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The Ammonia Maser
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The maser (Microwave Amplification by Stimulated Emission of Radiation) uses the stimulated emission process to produce coherent electromagnetic waves through amplification. The first maser was created by the Nobel Prize-winning Charles H. Townes in 1953, and was based on the umbrella inversion mode of the ammonia molecule NH_3 . The structure of this molecule consists of a pyramid with a nitrogen atom at the apex and one hydrogen atom at each corner of the triangular base, see Figure 1 a). The umbrella inversion of ammonia corresponds to the motion of the N atom relative to the H_3 symmetrical triangle, i. e., the nitrogen atom may be on both sides of the plane of hydrogen atoms. This phenomenon can be described by a symmetric double-well potential possessing two quantum states, corresponding to the two positions of the nitrogen atom, that are coupled.

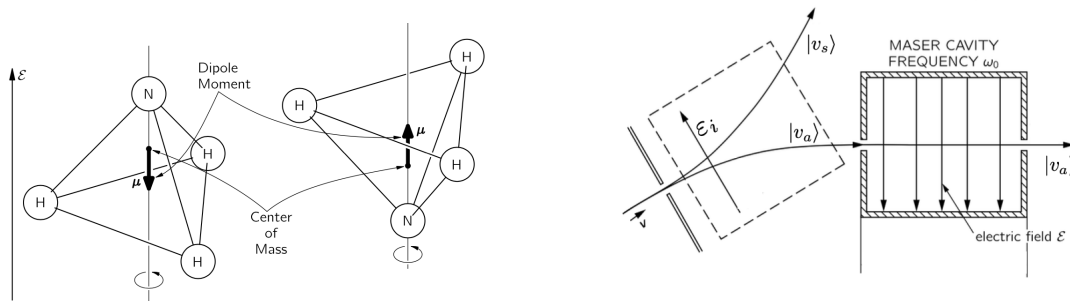


Figure 1: Sketches (not up to scale) of a) the two states for the ammonia molecule (left), and b) of the ammonia maser (right).

1. Ammonia can be described by the two quantum states

$$|v_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{y} \quad |v_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

having energy E_0 , which are coupled by a constant potential, $-A$, with $A = 0.04919$ meV.

- [1P] (a) obtain the Hamiltonian matrix H^0 describing this quantum system, the two eigenstates $|v_s\rangle$ and $|v_a\rangle$, their energies E_s^0 and E_a^0 , and their energy splitting $\hbar\omega_0 = |E_s^0 - E_a^0|$.
2. The first step to create the maser is to spatially separate the symmetric and antisymmetric states $|v_s\rangle$ and $|v_a\rangle$ of ammonia with an inhomogeneous electric field, which couples to the electric dipole moment μ , see Figure 1 b). To calculate this spatial separation:
 - [2P] (a) obtain the Hamiltonian matrix H describing ammonia in a static electric field $\vec{\varepsilon} = \varepsilon_s \hat{z}$, with ε_s being the electric field strength and \hat{z} the unit vector along the z -axis, and determine the energies of the two eigenstates, E_s and E_a ,
 - [1P] (b) determine these energies, E_s and E_a , in the weak and strong field regime, i. e., when the electric field interaction is much smaller and larger than the coupling between the two states,

- [2P] (c) in the weak field regime, obtain the force acting on the molecule for an electric field $\vec{\varepsilon} = \varepsilon_i \sqrt{z} \hat{z}$, with \hat{z} being the unit vector along the z -axis, and the spatial separation of the two states with opposite parity after 0.1 s and $\varepsilon_i = 0.2 \text{ MV/m}^{3/2}$. Assume that their initial velocity along this z -axis is zero.
3. In the second step, the molecules in the antisymmetric state enter a cavity with an oscillating electric field $\vec{\varepsilon} = 2\varepsilon_0 \cos(\omega t) \hat{z}$, with frequency ω and $\delta = \hbar\omega - \hbar\omega_0$. This cavity field induces a transition from the antisymmetric state to the symmetric one, and the energy released is fed into the oscillatory field. This process is called stimulated emission, and it allows for the conversion of molecular energy into the energy of an external electromagnetic field. In the weak field regime and for a resonant cavity field $\delta = 0$, determine:
- [2P] (a) for a molecule initially in the antisymmetric state, the probability to remain on this state or to perform a transition to the symmetric one,
- [1P] (b) the time needed by the ammonia to leave the cavity on the symmetric state after a single cycle for a cavity field strength $\varepsilon_0 = 0.01 \text{ V/m}$,
- [1P] (c) the length of this cavity if the molecules perform a single cycle from the asymmetric state to the symmetric one. Assume that they move along the x -axis, which is perpendicular to the cavity field, see Figure 1 b), at a temperature of $T = 300 \text{ K}$.

