

INTRODUCTION TO QUANTUM MECHANICS

PART-III THE HAMILTONIAN EQUATIONS and the SCHRODINGER EQUATION

CHAPTER-7

THE HAMILTONIAN EQUATIONS

How Do States Change with Time?

- 7.1 What are the base states?
- 7.2 How do states change with time?
 - 7.2.A The Time Evolution Operator
 - 7.2.B The Hamiltonian Matrix
- 7.3 General characteristic of the Hamiltonian Matrix
 - 7.3.A Symmetry of the H matrix
 - 7.3.B Stationary states
 - 7.3.C Interpretation of the Hamiltonian Matrix as the Energy Matrix
- 7.4 Two-State Systems
 - 7.4.A The ammonia Molecule
 - 7.4.A.a Case $H_{12} = H_{21} = 0$ Absence of crosstalk
 - 7.4.A.b Case: $H_{12} = H_{21} \neq 0$ Quantum Tunneling
 - Figuring out the Hamiltonian Matrix
 - Time evolution of the quantum states
 - Conservation of the total probability
 - Stationary states
 - 7.4.B Molecule in a static electric field
 - 7.4.C Molecule in a time dependent electric field
 - Operation of the ammonia maser
 - Transitions at resonance
 - 7.4.D Spin $\frac{1}{2}$ particle in a magnetic field

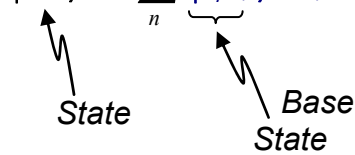
CHAPTER-7

THE HAMILTONIAN MATRIX¹

How Do States Change with Time?

7.1 What are the base states?

Chapter 4 described the concept of spectral Fourier decomposition, showing how any function $\Psi = \Psi(x)$ could be expressed in terms of harmonic functions $\{e^{ikx}, -\infty < k < \infty\}$, the latter being identified as a base. From there, the concept was generalized for basis composed not necessarily by harmonic functions. It was stated that, given an appropriate pre-determined basis-set of functions $\{|\varphi_n\rangle; n = 1, 2, 3, \dots\}$ satisfying the orthonormal inner product $\langle\varphi_n|\varphi_m\rangle = \delta_{mn}$, any state of motion Ψ of the system is equally described by a proper linear combination of the form (using the brackets notation),

$$|\Psi\rangle = \sum_n |\varphi_n\rangle A_n$$


Which base functions to choose will depend of course on the particular problem being studied. Even for the same problem a different basis set can be used,

$$|\Psi\rangle = \sum_n |\chi_n\rangle B_n$$

Note: In what follows we will consider base states that do not change with time. That is,

$$|\Psi(t)\rangle = \sum_n |\varphi_n\rangle A_n(t)$$

Also, when it is understood which specific states $|\varphi_n\rangle$ are we referring to, the following more simplified notation will be used,

$$|\Psi(t)\rangle = \sum_n |n\rangle A_n(t)$$

How do the base states $|\varphi_n\rangle$ look like?

It would be ideal to have analytical expressions describing these base functions, like, for example, in the Fourier expansion where we know the base constituted by the harmonic functions $\{e^{ikx}, -\infty < k < \infty\}$. But this will not be always the case. There are cases where the spatial variable x does not even exist (that is the case of the spin property for example).

It would be convenient then to develop a general formalism, without attaching ourselves too much to specific analytical variables, and rather conceive the states as a whole. We are fortunate that quantum mechanics allows that.

- For example, the complete description of an electron could be given simply by giving its momentum p (being understood that we mean a state described by the function $e^{i(p/\hbar)x}$) and its spin $|\uparrow\rangle$ or $|\downarrow\rangle$.

This gives the base: $\{ |p, \uparrow\rangle, |p, \downarrow\rangle; \text{ where } -\infty < p < \infty \}$.

- What about for two electrons?

That will require the specification of the 2 momenta and two spins. If one electron has momentum p_1 and the other p_2 , we still have four possible combinations respect to the spin

$$\{ |p_1, \uparrow; p_2, \uparrow\rangle; |p_1, \uparrow; p_2, \downarrow\rangle; |p_1, \downarrow; p_2, \uparrow\rangle; |p_1, \downarrow; p_2, \downarrow\rangle$$

$$\text{where } -\infty < p_1 < \infty \text{ and } -\infty < p_2 < \infty \}$$

As the number of electrons increases, the description of the base states becomes more elaborated.

- How to describe the states of a hydrogen atom?

If we did not know the hydrogen atom is made out of an electron and a proton, we could have specified the base states by giving the atom's momentum: $|p\rangle$.

But this description would have been incomplete? The hydrogen atom has internal parts. We have to specify,
the spin direction of the electron and its momentum

the spin direction of the proton and its momentum

Even after this correction, the above description would still be incomplete. Because, what about if the proton has internal parts? Currently it is accepted that it has. Further, even though it is currently accepted that the electron is a fundamental particle, maybe it will be discovered later that the electron does have internal parts ..., which would force us to introduced further corrections.

How do we know then whether or not we are having a complete set of base states?

The point is: we do not know the ultimate (complete) representation of the base states for the ultimate quantum mechanical description of the universe.

As an alternative, we generally work under some degree of approximation.

- Educated approximations

In non-relativistic quantum mechanics, if the energies involved in the problem are not too high so that the internal organization of the particles are not disturbed, then a reasonable approximation consists of ignoring such internal organization.

It would be sufficient to give the momenta and spin values of the electrons and nuclei.

It takes about 10 eV to excite a hydrogen atom into an internal excited state. Accordingly,

for situations where the energy involved is much lower than 10 eV, having for example a hydrogen atom moving slowly and bumping gently against other hydrogen atoms (staying always in the ground state) then such an atom can be considered as one particle and not worry about the internal motions (thus decreasing the number of details that we have to put into the nomenclature of the base states.)

- The ammonia molecule helps illustrate how to simplify the description of a complicated problem.

In an ammonia molecule, atoms located at the vertices of a pyramid; three hydrogen atoms in a plane and a nitrogen atom above or below that plane.

The description of this molecule can be complicated because it is possible to have an infinite number of motion states, namely,
 rotation around any axis
 translational motion in any direction
 vibrational motions

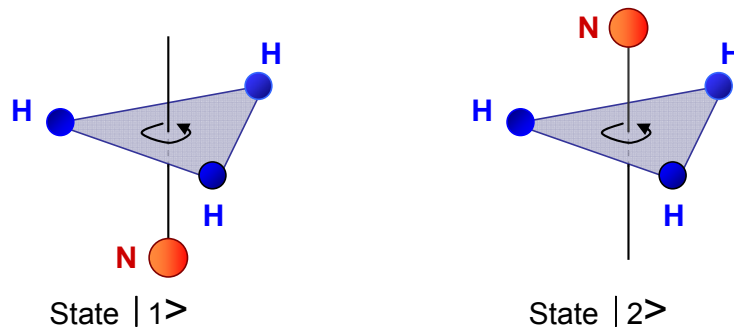


Fig. 7.1 The ammonia molecule. The figure shows two possible states for the molecule.

We want to make the approximation that the molecule is:
 rotating around its axis of symmetry with a certain angular momentum.
 undergoing translational motion with a certain momentum
 vibrating in a defined pattern

+

The molecule has two possible positions for the nitrogen atom (as shown in the figure above), which define the two base states we are mainly interested in this chapter, which are

State $|1\rangle$ defines the “down” state of the molecule (a given charge distribution corresponding to the case when the nitrogen is *below* the plane defined by the three hydrogen atoms.)

State $|2\rangle$ defines the “up” state of the molecule (a given charge distribution corresponding to the case when the nitrogen is *above* the plane defined by the three hydrogen atoms.)

We will assume that all the other states of motions do not affect the two particular states $|1\rangle$ and $|2\rangle$, the latter becoming our

interest of study. Thus, we are isolating a particular aspect (the behavior of states $|1\rangle$ and $|2\rangle$ out of a very complicated system.

Under this approximation, the state ψ of the nitrogen molecule, at any given time, is given by

$$\begin{aligned} |\psi(t)\rangle &= |1\rangle \underbrace{A_1(t)} + |2\rangle \underbrace{A_2(t)} \\ &= |1\rangle \underbrace{\langle 1|\psi(t)\rangle} + |2\rangle \underbrace{\langle 2|\psi(t)\rangle} \end{aligned}$$

[Note: We are not embarked, at this point, in the task of finding a detailed spatial charge-density distribution inside the molecule. That is not our objective right now. (We will assume here that the functions describing such charge-density distribution (associates with the two states $|1\rangle$ and $|2\rangle$ mentioned above) are given.

In this chapter we are rather interested in obtaining the *amplitude probability* that the molecule is found in any of the two base states. We will be able to do it, despite the fact that we do not know exactly what the charge-density distributions (associated to those states) are. Later on, when we had developed a more analytical formulation of the quantum mechanics and be able to figure out the exact spatial dependence of the charge distribution associated to the two base states, then we can come back and plug-in those analytical function into the description given in this section.]

7.2 How do a state Ψ evolve with time? ²

Let's assume that the set of states

$$\{ |n\rangle ; n = 1, 2, 3, \dots \} \quad (1)$$

constitutes a basis. That is, any state can be expressed as

$$|\Psi(t)\rangle = \sum_n |n\rangle A_n(t) \quad (2)$$

The central question in this section is:

How do the coefficients $A_n(t)$ change with time?

We would like to find a differential equation that governs $A_n(t)$. For that purpose, let's introduce the concept of the evolution operator.

7.2.A The Evolution Operator $\tilde{U}(t_2, t_1)$

Operators act on states, which result in a state.

Convention: We will use tilted bold fonts to identify operators.

\tilde{A} is an operator

$\tilde{A} |\Psi(t)\rangle$ operator \tilde{A} acting on the state $|\Psi(t)\rangle$

Definition of the evolution operator $\tilde{U}(t_2, t_1)$

$\tilde{U}(t_2, t_1)$ is defined as an operator that acting on a state at time t_1 gives the state at the time t_2 .

$$\underbrace{\tilde{U}(t_2, t_1)}_{\text{Operator}} \underbrace{|\Psi(t_1)\rangle}_{\text{State}} = \underbrace{|\Psi(t_2)\rangle}_{\text{State}} \quad (3)$$

By the way, we do not know how $\tilde{U}(t_2, t_1)$ looks like yet (in this section, we will just pretend that we know it.) Our interest is rather focused on finding what is its role in the quantum mechanics description of a state. In subsequent chapters we will see explicitly how to construct this operator.

