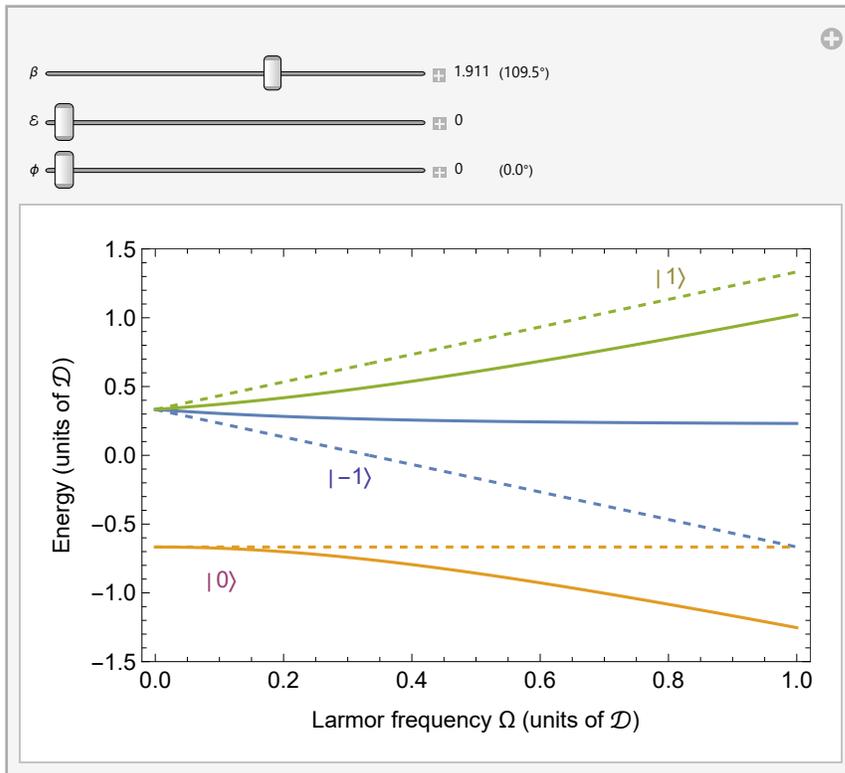
Out[35]=

Figure 3. Eigenenergies for the ground state of the NV center with a magnetic field applied at an angle β to the NV axis. The dashed lines show the curves for $\beta = 0$.

The eigenenergies are plotted as a function of β for a selectable value of Ω in **Figure 4**.
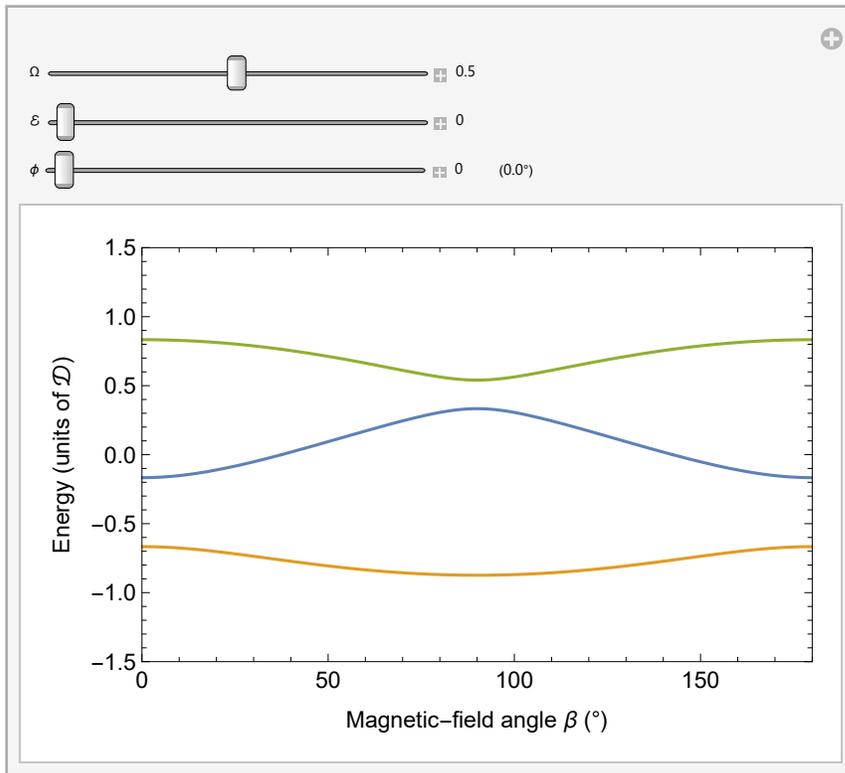
Out[36]=

Figure 4. Eigenenergies for the ground state of the NV center as a function of Ω (in units of $\mathcal{D}$), with a magnetic field applied at an angle β to the NV axis.

