Quantum Mechanics I

Week 6 (Solutions)

Spring Semester 2025

1 Spin precession in the Heisenberg representation

Consider the problem of spin precession already seen in the course. The Hamiltonian of the system is:

$$\hat{H} = -\left(\frac{eB}{mc}\right)\hat{S}_z = \omega \hat{S}_z. \tag{1.1}$$

A. We will solve this problem in the Heisenberg picture.

(a) First, calculate the exponential of the spin operators $e^{i\omega S_\alpha}$, where $\alpha = x, y, z$ and ω is a real constant. This operator will be important when working in the Heisenberg picture.

The exponential of a matrix is given by its series expansion. Therefore, $e^{i\omega \hat{S}_\alpha}$:

$$\begin{aligned}
e^{i\omega \hat{S}_\alpha} &= e^{i\frac{\hbar\omega}{2}\hat{\sigma}_\alpha} = \sum_{n=0}^{\infty} \frac{\left(i\frac{\hbar\omega}{2}\hat{\sigma}_\alpha\right)^n}{n!} \\
&= \left(\sum_{n \text{ even}} + \sum_{n \text{ odd}}\right) \frac{\left(i\frac{\hbar\omega}{2}\hat{\sigma}_\alpha\right)^n}{n!} \\
&= \sum_{n=0}^{\infty} \frac{\left(i\frac{\hbar\omega}{2}\hat{\sigma}_\alpha\right)^{2n}}{(2n)!} + \sum_{n=0}^{\infty} \frac{\left(i\frac{\hbar\omega}{2}\hat{\sigma}_\alpha\right)^{2n+1}}{(2n+1)!} \\
&= \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{\hbar\omega}{2}\right)^{2n}}{(2n)!}\mathbb{1} + i\sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{\hbar\omega}{2}\right)^{2n+1}}{(2n+1)!}\hat{\sigma}_\alpha \\
&= \cos\left(\frac{\hbar\omega}{2}\right)\mathbb{1} + i\sin\left(\frac{\hbar\omega}{2}\right)\hat{\sigma}_\alpha.
\end{aligned}$$

The operator $\mathbb{1}$ is the identity matrix and we used $\hat{\sigma}_\alpha^{2n} = \mathbb{1}$. We therefore find for the $\hat{S}_x$ and $\hat{S}_y$:

$$e^{i\omega \hat{S}_x} = \begin{pmatrix} \cos\left(\frac{\hbar\omega}{2}\right) & i\sin\left(\frac{\hbar\omega}{2}\right) \\ i\sin\left(\frac{\hbar\omega}{2}\right) & \cos\left(\frac{\hbar\omega}{2}\right) \end{pmatrix}, \quad e^{i\omega \hat{S}_y} = \begin{pmatrix} \cos\left(\frac{\hbar\omega}{2}\right) & \sin\left(\frac{\hbar\omega}{2}\right) \\ -\sin\left(\frac{\hbar\omega}{2}\right) & \cos\left(\frac{\hbar\omega}{2}\right) \end{pmatrix}, \tag{1.2}$$

and for the $\hat{S}_z$:

$$e^{i\omega\hat{S}_z} = \begin{pmatrix} \cos\left(\frac{\hbar\omega}{2}\right) + i\sin\left(\frac{\hbar\omega}{2}\right) & 0 \\ 0 & \cos\left(\frac{\hbar\omega}{2}\right) - i\sin\left(\frac{\hbar\omega}{2}\right) \end{pmatrix} = \begin{pmatrix} e^{i\frac{\hbar\omega}{2}} & 0 \\ 0 & e^{-i\frac{\hbar\omega}{2}} \end{pmatrix}. \tag{1.3}$$

(b) Using the Hamiltonian of Eq. (1.1), write the Heisenberg equations of motion for the time-dependent operators $\hat{S}_x(t)$, $\hat{S}_y(t)$ and $\hat{S}_z(t)$.

