We already discussed the physics of NH$_3$ Maser. Here we use this as a typical example of the time-independent perturbation problem.

1. Introduction

For the energy splitting scheme of NH$_3$ in the presence of an electric field, we apply the perturbation theory for solving the problems.

1  and 2  are not the eigenkets of \( \hat{\pi} \). Since

\[
\hat{\pi}|1\rangle = |2\rangle \quad \text{and} \quad \hat{\pi}|2\rangle = |1\rangle
\]
\[ \hat{\sigma} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \]

\( \hat{\pi} \) is regarded as the Pauli matrix \( \hat{\sigma}_x \). The eigenkets of \( \hat{\sigma}_x \) are \( \pm \rangle_x \).

\[ \hat{\sigma}_x \langle \pm \rangle_x = \pm \pm \langle \pm \rangle_x \]

with

\[ \langle + \rangle_x = \left| \varphi_x^{(0)} \right\rangle = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) ; \text{ symmetric state.} \]

\[ \langle - \rangle_x = \left| \varphi_x^{(0)} \right\rangle = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) ; \text{ antisymmetric state.} \]

These two states are the eigenkets of \( \hat{\pi} \).

We now consider the Hamiltonain \( \hat{H} \).

The symmetry of two physical configuration suggests that

\[ \langle 1 | \hat{H} | 1 \rangle = \langle 2 | \hat{H} | 2 \rangle = E_0 \]

What about the off-diagonal elements? The vanishing of \( \langle 2 | \hat{H} | 1 \rangle \) would mean that a molecule initially in the state \( |1\rangle \) would remain in that state. If \( \langle 2 | \hat{H} | 1 \rangle \neq 0 \), there is a small amplitude for the system to mix between the two states.

\[ \langle 2 | \hat{H} | 1 \rangle = -A \]

\[ \hat{H} = \frac{E_0 - A}{-A} \]

This Hamiltonian commutates with the parity operator: \([\hat{H}, \hat{\pi}] = 0\).

\[ \hat{\sigma}_x |\pm \rangle_x = \pm |\pm \rangle_x \]

2. **Eigenvalue problem**

\[ \hat{H} |\pm \rangle_x = (E_0 \hat{1} - A \hat{\sigma}_x) |\pm \rangle_x = (E_0 \mp A |\pm \rangle_x \]

2
\[ E_a^0 = E_0 + A \]
\[ E_s^0 = E_0 - A \]

\[ A^0 \] perturbation

\[ \langle 1 \rangle \]
\[ \langle 2 \rangle \]

\((\text{Application of electric field})\)

\[ \mu : \text{electric dipole moment} \]
\[ \text{energy} = \mu \varepsilon \]
\[ \text{energy} = -\mu \varepsilon \]

When the electric field is applied along the \( x \) axis (the axis of the electric dipole moment), the Hamiltonian is changed into

\[
\hat{H} = \begin{pmatrix}
E_0 + \mu \varepsilon & -A \\
-A & E_0 - \mu \varepsilon
\end{pmatrix} = E_0 \hat{1} + \mu \varepsilon \hat{\sigma}_z - A \hat{\sigma}_x
\]

The new Hamiltonian \( \hat{H} \) does not commutate with the parity operator \( \hat{\pi} \).

\[
\hat{H} = E_0 \hat{1} + \sqrt{(\mu \varepsilon)^2 + A^2} \left( -\frac{A}{\sqrt{(\mu \varepsilon)^2 + A^2}} \hat{\sigma}_z + \frac{\mu \varepsilon}{\sqrt{(\mu \varepsilon)^2 + A^2}} \hat{\sigma}_z \right)
\]
\[ n = \left( -\frac{A}{\sqrt{(\mu \epsilon)^2 + A^2}}, 0, \frac{\mu \epsilon}{\sqrt{(\mu \epsilon)^2 + A^2}} \right) \]