Hints:

- i) Assume that the ammonia dipole moment always lays on the same axis as the applied electric field.
- ii) To solve the time-dependent Schrödinger equation:
 - use the symmetric and antisymmetric basis states $c_s(t)$ and $c_a(t)$
 - perform the transformation $c_s(t) = \gamma_s(t)e^{-it\frac{E_0-A}{\hbar}}$ and $c_a(t) = \gamma_a(t)e^{-it\frac{E_0+A}{\hbar}}$,
 - apply the rotating wave approximation by neglecting the terms proportional to $e^{+it(\omega+\omega_0)}$ and $e^{-it(\omega+\omega_0)}$, which rapidly oscillate around zero and in any appreciable time scale of the system these oscillations quickly average to zero.

Data: Dipole moment of ammonia $\mu = 1.47D$, $\hbar = 1.054571817 \cdot 10^{-34} \text{ Js}$, $k_B = 1.380649 \cdot 10^{-23} \text{ J/K}$. The dalton or unified atomic mass unit is equal to $1.6605402 \cdot 10^{-27} \text{ kg}$, and the Debye is equal to $1D = 3.33564 \cdot 10^{-30} \text{ C m}$. $1 \text{ eV} = 1.60218 \cdot 10^{-19} \text{ J}$.

SOLUTION

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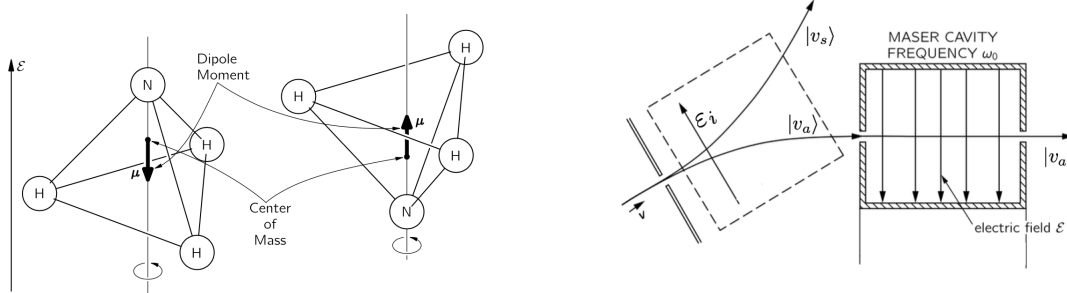


Figure 1: Sketches (not up to scale) of the two states for the ammonia molecule (left), and of the ammonia maser (right).

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having energy E_0 , and being coupled by the constant potential $-A$ with $A = 0.04919$ meV.

- [1P](a) Obtain the Hamiltonian matrix H^0 describing this quantum system, the two eigenstates $|v_s\rangle$ and $|v_a\rangle$, their energies E_s^0 and E_a^0 , and their energy splitting $\hbar\omega_0 = |E_s^0 - E_a^0|$.

Solution:

The Hamiltonian reads

$$H^0 = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix},$$

and the Schrödinger equation $H^0|\phi\rangle = E^0|\phi\rangle$. Diagonalizing the Hamiltonian matrix, we get the following symmetric and antisymmetric eigenstates and their energies

$$|v_s\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad E_s^0 = E_0 - A, \quad \text{and} \quad |v_a\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad E_a^0 = E_0 + A.$$

The energy splitting between them is $\hbar\omega_0 = |E_s^0 - E_a^0| = 2A$, which is $\hbar\omega_0 = 0.09838 \text{ meV} = 1.576 \cdot 10^{-23} \text{ J}$.

