4 Other 2-state systems

In the previous section, we have discussed in quite some detail a particular 2-state system which is a spin-$\frac{1}{2}$. Two states means that there are 2 orthonormal basis states, but of course, the system can be in infinitely many different states which are all the rays (normalised vectors up to an overall phase) which result from linear combinations of these two basis vectors. For the spin-$\frac{1}{2}$ the natural Hamiltonian was determined by the coupling of the magnetic moment $\vec{m} = \gamma \vec{S}$ to an external magnetic field $\vec{B}$. In this section we will discuss other 2-state systems with different Hamiltonians, resulting in different energy levels (eigenvalues of the Hamiltonian) and different time-evolutions.

4.1 Ground states of the ammonia molecule

The ammonia molecule NH_3 consists of 3 hydrogen atoms H that form a regular triangle and the nitrogen atom N which is positioned on a line going through the centre of the triangle and perpendicular to the triangle's plane. By symmetry, the N atom can be either at a certain distance x_0 above or below this plane. This description corresponds to the ground state of the molecule. The molecule also has all sorts of vibrational modes but they correspond to excited states. From statistical physics we know that in a gas at temperature T the relative numbers N_i of molecules having energies E_i are

$$\frac{N_i}{N_j} = \exp\left(-\frac{E_i - E_j}{k_B T}\right) , \tag{4.1}$$

where k_B is Boltzmann's constant. A good way to remember its value is that at room temperature (300 K) one has

$$k_B \times 300K \simeq \frac{1}{40} \, eV = 0.025 \, eV . \tag{4.2}$$

For the ammonia molecule the first excited state has an energy of about $0.1 \, eV$ above the ground state. At room temperature the ratio (4.1) then is about e^{-4} which is small but not very small. However, if we cool the gas to 100 K then this ratio drops to $e^{-12} \simeq 6 \times 10^{-6}$ which now is very small. We may then consider that (almost) all molecules are in their ground state and we can neglect the excited states. Actually it should be clear from the classical description of the ground state that there must be *two* equivalent ground states, the one with the N atom above the plane of the triangle and the one with it below. We will call the corresponding quantum states $|+\rangle$ and $|-\rangle$. They are clearly physically equivalent, but are of course distinct states. We can assume that they form an orthonormal basis for the description of this reduced system. We would like to say that they both have the same (ground state) energy, but this makes only sense if they are eigenstates of the Hamiltonian.

What is the expected Hamiltonian when we restrict to these two states $|\pm\rangle$? The Hamiltonian governs the time evolution via the Schrödinger equation. If the state $|+\rangle$ would remain $|+\rangle$ forever it would be an eigenstate of H, and similarly for the $|-\rangle$, and then $H|\pm\rangle = E|\pm\rangle$ with the same eigenvalue E since both states are just related by a mirror symmetry which should not

change the energies. However, there is actually a small but non-vanishing probability that the state $|+\rangle$ evolves to the state $|-\rangle$ and vice versa. (This is related to the tunnel effect to be discussed in subsection 7.6.) This means that $\langle -|\,H\,|+\rangle \equiv -a$ must be non-vanishing. Then also $\langle +|\,H\,|-\rangle = (\langle -|\,H\,|+\rangle)^* = -a^*$. We will assume that a is real and positive,[20] and, of course, a should be small compared to the 0.1 eV difference between the ground state and first excited vibrational mode. We will then assume that the matrix-elements of H are given by

$$\begin{pmatrix} \langle +|\,H\,|+\rangle & \langle +|\,H\,|-\rangle \\ \langle -|\,H\,|+\rangle & \langle -|\,H\,|-\rangle \end{pmatrix} = \begin{pmatrix} E_0 & -a \\ -a & E_0 \end{pmatrix} \equiv \mathtt{H} \ , \tag{4.3}$$

where we use the symbol $\mathtt{H}$ to denote the matrix of H. To make things very clear, giving these matrix elements of H in the orthonormal basis of the $|\pm\rangle$ is equivalent to the statements

$$H\,|+\rangle = E_0\,|+\rangle - a\,|-\rangle \quad , \quad H\,|-\rangle = -a\,|+\rangle + E_0\,|-\rangle \ . \tag{4.4}$$

Determining the eigenvalues and eigenvectors of the matrix $\mathtt{H}$ is equivalent to determining the eigenvalues and eigenvectors of the operator H. Indeed, as discussed in general before, if $|\phi_n\rangle$ is an eigenvector of H with eigenvalue E_n then $v_n = \begin{pmatrix} \langle +\,|\phi_n\rangle \\ \langle -\,|\phi_n\rangle \end{pmatrix}$ is the corresponding eigenvector of the matrix $\mathtt{H}$ with this same eigenvalue E_n.