As indicated in (2), at a given time t the state is described by,

$$|\Psi(t)\rangle = \sum_n |n\rangle A_n(t)$$

During an infinitesimal interval of time Δt the state evolves towards

$$|\Psi(t+\Delta t)\rangle = \sum_n |n\rangle A_n(t+\Delta t); \quad (4)$$

notice:

$$A_m(t+\Delta t) = \langle m | \Psi(t+\Delta t) \rangle \quad (4)'$$

On the other hand, according to (3)

$$|\Psi(t+\Delta t)\rangle = \tilde{U}(t+\Delta t, t) |\Psi(t)\rangle$$

which gives,,

$$\langle m | \Psi(t+\Delta t) \rangle = \langle m | \tilde{U}(t + \Delta t, t) | \Psi(t) \rangle \quad (5)$$

From (4) and (5),

$$A_m(t+\Delta t) = \langle m | \tilde{U}(t + \Delta t, t) | \Psi(t) \rangle$$

Using the expansion of $|\Psi(t)\rangle$ in terms of the base states,

$$\begin{aligned} A_m(t+\Delta t) &= \langle m | \tilde{U}(t + \Delta t, t) \sum_n | n \rangle A_n(t) \\ A_m(t+\Delta t) &= \sum_n \langle m | \tilde{U}(t + \Delta t, t) | n \rangle A_n(t) \end{aligned} \quad (6)$$

*This factor will
be defined as $U_{mn}(t + \Delta t, t)$*

General definition:

Let's construct a matrix $[U](t_2, t_1)$ whose components U_{mn} , are defined by

$$U_{mn}(t_2, t_1) \equiv \langle m | \tilde{U}(t_2, t_1) | n \rangle, \quad (7)$$

The definition is valid for arbitrary times t_2 and t_1 .

Notice, for the particular case in which the basis set had only three elements, the $[U]$ matrix would look like,

$$[U] = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{23} \\ U_{31} & U_{32} & U_{33} \end{pmatrix}$$

We want to emphasize the difference between the operator \tilde{U} and the matrix $[U]$.

The matrix $[U]$ is a particular representation of the operator \tilde{U} .
If a different base were chose, the matrix $[U]$ would change, but the operator \tilde{U} remains the same.

Using the definition given in (7), the results (6) can be expressed as,

$$A_m(t + \Delta t) = \sum_n U_{mn}(t + \Delta t, t) A_n(t) \quad (8)$$

As an example, for the particular case where only three base states are sufficient to describe the state of the particle, a matrix notation of the result (8) will look like,

$$\begin{pmatrix} A_1(t + \Delta t) \\ A_2(t + \Delta t) \\ A_3(t + \Delta t) \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{23} \\ U_{31} & U_{32} & U_{33} \end{pmatrix} \begin{pmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{pmatrix} \quad (8')$$

where $U_{mn} = U_{mn}(t + \Delta t, t)$

Notice, each $A_m(t + \Delta t)$ is a linear combination of the other three components $A_1(t)$, $A_2(t)$, $A_3(t)$.

7.2.B The Hamiltonian Matrix

We expect $A_m(t + \Delta t) \xrightarrow{\Delta t \rightarrow 0} A_m(t)$ for each m component.

Since expression (8) indicates that each $A_m(t + \Delta t)$ is a linear combination of all the other $A_n(t)$, it implies that the coefficients U_{mn} must satisfy,

$$U_{mn}(t + \Delta t, t) \xrightarrow{\Delta t \rightarrow 0} \begin{cases} 1 & \text{for } m = n \\ 0 & \text{for } m \neq n \end{cases} \quad (9)$$

That is, U_{mn} has this form,

$$U_{mn}(t + \Delta t, t) = \delta_{mn} + \Delta t K_{mn}(t)$$

or, equivalently,

$$[U](t + \Delta t, t) = [I] + \Delta t [K](t)$$

where $[I]$ is the unit matrix

For convenience (and to make this expression compatible with the results to be presented later) it is usual to extract the factor $(-i/\hbar)$ from the $[K]$ matrix components, out of which the $[H]$ matrix results,

$$[K] \equiv -\frac{i}{\hbar} [H] \quad (10)$$

[This is a key step. It is a definition quite conveniently introduced by Feynman as to make the equations for $[H]$ to be compatible with the Schrodinger equation. The latter will be introduced later.]

In terms of the components of the matrix $[H]$ one obtains,

$$U_{mn}(t + \Delta t, t) = \delta_{mn} - \Delta t \frac{i}{\hbar} H_{mn}(t) \quad (11)$$

which is equivalent to say

$$[U](t + \Delta t, t) = [I] + -\frac{i}{\hbar} \Delta t [H](t) \quad (11)'$$

Replacing (11) in (8),

$$A_m(t + \Delta t) = \sum_n \left(\delta_{mn} - \frac{i}{\hbar} (\Delta t) H_{mn}(t) \right) A_n(t)$$

$$A_m(t + \Delta t) = A_m(t) + \sum_n \left(-\frac{i}{\hbar} (\Delta t) H_{mn}(t) \right) A_n(t)$$

$$\frac{A_m(t + \Delta t) - A_m(t)}{\Delta t} = \sum_n \left(-\frac{i}{\hbar} H_{mn}(t) \right) A_n(t)$$

$$i\hbar \frac{dA_m(t)}{dt} = \sum_n H_{mn}(t) A_n(t) \quad \text{General case} \quad (12)$$

Or, equivalently, in matrix notation (for the particular case where only *three* base states are sufficient to describe the state of the particle,)

$$i\hbar \frac{d}{dt} \begin{pmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{pmatrix} = \begin{pmatrix} H_{11}(t) & H_{12}(t) & H_{13}(t) \\ H_{21}(t) & H_{22}(t) & H_{23}(t) \\ H_{31}(t) & H_{32}(t) & H_{33}(t) \end{pmatrix} \begin{pmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{pmatrix} \quad (\text{Case } n=3) \quad (13)$$

The matrix of coefficients H_{mn} is known as the Hamiltonian Matrix.

Below we show the matrix for the case in which there are only three base states.)

$$[H] \equiv \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} \text{ Hamiltonian Matrix (Case } n=3) \quad (14)$$

where $H_{mn} = H_{mn}(t)$

Equation (12) is the equivalent of Newton's law for the microscopic world. It constitutes the quantum mechanics law for the dynamics of the world.

To solve a particular problem all we have to do is to learn how to evaluate the coefficients H_{mn} of the Hamiltonian matrix

Once the Hamiltonian is known, expression (12) shows how all the coefficient $A_n(t)$ change with time; hence we know how the whole wavefunction $|\Psi(t)\rangle$ evolves with time: $|\Psi(t)\rangle = \sum_n |n\rangle A_n(t)$

Note on matrices (like $[H]$) and Operators (like \tilde{H}).

Later on it will become evident that the components constituting the Hamiltonian matrix $[H]$ depends on the particular basis of states being used. It is the Hamiltonian operator \tilde{H} that in fact describes the system; the matrix is just a particular representation of the operator in a given base state.

7.3 General characteristic of the Hamiltonian Matrix

Regardless of the particular problem involved, the Hamiltonian matrix holds general characteristics.

7.3.A The H matrix is symmetric

From expression (12) $i\hbar \frac{dA_k(t)}{dt} = \sum_n H_{kn}(t) A_n(t)$, taking the complex conjugates one obtains,

$$-i\hbar \frac{dA_k^*(t)}{dt} = \sum_n H_{kn}^*(t) A_n^*(t)$$

and multiplying by A_k ,

$$-i\hbar A_k \frac{dA_k^*(t)}{dt} = \sum_n H_{kn}^*(t) A_k A_n^*(t)$$

On the other hand, multiplying expression (12) by $A_k^*(t)$, one obtains,

$$i\hbar A_k^* \frac{dA_k(t)}{dt} = \sum_n H_{kn}(t) A_k^* A_n(t)$$

Hence,

$$i\hbar \frac{dA_k A_k^*}{dt} = \sum_n H_{kn}(t) A_k^*(t) A_n(t) - \sum_n H_{kn}^*(t) A_k(t) A_n^*(t) \quad (15)$$

Notice, in the right side of the equality above, we can not factor out the amplitude probability terms since $A_k^*(t) A_n(t)$ and $A_k(t) A_n^*(t)$ are, in general, different.

Adding all the terms $\frac{dA_k A_k^*}{dt}$, one obtains

$$\begin{aligned} \sum_k i\hbar \frac{dA_k A_k^*}{dt} &= \sum_k \sum_n H_{kn}(t) A_k^*(t) A_n(t) \\ &\quad - \sum_k \sum_n H_{kn}^*(t) A_k(t) A_n^*(t) \end{aligned}$$

Notice, on the right side of the equality above the indices n and k can interchange their names without altering the result.

$$\begin{aligned} \sum_k i\hbar \frac{dA_k A_k^*}{dt} &= \sum_k \sum_n H_{kn}(t) A_k^*(t) A_n(t) \\ &\quad - \sum_n \sum_k H_{nk}^*(t) A_n(t) A_k^*(t) \end{aligned}$$

This allows to obtain a simpler expression

$$\sum_k i\hbar \frac{dA_k A_k^*}{dt} = \sum_k \sum_n [H_{kn}(t) - H_{nk}^*(t)] A_k^*(t) A_n(t) \quad (16)$$

The probabilistic interpretation of the wavefunction $|\psi(t)\rangle = \sum_n |n\rangle A_n(t)$ indicates that the expression, $\sum_k A_k(t) A_k^*(t) = \sum_k |A_k(t)|^2$

gives the probability to find a particle in any of the base states. That probability should then be always equal to 1;

$$\sum_k A_k(t) A_k^*(t) = \sum_k |A_k(t)|^2 = 1 \quad (17)$$

that is, it must be independent of time. Accordingly $\frac{d}{dt} \left(\sum_k A_k A_k^* \right) = 0$ and, thus, expression (16) implies,

$$H_{kn} = H_{nk}^* \quad (18)$$

7.3.B Stationary states

Suppose a system is under some conditions that once it is in, for example, the state $|1\rangle$ it can not get into any other state $|n\rangle$ (and vice versa). This means that, in equation (12), the states $|n\rangle$ (for $n \neq 1$) do not get involved into the dynamics of state $|1\rangle$. Accordingly, the coefficients H_{1n} in (12) would be zero in those circumstances. The resultant equation would be,

$$i\hbar \frac{dA_1(t)}{dt} = H_{11} A_1(t) \quad (19)$$

Assuming that H_{11} does not depend on time, the solution for this equation is,

$$A_1(t) = A_1(0) e^{-i(H_{11}/\hbar) t} \quad (20)$$

From the de Broglie hypothesis learned in Chapter 4 (Section 4.3), we interpret the coefficient H_{11} as the energy of the state $|1\rangle$.