2. The first step to create the maser is to spatially separate the symmetric and antisymmetric states $|v_s\rangle$ and $|v_a\rangle$ of ammonia with an inhomogeneous electric field, which couples to the electric dipole moment μ , see Figure 1 b). To calculate this spatial separation:
 - [2P] (a) Obtain the Hamiltonian matrix H describing ammonia in a static electric field $\vec{\varepsilon} = \varepsilon_s \hat{z}$, with ε_s being the electric field strength and \hat{z} the unit vector along the z -axis, and determine the energies of the two eigenstates, E_s and E_a ,

Solution:

The dipole moment of ammonia couples to the electric field as $\vec{\mu} \cdot \vec{\varepsilon}$. As indicated in the first hint given at the end of the exercise, we consider that the dipole moment is always along the electric field axis. Taking into account that the two inversion modes have dipole moments with opposite directions, see Figure 1 a), the Hamiltonian of ammonia in the presence of the electric field reads

$$H = \begin{pmatrix} E_0 + \mu\varepsilon_s & -A \\ -A & E_0 - \mu\varepsilon_s \end{pmatrix},$$

Solving the corresponding Schrödinger equation, the eigenenergies are

$$E_s = E_0 - \sqrt{A^2 + \mu^2\varepsilon_s^2} \quad \text{and} \quad E_a = E_0 + \sqrt{A^2 + \mu^2\varepsilon_s^2}.$$

- [1P] (b) determine these field-dressed energies in the weak and strong field regime, i. e., when the electric field interaction is much smaller and larger than the coupling between the two states,

Solution:

The weak field regime appears if $\mu\varepsilon_s \ll A$, the eigenenergies can be written as

$$E_s = E_0 - A\sqrt{1 + \frac{\mu^2\varepsilon_s^2}{A^2}} \quad \text{and} \quad E_a = E_0 + A\sqrt{1 + \frac{\mu^2\varepsilon_s^2}{A^2}},$$

and we use the following approximation $\sqrt{1+x} \approx 1 + \frac{x}{2}$ for $|x| \ll 1$, in this case $x = \frac{\mu^2 \varepsilon_s^2}{A^2}$. In this weak field regime, the eigenenergies show a quadratic dependence on the field strength

$$E_s = E_0 - A - \frac{1}{2} \frac{\mu^2 \varepsilon_s^2}{A} \quad \text{and} \quad E_a = E_0 + A + \frac{1}{2} \frac{\mu^2 \varepsilon_s^2}{A}.$$

The strong field regime appears if $\mu \varepsilon_s \gg A$, the eigenenergies can be written as

$$E_s = E_0 - \mu \varepsilon_s \sqrt{1 + \frac{A^2}{\mu^2 \varepsilon_s^2}} \quad \text{and} \quad E_a = E_0 + \mu \varepsilon_s \sqrt{1 + \frac{A^2}{\mu^2 \varepsilon_s^2}},$$

Using, the following approximation $\sqrt{1 + \frac{A^2}{\mu^2 \varepsilon_s^2}} \approx 1 + \frac{A^2}{2\mu^2 \varepsilon_s^2}$, we obtain that in the strong field regime the energies, in first order, depend lineally on the field strength

$$E_s = E_0 - \mu \varepsilon_s - \frac{1}{2} \frac{A^2}{\mu \varepsilon_s} \quad \text{and} \quad E_a = E_0 + \mu \varepsilon_s + \frac{1}{2} \frac{A^2}{\mu \varepsilon_s}.$$

- [2P] (c) in the weak field regime, obtain the force acting on the molecule for an electric field $\vec{\varepsilon} = \varepsilon_i \sqrt{z} \hat{z}$, with \hat{z} being the unit vector along the z -axis, and the spatial separation of the two states with opposite parity after 0.1 s and $\varepsilon_i = 0.2 \text{ MV/m}^{3/2}$. Assume that their initial velocity along this z -axis is zero.

Solution:

The force acting on ammonia is $F = -\nabla E$. For the symmetric and antisymmetric states, it yields

$$F_s = \frac{1}{2} \frac{\mu^2}{A} \nabla \varepsilon^2 \quad \text{and} \quad F_a = -\frac{1}{2} \frac{\mu^2}{A} \nabla \varepsilon^2,$$

using $\varepsilon = \varepsilon_i \sqrt{z}$, we obtain

$$F_s = \frac{1}{2} \frac{\mu^2}{A} \varepsilon_i^2 \quad \text{and} \quad F_a = -\frac{1}{2} \frac{\mu^2}{A} \varepsilon_i^2.$$

and for the accelerations,

$$a_s = \frac{1}{2} \frac{\mu^2 \varepsilon_i^2}{A m_{NH_3}} \quad \text{and} \quad a_a = -\frac{1}{2} \frac{\mu^2 \varepsilon_i^2}{A m_{NH_3}}$$

with $m_{NH_3} = 3m_H + m_N$, m_H and m_N being the masses of the hydrogen and nitrogen atoms, respectively.

