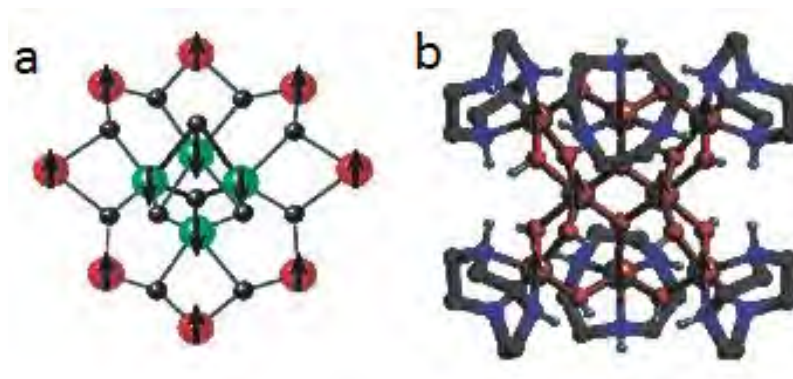


Solution Tutorial 2

1. A molecular magnet is an organic molecule that behaves like a tiny magnet due to its spin. The structure of one such molecule is shown in the figure.



Consider a molecule with spin $s = 2$. The approximate Hamiltonian describing the time dynamics for this molecule is

$$\hat{\mathcal{H}} = -\left(\frac{D}{\hbar}\right)\hat{S}_z^2, \quad (1)$$

where D is an anisotropy constant.

- Write the Hamiltonian in the Zeeman basis (basis of eigenstates of \hat{S}_z).
- What is the ground state energy of the molecule and what is its degeneracy?
- Using

$$\hat{S}_{\pm}|s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s \pm 1)} \hbar|s, m_s \pm 1\rangle.$$

find the matrix representation of $\hat{S}_+^2 + \hat{S}_-^2$.

- If the exact Hamiltonian is

$$\hat{\mathcal{H}} = -\left(\frac{D}{\hbar}\right)\hat{S}_z^2 + \left(\frac{A}{\hbar}\right)(\hat{S}_+^2 + \hat{S}_-^2), \quad (2)$$

and initial state is $|s, m_s\rangle = |2, 1\rangle$, what is the state after time t .

Answer

- (a) A spin 2 molecule has $s = 2$, so there are $(2s + 1) = 2(2) + 1 = 5$ allowed values of the magnetic quantum number m_s

$$m_s = 2, 1, 0, -1, -2.$$

and 5 eigenstates of \hat{S}_z^2 labeled as

$$|s, m_s\rangle = |2, 2\rangle, |2, 1\rangle, |2, 0\rangle, |2, -1\rangle, |2, -2\rangle.$$

with eigenvalues of \hat{S}_z^2 being

$$\hbar^2 m_s^2 = 4\hbar^2, \hbar^2, 0, +\hbar^2, +4\hbar^2.$$

So the eigenvalues of the Hamiltonian in Eq (??), are $-D\hbar m_s^2$. It thus follows that

$$\begin{aligned} \langle s, m_s | \hat{\mathcal{H}} | s, m_s \rangle &= -D\hbar m_s^2 \langle s, m_s | s, m_s \rangle \\ &= -D\hbar m_s^2 \\ \Rightarrow \langle 2, 2 | \hat{\mathcal{H}} | 2, 2 \rangle &= -4D\hbar, \quad \langle 2, 1 | \hat{\mathcal{H}} | 2, 1 \rangle = -D\hbar \\ \langle 2, 0 | \hat{\mathcal{H}} | 2, 0 \rangle &= 0, \quad \langle 2, -1 | \hat{\mathcal{H}} | 2, -1 \rangle = -D\hbar \\ \langle 2, -2 | \hat{\mathcal{H}} | 2, -2 \rangle &= -4D\hbar, \end{aligned}$$

and off-diagonal matrix elements of the Hamiltonian equal to zero. Hence the matrix representation of $\hat{\mathcal{H}}$ in the Zeeman basis is

$$\begin{aligned} \hat{\mathcal{H}} &= \begin{pmatrix} -4D\hbar & 0 & 0 & 0 & 0 \\ 0 & -D\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -D\hbar & 0 \\ 0 & 0 & 0 & 0 & -4D\hbar \end{pmatrix} \\ &= -D\hbar \begin{pmatrix} 4 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & 0 & +4 \end{pmatrix}. \end{aligned}$$

- (b) For D is positive, ground state is $|2, 2\rangle$ and $|2, -2\rangle$ with energy $-4D\hbar$. It is a two-fold degenerate state.

If D is negative, then ground state $|2, 0\rangle$, which is one-fold degenerate.

- (c) To find the matrix representation of $\hat{S}_+^2 + \hat{S}_-^2$, first we need to know the matrix representations of \hat{S}_+ and \hat{S}_- .