That is,

$|\Psi_1(t)\rangle = A_1(0) e^{-i(H_{11}/\hbar)t} |1\rangle$ gives the time dependence of a state $|\Psi_1\rangle$ with a **single definite energy** H_{11} and where only **one frequency** H_{11}/\hbar is involved. (21)

A state with such characteristics is called a **STATIONARY STATE**.

7.3.C Physical Interpretation of the Hamiltonian matrix

We will see later that for an arbitrary system it is possible to find a base set of stationary states ψ_k ($k= 1, 2, 3, \dots$), which correspondingly would have the following time dependence,

$$|\psi_k(t)\rangle = A_k(0) e^{-i(H_{kk}/\hbar)t} |k\rangle \quad (22)$$

where each coefficient H_{kk} is interpreted as the energy of the corresponding states. The connotation is then that the coefficients H_{kk} of the Hamiltonian matrix, in this case, are associated with the energy of the states. Hence, $[H]$ should be called the energy matrix.

(You may object why are we jumping into the conclusion of calling $[H]$ the energy matrix, since we have not figured out yet the interpretation of H_{mn} for $m \neq n$. Recall, however, that a matrix is always a representation of an operator in a given base. If we changed the base properly, we would get a diagonal matrix representation of the same operator, whose terms can then be interpreted as energy terms as done above. This justifies the interpretation of \tilde{H} as the energy operator.)

7.4 Two-State Systems

Finding the coefficients of the Hamiltonian matrix is the most important (and potentially the hardest part) in the description of a quantum system. To gain some familiarity, let's consider simple examples, starting with systems that can approximately be described by just two base states.

7.4.A The ammonia Molecule

The ammonia molecule was introduced in section 7.1 above.

State $|1\rangle$ defines the “down” state of the molecule (a given charge distribution corresponding to the case when the nitrogen is *below* the plane defined by the three hydrogen atoms.) (23)

State $|2\rangle$ defines the “up” state of the molecule (a given charge distribution corresponding to the case when the nitrogen is *above* the plane defined by the three hydrogen atoms.) (24)

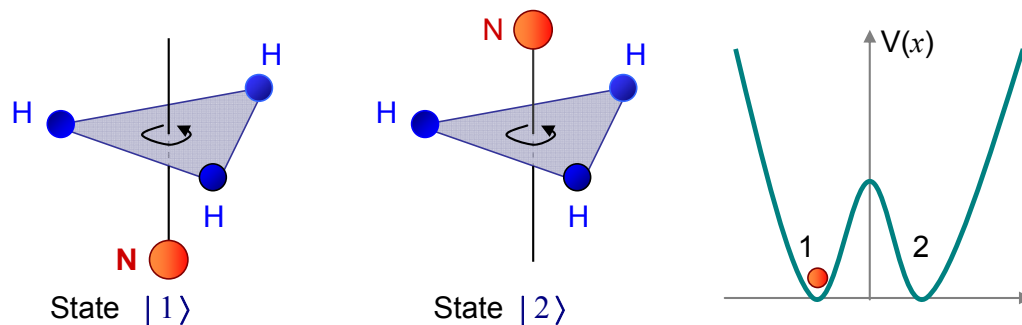


Fig. 7.2 Spatial configuration of states $|1\rangle$ and $|2\rangle$ for the NH_3 molecule. The curve on the right shows the potential energy of the N atom as a function of the distance from the plane containing the hydrogen atoms.

The ‘general’ state of the molecule is described as

$$|\psi(t)\rangle = |1\rangle A_1(t) + |2\rangle A_2(t)$$

- Assume that at $t=0$ a measurement indicates that the molecules is in the state $|1\rangle$.
- What is the probability that the molecule is found in the state $|2\rangle$ at some later time?

To answer this question we have to solve equation (12),

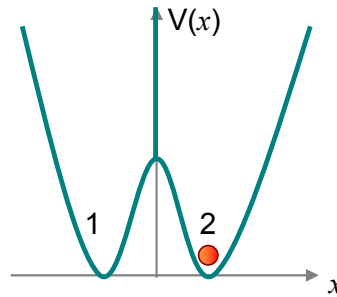
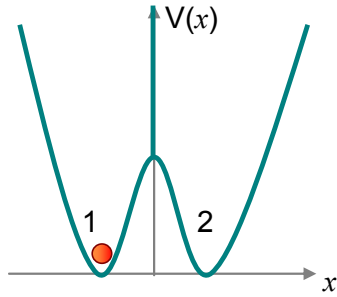
$i\hbar \frac{dA_m(t)}{dt} = \sum_{n=1}^2 H_{mn}(t) A_n(t)$, which is a system of differential equations

governing the coefficients A_1 and A_2 . But, paraphrasing Feynman, “the only ‘detail’ is that we do not know what to use for the coefficients H_{mn} .” However, given the nature of the problem we can make some educated guesses when trying to figure out the components H_{mn} of the Hamiltonian. We’ll do that in the following sections.

7.4.A.a Case: $H_{12} = H_{21} = 0$. Absence of “crosstalk”

This case is considered just for didactic purposes.

Using $H_{12} = 0$ in Eq. (12), implies that the state $|2\rangle$ does not get involved into the dynamic behavior of state $|1\rangle$ (It is like having an infinite potential barrier between states $|1\rangle$ and $|2\rangle$.)



Equation (12) then becomes,

$$i\hbar \frac{dA_1(t)}{dt} = H_{11} A_1(t)$$

If the ammonia were to remain at the state $|1\rangle$

Similarly, $H_{21} = 0$ implies

$$i\hbar \frac{dA_2(t)}{dt} = H_{22} A_2(t)$$

If the ammonia were to remain at the state $|2\rangle$

If we further assume that

H_{11} , H_{22} do not depend on time,

then the solutions for the above equations are,

$$A_1(t) = A_1(0)e^{-i(H_{11}/\hbar)t} \quad (25)$$

and

$$A_2(t) = A_2(0)e^{-i(H_{22}/\hbar)t} \quad (26)$$

What we have obtained then is two stationary states (a single definite energy and only one frequency is involved in a stationary state.)

$$|\psi_1\rangle = |1\rangle e^{-i(H_{11}/\hbar)t} \quad \text{and} \quad |\psi_2\rangle = |2\rangle e^{-i(H_{22}/\hbar)t} \quad (27)$$

The coefficients H_{11} and H_{22} can be interpreted as the energy of the stationary states $|1\rangle$ and $|2\rangle$ respectively.

The symmetry of the problem (see Fig. 7.2 above) suggests that the two coefficient H_{11} and H_{22} are equal; let's call it E_0 .

$$H_{11} = H_{22} \equiv E_0 \quad (28)$$

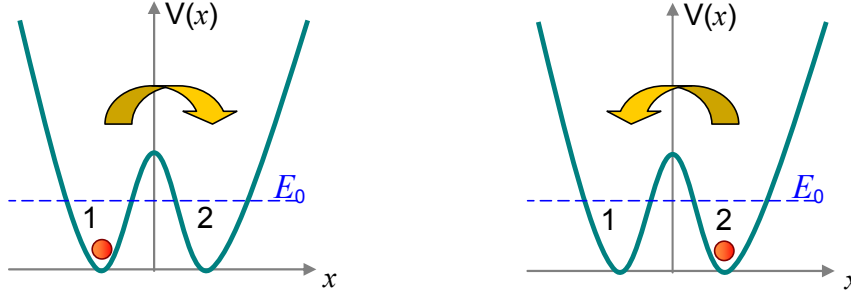
7.4.A.b Case: $H_{12} = H_{21} \neq 0$ Quantum Tunneling

Figuring out the Hamiltonian Matrix

It turns out that it is possible for the nitrogen atom to push its way through the plane defined by the three hydrogen atoms and flip to the other site. Such transition can be viewed as the nitrogen having to overcome an energy barrier. Although this can not be justified in terms of classical arguments, there is however a (quantum mechanics) amplitude probability that that can happen;

in quantum mechanics it is possible for a particle to cross a region that is classically forbidden energetically (quantum tunneling.)

In short, there is some small amplitude probability that the molecule starting in the state $|1\rangle$ gets into state $|2\rangle$; that is, the state $|2\rangle$ gets involved into the dynamics of the state $|1\rangle$, and vice versa.



This means that the coefficients $H_{12} = \langle 1 | \tilde{H} | 2 \rangle$ and $H_{21} = \langle 2 | \tilde{H} | 1 \rangle$ in equation (12) are different from zero. Writing the latter more explicitly we obtain

$$i\hbar \frac{dA_1(t)}{dt} = H_{11}A_1 + H_{12}A_2 \quad (29)$$

$$i\hbar \frac{dA_2(t)}{dt} = H_{21}A_1 + H_{22}A_2$$

Further, again due to symmetry arguments, it would be reasonable to assume that

$$H_{12} = H_{21} \equiv -W$$

There is some small amplitude probability that the molecule starting in the state $|1\rangle$ gets into state $|2\rangle$; and vice versa. (30)

where W is a constant different than zero (the negative sign is chosen arbitrarily, for later convenience).

Using (28) and (30) in (29) the differential equations take the form,

$$\begin{aligned} i\hbar \frac{dA_1(t)}{dt} &= E_0 A_1 - W A_2 \\ i\hbar \frac{dA_2(t)}{dt} &= -W A_1 + E_0 A_2 \end{aligned} \quad (31)$$

Here, one identifies the Hamiltonian matrix $[H]$,

$$[H] \equiv \begin{pmatrix} E_0 & -W \\ -W & E_0 \end{pmatrix} \quad (32)$$

Matrix representation of the Hamiltonian operator \tilde{H} in the base $\{ |1\rangle, |2\rangle \}$

We would like to emphasize that the matrix representing the Hamiltonian operator \tilde{H} would change if a different basis were to be chosen (as we will see below.)