The equation of motion for an operator $\hat{A}_H(t)$ in the Heisenberg picture is given by

$$\frac{d}{dt}\hat{A}_H(t) = \frac{i}{\hbar}[\hat{H}, \hat{A}_H(t)] + \left(\frac{\partial \hat{A}_S(t)}{\partial t}\right)_H, \tag{1.4}$$

where, in the case in which the operator $\hat{A}_S$ in the Schrödinger picture depends explicitly on time, the last quantity is given by

$$\left(\frac{\partial \hat{A}_S(t)}{\partial t}\right)_H = \hat{U}^\dagger(t)\frac{\partial \hat{A}_S(t)}{\partial t}\hat{U}(t), \tag{1.5}$$

where we used the Heisenberg notation $\hat{A}_H(t) = \hat{U}^\dagger(t)\hat{A}_S(t)\hat{U}(t)$, and the unitary time evolution operator $\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}$.

In particular, we note that the Hamiltonian $\hat{H}$ is the same in both pictures, as $[\hat{H}, U(t)] = 0$ and thus $U^\dagger(t)\hat{H}U(t) = \hat{H}$. For this reason, we use in the following that $[\hat{H}, \hat{A}(t)] = [\hat{H}(t), \hat{A}(t)] = \hat{U}^\dagger(t)[\hat{H}, \hat{A}]\hat{U}(t)$.

In this case, the equations are therefore given by:

$$\begin{aligned} \frac{d}{dt}\hat{S}_x(t) = \frac{i}{\hbar}[\hat{H}, \hat{S}_x(t)] &= -\frac{ieB}{\hbar mc}\hat{U}^\dagger(t)[\hat{S}_z, \hat{S}_x]\hat{U}(t) \\ &= \frac{eB}{mc}\hat{U}^\dagger(t)\hat{S}_y\hat{U}(t) = \frac{eB}{mc}\hat{S}_y(t) = -\omega\hat{S}_y(t). \end{aligned} \tag{1.6}$$

Similarly, we have

$$\frac{d}{dt}\hat{S}_y(t) = -\frac{eB}{mc}\hat{S}_x(t) = \omega\hat{S}_x(t), \quad \frac{d}{dt}\hat{S}_z(t) = 0. \tag{1.7}$$

The second derivatives are given by

$$\frac{d^2}{dt^2}\hat{S}_x(t) = -\omega^2\hat{S}_x(t), \quad \frac{d^2}{dt^2}\hat{S}_y(t) = -\omega^2\hat{S}_y(t), \tag{1.8}$$

which are differential equations of matrices.

(c) Solve the differential equations from the previous question, to obtain $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ as a function of time. Consider appropriate initial conditions.

These equations are solved for each matrix element individually. For $\hat{S}_x$, we have

$$\frac{d^2}{dt^2}(\hat{S}_x(t))_{ij} = -\omega^2(\hat{S}_x(t))_{ij} \quad \Rightarrow \quad (\hat{S}_x(t))_{ij} = A_{ij}\cos(\omega t) + B_{ij}\sin(\omega t). \tag{1.9}$$

As initial conditions we use

$$\hat{S}_x(t=0) = \hat{S}_x \quad \Rightarrow \quad A_{ij} = (\hat{S}_x)_{ij} \tag{1.10}$$

$$\left(\frac{d}{dt}\hat{S}_x\right)(t=0) = -\omega\hat{S}_y(t=0) = -\omega\hat{S}_y \quad \Rightarrow \quad B_{ij} = -(\hat{S}_y)_{ij}. \tag{1.11}$$

Therefore,

$$(\hat{S}_x(t))_{ij} = \cos(\omega t)(\hat{S}_x)_{ij} - \sin(\omega t)(\hat{S}_y)_{ij} \tag{1.12}$$

and in matrix notation

$$\begin{aligned} \hat{S}_x(t) &= \cos(\omega t)\hat{S}_x - \sin(\omega t)\hat{S}_y \\ &= \frac{\hbar}{2}\begin{pmatrix} 0 & \cos(\omega t) + i\sin(\omega t) \\ \cos(\omega t) - i\sin(\omega t) & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}. \end{aligned}$$