Using Eq (??), we can find

$$\begin{aligned}\hat{S}_+|2, 2\rangle &= 0 \\ \hat{S}_+|2, 1\rangle &= \sqrt{2(2+1) - 1(1+1)} \hbar|2, 2\rangle = 2\hbar|2, 2\rangle \\ \hat{S}_+|2, 0\rangle &= \sqrt{6}\hbar|2, 1\rangle \\ \hat{S}_+|2, -1\rangle &= \sqrt{6}\hbar|2, 0\rangle \\ \hat{S}_+|2, -2\rangle &= 2\hbar|2, -1\rangle.\end{aligned}$$

From which we infer that in Zeeman basis,

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix},$$

$$\hat{S}_- = \hat{S}_+^\dagger = \hbar \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Therefore,

$$\hat{S}_+^2 = \hbar^2 \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}$$

$$\begin{aligned}
&= \hbar^2 \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 2\sqrt{6} & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{6} & 0 & 0 \end{pmatrix}, \\
\hat{S}_-^2 = (\hat{S}_+^2)^\dagger &= \hbar^2 \begin{pmatrix} 0 & 0 & 2\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{6} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \\
\Rightarrow \hat{S}_+^2 + \hat{S}_-^2 &= \hbar^2 \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 2\sqrt{6} & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{6} & 0 & 0 \end{pmatrix} + \hbar^2 \begin{pmatrix} 0 & 0 & 2\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{6} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\
&= \hbar^2 \begin{pmatrix} 0 & 0 & 2\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 2\sqrt{6} & 0 & 0 & 0 & 2\sqrt{6} \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{6} & 0 & 0 \end{pmatrix}.
\end{aligned}$$

(d) Exact Hamiltonian is

$$\hat{\mathcal{H}} = -D\hbar \begin{pmatrix} 4 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & 0 & +4 \end{pmatrix} + A\hbar \begin{pmatrix} 0 & 0 & 2\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 2\sqrt{6} & 0 & 0 & 0 & 2\sqrt{6} \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{6} & 0 & 0 \end{pmatrix}$$

$$= \hbar \begin{pmatrix} -4D & 0 & 2\sqrt{6}A & 0 & 0 \\ 0 & \boxed{-D} & 0 & \boxed{6A} & 0 \\ 2\sqrt{6}A & 0 & 0 & 0 & 2\sqrt{6}A \\ 0 & \boxed{6A} & 0 & \boxed{-D} & 0 \\ 0 & 0 & 2\sqrt{6}A & 0 & -4D \end{pmatrix}$$

See the enclosed elements in the above matrix. The Hamiltonian connects $|2, 1\rangle$ to $|2, -1\rangle$ and vice versa. So if a system starts in $|2, 1\rangle$, it can only evolve into $|2, -1\rangle$. Hence we need to focus only at the elements shown above.

$$\hat{\mathcal{H}}_{\text{new}} = \hbar \begin{pmatrix} -D & 6A \\ 6A & -D \end{pmatrix},$$

where the ordering of elements is $\{|2, 1\rangle, |2, -1\rangle\}$. Other states don't matter if one starts in $|2, 1\rangle$. We need to express $|2, 1\rangle$ in the eigenstates of $\hat{\mathcal{H}}_{\text{new}}$.

The eigenvalues are determined by requiring

$$\det(\hat{\mathcal{H}}_{\text{new}} - \lambda \hat{\mathbf{1}}) = 0$$

$$\begin{vmatrix} -D - \lambda & 6A \\ 6A & -D - \lambda \end{vmatrix} = 0,$$

which yields $\lambda = -D \pm 6A$.

We can now find the eigenstates corresponding to these eigenvalues.

For $\lambda_1 = -D + 6A$,

$$\begin{pmatrix} -D & 6A \\ 6A & -D \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = (-D + 6A) \begin{pmatrix} e_1 \\ e_2 \end{pmatrix},$$

yielding

$$-De_1 + 6Ae_2 = (-D + 6A)e_1$$

$$6Ae_1 - De_2 = (-D + 6A)e_2.$$

from which we discover $e_1 = e_2$. By setting $e_1 = 1$ we obtain

$$\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Likewise for the other eigenstates, $\lambda_2 = -D - 6A$, we find

$$\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

We can normalize these states to obtain the eigenstates,

$$\begin{aligned} |v_1\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} && \text{with eigenvalue } -D + 6A, \text{ and} \\ |v_2\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} && \text{with eigenvalue } -D - 6A. \end{aligned}$$

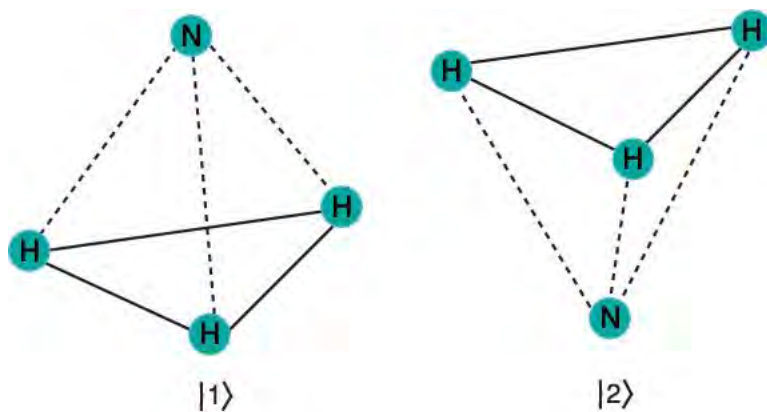
In the small subspace spanned by $\{|2, 1\rangle, |2, -1\rangle\}$ basis, our initial state is

$$|2, 1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} (|v_1\rangle + |v_2\rangle).$$