Time evolution of the quantum states (Solving Eq. (31))

Adding the two equations in (31),

$$\begin{aligned} i\hbar \frac{d[A_1 + A_2]}{dt} &= E_0[A_1 + A_2] - W[A_1 + A_2] \\ i\hbar \frac{d[A_1 + A_2]}{dt} &= (E_0 - W)[A_1 + A_2] \end{aligned} \quad (33)$$

which gives the solution,

$$[A_1 + A_2] = a e^{-(i/\hbar)(E_0 - W)t}, \quad \text{where } a = \text{arb const} \quad (34)$$

Subtracting the equations in (31),

$$\begin{aligned} i\hbar \frac{d[A_1 - A_2]}{dt} &= E_0[A_1 - A_2] + W[A_1 - A_2] \\ i\hbar \frac{d[A_1 - A_2]}{dt} &= (E_0 + W)[A_1 - A_2] \end{aligned} \quad (35)$$

which gives the solution,

$$[A_1 - A_2] = b e^{-(i/\hbar)(E_0 + W)t}, \quad \text{where } b = \text{arb const} \quad (36)$$

From (34) and (36), one obtains the general solution for Eq. (31),

$$A_1(t) = \frac{a}{2} e^{-(i/\hbar)(E_0 - W)t} + \frac{b}{2} e^{-(i/\hbar)(E_0 + W)t} \quad (37)$$

$$A_2(t) = \frac{a}{2} e^{-(i/\hbar)(E_0 - W)t} - \frac{b}{2} e^{-(i/\hbar)(E_0 + W)t}$$

with arbitrary constants a and b .

The above are the amplitude probabilities intervening in the description of a general state,

$$|\psi(t)\rangle = |1\rangle A_1(t) + |2\rangle A_2(t)$$

Evolution of a state while conserving the total probability


The general state is described by $|\psi(t)\rangle = |1\rangle A_1(t) + |2\rangle A_2(t)$.

Returning to our original question:

If at $t=0$ the molecule is in the state $|1\rangle$, what is the probability that the molecule is found in the state $|2\rangle$ at a later time?

This initial condition requires that: $A_1(0) = 1$ and $A_2(0) = 0$. This is satisfied by the general solutions (37) if $a = b = 1$, thus giving,

$$\begin{aligned} A_2(t) &= \frac{a}{2} e^{-(i/\hbar)(E_0 - W)t} - \frac{a}{2} e^{-(i/\hbar)(E_0 + W)t} \\ &= \frac{1}{2} e^{-(i/\hbar)(E_0)t} \left[e^{(i/\hbar)(W)t} - e^{-(i/\hbar)(W)t} \right] \\ A_2(t) &= i e^{-(i/\hbar)(E_0)t} \sin\left(\frac{W}{\hbar}t\right) \end{aligned} \quad (38)$$



The corresponding probability to find the molecule in the state $|2\rangle$ at the time t is ,

$$P_2(t) \equiv |A_2(t)|^2 = \text{Sin}^2\left(\frac{W}{\hbar}t\right) \quad (39)$$

Notice the oscillatory character of $P_2(t)$, sometimes with a maximum value of 1 and then back to zero.

Similarly, expression (37) with $a = b = 1$ gives,

$$\begin{aligned} A_1(t) &= \frac{1}{2}e^{-(i/\hbar)(E_0 - W)t} + \frac{1}{2}e^{-(i/\hbar)(E_0 + W)t} \\ &= \frac{1}{2}e^{-(i/\hbar)(E_0)t} \left[e^{(i/\hbar)(W)t} + e^{-(i/\hbar)(W)t} \right] \\ A_1(t) &= e^{-(i/\hbar)(E_0)t} \text{Cos}\left(\frac{W}{\hbar}t\right) \end{aligned} \quad (40)$$

The corresponding probability to find the particle back in the state $|1\rangle$ at the time t is,

$$P_1(t) \equiv |A_1(t)|^2 = \text{Cos}^2\left(\frac{W}{\hbar}t\right) \quad (41)$$

In summary,

What we have found is that for a state $|\psi(t)\rangle = |1\rangle A_1(t) + |2\rangle A_2(t)$ with initial condition $A_1(0) = 1$ and $A_2(0) = 0$, the probability $P_1(t) \equiv |A_1(t)|^2$ is dumped into state $|2\rangle$ until P_1 is zero; then the role of $P_1(t) \equiv |A_1(t)|^2$ and $P_2(t) \equiv |A_2(t)|^2$ inverts itself. All this happens at a angular frequency $\omega = W / \hbar$.

Notice also that at all times the total probability $P_1(t) + P_2(t)$ (to find the molecule in any of its two states) is constant and equal to 1.

$$\begin{aligned}
|\psi(t)\rangle &= |1\rangle A_1(t) + |2\rangle A_2(t) \\
\text{with } A_1(t) &= e^{-(i/\hbar)(E_0)t} \cos\left(\frac{W}{\hbar}t\right) \\
A_2(t) &= ie^{-(i/\hbar)(E_0)t} \sin\left(\frac{W}{\hbar}t\right) \\
\text{At } t=0: |\psi(0)\rangle &= |1\rangle
\end{aligned}
\tag{42}$$

$\omega = W/\hbar$

Stationary states

Below we show that even when $H_{12} = H_{21} \neq 0$ we can find stationary states; that is, states with a single definite energy and only one frequency. Indeed, expressions (33) and (35) above (and reproduced below in expression (43)) alert on this possibility.

$$\begin{aligned}
i\hbar \frac{d[A_1 + A_2]}{dt} &= (E_0 - W) [A_1 + A_2] \\
i\hbar \frac{d[A_1 - A_2]}{dt} &= (E_0 + W) [A_1 - A_2]
\end{aligned}
\tag{43}$$

These expressions suggest to define the following 'new' states $|S_I'\rangle$ and $|S_{II}'\rangle$ (in terms of the 'old' states $|1\rangle$ and $|2\rangle$),

$$|S_I'\rangle \equiv |1\rangle + |2\rangle$$

$$|S_{II}'\rangle \equiv |1\rangle - |2\rangle$$

for, that way, the equation (43) would reveal the existence of stationary states (as we will see below).

But first notice that these states would not be normalized (notice, for example, that $\langle S_I' | S_I' \rangle = 2$.) This, however, can be corrected by defining,

$$|S_I\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad \text{and} \quad |S_{II}\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \quad (44)$$

The wavefunction can equivalently be expressed in either base,

$$\begin{aligned} |\psi(t)\rangle &= |1\rangle A_I(t) + |2\rangle A_2(t) \\ &\text{or,} \\ &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \end{aligned} \quad (45)$$

How do the amplitudes $B_I(t)$ and $B_{II}(t)$ change with time?

Since we know the time dependence of $A_1(t)$ and $A_2(t)$, all we have to do is to find a relationship between the A -amplitudes and the B -amplitudes. This is obtained by replacing (44) in (45),

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) B_I(t) + \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) B_{II}(t) \\ &= \frac{1}{\sqrt{2}} [B_I(t) + B_{II}(t)] |1\rangle + \frac{1}{\sqrt{2}} [B_I(t) - B_{II}(t)] |2\rangle \end{aligned}$$

which implies,

$$A_1(t) = \frac{1}{\sqrt{2}} [B_I(t) + B_{II}(t)] \quad \text{and} \quad A_2(t) = \frac{1}{\sqrt{2}} [B_I(t) - B_{II}(t)]$$

(46)

as well as

$$B_I(t) = \frac{1}{\sqrt{2}} [A_1(t) + A_2(t)] \quad \text{and} \quad B_{II}(t) = \frac{1}{\sqrt{2}} [A_1(t) - A_2(t)]$$

Replacing (46) in (43), the following relationship is obtained,

$$i\hbar \frac{d}{dt} B_I(t) = [E_0 - W] B_I(t) + [0] B_{II}(t) \quad (47)$$

$$i\hbar \frac{d}{dt} B_{II}(t) = [0] B_I(t) + [E_0 + W] B_{II}(t)$$

We find that the same Hamiltonian operator \tilde{H} alluded in (32) acquires a different matrix representation when using the new base $\{ |S_I\rangle, |S_{II}\rangle \}$ defined in (44),

$$[\mathbf{H}'] \equiv \begin{pmatrix} E_0 - W & 0 \\ 0 & E_0 + W \end{pmatrix} \quad (48)$$

Matrix representation of the Hamiltonian operator $\tilde{\mathbf{H}}$ in the base $\{ |S_I\rangle, |S_{II}\rangle \}$

Compare this expression with (32). The Hamiltonian operator is the same $\tilde{\mathbf{H}}$ (the same problem being solved), but the matrix representing it are different (since different basis are being used in (32) and (48).)

The stationary solutions of Eq. (47) have the form,

Solution-1:

$$B_I(t) = B_I(0)e^{-(i/\hbar)(E_0 - W)t}, \quad B_{II}(t) = 0 \quad (49)$$

Solution-2:

$$B_I(t) = 0, \quad B_{II}(t) = B_{II}(0)e^{-(i/\hbar)(E_0 + W)t} \quad (50)$$

Thus, we have found that the ammonia molecule admits two stationary states,

$$\begin{aligned} |\Psi_I(t)\rangle &= B_I(0)e^{-(i/\hbar)(E_0 - W)t} |S_I\rangle \\ |\Psi_{II}(t)\rangle &= B_{II}(0)e^{-(i/\hbar)(E_0 + W)t} |S_{II}\rangle \end{aligned} \quad (51)$$

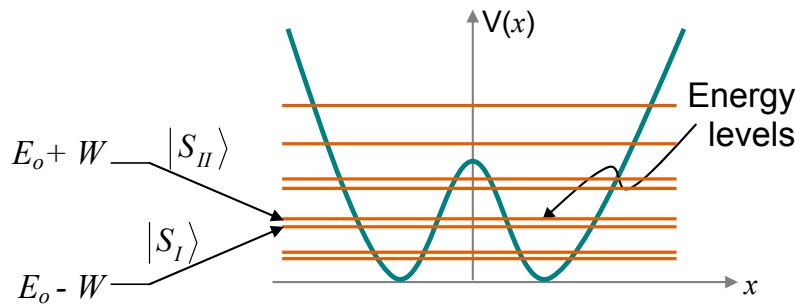


Fig. 7.3 Because there is some chance ($W \neq 0$) that the nitrogen atom can tunnel from one position to the other (see diagram in Fig. 7.2) the energy levels of the molecule are

split. (In the text description we have referred to only one of these levels; but many other are split as well.) The horizontal bars have been drawn to run across the two potential wells as to indicate that the energy levels are associated to the whole molecule (and not just each individual potential well.)

We can envision a way to measure experimentally the value of $W \equiv -H_{12} = H_{21}$ (the amplitude probability that the molecules can flip between state $|1\rangle$ and $|2\rangle$) and, in passing, allude its application to the maser:

Excitation of an electron inside an atom typically requires excitation by photons of energies in the range of the visible and ultraviolet range.