Let us then determine the eigenvalues and eigenvectors of the matrix $\mathtt{H}$. Since the eigenvector equation $\mathtt{H}v = Ev$ is equivalent to $(\mathtt{H} - E\,\mathbf{1})v = 0$, a non-vanishing solution v to this homogeneous linear system can only exist if the matrix $\mathtt{H} - E\,\mathbf{1}$ has vanishing determinant, hence

$$0 = \det(\mathtt{H} - E\,\mathbf{1}) = \det\begin{pmatrix} E_0 - E & -a \\ -a & E_0 - E \end{pmatrix} = (E_0 - E)^2 - a^2 \quad \Rightarrow \quad E = E_0 \pm a \ . \tag{4.5}$$

We will call the two eigenvalues E_S and E_A for reasons to become clear soon :

$$E_S = E_0 - a \quad , \quad E_A = E_0 + a \ . \tag{4.6}$$

Let us then determine the corresponding eigenvectors v_S and v_A by

$$0 = (\mathtt{H} - E_S\mathbf{1})v_S = \begin{pmatrix} a & -a \\ -a & a \end{pmatrix} v_S \quad , \quad 0 = (\mathtt{H} - E_A\mathbf{1})v_A = \begin{pmatrix} -a & -a \\ -a & -a \end{pmatrix} v_A \ . \tag{4.7}$$

Of course, these equations do determine the components of v_S and v_A only up to the normalisation and a choice of phase. We choose the phases so that they are real, and also normalise them to one. Then

$$v_S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad , \quad v_A = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \ . \tag{4.8}$$

The corresponding kets are

$$|S\rangle = \frac{1}{\sqrt{2}}\big(|+\rangle + |-\rangle\big) \quad , \quad |A\rangle = \frac{1}{\sqrt{2}}\big(|+\rangle - |-\rangle\big) \ . \tag{4.9}$$

---

[20]We may redefine the states $|\pm\rangle \to e^{\pm i\gamma}\,|\pm\rangle$ and this will change $a \to e^{2i\gamma}a$. Hence by choosing an appropriate γ we may make a real and positive.

This explains the origin of the labels S and A because they are symmetric and antisymmetric combinations of the "localised" states $|+\rangle$ and $|-\rangle$. However, as observed before, we may redefine the kets by phases. We could e.g. redefine $|-\rangle$ by an overall minus sign and then what looked like the symmetric combination will appear as the antisymmetric one and vice versa. What is of more physical relevance are the eigenvalues E_S and E_A. One has $E_S < E_A$ and one could say that the value E_0 has been split into $E_0 + a$ and $E_0 - a$.

We have found that the states $|\pm\rangle$ corresponding to the nitrogen atom localised above or below the plane of the three hydrogens are not eigenstates of the Hamiltonian, but the latter are the symmetric and antisymmetric combinations $|S\rangle$ and $|A\rangle$. The time evolution of any state is simple if expressed in the basis of eigenstates of the Hamiltonian. Just as in the previous section for the spin we can write the time evolution as

$$|\psi(0)\rangle = \alpha_S(0)|S\rangle + \alpha_A(0)|A\rangle \quad \Rightarrow \quad |\psi(t)\rangle = e^{-iE_St/\hbar}\alpha_S(0)|S\rangle + e^{-iE_At/\hbar}\alpha_A(0)|A\rangle \ . \quad (4.10)$$

Assume that at $t = 0$ the molecule was in the localised state $|+\rangle = \frac{1}{\sqrt{2}}\big(|S\rangle + |A\rangle\big)$, so that $\alpha_S(0) = \alpha_A(0) = \frac{1}{\sqrt{2}}$. Then