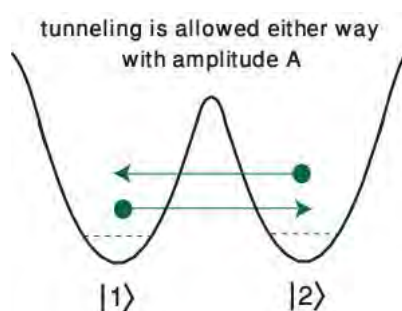
Hence, with time the state evolves to

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}} \left(e^{-i\lambda_1 t} |v_1\rangle + e^{-i\lambda_2 t} |v_2\rangle \right) \\ &= \frac{1}{\sqrt{2}} \left(e^{-i(-D+6A)t} |v_1\rangle + e^{-i(-D-6A)t} |v_2\rangle \right) \\ &= \frac{1}{\sqrt{2}} \left(e^{iDt} e^{-i6At} |v_1\rangle + e^{iDt} e^{i6At} |v_2\rangle \right) \\ &= \frac{1}{\sqrt{2}} e^{iDt} \left(e^{-i6At} |v_1\rangle + e^{i6At} |v_2\rangle \right) \\ &= \frac{1}{2} e^{iDt} \left[e^{-i6At} (|2, 1\rangle + |2, -1\rangle) + e^{i6At} (|2, 1\rangle - |2, -1\rangle) \right] \\ &= \frac{1}{2} e^{iDt} \left[\left(e^{i6At} + e^{-i6At} \right) |2, 1\rangle - \left(e^{i6At} - e^{-i6At} \right) |2, -1\rangle \right] \\ &= \frac{1}{2} e^{iDt} \left[2 \cos(6At) |2, 1\rangle - 2i \sin(6At) |2, -1\rangle \right]. \end{aligned}$$

2. Ammonia is a pyramidal molecule shown in the figure. There are two possible configurations for a rigid molecule: the N atom is above or below the plane of H atoms. These states are respectively labeled $|1\rangle$ and $|2\rangle$.

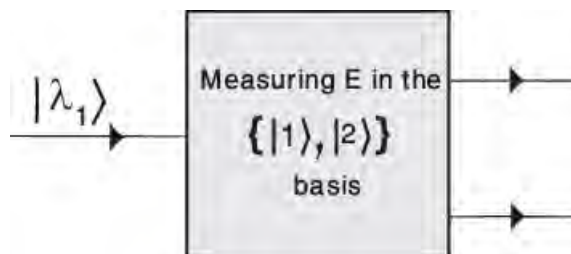


The energies of these states $|1\rangle$ and $|2\rangle$ are equal, say E_0 . It is possible that the molecule tunnels between these states. The amplitude of tunneling is determined by a real number A such that $\langle 2|\hat{\mathcal{H}}|1\rangle = \langle 1|\hat{\mathcal{H}}|2\rangle = -A$, where A is a measure of the tunneling probability.



- Write the Hamiltonian matrix in the $\{|1\rangle, |2\rangle\}$ basis.
- Express this Hamiltonian in terms of identity and Pauli spin operators.
- Show that a Hamiltonian $a\hat{\mathbf{1}} + b\hat{\sigma}_x$ results in the same time evolution as the Hamiltonian $b\hat{\sigma}_x$, where a and b are scalars.
- Find the eigenstates and eigenvalues of the Hamiltonian. If the energy is measured in the $\{|1\rangle, |2\rangle\}$ basis, what are the possible outcomes?
- Let's label the eigenstates you have found in part (d) as $|\lambda_1\rangle$ and $|\lambda_2\rangle$. What is the energy gap between $|\lambda_1\rangle$ and $|\lambda_2\rangle$? For example, you may like to draw an energy level diagram.

- (f) Express both $|\lambda_1\rangle$ and $|\lambda_2\rangle$ in terms of $|1\rangle$ and $|2\rangle$.
- (g) What does an eigenstate, say $|\lambda_1\rangle$ correspond to? For example, if you were to measure the energy in the $\{|1\rangle, |2\rangle\}$ basis, what would be your possible outcomes, the newly prepared states and their probabilities? The relevant conceptual diagram is shown below.



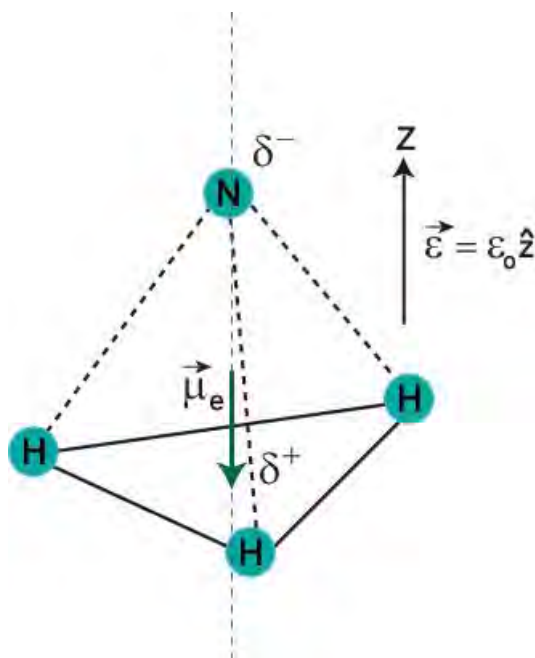
- (h) Suppose the molecule starts in the state $|1\rangle$. What is the state $|\psi(t)\rangle$ after time t ? How long would you need to wait to completely transform the state to $|2\rangle$? How does the frequency of the oscillation $|1\rangle \mapsto |2\rangle \mapsto |1\rangle$ relate to the energy gap (and A) found in part (e). This is a Rabi oscillation between $|1\rangle$ and $|2\rangle$!

Typically experiments indicate that the energy gap between $|\lambda_1\rangle$ and $|\lambda_2\rangle$ is $\sim 10^{-4}$ Hz.

- (i) Find a typical value for A . Select the proper units.

Next, we place the molecule inside a dc electric field, $\vec{\mathcal{E}}_0$, oriented along the z -axis. The axis connecting the centre of the base of the pyramid and the centre of the N atom is also along the z -axis, and is shown in the figure overleaf. The molecule has an intrinsic electric dipole moment $\vec{\mu}_e$ that can be parallel or antiparallel to $\vec{\mathcal{E}}_0$.