To excite the **vibration modes** of a molecule involves photons in the **infrared**.

Excitation of the **rotational motion** requires photons in the **far-infrared**.

In the ammonia molecule, the difference in energy of the stationary states described above is equal to $E_{II} - E_{II} = 2W \equiv hf$. The frequency f lies in the range of **microwaves**; $f = 24,000 \text{ MHz}$ or $\lambda \sim 1 \text{ cm}$

7.4.B Ammonia molecule in a static electric field

What is the Hamiltonian associated to the ammonia molecules problem when an electric field is present?

First, we notice that, due to the internal charge distribution, the ammonia molecule has an electrical dipole μ (see schematic in Fig. 7.4 below.) *“When the nitrogen flips from one side to the other, the center of mass will not move, but the electric dipole moment will flip over. As a result, the energy of the ammonia molecule in the electric field will depend on the molecular orientation.”*

In the absence of an external electric field (studied in the previous section) the existence of μ is immaterial. But, in the presence of an external electric field \mathcal{E} , the states $|1\rangle$ and $|2\rangle$ will have their energy E_o lowered and raised, respectively, by an amount $\mu \mathcal{E}$. Thus, in a

first approximation, if we ignored the amplitude probability for the molecules to flip from one configuration to the other, we would have stationary states of energy $E_o \pm \mu \mathcal{E}$. That is,

$$H_{11} = E_o - \mu \mathcal{E} \quad \text{and} \quad H_{22} = E_o + \mu \mathcal{E} \quad (52)$$

(That is, we are proceeding to assign the values of H_{11} and H_{22} in a similar way as when we arrived to expression (28) in section 7.4.A.a above.)

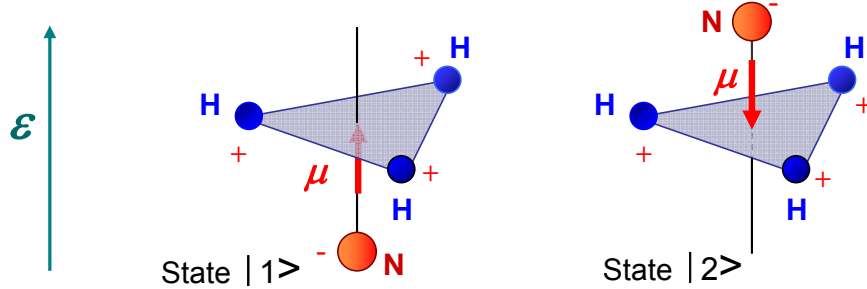


Fig. 7.4 Schematic representation of charge distribution, which gives rise to a net electric dipole μ . In the presence of an external electric field \mathcal{E} the state $|1\rangle$ has a lower energy than state $|2\rangle$.

- When considering an amplitude probability that the nitrogen atom can jump from one position to the other across the plane defined by the hydrogen atoms, we will assume that the electric field does not affect drastically the values of H_{12} . Thus,

$$H_{12} = H_{21} \equiv -W$$

In this case, the dynamic equation (12) becomes,

$$\begin{aligned} i\hbar \frac{dA_1(t)}{dt} &= (E_o - \mu \mathcal{E}) A_1 - W A_2 \\ i\hbar \frac{dA_2(t)}{dt} &= -W A_1 + (E_o + \mu \mathcal{E}) A_2 \end{aligned} \quad (53)$$

which gives the amplitudes A_1 and A_2 that describe the wavefunction in the base $\{|1\rangle, |2\rangle\}$;

$$|\psi(t)\rangle = |1\rangle A_1(t) + |2\rangle A_2(t)$$

Solving Eq. (53)

Adding the two equations in (53),

$$i\hbar \frac{d[A_1 + A_2]}{dt} = (E_0 - W) [A_1 + A_2] - \mu\mathcal{E}[A_1 - A_2] \quad (54)$$

$$i\hbar \frac{d[A_1 - A_2]}{dt} = -\mu\mathcal{E}[A_1 + A_2] + (E_0 + W)[A_1 - A_2]$$

This result suggests to define the new base,

$$|S_I\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad \text{and} \quad |S_{II}\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \quad (55)$$

A general wavefunction $|\psi(t)\rangle$ can be expressed in terms of the either base,

$$\begin{aligned} |\psi(t)\rangle &= |I\rangle A_I(t) + |2\rangle A_2(t) \\ &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \end{aligned} \quad (56)$$

where $B_I(t) = \frac{1}{\sqrt{2}}[A_1(t) + A_2(t)]$ and $B_{II}(t) = \frac{1}{\sqrt{2}}[A_1(t) - A_2(t)]$

From (54) the equation for the B-amplitudes becomes,

$$i\hbar \frac{d[B_I]}{dt} = (E_0 - W) [B_I] - \mu\mathcal{E} [B_{II}] \quad (57)$$

$$i\hbar \frac{d[B_{II}]}{dt} = -\mu\mathcal{E} [B_I] + (E_0 + W)[B_{II}]$$

$$[H''] \equiv \begin{pmatrix} E_0 - W & -\mu\mathcal{E} \\ -\mu\mathcal{E} & E_0 + W \end{pmatrix}$$

Matrix representation of the Hamiltonian operator $\tilde{\mathcal{H}}$ in the base $\{|S_I\rangle, |S_{II}\rangle\}$

Thus in this case (when $\mathcal{E} \neq 0$) the Hamiltonian matrix is not diagonal neither in the $\{|1\rangle, |2\rangle\}$ nor the $\{|S_I\rangle, |S_{II}\rangle\}$ basis.

Looking for stationary states (solving Eq. (57))

Stationary states are characterized by a single frequency.
In order for the state

$$|\psi(t)\rangle = |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t)$$

to describe a stationary state we have to require in equation (57) that both amplitudes $B_I(t)$ and $B_{II}(t)$ have the same frequency dependence.

Accordingly, let's consider a solution of the form,

$$B_I(t) = b_I e^{-(i/\hbar)(E)t} \quad \text{and} \quad B_{II}(t) = b_{II} e^{-(i/\hbar)(E)t} \quad (58)$$

with b_I , b_{II} , and E being constants to be determined

If we succeeded in finding the proper b_I , b_{II} , and E values, the wavefunction would look like,

$$\begin{aligned} |\psi(t)\rangle &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \\ &= |S_I\rangle b_I e^{-(i/\hbar)(E)t} + |S_{II}\rangle b_{II} e^{-(i/\hbar)(E)t} \\ &= [|S_I\rangle b_I + |S_{II}\rangle b_{II}] e^{-(i/\hbar)(E)t} \end{aligned}$$

In effect, the wavefunction would be varying as a function of time with just one frequency (which is characteristics of stationary states.)

Replacing (58) in (57) gives,

$$\begin{aligned} E b_I &= (E_0 - W) b_I - \mu \mathcal{E} b_{II} \\ E b_{II} &= -\mu \mathcal{E} b_I + (E_0 + W) b_{II} \end{aligned}$$

Rearranging the terms,

$$\begin{aligned} [E - (E_0 - W)] b_I &= -\mu \mathcal{E} b_{II} \\ [E - (E_0 + W)] b_{II} &= -\mu \mathcal{E} b_I \end{aligned} \quad (59)$$

The expression above indicates that b_I and b_{II} can not be chosen independently (if we want to obtain stationary states.)

Equating the ratio b_I / b_{II} from each of the two expressions above, one obtains,

$$\frac{-\mu \mathcal{E}}{[E - (E_0 - W)]} = \frac{[E - (E_0 + W)]}{-\mu \mathcal{E}}$$

$$[E - (E_0 - W)][E - (E_0 + W)] = (\mu\mathcal{E})^2$$

$$[(E - E_0) + W][(E - E_0) - W] = (\mu\mathcal{E})^2$$

$$(E - E_0)^2 - W^2 = (\mu\mathcal{E})^2$$

$$(E - E_0)^2 = W^2 + (\mu\mathcal{E})^2$$

$$E - E_0 = \pm \sqrt{W^2 + (\mu\mathcal{E})^2}$$

The last expression indicates that two stationary states are possible, whose energies are given by,

$$E_L = E_0 - \sqrt{W^2 + (\mu\mathcal{E})^2} \quad (60)$$

$$E_U = E_0 + \sqrt{W^2 + (\mu\mathcal{E})^2}$$

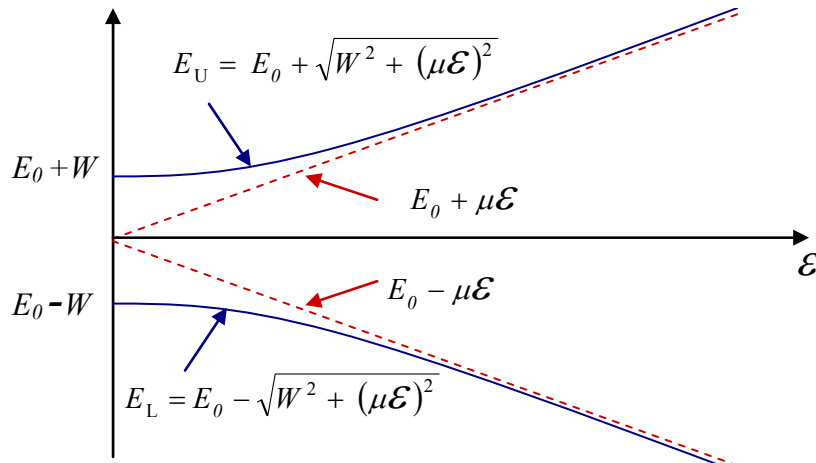


Fig. 7.5 Split energy levels of the ammonia molecules as a function of the magnitude of the applied external electric field \mathcal{E} .