Transition frequencies

Microwave transition frequencies correspond to the differences between the eigenenergies.

To follow the derivation of the transition frequencies from the eigenenergies obtained above, click the cell below; otherwise, proceed to the following plots and discussion of the results.

Derivation of transition frequencies

The transition frequencies are plotted in **Figure 5**, for a selectable magnetic-field angle β, along with the transition frequencies for $\beta = 0$ for comparison (dashed lines). The labels indicate the sublevels taking part in the transitions when $\beta = 0$. Note that the transition $|-1\rangle \rightarrow |1\rangle$ is actually forbidden for $\beta = 0$.
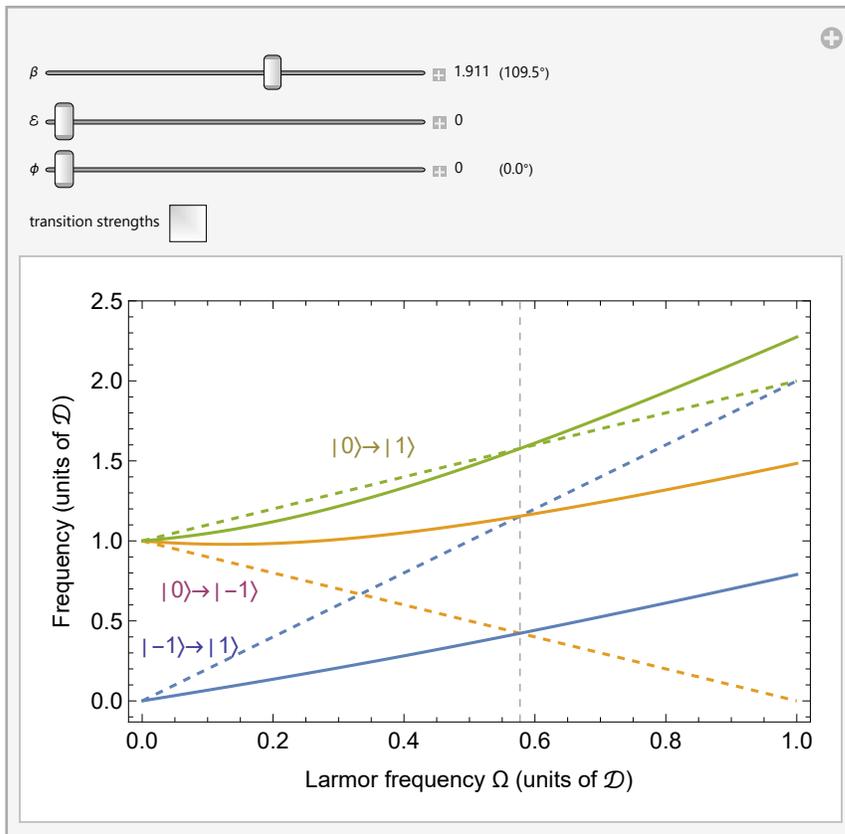
Out[50]=

Figure 5. Microwave transition frequencies between the ground state sublevels as a function of Larmor frequency, with the magnetic field applied at an angle β to the NV axis. The dashed lines show the transition frequencies for $\beta = 0$. Note that the transition between $|-1\rangle$ and $|1\rangle$, with frequency $2\,\Omega$, is forbidden for $\beta = 0$. The vertical dashed line shows the intersections between the transition-frequency curves and the curves for $\beta = 0$. Selecting "transition strengths" shows the transition strengths corresponding to the various transition frequencies as the widths of the curves.