- (j) How do the energies of the states $|1\rangle$ and $|2\rangle$ change in the presence of the electric field? You may recall that the energy of an electric dipole inside an electric field is $-\mu_e \cdot \vec{\mathcal{E}}_0$.
- (k) Write the Hamiltonian in the $\{|1\rangle, |2\rangle\}$ basis in the presence of the electric field? Suppose $|\vec{\mathcal{E}}_0|$ is so small that it does not effect A .



- (l) Are $|\lambda_1\rangle$ and $|\lambda_2\rangle$ still eigenstates of the Hamiltonian in the presence of the electric field?
- (m) If $\mu_e |\mathcal{E}_0| \ll A$, find the eigenvalues and hence energies of the eigenstates. How does the gap depend on $|\vec{\mathcal{E}}_0|$. Draw the energy gap in terms of $|\vec{\mathcal{E}}_0|$.
- (n) Using your result from (i) and the value

$$\begin{aligned} |\vec{\mu}_e| &= 1.3 \text{ Debye} \\ &= 1.3 \times 3.33 \times 10^{-30} \text{ C m}, \end{aligned}$$

decide whether $\mu_e |\mathcal{E}_0| \ll A$ is a valid assumption, for $|\mathcal{E}_0| \sim 10^{-10} \text{ V/m}$.

- (o) Now suppose the electric field is time-dependent and given by

$$\vec{\mathcal{E}}_0 = \mathcal{E}_0 \cos(\omega_0 t) \hat{z}.$$

Write the Hamiltonian in the $\{|1\rangle, |2\rangle\}$ basis.

- (p) Write this Hamiltonian in the $\{|\lambda_1\rangle, |\lambda_2\rangle\}$ basis.
- (q) For the NMR experiment, a $\phi_p = 0$ pulse is applied, and in class we've shown that the Hamiltonian in the rotating frame is

$$(\omega_0 - \omega_{\text{TR}}) \hat{S}_z + \frac{\omega_1}{2} \hat{S}_x, \quad (3)$$

where ω_o is the larmor frequency and ω_{TR} is the transmitter frequency. (In class, we've actually derived the result for perfect resonance $\omega_o = \omega_{\text{TR}}$). Derive the Hamiltonian given in Eq (3).

- (r) Comparing your Hamiltonian in part (p) with Eq (3) and your result from part(c), find the Rabi oscillation frequency for the NH_3 molecule in terms of $|\vec{\mathcal{E}}_o|$. Find this frequency for an applied field of $\mathcal{E}_o = 1 \times 10^{-10}$ V/m.
- (s) Explain in simple language what is happening to the NH_3 molecule.

Answer

- (a) The Hamiltonian matrix in the $\{|1\rangle, |2\rangle\}$ basis is given by

$$\hat{\mathcal{H}} = \begin{pmatrix} \langle 1|\hat{\mathcal{H}}|1\rangle & \langle 1|\hat{\mathcal{H}}|2\rangle \\ \langle 2|\hat{\mathcal{H}}|1\rangle & \langle 2|\hat{\mathcal{H}}|2\rangle \end{pmatrix} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}. \quad (4)$$

Now how do we get this matrix? The off-diagonal terms $\langle 2|\hat{\mathcal{H}}|1\rangle$ and $\langle 1|\hat{\mathcal{H}}|2\rangle$ are given and show the possibility of the state $|1\rangle$ tunneling into $|2\rangle$ with time, and vice. verse. It is also given that the energy of $|1\rangle$ is E_0 . This means that if the molecule is in the state $|1\rangle$, the expectation value of the energy $\langle 1|\hat{\mathcal{H}}|1\rangle$ will be E_0 and likewise for $|2\rangle$. Note that $|1\rangle$ and $|2\rangle$ are *not* eigenstates of the Hamiltonian.

- (b) The Hamiltonian can be written in terms of the Pauli matrices as

$$\hat{\mathcal{H}} = E_0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - A \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = E_0 \hat{\mathbf{1}} - A \hat{\sigma}_x.$$

- (c) Suppose $|\psi(0)\rangle$ is the initial state of the system at time $t = 0$, then at time t the state is

$$\begin{aligned} |\psi(t)\rangle &= e^{-i\hat{\mathcal{H}}t/\hbar} |\psi(0)\rangle \\ &= e^{-i(a\hat{\mathbf{1}}+b\hat{\sigma}_x)t/\hbar} |\psi(0)\rangle \quad \text{for } \hat{\mathcal{H}} = a\hat{\mathbf{1}} + b\hat{\sigma}_x \end{aligned}$$

$[\hat{\mathbf{1}}, \hat{\sigma}_x] = 0$, so we can write the exponent as

$$e^{-i(a\hat{\mathbf{1}}+b\hat{\sigma}_x)t/\hbar} = e^{-ia\hat{\mathbf{1}}t/\hbar} e^{-ib\hat{\sigma}_x t/\hbar}.$$

Since $\hat{\mathbf{1}}^2 = \hat{\mathbf{1}}$,

$$\begin{aligned} e^{-ia\hat{\mathbf{1}}t/\hbar} &= \cos\left(\frac{at}{\hbar}\right)\hat{\mathbf{1}} - i\sin\left(\frac{at}{\hbar}\right)\hat{\mathbf{1}} \\ &= e^{-iat/\hbar}\hat{\mathbf{1}}. \end{aligned}$$

Hence

$$\begin{aligned} |\psi(t)\rangle &= e^{-ia\hat{\mathbf{1}}t/\hbar}e^{-ib\hat{\sigma}_xt/\hbar}|\psi(0)\rangle \\ &= e^{-iat/\hbar}(e^{-ib\hat{\sigma}_xt/\hbar}|\psi(0)\rangle), \end{aligned}$$

which is identical to $e^{-ib\hat{\sigma}_xt/\hbar}|\psi(0)\rangle$, because $e^{-iat/\hbar}$ is merely an inconsequential phase factor.