Similarly, we find

$$\begin{aligned} \hat{S}_y(t) &= \cos(\omega t)\hat{S}_y + \sin(\omega t)\hat{S}_x \\ &= \frac{\hbar}{2}\begin{pmatrix} 0 & -i\cos(\omega t) + \sin(\omega t) \\ i\cos(\omega t) + \sin(\omega t) & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -ie^{i\omega t} \\ ie^{-i\omega t} & 0 \end{pmatrix}. \end{aligned}$$

The equation for $\hat{S}_z(t)$ yields $S_z(t) = S_z$.

We can verify that $\hat{S}_\alpha(t) = \hat{U}^\dagger(t)\hat{S}_\alpha\hat{U}(t)$, for all $\alpha \in \{x, y, z\}$.

B. An electron is subjected to a uniform and time-independent magnetic field $\mathbf{B} = B\mathbf{z}$. At $t = 0$, the electron is an eigenstate of $\hat{S}_n$ ($\equiv \hat{\mathbf{S}}\cdot\mathbf{n}$) with eigenvalue $\frac{\hbar}{2}$, i.e. $|\psi\rangle = |S_n;+\rangle$. Here $\mathbf{n}$ is a unit vector on the plane $x-z$, and can be parameterized by $\mathbf{n} = (\sin\theta, 0, \cos\theta)$.

(a) Obtain the probability of finding the electron in the state $s_x = \frac{\hbar}{2}$ as a function of time.

At the initial time $t = 0$, the electron is in the Eigenstate of the operator $\hat{S}_n = \frac{\hbar}{2}(\sin\theta\,\sigma_x + \cos\theta\,\sigma_z)$ with positive Eigenvalue $\frac{\hbar}{2}$. After the last exercise on the Bloch sphere, we know that this Eigenstate is given by $|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + \sin\frac{\theta}{2}|1\rangle$, where $|0\rangle$ and $|1\rangle$ are Eigenstates of the σ_z operator.

The probability to find the state $|S_x;+\rangle = \frac{1}{\sqrt{2}}|0\rangle + \frac{1}{\sqrt{2}}|1\rangle$ at time t is

$$
\begin{aligned}
P = \left|\langle S_x;+|\hat{U}(t)|\psi\rangle\right|^2 &= \left|\frac{1}{\sqrt{2}}e^{-i\omega t/2}\cos\frac{\theta}{2} + \frac{1}{\sqrt{2}}e^{i\omega t/2}\sin\frac{\theta}{2}\right|^2 && (1.13)\\
&= \frac{1}{2}\left(1 + \cos\frac{\theta}{2}\sin\frac{\theta}{2}(e^{i\omega t} + e^{-i\omega t})\right) && (1.14)\\
&= \frac{1}{2}\left(1 + \sin\theta\cos\omega t\right). && (1.15)
\end{aligned}
$$

Note that this result can be obtained, equivalently, both in the Schrödinger and in the Heisenberg pictures. In the Schrödinger picture, we interpret $\hat{U}(t)|\psi\rangle = |\psi(t)\rangle$ as the quantum state of the system at time t. The time-dependent state can be found by solving the Schrödinger equation

$$
i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle \tag{1.16}
$$

with the initial conditions $|\psi(0)\rangle = \cos\frac{\theta}{2}|0\rangle + \sin\frac{\theta}{2}|1\rangle$. The solution is $|\psi(t)\rangle = \cos\frac{\theta}{2}e^{-i\frac{\omega}{2}t}|0\rangle + \sin\frac{\theta}{2}e^{i\frac{\omega}{2}t}|1\rangle$. The probability is then computed from the absolute square of the amplitude $\langle S_x;+|\psi(t)\rangle$, where $|S_x;+\rangle$ is the eigenvector of the operator S_x in the Schrödinger picture (which is time-independent).