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\big(e^{-iE_St/\hbar}|S\rangle + e^{-iE_At/\hbar}|A\rangle\big) = \frac{e^{-iE_0t/\hbar}}{\sqrt{2}}\big(e^{iat/\hbar}|S\rangle + e^{-iat/\hbar}|A\rangle\big) \ . \quad (4.11)$$

The probability to find the molecule at time t in the other localised state $|-\rangle = \frac{1}{\sqrt{2}}\big(|S\rangle - |A\rangle\big)$ is

$$\mathcal{P}_{+\to-} = \big|\langle-|\psi(t)\rangle\big|^2 = \Big|\frac{1}{2}\big(e^{iat/\hbar} - e^{-iat/\hbar}\big)\Big|^2 = \sin^2\frac{at}{\hbar} \ . \quad (4.12)$$

This probability oscillates between 0 and 1. It's first maximum is at $\frac{at}{\hbar} = \frac{\pi}{2}$, i.e. at $t = \frac{\pi\hbar}{2a}$.

We can also introduce an observable "position of the nitrogen" which we call X by defining $X|\pm\rangle = \pm x_0|\pm\rangle$. This means that in this basis

$$X = x_0\Big(|+\rangle\langle+| - |-\rangle\langle-|\Big) \ . \quad (4.13)$$

Let us compute the mean position of the nitrogen in the state (4.11) which we reexpress in the basis $|\pm\rangle$:

$$
\begin{aligned}
|\psi(t)\rangle &= \frac{1}{2}e^{-iE_St/\hbar}(|+\rangle + |-\rangle) + \frac{1}{2}e^{-iE_At/\hbar}(|+\rangle - |-\rangle)) \\
&= \frac{1}{2}\big(e^{-iE_St/\hbar} + e^{-iE_At/\hbar}\big)|+\rangle + \frac{1}{2}\big(e^{-iE_St/\hbar} - e^{-iE_At/\hbar}\big)|-\rangle \\
&= e^{-iE_0t/\hbar}\Big(\frac{1}{2}\big(e^{iat/\hbar} + e^{-iat/\hbar}\big)|+\rangle + \frac{1}{2}\big(e^{iat/\hbar} - e^{-iat/\hbar}\big)|-\rangle \\
&= e^{-iE_0t/\hbar}\Big(\cos\frac{at}{\hbar}|+\rangle + i\sin\frac{at}{\hbar}\Big)|-\rangle \ . \quad (4.14)
\end{aligned}
$$

Then

$$
\begin{aligned}
\langle X\rangle_\Psi &= \langle\psi(t)|X|\psi(t)\rangle \\
&= \Big(\cos\frac{at}{\hbar}\langle+| - i\sin\frac{at}{\hbar}\Big)\langle-|\Big)x_0\Big(|+\rangle\langle+| - |-\rangle\langle-|\Big)\Big(\cos\frac{at}{\hbar}|+\rangle + i\sin\frac{at}{\hbar}\Big)|-\rangle \\
&= x_0\Big(\cos^2\frac{at}{\hbar} - \sin^2\frac{at}{\hbar}\Big) = x_0\cos\frac{2at}{\hbar} \ . \quad (4.15)
\end{aligned}
$$

We see that $\langle X \rangle_\Psi$ oscillates with an angular frequency $\frac{2a}{\hbar}$ where $2a$ is the energy difference between the two eigenstates. At $t = 0$ we have $\langle X \rangle_\Psi = x_0$ consistent with the fact that the molecule is in the localised state $|+\rangle$. At time $t = \frac{\pi\hbar}{2a}$ we have $\langle X \rangle_\Psi = -x_0$, again consistent with the fact that at this time the probability (4.12) to be in the localised state $|-\rangle$ equals one. For the intermediate times $0 < t < \frac{2a}{\hbar}$ the state is a superposition of the eigenstates of the "position" operator and the probability (4.12) is neither 0 nor 1, and the mean position is strictly larger than $-x_0$ and strictly less than x_0.