(d) The eigenvalues are determined by requiring

$$\begin{aligned} \det(\hat{\mathcal{H}} - \lambda\hat{\mathbf{1}}) &= 0 \\ \begin{vmatrix} E_0 - \lambda & -A \\ -A & E_0 - \lambda \end{vmatrix} &= 0, \end{aligned}$$

which yields $\lambda = E_0 \pm A$.

We can now find the eigenstates corresponding to these eigenvalues.

For $\lambda_1 = E_0 - A$,

$$\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = (E_0 - A) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix},$$

yielding

$$\begin{aligned} E_0v_1 - Av_2 &= (E_0 - A)v_1 \\ -Av_1 + E_0v_2 &= (E_0 - A)v_2. \end{aligned}$$

Solving these simultaneously we obtain

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Likewise for the other eigenstates, $\lambda_2 = E_0 + A$, we find

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

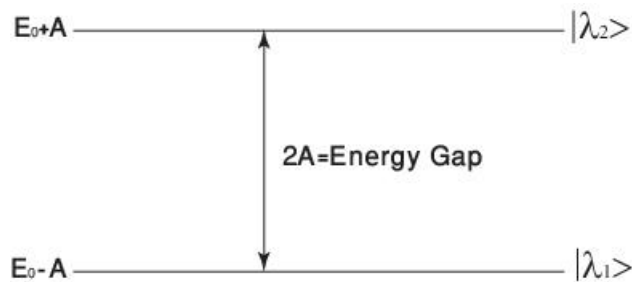
We can normalize these states to obtain the eigenstates,

$$|\lambda_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{with eigenvalue } E_0 - A, \quad \text{and}$$

$$|\lambda_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{with eigenvalue } E_0 + A.$$

If the energy is measured in the $\{|\lambda_1\rangle, |\lambda_2\rangle\}$ basis, the outcomes are $E_0 - A$ and $E_0 + A$. If the energy is measured in the $\{|1\rangle, |2\rangle\}$ basis, both outcomes are E_0 as discussed in part (g).

- (e) We have labeled the eigenstates found above as $|\lambda_1\rangle$ and $|\lambda_2\rangle$. The possibility of tunneling between the states $|1\rangle$ and $|2\rangle$ has created two eigenstates $|\lambda_1\rangle$ and $|\lambda_2\rangle$ with an energy gap of $2A$. If there were no tunneling, the eigenstates would be $|1\rangle$ and $|2\rangle$ and they would be degenerate, each with the same energy E_0 .



- (f) The energy eigenstate in terms of $|1\rangle$ and $|2\rangle$ can be written as

$$|\lambda_1\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

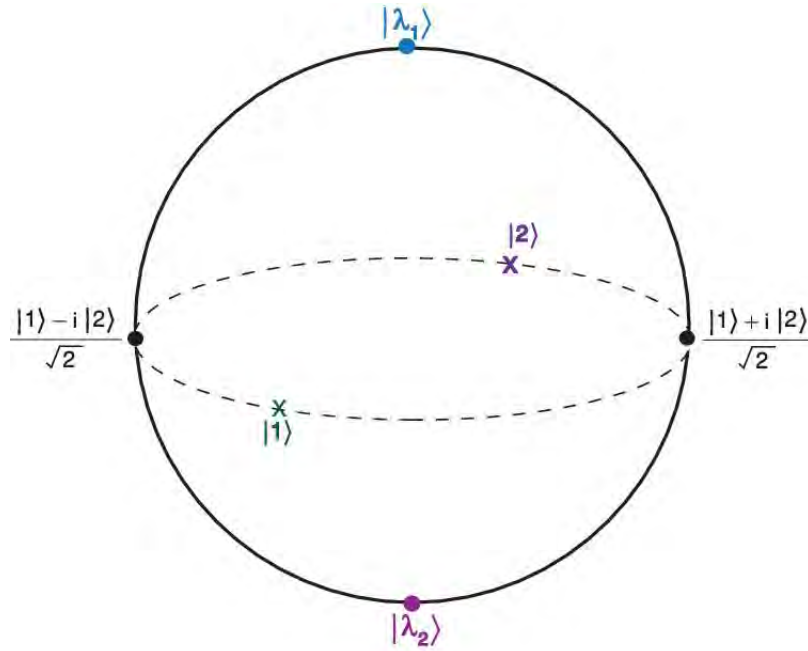
$$|\lambda_2\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle).$$

Conversely, $|1\rangle$ and $|2\rangle$ can also be expressed in terms of the eigenstates $|\lambda_1\rangle$ and $|\lambda_2\rangle$, as

$$|1\rangle = \frac{1}{\sqrt{2}}(|\lambda_1\rangle + |\lambda_2\rangle),$$

$$|2\rangle = \frac{1}{\sqrt{2}}(|\lambda_1\rangle - |\lambda_2\rangle).$$

The states of the two-dimensional system can also be conventionally represented on a Bloch sphere, indicating that the NH_3 molecule's conformation is equivalent to a "fictitious spin", describable by the spin operators $\hat{S}_x, \hat{S}_y, \hat{S}_z$.