\[ \hat{H} = E_0 \hat{1} + \sqrt{(\mu \epsilon)^2 + A^2} \hat{\sigma} \cdot n \]

\[ \hat{\sigma} \cdot n \left| \pm \right\rangle_n = \pm \left| \pm \right\rangle_n \]

where

\[ \left| + \right\rangle_n = \cos \frac{\theta}{2} \left| 1 \right\rangle + \sin \frac{\theta}{2} \left| 2 \right\rangle \]

and

\[ \left| - \right\rangle_n = -\sin \frac{\theta}{2} \left| 1 \right\rangle + \cos \frac{\theta}{2} \left| 2 \right\rangle \]

where

\[ \sin \theta = -\frac{A}{\sqrt{(\mu \epsilon)^2 + A^2}} \quad \cos \theta = \frac{\mu \epsilon}{\sqrt{(\mu \epsilon)^2 + A^2}} \]
Thus we have

\[ \hat{H} \left| \pm \right\rangle_n = (E_0 \pm \sqrt{(\mu \varepsilon)^2 + A^2}) \left| \pm \right\rangle_n \]

\[ E^0_s = E_0 + A \quad \text{electric field } \varepsilon \]

\[ E^0_a = E_0 - A \quad \text{(symmetric)} \]

\[ E_a = E_0 + \sqrt{(\mu \varepsilon)^2 + A^2} \]

\[ E_s = E_0 - \sqrt{(\mu \varepsilon)^2 + A^2} \]

In a weak electric field

\[ E_s = E_0 - A \sqrt{1 + \frac{\mu^2 \varepsilon^2}{A^2}} = E_0 - \frac{\mu^2 \varepsilon^2}{2A^2} + ... \]

\[ E_a = E_0 + A \sqrt{1 + \frac{\mu^2 \varepsilon^2}{A^2}} = E_0 + \frac{\mu^2 \varepsilon^2}{2A^2} + ... \]

3. Perturbation-1

Suppose that

\[ \hat{H} = \hat{H}_0 + \hat{H}_1 = \begin{pmatrix} E_0 + \mu \varepsilon & -A \\ -A & E_0 - \mu \varepsilon \end{pmatrix} = \begin{pmatrix} E_0 + \mu \varepsilon & 0 \\ 0 & E_0 - \mu \varepsilon \end{pmatrix} + \begin{pmatrix} 0 & -A \\ -A & 0 \end{pmatrix} \]

where

\[ \hat{H}_0 = \begin{pmatrix} E_0 + \mu \varepsilon & 0 \\ 0 & E_0 - \mu \varepsilon \end{pmatrix} \]

\[ \hat{H}_1 = \begin{pmatrix} 0 & -A \\ -A & 0 \end{pmatrix} \]

under the basis of \( |1\rangle \) and \( |2\rangle \). Here \( \hat{H}_0 \) is the unperturbed Hamiltonian and \( \hat{H}_1 \) is the perturbing Hamiltonian. \( |1\rangle \) and \( |2\rangle \) are the eigenket of \( \hat{H}_0 \).

\[ \hat{H}_0 |1\rangle = (E_0 + \mu \varepsilon) |1\rangle, \quad \hat{H}_0 |2\rangle = (E_0 - \mu \varepsilon) |2\rangle \]
with
\[ E_1^{(0)} = E_0 + \mu \varepsilon, \quad E_2^{(0)} = E_0 - \mu \varepsilon \]

Thus the unperturbed system is a non-degenerate system with \(|1\rangle\) and \(|2\rangle\). So we can use the non-degenerate perturbation theory for this problem.