Note that we could have proceeded differently to compute $\langle X \rangle_\Psi$. instead of expressing $|\psi(t)\rangle$ in the eigenbasis of the position operator, we could have expressed the position operator in the eigenbasis of the Hamiltonian. From our experience with the different basis' for the spin-$\frac{1}{2}$ one might guess the answer and then check that it is correct. Using (4.9) one has

$$
\begin{aligned}
x_0 \Big(|S\rangle \langle A| + |A\rangle \langle S| \Big) &= \frac{x_0}{2} \Big(\big(|+\rangle + |-\rangle \big) \big(\langle +| - \langle -| \big) + \big(|+\rangle - |-\rangle \big) \big(\langle +| + \langle -| \big) \Big) \\
&= x_0 \Big(|+\rangle \langle +| - |-\rangle \langle -| \Big) = X \ , \tag{4.16}
\end{aligned}
$$

so that

$$
\begin{aligned}
\langle X \rangle_\Psi &= \langle \psi(t)| \, X \, |\psi(t)\rangle \\
&= \frac{1}{2} \big(e^{iE_S t/\hbar} \langle S| + e^{iE_A t/\hbar} \langle A| \big) \, x_0 \, \big(|S\rangle \langle A| + |A\rangle \langle S| \big) \big(e^{-iE_S t/\hbar} |S\rangle + e^{-iE_A t/\hbar} |A\rangle \big) \\
&= \frac{x_0}{2} \big(e^{i(E_S - E_A)t/\hbar} + e^{i(E_A - E_S)t/\hbar} \big) = x_0 \cos \frac{(E_S - E_A)t}{\hbar} = x_0 \cos \frac{2at}{\hbar} \ , \tag{4.17}
\end{aligned}
$$

of course, in agreement with (4.15).

4.2 Coupling the ammonia molecule to an electric field

The ammonia molecule has an electric dipole moment resulting from an excess of negative electric charge "localised" around the nitrogen atom and an excess of positive electric charge around the hydrogen atoms. So the dipole moment is oriented perpendicular to the plane of the hydrogens and "points" in the direction opposite to the nitrogen atom. This dipole moment is $d = qx_0$ where q is the (negative) excess charge on the nitrogen atom and x_0 this distance of this atom from the plane of the hydrogens. To simplify the discussion suppose this dipole moment is oriented along the x-axis. Proceeding by analogy, there should be an observable "electric dipole moment" $D = qX$ with X defined as above. If there is an electric field $\mathcal{E}$ in this same x-direction, the energy of the classical electric dipole d in this electric field is $-d\mathcal{E}$. More generally, the energy is $-\vec{d} \cdot \vec{\mathcal{E}}$ and this will tend to align the dipole with the field. Here we will simply assume that the corresponding Hamiltonian is given by

$$
H_{\text{dipole}} = -q\mathcal{E}X = -\eta \Big(|+\rangle \langle +| - |-\rangle \langle -| \Big) = -\eta \Big(|S\rangle \langle A| + |A\rangle \langle S| \Big) \ , \quad \eta \equiv d\mathcal{E} = qx_0\mathcal{E} \ , \tag{4.18}
$$

with $d\mathcal{E}$ considered as a number (with units of eV). Let us now designate the previous Hamiltonian given in (4.3) by H_0, so that the total Hamiltonian is simply the sum of H_0 and H_{dipole}. This is by

no means obvious, but should reflect the fact that classically the energy is an additive quantity. So

$$H = H_0 + H_{\text{dipole}} \ . \tag{4.19}$$

From (4.3) and (4.18) one then reads that in the $|\pm\rangle$ basis the corresponding matrix is $\mathtt{H} = \begin{pmatrix} E_0 - \eta & -a \\ -a & E_0 + \eta \end{pmatrix}$. Equivalently, one can also compute the matrix elements of H in the basis $\{|S\rangle, |A\rangle\}$ which we denote by $\widetilde{\mathtt{H}}$ and which is

$$\widetilde{\mathtt{H}} = \begin{pmatrix} E_0 - a & -\eta \\ -\eta & E_0 + a \end{pmatrix} \ . \tag{4.20}$$