- (g) $|1\rangle$ and $|2\rangle$ are not eigenstates of the Hamiltonian, though the experiment attempts to measure the energy in the $\{|1\rangle, |2\rangle\}$ basis. From the Bloch sphere shown, we realize that the $\{|1\rangle, |2\rangle\}$ basis is an eigenbasis of \hat{S}_x , not \hat{S}_z whose eigenstates are $|\lambda_1\rangle$ and $|\lambda_2\rangle$. Hence we are measuring energy not in the eigenbasis of the Hamiltonian. The energy measurement process, sorts out the molecules into $|1\rangle$ and $|2\rangle$ molecules, effectively projecting the input state onto $|1\rangle$ and $|2\rangle$. Each of these states has an energy E_0 . If $|\lambda_1\rangle$ is the input, the probabilities of $|1\rangle$ and $|2\rangle$ states being prepared are

$$|\langle 1|\lambda_1\rangle|^2 = \frac{1}{2} \quad \text{and} \quad |\langle 2|\lambda_1\rangle|^2 = \frac{1}{2},$$

respectively.

- (h) If $|\psi(0)\rangle = |1\rangle = \frac{1}{\sqrt{2}}(|\lambda_1\rangle + |\lambda_2\rangle)$, then after time t , the state evolves to

$$\begin{aligned} |\psi(t)\rangle &= e^{-i\hat{H}t/\hbar}|1\rangle, \\ &= \frac{e^{-i\hat{H}t/\hbar}}{\sqrt{2}}(|\lambda_1\rangle + |\lambda_2\rangle) \\ &= \frac{e^{-i(E_0-A)t/\hbar}}{\sqrt{2}}|\lambda_1\rangle + \frac{e^{-i(E_0+A)t/\hbar}}{\sqrt{2}}|\lambda_2\rangle \\ &= e^{-i(E_0-A)t/\hbar} \left(\frac{|\lambda_1\rangle}{\sqrt{2}} + \frac{e^{-2iAt/\hbar}}{\sqrt{2}}|\lambda_2\rangle \right), \end{aligned}$$

where $e^{-i(E_0-A)t/\hbar}$ is a global phase factor. Thus, the molecule's state $|1\rangle$ is not a stationary state of the Hamiltonian.

To answer this question completely we need to transform back to $\{|1\rangle, |2\rangle\}$ basis.

Ignoring the global phase,

$$\begin{aligned}
 |\psi(t)\rangle &= \frac{1}{\sqrt{2}}(|\lambda_1\rangle + e^{-2i\frac{At}{\hbar}}|\lambda_2\rangle) \\
 &= \frac{1}{2}\left(|1\rangle + |2\rangle + e^{-2i\frac{At}{\hbar}}(|1\rangle - |2\rangle)\right) \\
 &= \frac{1}{2}\left((1 + e^{-2i\frac{At}{\hbar}})|1\rangle + (1 - e^{-2i\frac{At}{\hbar}})|2\rangle\right) \\
 &= e^{-i\frac{At}{\hbar}}\left(\left(\frac{e^{i\frac{At}{\hbar}} + e^{-i\frac{At}{\hbar}}}{2}\right)|1\rangle + \left(\frac{e^{i\frac{At}{\hbar}} - e^{-i\frac{At}{\hbar}}}{2}\right)|2\rangle\right) \\
 &= e^{-i\frac{At}{\hbar}}\left(\cos\left(\frac{At}{\hbar}\right)|1\rangle + i\sin\left(\frac{At}{\hbar}\right)|2\rangle\right).
 \end{aligned}$$

This is how the initial state $|1\rangle$ transforms in time. For complete transformation to $|2\rangle$, we require

$$\begin{aligned}
 \cos\left(\frac{At}{\hbar}\right) &= \frac{\pi}{2}, \\
 \Rightarrow t &= \frac{\pi\hbar}{2A}.
 \end{aligned}$$

The time period of oscillation is determined from

$$\frac{AT}{\hbar} = \pi \Rightarrow T = \frac{\pi\hbar}{A}.$$

Hence the frequency of oscillation (in rad/s) is given by $(2\pi A/\pi\hbar) = 2A/\hbar$. One sees that the state is oscillating between $|1\rangle$ and $|2\rangle$.

- (i) Energy gap = $2A = \hbar\omega = hf = 6.62 \times 10^{-34} \times 10^{-4}$ Hz.

$$A = 3.3 \times 10^{-38} \text{ J.}$$

- (j) When the ammonia molecule is placed in dc electric field $\vec{\mathcal{E}}_0 = \mathcal{E}_0\hat{z}$, then the energy of ammonia molecule, depending on whether it is in $|1\rangle$ state or in $|2\rangle$ state, varies as

$$\begin{aligned}
 E &= E_0 + E_{\text{dipole}} \\
 E_{|1\rangle} &= E_0 + (-\mu_e \cdot \vec{\mathcal{E}}_0) = E_0 + \mu_e\mathcal{E}_0 \quad \text{and} \\
 E_{|2\rangle} &= E_0 + (-\mu_e \cdot \vec{\mathcal{E}}_0) = E_0 - \mu_e\mathcal{E}_0.
 \end{aligned}$$

$E_{|1\rangle}$ is higher because in the $|1\rangle$ state, the electric dipole vector is opposite to the applied field, the angle between $\vec{\mu}_e$ and $\vec{\mathcal{E}}_0$ being 180° , making the dipole energy positive.

- (k) The presence of this electric field modifies the matrix representation of the Hamiltonian in the $\{|1\rangle, |2\rangle\}$ basis:

$$\hat{\mathcal{H}} = \begin{pmatrix} \langle 1|\hat{\mathcal{H}}|1\rangle & \langle 1|\hat{\mathcal{H}}|2\rangle \\ \langle 2|\hat{\mathcal{H}}|1\rangle & \langle 2|\hat{\mathcal{H}}|2\rangle \end{pmatrix} = \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 \end{pmatrix},$$

where we assume the external field is sufficiently weak that it does not affect the tunneling amplitude, and hence the off-diagonal terms.