Figure 6 shows the transition frequencies as a function of β for a selectable Larmor frequency Ω. The horizontal dashed lines show the transition frequencies for $\beta = 0$.
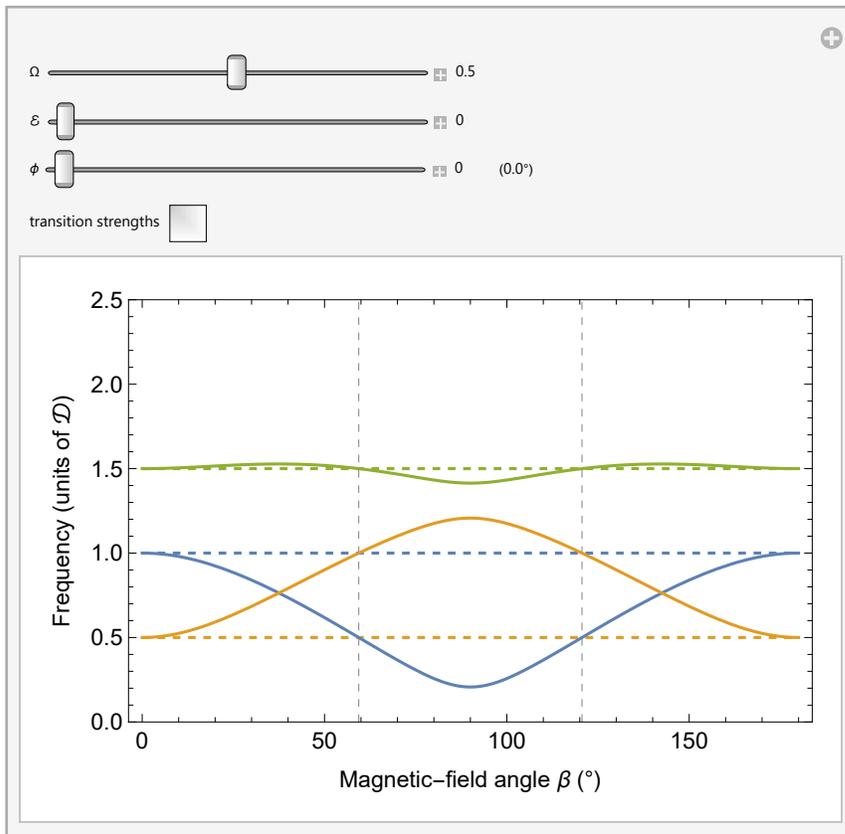
Out[51]=

Figure 6. Microwave transition frequencies between the ground state sublevels as a function of magnetic-field angle. The dashed lines show the transition frequencies for $\beta = 0$. The vertical dashed lines show the intersections between the transition-frequency curves and the $\beta = 0$ lines. Selecting "transition strengths" shows the transition strengths corresponding to the various transition frequencies as the widths of the curves.

As seen in **Figure 5**, for a given nonzero value of β, the curves intersect those for $\beta = 0$ at a particular Larmor frequency Ω (indicated with a vertical dashed line). Likewise, in **Figure 6**, there is a range of Ω values for which all three frequencies are equal to those at $\beta = 0$ at two nonzero values of β. This fact can be physically significant: For example, if a magnetic field is applied along a particular NV axis, the field will either be parallel or at an angle of $\simeq 109\,°$ to each NV axis in the crystal, as noted above. When the transition frequencies for the two subensembles of NV centers become equal, a phenomenon known as cross relaxation can occur, which increases the spin-polarization relaxation rate.

For a discussion and visualization of the origin of this frequency recurrence phenomenon, click the cell below. This discussion builds off of the results obtained in the above derivations of eigenenergies and transition frequencies.

Discussion of frequency recurrence

Transition strengths

The relative strength of a magnetic-dipole transition between two sublevels $\langle \psi_1 |$ and $\langle \psi_2 |$ is given by $|\langle \psi_1 | \mathbf{S} | \psi_2 \rangle|^2$. For example, for $\beta = 0$, the relative strength of the $\langle 0 | \rightarrow \langle 1 |$ transition is given by

In[59]:=
```
Sum[Abs[{0, 1, 0}.S[[i]].{1, 0, 0}]^2, {i, 3}]
```

Out[59]=
```
1
```

while the strength of the $\langle-1| \rightarrow \langle1|$ transition is

In[60]:=
```
Sum[Abs[{0, 0, 1}.S[[i]].{1, 0, 0}]^2, {i, 3}]
```

Out[60]=
```
0
```

indicating that this transition is forbidden. When $\beta \neq 0$, the transition strengths are found using the eigenstates obtained from diagonalizing the Hamiltonian. Selecting "transition strengths" in **Figures 5** and **6** will display the relative transition strengths as the widths of the corresponding transition-frequency curves.

To follow the calculation of eigenstates and transition strengths for the NV system, click the cell below.

> Calculation of eigenstates and transition strengths

Acknowledgements

References

Kopp, J. (2008), "Efficient numerical diagonalization of Hermitian 3×3 matrices", International Journal of Modern Physics C 19(03), 523-548.