This looks exactly like $\mathtt{H}$ with the roles of a and η exchanged. This was to be expected : if one neglects a, then the $|\pm\rangle$ basis are eigenstates of the Hamiltonian with energies $E_0 \mp \eta$, and switching on a provokes transitions between these two states. If one neglects the electric field, i.e. η, the eigenstates of the Hamiltonian are the $\{|S\rangle, |A\rangle\}$ with energies $E_0 \mp a$, and switching on η provokes transitions between these two states. The fact that a and η get exchanged simply by changing basis, means that they must appear symmetrically in the eigenvalues of the full Hamiltonian, since the eigenvalues can not depend on the choice of basis. The only formula which reduces to the previous one in either case and is symmetric is (recall that $\eta < 0$ so that $\sqrt{\eta^2} = -\eta$)

$$E_\pm = E_0 \pm \sqrt{a^2 + \eta^2} \ . \tag{4.21}$$

Let us check this. The eigenvalues are determined by the equation $\det(\mathtt{H} - E\mathbf{1}) = 0$ or $\det(\widetilde{\mathtt{H}} - E\mathbf{1}) = 0$. Both lead to $(E_0 - E)^2 - a^2 - \eta^2 = 0$ which indeed leads to (4.21). Of course, the components of the eigenvectors of H depend on the choice of basis. Let us adopt the $\{|S\rangle, |A\rangle\}$ basis and let us parametrise a and η as

$$a = \sqrt{a^2 + \eta^2} \cos\theta \quad , \quad \eta = \sqrt{a^2 + \eta^2} \sin\theta \quad , \quad \frac{\eta}{a} = \tan\theta \ , \tag{4.22}$$

so that

$$\widetilde{\mathtt{H}} = E_0 \mathbf{1} - \sqrt{a^2 + \eta^2}\, T \quad , \quad T = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \ . \tag{4.23}$$

Using again the trigonometric identities $\cos\theta = \cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2}$ and $\sin\theta = 2\cos\frac{\theta}{2}\sin\frac{\theta}{2}$ one easily sees that the eigenvectors of T are

$$v_1 = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix} \quad , \quad v_2 = \begin{pmatrix} -\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix} \quad , \quad Tv_1 = v_1 \quad , \quad Tv_2 = -v_2 \ . \tag{4.24}$$

Note that we can interpret $\frac{\hbar}{2}T$ as the matrix of $\vec{u} \cdot \vec{S}$ at $\varphi = 0$, see (3.30), and it is then no surprise that the v_1 and v_2 are nothing else than the corresponding eigenvectors $|+\rangle_{\vec{u}}$ and $|-\rangle_{\vec{u}}$, see (3.31). Obviously, these same v_1 and v_2 are also eigenvectors of $\widetilde{\mathtt{H}}$ with eigenvalues $E_\mp = E_0 \mp \sqrt{a^2 + \eta^2}$. We can also translate this back into the ket formalism as

$$|\psi_-\rangle = \cos\frac{\theta}{2}|S\rangle + \sin\frac{\theta}{2}|A\rangle \quad , \quad |\psi_+\rangle = -\sin\frac{\theta}{2}|S\rangle + \cos\frac{\theta}{2}|A\rangle \ ,$$

$$H|\psi_\mp\rangle = E_\mp|\psi_\mp\rangle \quad , \quad E_\mp = E_0 \mp \sqrt{a^2 + \eta^2} \ . \tag{4.25}$$

If we switch off the electric field, $\eta = 0$, then $\theta = 0$ and $|S\rangle$ and $|A\rangle$ are eigenstates of the Hamiltonian. Suppose the electric field is weak, $|\eta| \ll a$ then $\sqrt{a^2 + \eta^2} \simeq a + \frac{\eta^2}{2a}$ and $E_+ = E_0 + a + \frac{\eta^2}{2a} = E_A + \frac{\eta^2}{2a}$ and $E_- = E_0 - a - \frac{\eta^2}{2a} = E_S - \frac{\eta^2}{2a}$. Furthermore $\frac{\eta}{a} = \tan\theta$ is small, so that θ is small and $\cos\frac{\theta}{2} \simeq 1$ and $\sin\frac{\theta}{2} \simeq \frac{\theta}{2} \simeq \frac{1}{2}\tan\theta = \frac{\eta}{2a}$. Then (4.25) becomes

$$|\psi_-\rangle \simeq |S\rangle + \frac{\eta}{2a}|A\rangle \qquad , \qquad |\psi_+\rangle = |A\rangle - \frac{\eta}{2a}|S\rangle \ ,$$

$$H|\psi_\mp\rangle = E_\mp|\psi_\mp\rangle \qquad , \qquad E_\mp = E_0 \mp \left(a + \frac{\eta^2}{2a}\right) . \tag{4.26}$$