- (l) No! Let's check it.

$$\begin{aligned} \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 \end{pmatrix} |\lambda_1\rangle &= \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 - A \\ E_0 - \mu_e \mathcal{E}_0 - A \end{pmatrix} \neq c \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \end{aligned}$$

where c is some scalar. So $|\lambda_1\rangle$ is no longer an eigenstate of the Hamiltonian in the presence of a dc electric field. The same is true for $|\lambda_2\rangle$.

- (m) The eigenvalues are determined by requiring

$$\begin{vmatrix} E_0 + \mu_e \mathcal{E}_0 - \lambda & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 - \lambda \end{vmatrix} = 0$$

which yields

$$\lambda = E_0 \pm \sqrt{(\mu_e \mathcal{E}_0)^2 + A^2} = E_0 \pm A \sqrt{1 + \left(\frac{\mu_e \mathcal{E}_0}{A}\right)^2}.$$

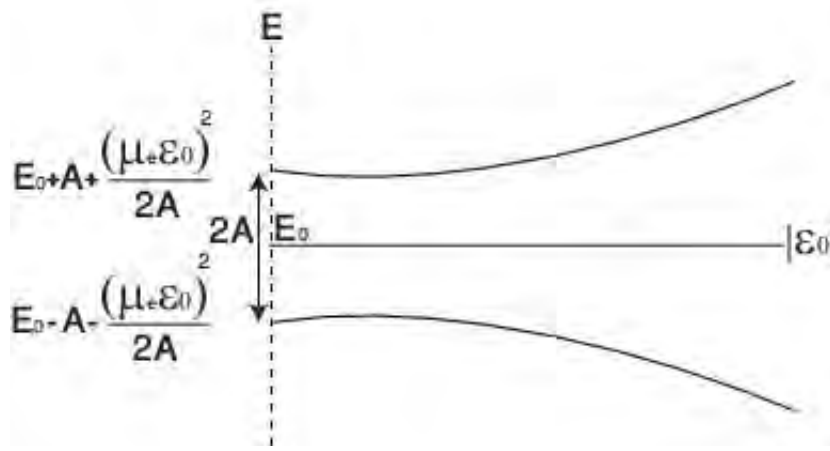
For $\mu_e |\mathcal{E}_0| \ll A$, we use the binomial expansion to obtain

$$\lambda = E_0 \pm A \left(1 + \frac{\mu_e^2 \mathcal{E}_0^2}{2A^2}\right) = E_0 \pm A \pm \frac{\mu_e^2 |\mathcal{E}_0|^2}{2A}.$$

The energy gap between two states is

$$\begin{aligned} \text{Energy gap} &\simeq E_2 - E_1 \\ &= \left(E_0 + A + \frac{\mu_e^2 |\mathcal{E}_0|^2}{2A}\right) - \left(E_0 - A - \frac{\mu_e^2 |\mathcal{E}_0|^2}{2A}\right) \\ &= 2A + \frac{\mu_e^2 |\mathcal{E}_0|^2}{A}. \end{aligned}$$

and is shown in the figure below. Note that the gap spacing increases as $|\mathcal{E}_0|$ increases.



- (n) Given that; magnitudes of electric field \mathcal{E}_0 and dipole moment μ_e is

$$\begin{aligned}\mu_e &= 1.3 \times 3.33 \times 10^{-30} \text{ C m}, & \mathcal{E}_0 &\sim 10^{-10} \text{ V/m} \\ \Rightarrow \mu_e \mathcal{E}_0 &= (1.3 \times 3.33 \times 10^{-30})(10^{-10}) = 4.32 \times 10^{-40} \text{ J}.\end{aligned}$$

Since tunneling amplitude $A = 3.3 \times 10^{-38} \text{ J}$ (derived in part (i)), $\mu_e |\mathcal{E}_0| \ll A$ is indeed a valid assumption.

- (o) The Hamiltonian in the $\{|1\rangle, |2\rangle\}$ basis is

$$\hat{\mathcal{H}} = \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 \cos(\omega_0 t) \end{pmatrix}.$$

- (p) There are two different approaches to finding the hamiltonian in the $\{|\lambda_1\rangle, |\lambda_2\rangle\}$ basis. We only mention one.

$$\begin{aligned}\langle \lambda_1 | 1 \rangle &= \frac{1}{\sqrt{2}} & \langle \lambda_1 | 2 \rangle &= \frac{1}{\sqrt{2}}, \\ \langle \lambda_2 | 1 \rangle &= \frac{1}{\sqrt{2}} & \langle \lambda_2 | 2 \rangle &= -\frac{1}{\sqrt{2}}.\end{aligned}$$

The similarity transform is

$$\hat{S}_{\text{old} \rightarrow \text{new}} = \begin{pmatrix} \langle \lambda_1 | 1 \rangle & \langle \lambda_1 | 2 \rangle \\ \langle \lambda_2 | 1 \rangle & \langle \lambda_2 | 2 \rangle \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}.$$

Hence the Hamiltonian in the new $\{|\lambda_1\rangle, |\lambda_2\rangle\}$ basis is

$$\begin{aligned}
\hat{\mathcal{H}}' &= \hat{S}\hat{\mathcal{H}}\hat{S}^\dagger \\
&= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) & -A \\ -A & E_0 - \mu_e \mathcal{E}_0 \cos(\omega_0 t) \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\
&= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) - A & E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) + A \\ -A + E_0 - \mu_e \mathcal{E}_0 \cos(\omega_0 t) & -A - E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) \end{pmatrix} \\
&= \begin{pmatrix} E_0 - A & \mu_e \mathcal{E}_0 \cos(\omega_0 t) \\ \mu_e \mathcal{E}_0 \cos(\omega_0 t) & E_0 + A \end{pmatrix}.
\end{aligned}$$