The first order perturbation:
\[ E_1^{(1)} = \langle 1 | \hat{H}_1 | 1 \rangle = 0 \]
\[ E_2^{(1)} = \langle 2 | \hat{H}_1 | 2 \rangle = 0 \]

The second order perturbation
\[ E_1^{(2)} = \frac{\langle 2 | \hat{H}_1 | 1 \rangle^2}{E_1^{(0)} - E_2^{(0)}} = \frac{A^2}{2 \mu \varepsilon} \]
\[ E_2^{(2)} = \frac{\langle 1 | \hat{H}_1 | 2 \rangle^2}{E_2^{(0)} - E_1^{(0)}} = -\frac{A^2}{2 \mu \varepsilon} \]

Then we have
\[ E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = E_0 + \mu \varepsilon + \frac{A^2}{2 \mu \varepsilon} \quad \text{(high energy)} \]
\[ E_2 = E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = E_0 - \mu \varepsilon - \frac{A^2}{2 \mu \varepsilon} \quad \text{(low energy)} \]

The wave function:
\[ |\psi_1\rangle = |1\rangle + |2\rangle \frac{\langle 2 | \hat{H}_1 | 1 \rangle}{E_1^{(0)} - E_2^{(0)}} = |1\rangle - \frac{A}{2 \mu \varepsilon} |2\rangle \]
\[ |\psi_2\rangle = |2\rangle + |1\rangle \frac{\langle 1 | \hat{H}_1 | 2 \rangle}{E_2^{(0)} - E_1^{(0)}} = \frac{A}{2 \mu \varepsilon} |1\rangle + |2\rangle \]
4. Perturbation under the new basis

First we start to find new eigenket of the $\hat{H}_0$ defined by

\[
\hat{H}_0 = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} = E_0 \hat{1} - A \hat{\sigma}_x,
\]

under the basis of \{1\} and \{2\}, where

\[
\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.
\]

The perturbation Hamiltonian is given by

\[
\hat{H}_1 = \begin{pmatrix} \mu \varepsilon & 0 \\ 0 & -\mu \varepsilon \end{pmatrix}
\]

under the basis of \{1\} and \{2\}, where $|\mu \varepsilon| << A$.

\[
\hat{H}_0 |+\rangle_x = (E_0 \hat{1} - A \hat{\sigma}_x) |+\rangle_x = (E_0 - A) |+\rangle_x
\]

\[
\hat{H}_0 |-\rangle_x = (E_0 \hat{1} - A \hat{\sigma}_x) |-\rangle_x = (E_0 + A) |+\rangle_x
\]

Then we have

(i)
Eigenvalue: \( E_s^{(0)} = E_0 - A \)

Eigenvector: \[ |\psi_s^{(0)}\rangle = |+\rangle_s = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \]

(ii)

Eigenvalue: \( E_a^{(0)} = E_0 + A \)

Eigenvector: \[ |\psi_a^{(0)}\rangle = |-\rangle_s = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \]

We note that the unitary operator is defined as

\[ |\psi_s^{(0)}\rangle = \hat{U} |1\rangle_s, \quad |\psi_a^{(0)}\rangle = \hat{U} |2\rangle_s \]

where

\[ \hat{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \quad \hat{U}^+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \]

We now consider the perturbation \( \hat{H}_1 \) defined by

\[ \hat{H}_1 = \begin{pmatrix} \mu \varepsilon & 0 \\ 0 & -\mu \varepsilon \end{pmatrix} \]

under the basis of \( \{ |1\rangle \text{ and } |2\rangle \} \), where \( |\mu \varepsilon| << A \). The Hamiltonians can be rewritten as

\[ \hat{U}^+ H_0 \hat{U} = \begin{pmatrix} E_0 - A & 0 \\ 0 & E_0 + A \end{pmatrix}, \quad \hat{U}^+ H_1 \hat{U} = \begin{pmatrix} 0 & \mu \varepsilon \\ \varepsilon \mu & 0 \end{pmatrix} \]

under the basis of \( \{ |\psi_s^{(0)}\rangle \text{ and } |\psi_a^{(0)}\rangle \} \). We now use the non-degenerate perturbation theory.