Let us compute the mean value of the dipole moment (recall $\eta = d\mathcal{E} = qx_0\mathcal{E}$)

$$\langle D\rangle_{\psi_\mp} = \langle\psi_\mp| qX |\psi_\mp\rangle = \frac{\eta}{\mathcal{E}}\langle\psi_\mp| \Big(|S\rangle\langle A| + |A\rangle\langle S| \Big) |\psi_\mp\rangle = \pm\frac{\eta}{\mathcal{E}}\frac{\eta}{a} = \pm\frac{d^2}{a}\mathcal{E} \tag{4.27}$$

We see that in the state of lower energy, $|\psi_-\rangle$, the dipole moment is aligned with the electric field, and in the state of higher energy, $|\psi_+\rangle$, it is anti-aligned. This is of course consistent with the fact that $H_{\text{dipole}} = -D\mathcal{E}$. Note however that the energies $E_\mp$ are *not* $E_{S/A} - \langle D\rangle_{\psi_\mp}\mathcal{E}$ but that there is an additional factor $\frac{1}{2}$ in the second term. This is because the states $|\psi_\mp\rangle$ are *not* eigenstates[21] of X so that $D|\psi_\mp\rangle \neq \langle D\rangle_{\psi_\mp}|\psi_\mp\rangle$.

Consider now a beam of ammonia molecules going through a region of inhomogeneous electric field. Much as with the discussion of the Stern-Gerlach experiment, an inhomogeneous electric field gives rise to a force as $\vec{F} = -\vec{\nabla}E$ and since the two eigenstates have different energies $E_\mp = E_0 \mp \left(a + \frac{\eta^2}{2a}\right) = E_0 \mp \left(a + \frac{d_0^2\mathcal{E}^2}{2a}\right)$ one gets a force

$$\vec{F}_\mp = \pm\frac{d_0^2}{2a}\vec{\nabla}\mathcal{E}^2 . \tag{4.28}$$

This will split the beam in two beams and one can then single out either the molecules in the state $|\psi_-\rangle \simeq |S\rangle$ or in the state $|\psi_+\rangle \simeq A$.

4.3 The principle of the ammonia maser

We can now briefly discuss the ammonia maser. MASER stands for "microwave amplification by stimulated emission of radiation". As just described, one prepares the ammonia molecules in the state $|A\rangle$. This is the state of higher energy (excited states) and the molecules will eventually undergo the transition to the lower energy state $|S\rangle$ and emit photons of the corresponding energy $E_A - E_S = 2a \equiv \hbar\omega_0$. However, the probability for this spontaneous emission is very low, and correspondingly it takes a long time to occur (the mean lifetime is about one month).

Let us study what happens instead if these molecules find themselves in an oscillating electric field (microwave) of frequency ω. This sounds familiar from our study of magnetic resonance and, indeed, we will see quite a few similarities. To simplify, we again assume that the dipole moments

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[21]To appreciate this remark note that *if* a (normalised) ket $|\psi\rangle$ is eigenstate of an observable A with eigenvalue a, then $\langle A\rangle_\psi = \langle\psi|A|\psi\rangle = a\langle\psi|\psi\rangle = a$ so that one has $A|\psi\rangle = a|\psi\rangle = \langle A\rangle_\psi|\psi\rangle$. Conversely, if $A|\psi\rangle = \langle A\rangle_\psi|\psi\rangle$ then $\langle A\rangle_\psi$ is an eigenvalue of A and obviously $|\psi\rangle$ the corresponding eigenvector.

are all parallel to the direction of the electric field of this microwave. The Hamiltonian in the basis $\{|S\rangle, |A\rangle\}$ then looks exactly like (4.29) but with $\eta \to \eta \cos \omega t$:

$$\widetilde{\mathrm{H}}(t) = \begin{pmatrix} E_0 - a & -\eta \cos \omega t \\ -\eta \cos \omega t & E_0 + a \end{pmatrix} . \tag{4.29}$$

If we write $|\psi(t)\rangle = a_S(t)|S\rangle + a_A(t)|A\rangle$ the Schrödinger equation reads

$$i\hbar \dot{a}_S = (E_0 - a)a_S - \eta \cos \omega t \, a_A \quad , \quad i\hbar \dot{a}_A = (E_0 + a)a_A - \eta \cos \omega t \, a_S . \tag{4.30}$$