Their numerical values of the accelerations are $a_s = -a_a = 2.161 \text{ ms}^{-2}$, where we have used $\varepsilon_i = 0.2 \text{ MV/m}^{3/2}$, $\mu = 1.47 \text{ D} = 4.0934 \cdot 10^{-30} \text{ cm}$, and $m_{NH_3} = 17 \text{ Da} = 2.823 \cdot 10^{-26} \text{ kg}$.

The position of the ammonia molecules along the z -axis is $z = z_0 + v_0 t + t^2 a/2$. As indicated in the problem $v_0 = 0$, and we can take $z_0 = 0$ without loss of generality, we obtain that in 0.1 s each state is shifted 1.08 cm in opposite directions, and their spatial separation is 2.16 cm.

3. In the second step, the molecules in the antisymmetric state enter a cavity with an oscillating electric field $\vec{\varepsilon} = 2\varepsilon_0 \cos(\omega t)\hat{z}$, with frequency ω , and $\delta = \hbar\omega - \hbar\omega_0$. This cavity field induces a transition from the antisymmetric state to the symmetric one, and the energy released is fed into the oscillatory field. This process is called stimulated emission, and it allows for the conversion of molecular energy into the energy of an external electromagnetic field. In the weak field regime and for a resonant cavity field $\delta = 0$, determine:

Solution:

For the questions of this part, we need to solve time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt}|\psi\rangle = H|\psi\rangle \quad \text{with} \quad H = \begin{pmatrix} E_0 + \mu\varepsilon_s(t) & -A \\ -A & E_0 - \mu\varepsilon_s(t) \end{pmatrix},$$

which is a systems of coupled differential equations

$$i\hbar \frac{dc_1(t)}{dt} = [E_0 + 2\mu\varepsilon_0 \cos(\omega t)] c_1(t) - A c_2(t) \quad (1)$$

$$i\hbar \frac{dc_2(t)}{dt} = [E_0 - 2\mu\varepsilon_0 \cos(\omega t)] c_2(t) - A c_1(t) \quad (2)$$

We transform them to the basis $c_s(t) = c_1(t) + c_2(t)$ and $c_a(t) = c_1(t) - c_2(t)$, obtaining

$$i\hbar \frac{dc_s(t)}{dt} = (E_0 - A)c_s(t) + 2\mu\varepsilon_0 \cos(\omega t)c_a(t) \quad (3)$$

$$i\hbar \frac{dc_a(t)}{dt} = (E_0 + A)c_a(t) + 2\mu\varepsilon_0 \cos(\omega t)c_s(t) \quad (4)$$

This systems of differential equations is further simplified with the change

$$c_s(t) = \gamma_s(t)e^{-it\frac{E_0-A}{\hbar}} \quad \text{and} \quad c_a(t) = \gamma_a(t)e^{-it\frac{E_0+A}{\hbar}},$$

where $\gamma_s(t)$ and $\gamma_a(t)$ satisfy

$$i\hbar \frac{d\gamma_s(t)}{dt} = 2\mu\varepsilon_0 \cos(\omega t)\gamma_a(t)e^{-it\frac{2A}{\hbar}} \quad (5)$$

$$i\hbar \frac{d\gamma_a(t)}{dt} = 2\mu\varepsilon_0 \cos(\omega t)\gamma_s(t)e^{it\frac{2A}{\hbar}} \quad (6)$$

Using the expression of the cosine in terms of exponentials, these equations read

$$i\hbar \frac{d\gamma_s(t)}{dt} = \mu\varepsilon_0 [e^{-it(\omega-\omega_0)} + e^{+it(\omega+\omega_0)}] \gamma_a(t) \quad (7)$$

$$i\hbar \frac{d\gamma_a(t)}{dt} = \mu\varepsilon_0 [e^{it(\omega-\omega_0)} + e^{-it(\omega+\omega_0)}] \gamma_s(t) \quad (8)$$

where we have used $\hbar\omega_0 = 2A$. The terms $e^{+it(\omega+\omega_0)}$ and $e^{-it(\omega+\omega_0)}$ rapidly oscillate around zero, the rotating wave approximation neglects them on the basis that on any appreciable time scale of the system these oscillations will quickly average to zero. As a consequence, the system of differential equation reads

$$i\hbar \frac{d\gamma_s(t)}{dt} = \mu\varepsilon_0 e^{-it(\omega-\omega_0)} \gamma_a(t) \quad (9)$$

$$i\hbar \frac{d\gamma_a(t)}{dt} = \mu\varepsilon_0 e^{it(\omega-\omega_0)} \gamma_s(t) \quad (10)$$