Stationary state of energy $E_L = E_0 - \sqrt{W^2 + (\mu\mathcal{E})^2}$

Replacing $E = E_L$ in (59),

$$[-\sqrt{W^2 + (\mu\mathcal{E})^2} + W]b_I = -\mu\mathcal{E}b_{II}$$

$$\frac{-\sqrt{W^2 + (\mu\mathcal{E})^2} - W}{-\mu\mathcal{E}}b_{II} = b_I$$

The stationary state has the form

$$\begin{aligned}
|\psi_L(t)\rangle &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \\
&= |S_I\rangle b_I e^{-(i/\hbar)(E_L)t} + |S_{II}\rangle b_{II} e^{-(i/\hbar)(E_L)t} \\
&= [|S_I\rangle b_I + |S_{II}\rangle b_{II}] e^{-(i/\hbar)(E_L)t}
\end{aligned}$$

If we choose $b_I = \mu\mathcal{E}$ then $b_{II} = \sqrt{W^2 + (\mu\mathcal{E})^2} - W$, we obtain a no-normalized state,

$$|\psi_L(t)\rangle = [\mu\mathcal{E}|S_I\rangle + (\sqrt{W^2 + (\mu\mathcal{E})^2} - W)|S_{II}\rangle] e^{-(i/\hbar)(E_L)t} \quad (61)$$

For small \mathcal{E} ($\mu\mathcal{E} \ll W$),

$$\begin{aligned}
\sqrt{W^2 + (\mu\mathcal{E})^2} &= W\sqrt{1 + (\mu\mathcal{E}/W)^2} = W[1 + (1/2)(\mu\mathcal{E}/W)^2] \\
\sqrt{W^2 + (\mu\mathcal{E})^2} - W &= (1/2)(\mu\mathcal{E})^2/W
\end{aligned}$$

and the non-normalized state takes the form,

$$|\psi_L(t)\rangle = [|S_I\rangle + (\mu\mathcal{E}/2W)|S_{II}\rangle] e^{-(i/\hbar)(E_L)t} \quad (62)$$

Stationary state of energy $E_U = E_0 + \sqrt{W^2 + (\mu\mathcal{E})^2}$

Replacing $E = E_U$ in (59),

$$\begin{aligned}
[\sqrt{W^2 + (\mu\mathcal{E})^2} + W] b_I &= -\mu\mathcal{E} b_{II} \\
[\sqrt{W^2 + (\mu\mathcal{E})^2} - W] b_{II} &= -\mu\mathcal{E} b_I
\end{aligned}$$

The stationary state has the form

$$\begin{aligned}
|\psi_U(t)\rangle &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \\
&= |S_I\rangle b_I e^{-(i/\hbar)(E_U)t} + |S_{II}\rangle b_{II} e^{-(i/\hbar)(E_U)t} \\
&= [|S_I\rangle b_I + |S_{II}\rangle b_{II}] e^{-(i/\hbar)(E_U)t}
\end{aligned}$$

If we choose $b_I = -\mu\mathcal{E}$ then $b_{II} = \sqrt{W^2 + (\mu\mathcal{E})^2} + W$, we obtain a no-normalized state,

$$|\psi_U(t)\rangle = [-\mu\mathcal{E}|S_I\rangle + (\sqrt{W^2 + (\mu\mathcal{E})^2} + W)|S_{II}\rangle] e^{-(i/\hbar)(E_U)t} \quad (63)$$

For small \mathcal{E} ($\mu\mathcal{E} \ll W$),

$$|\psi_U(t)\rangle = [-\mu\mathcal{E}|S_I\rangle + (2W + (1/2)(\mu\mathcal{E})^2/W)|S_{II}\rangle] e^{-(i/\hbar)(E_U)t} \quad (64)$$

Notice, when $\mathcal{E} \rightarrow 0$ the states should reduce to the ones given in (51); in effect, from (62) and (64) we obtain,

$$\begin{aligned} |\psi_L(t)\rangle &\xrightarrow{\mathcal{E} \rightarrow 0} |S_I\rangle e^{-(i/\hbar)(E_0 - W)t} \\ |\psi_U(t)\rangle &\xrightarrow{\mathcal{E} \rightarrow 0} |S_{II}\rangle e^{-(i/\hbar)(E_0 + W)t} \end{aligned}$$

Spatial separation of ammonia molecules

For typical electric fields used in the lab, the energy $\mu\mathcal{E}$ is much smaller than W . The value of the energy levels can then be approximated by $E = E_0 \pm W \sqrt{1 + \left(\frac{\mu\mathcal{E}}{W}\right)^2} = E_0 \pm W \left[1 + \frac{1}{2}\left(\frac{\mu\mathcal{E}}{W}\right)^2\right]$

$$E_L = E_0 - W - \frac{\mu^2}{2W} \mathcal{E}^2$$

and similarly,

$$E_U = E_0 + W + \frac{\mu^2}{2W} \mathcal{E}^2$$

We find that the (potential) energy varies proportionally to \mathcal{E}^2 . We can infer then that in the presence of an electric field, a force will be acting on the ammonia molecules whose value will be given by,

$$\vec{F} = -\nabla \text{Energy} = \pm \nabla \frac{\mu^2}{2W} \mathcal{E}^2 = \pm \frac{\mu^2}{2W} \nabla(\mathcal{E}^2) \quad (65)$$

7.4.C Molecule in a time-dependent electric field

Operation of the ammonia maser

- Find a way to separate the states $|\psi_L(t)\rangle$ and $|\psi_U(t)\rangle$.

This is attained by passing a collimated beam of atoms through an electric field gradient, which will exert a force depending on the ammonia molecule state, as described in (65) above.

- At the entrance of the resonant cavity, the atoms would be at the state $|\psi_U(t)\rangle$ (see Fig.7.6 below.)

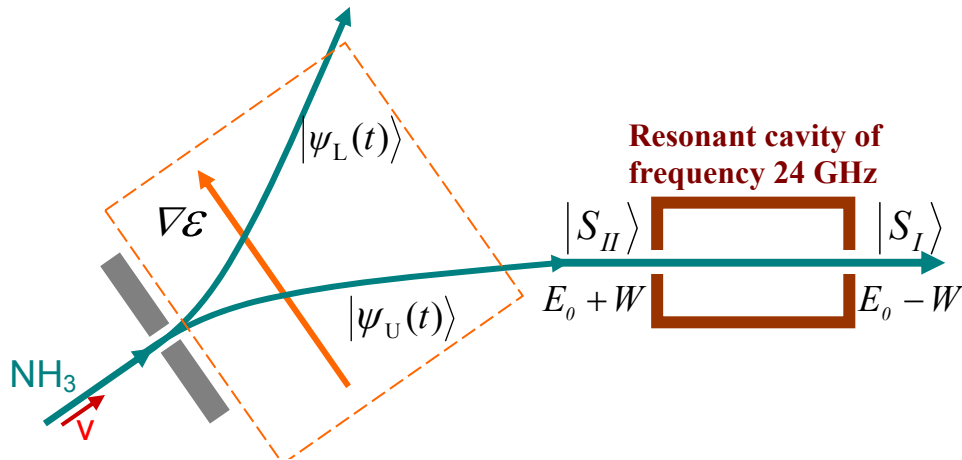


Fig. 7.6 Schematic description of the ammonia maser. A gradient electric field splits the atoms, as to produce a beam of atoms in the $|S_{II}\rangle$ state entering the resonant cavity. Upon interacting with a time-dependent electric field inside the cavity, the atoms transit from state $|S_{II}\rangle$ to state $|S_I\rangle$, thus delivering an energy $E_{II} - E_I = 2W$ to the cavity.

- At the resonant cavity, the atoms will find a time-dependent electric field, which will induce the transition of the ammonia molecules from the $|\psi_U(t)\rangle$ state towards the state $|\psi_L(t)\rangle$.
The interaction between the ammonia molecule and a time dependent electric field (established inside the cavity) will be described below in more detail.
- This transition will deliver energy to the cavity, which will later interact with the new incoming atoms.
(The length of the cavity is made just long enough for the molecule certainly makes the transition, thus entering the cavity in the state $|\psi_U(t)\rangle$ and leaving the cavity in the state $|\psi_L(t)\rangle$.)

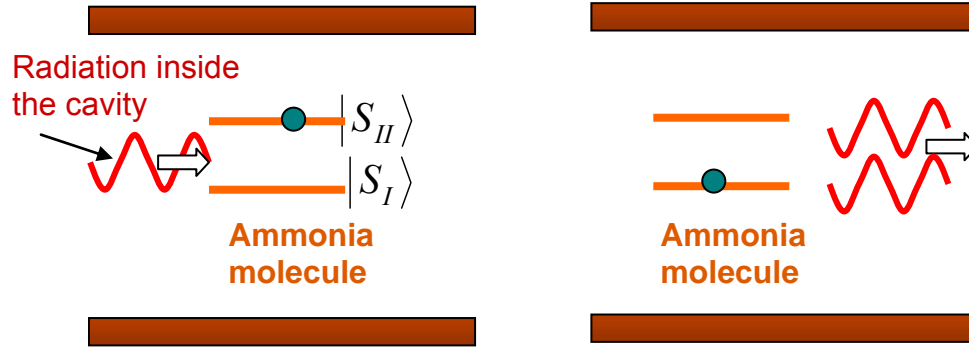


Fig. 7.7 Excitation of the ammonia molecules with a time dependent electric field. The peculiarity in the stimulated emission is that the resulting two photons are in phase.

What we need to understand now is the interaction between the molecules and a time-dependent electric field existent in the cavity. Such understanding can be obtained following a procedure identical to the case of the static, but until expression (57). Here we reproduce that expression but making explicit the fact that this time the electric field \mathcal{E} depends on time.

$$i\hbar \frac{d[B_I]}{dt} = (E_0 - W) [B_I] - \mu \mathcal{E}(t) [B_{II}] \quad (66)$$

$$i\hbar \frac{d[B_{II}]}{dt} = -\mu \mathcal{E}(t) [B_I] + (E_0 + W) [B_{II}]$$

which gives the amplitudes B_I and B_{II} that describe the wavefunction in the base $|S_I\rangle, |S_{II}\rangle$;

$$|\psi(t)\rangle = |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t)$$

$$[H](t) \equiv \begin{pmatrix} E_0 - W & -\mu \mathcal{E}(t) \\ -\mu \mathcal{E}(t) & E_0 + W \end{pmatrix} \quad (67)$$

Matrix representation of the Hamiltonian operator $\tilde{\mathcal{H}}$ in the base $\{|S_I\rangle, |S_{II}\rangle\}$

When the electric field \mathcal{E} is zero,

we have found solutions of the form (according to (51) above)

$$B_I(t) = B_I(0) e^{-(i/\hbar)(E_0 - W)t},$$

and

$$B_{II}(t) = B_{II}(0) e^{-(i/\hbar)(E_0 + W)t}$$

When an external electric field $\mathcal{E} = \text{constant}$ is applied,

we also found similar solutions. Indeed, according to (58) the solutions have the form.

$$B_I(t) = b_I e^{-(i/\hbar)(E)t}$$

and

$$B_{II}(t) = b_{II} e^{-(i/\hbar)(E)t}$$

where b_I and b_{II} were constants, and $E = E_0 \pm W$

This time, to take into account that the electric field is changing with time, let's consider solutions of the form,

$$B_I(t) = b_I(t) e^{-(i/\hbar)(E_I)t} \quad \text{and} \quad B_{II}(t) = b_{II}(t) e^{-(i/\hbar)(E_{II})t} \quad (68)$$

where $E_I \equiv E_0 - W$, $E_{II} \equiv E_0 + W$

Notice b_I and b_{II} are now functions that depend on time (to be determined.)