One then tries to make some redefinitions of the functions a_S and a_A to solve this system.[22] We set $a_S(t) = \widetilde{a}_S(t)e^{-i(E_0-a)t/\hbar}$ and $a_A(t) = \widetilde{a}_A(t)e^{-i(E_0+a)t/\hbar}$. (In the absence of electric field one would simply find that $\widetilde{a}_S$ and $\widetilde{a}_A$ are constant.) Then $(2a = \hbar\omega_0)$

$$i\hbar \dot{\widetilde{a}}_S = -\frac{\eta}{2}\left(e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}\right)\widetilde{a}_A \quad , \quad i\hbar \dot{\widetilde{a}}_A = -\frac{\eta}{2}\left(e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}\right)\widetilde{a}_S . \tag{4.31}$$

In general, this does not have any simple analytic solution.[23] But assume that $\omega \simeq \omega_0$. This means that $e^{\pm i(\omega+\omega_0)t}$ oscillates much more quickly than $e^{\pm i(\omega-\omega_0)t}$, and then the former can be neglected with respect to the latter, to a good approximation.[24] Then

$$i\hbar \dot{\widetilde{a}}_S \simeq -\frac{\eta}{2} e^{i(\omega-\omega_0)t}\widetilde{a}_A \quad , \quad i\hbar \dot{\widetilde{a}}_A \simeq -\frac{\eta}{2} e^{-i(\omega-\omega_0)t}\widetilde{a}_S . \tag{4.32}$$

We let $\eta = -\hbar\omega_1$ and doing one further change $\widetilde{\alpha}_S = e^{i(\omega-\omega_0)t/2}\beta_S$, $\widetilde{\alpha}_A = e^{-i(\omega-\omega_0)t/2}\beta_A$ results in

$$i\dot{\beta}_S \simeq -\frac{\omega_0 - \omega}{2}\beta_S + \frac{\omega_1}{2}\beta_A \quad , \quad i\hbar\dot{\beta}_A \simeq \frac{\omega_0 - \omega}{2}\beta_A + \frac{\omega_1}{2}\beta_S . \tag{4.33}$$

This is now a system with constant coefficients which one can easily solve. But comparing with (3.69) we see that we get exactly the same equation as when discussing Rabi's formula for the magnetic resonance if we identify $\beta_S \sim \beta_-$ and $\beta_A \sim \beta_+$. We can then immediately translate the result (3.75) obtained before and give the transition probability from the state $|A\rangle$ to the state $|S\rangle$ (our various redefinitions only changed the phases, so they do not affect the probabilities) as

$$\mathcal{P}_{A \to S}(t) = \frac{\omega_1^2}{(\omega_0 - \omega)^2 + \omega_1^2} \sin^2 \frac{\Omega t}{2} \quad , \quad \Omega = \sqrt{(\omega_0 - \omega)^2 + \omega_1^2} . \tag{4.34}$$

---

[22]The reader may have noticed that this task would be much simpler if we had taken a complex electric field $\mathcal{E}e^{-i\omega t}$ instead of $\mathcal{E}\cos\omega t$. The reason we did not do this is because the electric field is real ! So why is it that one can sometimes work with the complex electric field $\mathcal{E}_c$ and sometimes not ? Of course, the "true" electric field is just the real part of this complex field : $\mathcal{E} = \frac{1}{2}(\mathcal{E}_c + \mathcal{E}_c^*)$. When dealing with Maxwell's equations one is dealing with linear and real equations. Hence if $\mathcal{E}_c$ is a solution to Maxwell's equations, then so is $\mathcal{E}_c^*$ and so is their sum. Here, however, we are dealing with Schrödinger's equation which is linear in ψ, but not simultaneously in ψ and $\mathcal{E}$, and moreover it is intrinsically complex.

[23]Of course, formally, as discussed in subsection 2.9, one can express the solution in terms of the time-ordered exponential of $\frac{1}{i\hbar}\int_{t_0}^t \mathrm{d}t' \begin{pmatrix} 0 & \gamma(t') \\ \gamma(t')^* & 0 \end{pmatrix}$ where $\gamma(t) = -\frac{\eta}{2}\left(e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}\right)$.