In the Heisenberg picture, in contrast, we consider the state $|\psi\rangle$ to be time-independent. The probability is given by the square of the amplitude $\langle S_x(t);+|\psi\rangle$ where $|S_x(t);+\rangle$ is the eigenvector of the Heisenberg operator $\hat{S}_x(t)$ (which is time-dependent).

The two pictures give the same results. In fact, the operator $\hat{S}_x(t)$ can be written as $\hat{U}^\dagger(t)\hat{S}_x\hat{U}(t)$. From this, it follows that the eigenvectors of the Heisenberg operator are related to the corresponding eigenvectors in the Schrödinger picture as

$$
|S_x(t);+\rangle = \hat{U}^\dagger(t)|S_x;+\rangle\ . \tag{1.17}
$$

Indeed,

$$
\begin{aligned}
\hat{S}_x(t)|S_x(t);+\rangle &= \hat{U}^\dagger(t)\hat{S}_x\hat{U}(t)\hat{U}^\dagger(t)|S_x;+\rangle\\
&= \hat{U}^\dagger(t)\hat{S}_x|S_x;+\rangle\\
&= \frac{\hbar}{2}\hat{U}^\dagger(t)|S_x;+\rangle = \frac{\hbar}{2}|S_x(t);+\rangle\ ,
\end{aligned} \tag{1.18}
$$

so $|S_x(t);+\rangle = \hat{U}^\dagger(t)\left|\hat{S}_x;+\right\rangle$ is an eigenvector with eigenvalue $+\hbar/2$ of $\hat{S}_x(t)$.

Explicitly,

$$
|S_x(t);+\rangle = \frac{1}{\sqrt{2}}(e^{i\frac{\omega}{2}t}|0\rangle + e^{-i\frac{\omega}{2}t}|1\rangle) \tag{1.19}
$$

Both the Schrödinger picture and the Heisenberg picture lead to the same expression for the probability amplitude: $\langle S_x;+|\psi(t)\rangle = \langle S_x;+|\hat{U}(t)|\psi\rangle$, $\langle S_x(t);+|\psi\rangle = \langle S_x;+|(\hat{U}^\dagger(t))^\dagger|\psi\rangle = \langle S_x;+|\hat{U}(t)|\psi\rangle$. (Note that the "bra" corresponding to $|S_x(t);+\rangle = \hat{U}^\dagger(t)|S_x;+\rangle$ is $\langle S_x(t);+| = \langle S_x;+|(\hat{U}^\dagger(t))^\dagger$.)

The equivalence between Schrödinger and Heisenberg pictures is completely general: the two pictures are equivalent in *any* quantum-mechanical problem.

(b) Find the mean value of $\hat{S}_x$ as a function of time.

The time evolution of the operator $\hat{S}_x(t)$ is given by equation (12). Therefore, the average value of the operator $\hat{S}_x(t)$ in the state $|\psi\rangle$ at time t is

$$\langle\psi|\hat{S}_x(t)|\psi\rangle = \frac{\hbar}{2}\begin{pmatrix}\cos\frac{\theta}{2} & \sin\frac{\theta}{2}\end{pmatrix}\begin{pmatrix}0 & e^{i\omega t}\\ e^{-i\omega t} & 0\end{pmatrix}\begin{pmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\end{pmatrix} \tag{1.20}$$

$$= \frac{\hbar}{2}\sin\frac{\theta}{2}\cos\frac{\theta}{2}(e^{i\omega t}+e^{-i\omega t}) = \frac{\hbar}{2}\sin\theta\cos(\omega t). \tag{1.21}$$

(c) Show that the solution corresponds to what you expect for the two extreme values $\theta = 0$ and $\theta = \frac{\pi}{2}$.

For $\theta = 0$ the spin is aligned along the positive $\hat{z}$ direction, there is no precession, and the probability of measuring $s_x = \frac{\hbar}{2}$ is $\frac{1}{2}$. Consequently, the expectation value of $\hat{S}_x$ is zero.

For $\theta = \frac{\pi}{2}$ the state is given by $|S_x(t);+\rangle$. Therefore, we have $P = 1$ for $t = 0$ and $P = 0$ for $t = \frac{\pi}{\omega}$. Furthermore, the expectation value of $\hat{S}_x$ is the classical precession of a vector in the $x - z$ plane.