Another approach gives the same Hamiltonian $\{|\lambda_1\rangle, |\lambda_2\rangle\}$ basis;

$$\begin{aligned}
\hat{\mathcal{H}}_{11} &= \frac{1}{2} \left(\langle 1| + \langle 2| \right) \hat{\mathcal{H}} \left(|1\rangle + |2\rangle \right) \\
&= \frac{1}{2} \left(\langle 1|\hat{\mathcal{H}}|1\rangle + \langle 1|\hat{\mathcal{H}}|2\rangle + \langle 2|\hat{\mathcal{H}}|1\rangle + \langle 2|\hat{\mathcal{H}}|2\rangle \right) \\
&= \frac{1}{2} \left(E_0 + \mu_e \mathcal{E}_0 \cos(\omega_0 t) - 2A + E_0 - \mu_e \mathcal{E}_0 \cos(\omega_0 t) \right) = E_0 - A,
\end{aligned}$$

similarly other matrix elements can be found.

(q) Hamiltonian in lab frame for the spin 1/2 system is

$$\begin{aligned}
\hat{\mathcal{H}}_{\text{spin}} &\approx \omega_0 \hat{S}_z + \omega_1 (\hat{S}_x \cos(\omega_{\text{TR}} t)) \\
&= \omega_0 \hat{S}_z + \frac{\omega_1}{2} \left(\hat{S}_x \cos(\omega_{\text{TR}} t) + \hat{S}_y \sin(\omega_{\text{TR}} t) \right) + \frac{\omega_1}{2} \left(\hat{S}_x \cos(\omega_{\text{TR}} t) - \hat{S}_y \sin(\omega_{\text{TR}} t) \right).
\end{aligned} \tag{5}$$

The last big parentheses shows the non-resonant part which can be ignored.

Hence

$$\begin{aligned}
\hat{\mathcal{H}} &\approx \omega_0 \hat{S}_z + \frac{\omega_1}{2} \left(\hat{S}_x \cos(\omega_{\text{TR}} t) + \hat{S}_y \sin(\omega_{\text{TR}} t) \right) \\
&= \omega_0 \hat{S}_z + \frac{\omega_1}{2} \left(e^{-i\omega_{\text{TR}} t \hat{S}_z / \hbar} \hat{S}_x e^{i\omega_{\text{TR}} t \hat{S}_z / \hbar} \right).
\end{aligned}$$

Now in a rotating frame rotating with the frequency ω_{TR} (instead of ω_0), the Hamiltonian is,

$$\begin{aligned}
\tilde{\hat{\mathcal{H}}} &= e^{i\omega_{\text{TR}} t \hat{S}_z / \hbar} \hat{\mathcal{H}} e^{-i\omega_{\text{TR}} t \hat{S}_z / \hbar} - \omega_{\text{TR}} \hat{S}_z \\
&= e^{i\omega_{\text{TR}} t \hat{S}_z / \hbar} \left[\omega_0 \hat{S}_z + \frac{\omega_1}{2} \left(e^{-i\omega_{\text{TR}} t \hat{S}_z / \hbar} \hat{S}_x e^{i\omega_{\text{TR}} t \hat{S}_z / \hbar} \right) \right] e^{-i\omega_{\text{TR}} t \hat{S}_z / \hbar} - \omega_{\text{TR}} \hat{S}_z \\
&= (\omega_0 - \omega_{\text{TR}}) \hat{S}_z + \frac{\omega_1}{2} \hat{S}_x.
\end{aligned}$$

(r) From part (p), we have

$$\hat{\mathcal{H}}_{\text{ammonia molecule}} = E_0 \hat{\mathbf{1}} - \frac{2A}{\hbar} \hat{S}_z + \frac{2\mu_e |\mathcal{E}_0| \cos(\omega_0 t)}{\hbar} \hat{S}_x.$$

From part (c), we know already that the $\hat{\mathbf{1}}$ term is immaterial; hence

$$\hat{\mathcal{H}}_{\text{ammonia molecule}} = -\frac{2A}{\hbar} \hat{S}_z + \frac{2\mu_e |\mathcal{E}_0| \cos(\omega_0 t)}{\hbar} \hat{S}_x, \quad (6)$$

which is identical to the spin 1/2 placed inside a magnetic field (Eq (5) with $\omega_{\text{TR}} = \omega_0$). Hence, we can transform $\hat{\mathcal{H}}_{\text{ammonia molecule}}$ into the rotating frame (with $\omega_{\text{TR}} = \omega_0$) perfectly identically to the spin 1/2 system, resulting in

$$\tilde{\mathcal{H}}_{\text{ammonia molecule}} = \frac{\omega_1}{2} \hat{S}_x.$$

The Rabi oscillation frequency for the spin 1/2 system is $\omega_1/2$. By comparing Eq (5) with Eq (6), we establish that $\omega_1 = 2\mu_e |\mathcal{E}_0|/\hbar$, leading to a Rabi frequency of

$$\frac{\omega_1}{2} = \frac{\mu_e |\mathcal{E}_0|}{\hbar} = 4.11 \times 10^{-6} \text{ rad s}^{-1} = 6.54 \times 10^{-7} \text{ Hz}.$$

(s) A dc electric field is changing the energy gap between the $|1\rangle$ and $|2\rangle$ states.

A small ac electric field is causing Rabi oscillations (transitions) between two orthogonal states, $|\lambda_1\rangle$ and $|\lambda_2\rangle$.