[24]Indeed, think of solving a first order differential equation $\dot{f} = (g_1(t) + g_2(t))f(t)$. To obtain $f(t)$ one starts at some initial value $f(t_0)$, subdivides $t-t_0$ into N intervals of size δt with intermediate times t_n and then successively approximates $f(t_n + \delta t) = f(t_n) + \delta t(g_1(t_n) + g_2(t_n))f(t_n)$. If g_1 changes little, but g_2 oscillates quickly, the effect of g_2 over a few intervals will average out, while the effect of g_1 will be cumulative. This means that in a first approximation one can neglect the quickly oscillating g_2.

If one tunes the microwave frequency ω to be very close to the proper ammonia frequency ω_0 this probabiity is close to 1 after a time $t = \frac{\pi}{\Omega} \simeq \frac{\pi}{\omega_1} = \frac{\pi\hbar}{|\eta|} = \frac{h}{2|d_0\mathcal{E}|}$. This means that within this time almost all ammonia molecules will undergo the transition to the ground state emitting the radiation of the precise frequency ω_0 corresponding to $\nu = \frac{\omega_0}{2\pi} = 24\,\text{GHz}$. This is called stimulated emission. The overall factor for the probability is characteristic of a resonance with width ω_1. The smaller the electric field $\mathcal{E}$, i.e. the smaller ω_1, the narrower is this resonance and the longer it takes to make the transition to the ground state. The whole point is that a stimulating microwave frequency close to ω_0 results in the emission of the exact frequency ω_0. This phenomenon can be used in a variety of ways : to amplify some weak signals of the appropriate frequency, or to provide an oscillator of very stable frequency. This same principle is at the origin of atomic clocks. A solid state maser was used by Penzias and Wilson in 1965 when they discovered the cosmic microwave background radiation corresponding to black body radiation at a temperature of about 3 K.[25]

4.4   General time-independent 2-state systems

We have seen, for the ammonia maser, that once we had transformed the Schrödinger equation into a system with constant coefficients, this system turned out to be the same as encountered earlier when studying the spin-$\frac{1}{2}$. We will now show that this is a necessary analogy.

Consider any 2-state system with a time-independent Hamiltonian. With respect to some fixed orthonormal basis, the corresponding matrix must be a 2×2 hermitian matrix. Now any such matrix is a linear combination of the identity matrix and the three Pauli matrices with real coefficients E_0 and b_j :

$$\mathtt{H} = E_0\,\mathbf{1}_{2\times 2} + \sum_{j=x,y,z} b_j\sigma_j \equiv E_0\,\mathbf{1}_{2\times 2} + \vec{b}\cdot\vec{\sigma} = E_0\,\mathbf{1}_{2\times 2} + b\,\vec{u}\cdot\vec{\sigma} \ , \tag{4.35}$$

where $b = |\vec{b}|$ and $\vec{u} = \frac{\vec{b}}{b}$. The matrix $\sigma_{\vec{u}} = \vec{u}\cdot\vec{\sigma}$ was given in (3.30) if the unit vector $\vec{u}$ is parametrised in spherical coordinates in terms of θ and φ. Its eigenvectors are the $v_\pm(\vec{u})$ given in (3.31) and the eigenvalues are ± 1.

It should be obvious that $\mathtt{H}$ and $\vec{u}\cdot\vec{\sigma}$ have the same eigenvectors $v_\pm(\vec{u})$ and that the eigenvalues of $\mathtt{H}$ are $E_\pm = E_0 \pm b$:

$$\mathtt{H}\,v_\pm(\vec{u}) = (E_0 \pm b)\,v_\pm(\vec{u}) \ . \tag{4.36}$$

The eigenvalues are very easily obtained this way. But to figure out explicitly the eigenvectors $v_\pm(\vec{u})$ in terms of the components of $\vec{b}$ can be a bit cumbersome, and it may be easier to compute their components directly from (4.36). Let us remind the reader that, for each eigenvalue, (4.36) constitutes two equivalent linear equations and it is enough to solve one of them which determines the ratio of the two components of the eigenvector. The overall scale is fixed by the normalisation, and the overall phase is arbitrary.

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[25]More precisely, the CMB corresponds to a temperature of 2.73 K. A good way to remember this is to realize that this is $\frac{1}{100}$ times the temperature at which ice melts, 273 K, formerly called 0º C ...