Replacing (68) in (66) gives,

$$\begin{aligned} \left(E_I b_I + i\hbar \frac{db_I}{dt} \right) e^{-(i/\hbar)(E_I)t} &= E_I b_I e^{-(i/\hbar)(E_I)t} - \mu \mathcal{E} b_{II} e^{-(i/\hbar)(E_{II})t} \\ \left(E_{II} b_{II} + i\hbar \frac{db_{II}}{dt} \right) e^{-(i/\hbar)(E_{II})t} &= -\mu \mathcal{E} b_I e^{-(i/\hbar)(E_I)t} + E_{II} b_{II} e^{-(i/\hbar)(E_{II})t} \end{aligned}$$

Multiplying the first equation by $e^{(i/\hbar)(E_I)t}$ and the second equation by $e^{(i/\hbar)(E_{II})t}$, respectively, one obtains,

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}(t) b_{II} e^{-i\omega_o t} \quad (69)$$

$$i\hbar \frac{db_{II}}{dt} = -\mu \mathcal{E}(t) b_I e^{i\omega_o t}$$

where we have used

$$E_{II} - E_I = 2W \equiv \hbar \omega_o \quad (70)$$

Assuming an electric field of the form

$$\mathcal{E}(t) = 2\mathcal{E}_o \cos \omega t = e^{i\omega t} + e^{-i\omega t} \quad (71)$$

(we are assuming there is this type of radiation inside the cavity,) expression (69) becomes,

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_o b_{II} \left[e^{i(\omega - \omega_o)t} + e^{-i(\omega + \omega_o)t} \right] \quad (72)$$

$$i\hbar \frac{db_{II}}{dt} = -\mu \mathcal{E}_o b_I \left[e^{i(\omega + \omega_o)t} + e^{-i(\omega - \omega_o)t} \right]$$

If \mathcal{E}_o is small, we expect $\frac{db_I}{dt}$ and $\frac{db_{II}}{dt}$ to be slowly varying functions of time. In a formal integration of the expression above, we would have $i\hbar b_I(t) = -\mu \mathcal{E}_o \int^t b_{II}(t') e^{i(\omega - \omega_o)t'} - \mu \mathcal{E}_o \int^t b_{II}(t') e^{-i(\omega + \omega_o)t'}$. The term varying at frequency $\omega + \omega_o$ changes so rapidly around zero, that it will not contribute appreciable to the average rate of change of $b_I(t)$, compared to the term oscillating at frequency $\omega - \omega_o$. Thus, we will use the following approximation,

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_o b_{II} \left[e^{i(\omega - \omega_o)t} \right] \quad (73)$$

$$i\hbar \frac{db_{II}}{dt} = -\mu \mathcal{E}_o b_I \left[e^{-i(\omega - \omega_o)t} \right]$$

Particular case: Transitions at resonance

Let's consider the case in which the existent radiation in the cavity has a frequency ω equal to $(E_{II} - E_I)/\hbar = 2W/\hbar \equiv \omega_o$

For $\omega = \omega_o$. expression (73) reduces to

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_o b_{II} \quad , \quad \text{and} \quad i\hbar \frac{db_{II}}{dt} = -\mu \mathcal{E}_o b_I$$

The rate at which b_I and b_{II} change with time is determined by amplitude \mathcal{E}_o of the external electric field and the electric dipole μ of the ammonia molecule.

To decouple these two equations, we evaluate the derivative of the first equation $i\hbar \frac{d^2 b_I}{dt^2} = -\mu \mathcal{E}_o \frac{db_{II}}{dt}$, where we replace the second equation $i\hbar \frac{d^2 b_I}{dt^2} = -\mu \mathcal{E}_o \frac{db_{II}}{dt} = -\mu \mathcal{E}_o \left[-\frac{\mu \mathcal{E}_o}{i\hbar} b_I \right]$ which gives

$$\frac{d^2 b_I}{dt^2} + \left(\frac{\mu \mathcal{E}_o}{\hbar} \right)^2 b_I = 0 \quad (74)$$

An identical equation is obtained for b_{II} .

A general solution for b_I is,

$$b_I(t) = p \left[\cos\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) \right] + q \left[\sin\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) \right] \quad (75)$$

Accordingly, the corresponding solution for b_{II} will be,

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_o b_{II}$$

$$b_{II}(t) = \frac{i\hbar}{-\mu \mathcal{E}_o} \frac{db_I}{dt} = \frac{i\hbar}{-\mu \mathcal{E}_o} \frac{d}{dt} \left[p \cos\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) + q \sin\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) \right]$$

$$b_{II}(t) = p \left[i \sin\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) \right] - q \left[i \cos\left(\frac{\mu \mathcal{E}_o}{\hbar} t\right) \right] \quad (76)$$

In summary,

For the ammonia molecules inside an electric field of frequency ω equal to the resonance frequency ω_0

$$\mathcal{E}(t) = 2\mathcal{E}_0 \cos \omega_0 t$$

$$(\text{where } \omega_0 = (E_{II} - E_I)/\hbar = 2W/\hbar)$$

the molecule's wavefunction evolves as

$$\begin{aligned} |\psi(t)\rangle &= |S_I\rangle B_I(t) + |S_{II}\rangle B_{II}(t) \\ &= |S_I\rangle b_I(t) e^{-(i/\hbar)(E_I)t} + |S_{II}\rangle b_{II}(t) e^{-(i/\hbar)(E_{II})t} \end{aligned}$$

where

$$b_I(t) \text{ and } b_{II}(t) \text{ are given in (75) and (76).}$$

If at $t=0$ the system is at the state of higher energy $|S_{II}\rangle$, it means $b_I(0) = 0$ and $b_{II}(0) = 1$.

The proper solution, given in (75) and (76), requires that $q = i$ and $p = 0$, which gives,

$$b_I(t) = i \left[\sin\left(\frac{\mu\mathcal{E}_0}{\hbar} t\right) \right], \quad b_{II}(t) = \left[\cos\left(\frac{\mu\mathcal{E}_0}{\hbar} t\right) \right];$$

Accordingly, the probability that the molecule being at the state $|S_{II}\rangle$ at $t=0$ make a transition to, or be found at, state $|S_I\rangle$ at a later time t will be,

$$P_I(t) = \sin^2\left(\frac{\mu\mathcal{E}_0}{\hbar} t\right) \quad (77)$$

$$(\text{Probability for the transition } |S_{II}\rangle \rightarrow |S_I\rangle)$$

and the probability that the molecule remains in the state $|S_{II}\rangle$ at a later time t will be,

$$P_{II}(t) = \cos^2\left(\frac{\mu\mathcal{E}_0}{\hbar} t\right) \quad (78)$$

Now we can understand better the diagram in Fig 7.6 describing the operation of the maser.

Since the molecular beam advances at velocity v , a molecule will take a time T to cross the cavity.

If the cavity is made long enough so that $(\mu\mathcal{E}_o/\hbar)T = \pi/2$ then for a molecule entering the cavity at $t=0$ in the state $|S_{II}\rangle$ there is a certainty, according to (78), that at $t=T$ it will leave the cavity in the state $|S_I\rangle$. [This estimation is based on the assumption that the electromagnetic field inside the cavity is oscillating exactly at the right frequency $\omega_o = (E_{II} - E_I)/\hbar$, which induces the transition from the upper level to the lower energy level as shown in Fig. 7.7).

These molecular transitions must deliver enough energy to maintain the cavity oscillations, cover the cavity losses, and the energy drawn from the cavity (that is, experimentally we must provide to the cavity enough molecules in the state of energy E_{II}).

Other ways of making masers.

Instead of separating the atoms in state $|S_{II}\rangle$ from those in state $|S_I\rangle$ (as displayed in Fig. 7.6), one can have all the atoms in their different states in the cavity and rather find a way to pump the atoms in state $|S_I\rangle$ to state $|S_{II}\rangle$. One way is the so called three-state maser.

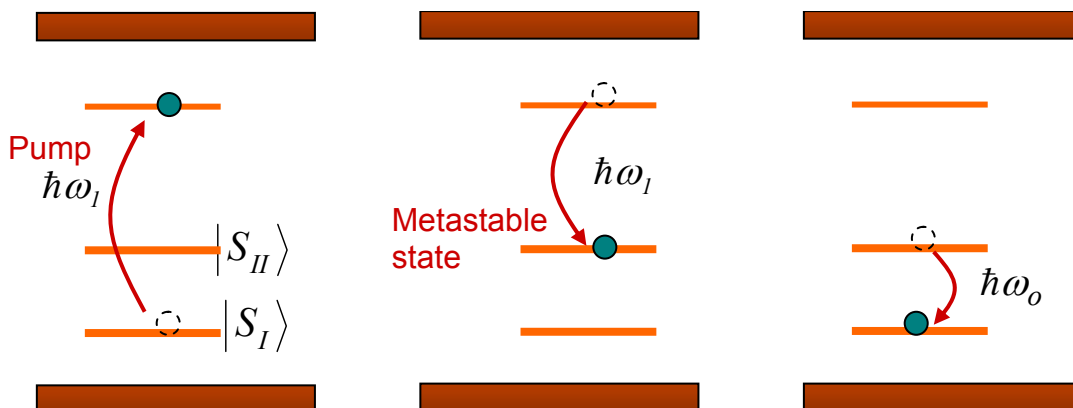


Fig. 7.8. Strategy for achieving enough high population of the state $|S_{II}\rangle$. The meta-stable state has a long lifetime (the molecule stays there for a

relatively long time, so enough high population is achieved. Aside from this three-state strategy, the system (maser) works as a two-state system.

General case: Transitions off resonance, $\omega \neq \omega_0$.

In this case, we consider that the frequency ω of the radiation in the cavity is different than $\omega_0 = (E_{II} - E_I) / \hbar$.

We want to calculate the probability that the ammonia molecule will transit from state $|S_{II}\rangle$ to $|S_I\rangle$ or vice versa.