The cavity field is resonant if $\hbar\omega = \hbar\omega_0 = 2A$, and these equations are further simplified as

$$i\hbar \frac{d\gamma_s(t)}{dt} = \mu\varepsilon_0 \gamma_a(t) \quad (11)$$

$$i\hbar \frac{d\gamma_a(t)}{dt} = \mu\varepsilon_0 \gamma_s(t) \quad (12)$$

To solve them, we derivate the first equation and substitute the second one on the first one obtaining

$$\frac{d^2\gamma_s(t)}{d^2t} = -\frac{\mu^2\varepsilon_0^2}{\hbar^2} \gamma_s(t) \quad (13)$$

The solutions are

$$\gamma_s(t) = c_1 \cos\left(\frac{\mu\varepsilon_0}{\hbar}t\right) + c_2 \sin\left(\frac{\mu\varepsilon_0}{\hbar}t\right) \quad (14)$$

$$\gamma_a(t) = ic_2 \cos\left(\frac{\mu\varepsilon_0}{\hbar}t\right) - ic_1 \sin\left(\frac{\mu\varepsilon_0}{\hbar}t\right) \quad (15)$$

where c_1 and c_2 are constants to be determined by the initial conditions. For $t = 0$, the ammonia is on the asymmetric state $\gamma_a(t = 0) = 1$ and $\gamma_s(t = 0) = 0$, obtaining $c_1 = 0$, $c_2 = -i$, and

$$\gamma_s(t) = -i \sin\left(\frac{\mu\varepsilon_0}{\hbar}t\right) \quad \text{and} \quad \gamma_a(t) = \cos\left(\frac{\mu\varepsilon_0}{\hbar}t\right) \quad (16)$$

[2P] (a) for a molecule initially on the antisymmetric state, the probability to remain on this state or to perform a transition to the symmetric one,

Solution:

The probability that ammonia remains on the antisymmetric state is $P_a(t) = |\gamma_a(t)|^2 = \cos^2\left(\frac{\mu\varepsilon_0 t}{\hbar}\right)$.

The probability that ammonia performs a transition to the symmetric state is $P_s(t) = |\gamma_s(t)|^2 = \sin^2\left(\frac{\mu\varepsilon_0 t}{\hbar}\right)$.

- [1P] (b) the time needed by the ammonia to leave the cavity on the symmetric state after a single cycle for a cavity field strength $\varepsilon_0 = 0.01$ V/m,

Solution:

The ammonia leaves the cavity on the symmetric state if $P_s(T) = 1$, i. e., $\sin^2\left(\frac{\mu\varepsilon_0 T}{\hbar}\right) = 1$, which holds if $T = \frac{n\pi\hbar}{2\mu\varepsilon_0}$ with $n = 1, 3, \dots$. Taking $n = 1$ and $\varepsilon_0 = 0.01$ V/m, it yields $T = 3.38$ ms.

- [1P] (c) the length of this cavity if the molecules perform a single cycle from the asymmetric state to the symmetric one. Assume that they move along the x -axis, which is perpendicular to the cavity field, see Figure 1 b), at a temperature of $T = 300$ K.

Solution:

For a Maxwell-Boltzmann distribution, the most probable velocity is given by

$$v = \sqrt{\frac{2k_B T}{m_{NH_3}}}. \quad (17)$$

For $T = 300$ K, it yields $v = 541.71$ m/s. For the length of the cavity, we use this velocity and the time needed to perform a single cycle within the cavity computed in the previous question $T = 3.38$ ms. Thus, the cavity length is $L = vt = 1.83$ m.

Data: Dipole moment of ammonia $\mu = 1.47D$, $\hbar = 1.054571817 \cdot 10^{-34}$ Js, $k_B = 1.380649 \cdot 10^{-23}$ J/K. The dalton or unified atomic mass unit is equal to $1.6605402 \cdot 10^{-27}$ kg, and the Debye is equal to $1D = 3.33564 \cdot 10^{-30}$ C m. $1 \text{ eV} = 1.60218 \cdot 10^{-19}$ J.

Historic remark: This problem is based on the lecture about The Ammonia Maser given in 1963 by Richard Feynman at The California Institute of Technology, see https://www.feynmanlectures.caltech.edu/III_09.html, Figure 1 a) and Figure 1 b) were adapted from this web page.