(i) The first order perturbation:

\[ E_s^{(1)} = \langle \psi_s^{(0)} | \hat{H}_1 |\psi_s^{(0)}\rangle = 0 \]

\[ E_a^{(1)} = \langle \psi_a^{(0)} | \hat{H}_1 |\psi_a^{(0)}\rangle = 0 \]
(ii) The second order perturbation

\[ E_s^{(2)} = \frac{\langle\psi_s^{(0)} | \hat{H} | \psi_s^{(0)} \rangle^2}{E_s^{(0)} - E_s^{(0)}} = -\frac{\mu^2 \varepsilon^2}{2A} \]

\[ E_a^{(2)} = \frac{\langle\psi_s^{(0)} | \hat{H} | \psi_a^{(0)} \rangle^2}{E_a^{(0)} - E_s^{(0)}} = \frac{\mu^2 \varepsilon^2}{2A} \]

Then we have

\[ E_s = E_s^{(0)} + E_s^{(1)} + E_s^{(2)} = E_0 - A - \frac{\mu^2 \varepsilon^2}{2A} \] (lower energy)

\[ E_a = E_a^{(0)} + E_a^{(1)} + E_a^{(2)} = E_0 + A + \frac{\mu^2 \varepsilon^2}{2A} \] (higher energy)

The wave function:

\[ |\psi_s\rangle = |\psi_s^{(0)}\rangle + \frac{\langle\psi_s^{(0)} | \hat{H} | \psi_s^{(0)} \rangle}{E_s^{(0)} - E_a^{(0)}} |\psi_s^{(0)}\rangle = |\psi_s^{(0)}\rangle - \frac{\varepsilon \mu}{2A} |\psi_a^{(0)}\rangle \]

\[ |\psi_a\rangle = |\psi_a^{(0)}\rangle + \frac{\langle\psi_s^{(0)} | \hat{H} | \psi_a^{(0)} \rangle}{E_a^{(0)} - E_s^{(0)}} |\psi_s^{(0)}\rangle = |\psi_a^{(0)}\rangle + \frac{\varepsilon \mu}{2A} |\psi_s^{(0)}\rangle \]
5. **Eigenvalue problem (exact solution)**

We solve the eigenvalue problem using the Mathamtica.

(i) **Eigenvalue:** \( E_0 + \sqrt{A^2 + \epsilon^2 \mu^2} \) (higher energy)

Eigenket: \( |\psi_a\rangle \approx (\epsilon \mu + \sqrt{A^2 + \epsilon^2 \mu^2})|1\rangle - |2\rangle \)

(ii) **Eigenvalue:** \( E_0 - \sqrt{A^2 + \epsilon^2 \mu^2} \) (lower energy)

Eigenket: \( |\psi_s\rangle = -(\epsilon \mu - \sqrt{A^2 + \epsilon^2 \mu^2})|1\rangle + |2\rangle \)

where the eigenkets are not normalized.

6. **Application**

Let us consider \( \text{NH}_3 \) in a region where \( \epsilon \) is weak but where \( \epsilon^2 \) has a strong gradient in the \( x \)-direction (i.e., along the axis of molecules).

\[
\frac{d}{dx}(\epsilon^2) = \lambda
\]

The molecules in the state \( |\varphi_s\rangle \) are subjected to a force parallel to the \( x \) axis:

\[
F_s = -\frac{dE_s}{dx} = \frac{1}{2} \lambda \frac{\mu^2}{A}
\]

Similarly, the molecules in the state \( |\varphi_a\rangle \) are subjected to an opposite force:
\[ F_a = -\frac{dE_a}{dx} = -\frac{1}{2} \frac{\lambda \mu^2}{A} \]

This is the basis of the method which is used in the ammonia maser to sort the molecules and select those in the higher energy state.

In the ammonia maser, the beam with molecules in the state \( |\phi_a^{(0)}\rangle \) and with the higher energy is sent through a resonant cavity.