Let's go back to the general equations given in expression (73) above, and reproduced here,

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_0 b_{II} \left[e^{i(\omega - \omega_0)t} \right] \quad (73)$$

$$i\hbar \frac{db_{II}}{dt} = -\mu \mathcal{E}_0 b_I \left[e^{-i(\omega - \omega_0)t} \right]$$

Rather than finding the most general solution, we will consider the case in which,

$$\frac{\mu \mathcal{E}_0}{\hbar} t \ll 1 \quad (79)$$

That is, starting from a given initial conditions at $t=0$ for b_I and b_{II} , we want to know how these two parameters change with time right after $t=0$ during an interval that satisfies (79).

Notice that in the time regime expressed in (79), even in the case of resonance, where $\omega = \omega_0$, the transition probability from one state to another state (given in expression (77)) is very small. We will exploit this fact when solving (73). In effect, let's consider again that at $t=0$, $b_I(0) = 0$ and $b_{II}(0) = 1$. Since b_{II} changes very little, we will use $b_{II}(t) = 1$ in the first equation of (73)

$$i\hbar \frac{db_I}{dt} = -\mu \mathcal{E}_0 b_{II} \left[e^{i(\omega - \omega_0)t} \right] = -\mu \mathcal{E}_0 \left[e^{i(\omega - \omega_0)t} \right]$$

whose solution is,

$$b_I(t) - b_I(0) = \frac{\mu \mathcal{E}_0}{\hbar(\omega - \omega_o)} \left[e^{i(\omega - \omega_o)t} - 1 \right]$$

$$b_I(t) = \frac{\mu \mathcal{E}_0}{\hbar(\omega - \omega_o)} \left[e^{i(\omega - \omega_o)t} - 1 \right]$$

$$\begin{aligned} |b_I(t)|^2 &= \left[\frac{\mu \mathcal{E}_0}{\hbar(\omega - \omega_o)} \right]^2 (e^{i(\omega - \omega_o)t} - 1)(e^{-i(\omega - \omega_o)t} - 1) \\ &= (2 - e^{i(\omega - \omega_o)t} - e^{-i(\omega - \omega_o)t}) \\ &= (2 - 2\cos((\omega - \omega_o)t)) \end{aligned}$$

Using the identity $\cos(a+b) = \cos(a)\cos(b) - \sin(a)\sin(b)$

$$\begin{aligned} \cos(2a) &= \cos^2(a) - \sin^2(a) \\ &= 1 - 2\sin^2(a) \end{aligned}$$

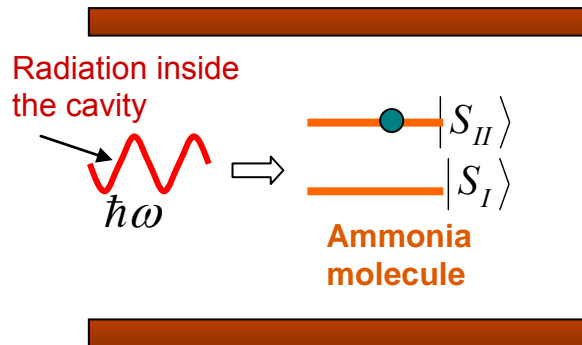
$$\sin^2(a) = (1/2) [1 - \cos(2a)]$$

Hence,

$$|b_I(t)|^2 = \left[\frac{\mu \mathcal{E}_0}{\hbar(\omega - \omega_o)} \right]^2 4\sin^2\left(\frac{\omega - \omega_o}{2}t\right) \quad (80)$$

For convenience, the expression above is equivalently expressed as,

$$|b_I(t)|^2 = \left[\frac{\mu \mathcal{E}_0}{\hbar} t \right]^2 \frac{\sin^2\left(\frac{\omega - \omega_o}{2}t\right)}{\left[\frac{\omega - \omega_o}{2}t\right]^2} \quad (81)$$



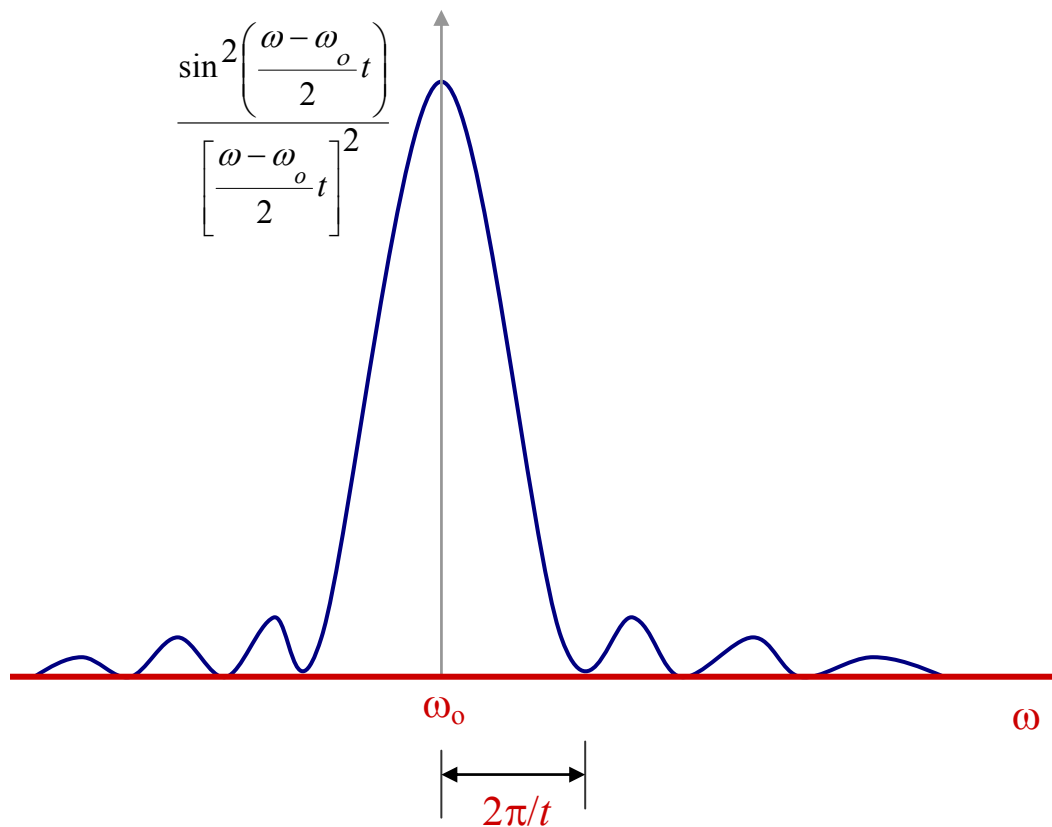


Fig. 7.9. For a fixed value of t , variation of as a function of the frequency

How sharp is this peak?

We notice the graph is essentially equal to zero outside the bandwidth $\Delta\omega = 2\pi/t$.

Let's assume an ammonia molecule that enters the cavity in the state $|S_{II}\rangle$ stays in the cavity for about $t = 1$ ms. The probability for the molecule to make a transition to the state $|S_{II}\rangle$ drops practically to a value equal to zero for frequencies outside a deviation of $\Delta\omega = 2\pi/1\text{ms}$.

Since $\omega_o = 2\pi \times 24 \times 10^9$ Hz, this deviation represents a fraction equal to

$$\frac{\Delta\omega}{\omega_o} = \frac{1}{24 \times 10^6} \sim 4 \times \frac{1}{10^8} \quad (82)$$

Thus, the frequency ω in the cavity has to be really very close to ω_0 in order to have a significant probability for the transition from state $|S_{II}\rangle$ to $|S_I\rangle$ to take place.

Absorption of electromagnetic energy

Expression (81) can also be expressed in term of the radiation intensity in the cavity,

$$I = 2\varepsilon_0 c \mathcal{E}_0^2$$

$$|b_I(t)|^2 = \frac{\mu^2}{\hbar^2} t^2 \frac{I}{2\varepsilon_0 c} \frac{\sin^2\left(\frac{\omega - \omega_0}{2} t\right)}{\left[\frac{\omega - \omega_0}{2} t\right]^2} \quad (83)$$

Since typically the radiation is not monochromatic, it is better to express the probability in terms of the spectral intensity density $\mathcal{J}(\omega)$ (intensity per unit frequency interval)

$$\begin{aligned} |b_I(t)|^2 &= \frac{\mu^2}{\hbar^2} t^2 \frac{1}{2\varepsilon_0 c} \int_0^\infty \mathcal{J}(\omega) \frac{\sin^2\left(\frac{\omega - \omega_0}{2} t\right)}{\left[\frac{\omega - \omega_0}{2} t\right]^2} d\omega \\ &= \frac{\mu^2}{\hbar^2} t^2 \frac{\mathcal{J}(\omega_0)}{2\varepsilon_0 c} \int_0^\infty \frac{\sin^2\left(\frac{\omega - \omega_0}{2} t\right)}{\left[\frac{\omega - \omega_0}{2} t\right]^2} d\omega \end{aligned}$$

$$= \frac{\mu^2}{\hbar^2} t^2 \frac{\mathcal{J}(\omega_o)}{2\varepsilon_o c} \frac{2\pi}{t}$$

$$|b_I(t)|^2 = \pi \frac{\mu^2}{\hbar^2} \frac{\mathcal{J}(\omega_o)}{\varepsilon_o c} t \quad (84)$$

Probability for the transition $|S_{II}\rangle \rightarrow |S_I\rangle$

Ammonia electric dipole: $\mu = 5.0 \cdot 10^{-30}$ Cm,

$$\hbar = 1.05 \cdot 10^{-34} \text{ Js}$$

$$\hbar / (\mu \varepsilon_o) = (2 \cdot 10^{-5} \text{ J*s} / \text{C*m*\varepsilon_o})$$

$$\text{For } \varepsilon_o = 1 \text{ N/C} \implies \mu \varepsilon_o = 5.0 \cdot 10^{-30} \text{ J} = 3.1 \cdot 10^{-11} \text{ eV}$$

$$\hbar / (\mu \varepsilon_o) = 2 \cdot 10^{-5} \text{ s}$$

We realize that it is the beat frequencies what counts. The high frequency related to the energy states are the carriers. The frequency resulting from the difference in energy levels is what sets the amplitude or strength at which the probability changes. Andres

¹ The Feynman Lectures, Vol III, Chapter 8

² The Feynman Lectures, Vol III, Chapter 8

See also B. H. Bransden & C. J. Joachain, "Quantum mechanics," 2nd Edition, Prentice Hall (2000). Page 232.