2 The Ammonia molecule

The Ammonia molecule (NH_3) is an interesting case of complex system that nonetheless admits a relatively simple description in terms of a two level system. In the following we will make the assumption that we have a single molecule at rest, that is spinning around the axis formed by the triangular plane containing the Hydrogen atoms and the Nitrogen atom. (see Figure 1 for a visualization of the pyramidal structure of this molecule). In this situation, there are two equivalent positions for the Nitrogen atom: either in the upper part of the Hydrogen plane or in the lower part.

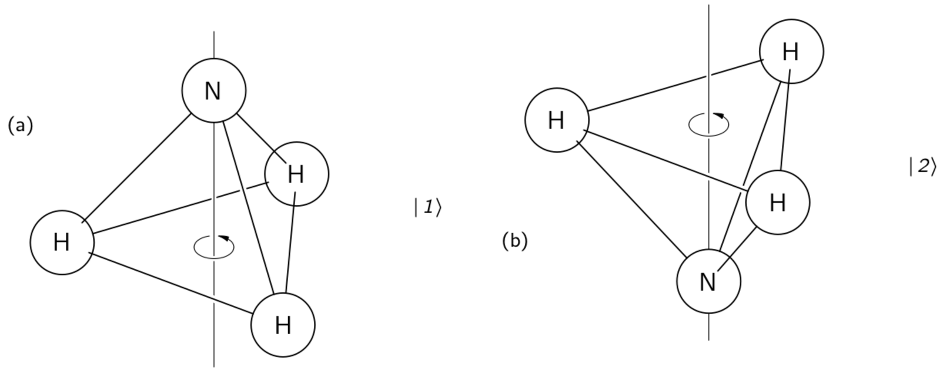

Figure 1: The ammonia molecule has two equivalent geometrical arrangements, one with the nitrogen up (left) and one with the nitrogen down (right).

A. Restricting our attention to only these two possible geometric configurations, we are going to associate two basis states $|1\rangle$ and $|2\rangle$, respectively to the up and down Nitrogen configurations, thus

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.1}$$

The Hamiltonian of the system is:

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}. \tag{2.2}$$

The two configurations are equivalent, thus the average energy E_0 of these two states is the same. The off-diagonal element A is a real-valued, positive phenomenological constant, and represents the process that transforms one state to the other. This follows from the fact that in nature, both configurations are observed.

(a) Find the eigenvalues and eigenvectors of this Hamiltonian.

The energy eigenvalues are found by diagonalizing this matrix, solving

$$\det \begin{pmatrix} E_0 - E & -A \\ -A & E_0 - E \end{pmatrix} = (E_0 - E)^2 - A^2 = 0\,, \tag{2.3}$$

which has the two solutions

$$E_\pm = E_0 \pm A. \tag{2.4}$$

The corresponding two eigen-kets are also found, expressed in the basis $\{|1\rangle\,, |2\rangle\}$:

$$|+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad |-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{2.5}$$

(b) Find the matrix representation of the unitary time-evolution operator in the original basis $\{|1\rangle\,, |2\rangle\}$.

The Hamiltonian we are considering is time-independent, thus the time evolution operator is

$$\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}. \tag{2.6}$$

and we can also find its matrix elements in the $|1\rangle, |2\rangle$ basis. For example, we can use the completeness of the energy eigen-kets:

$$\begin{aligned}
\langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|1\rangle &= \langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|+\rangle\langle +|1\rangle + \langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|-\rangle\langle -|1\rangle \\
&= e^{-\frac{i}{\hbar}E_+t}|\langle +|1\rangle|^2 + e^{-\frac{i}{\hbar}E_-t}|\langle -|1\rangle|^2 \\
&= \frac{1}{2}e^{-\frac{i}{\hbar}E_0t}\left(e^{-\frac{i}{\hbar}At} + e^{+\frac{i}{\hbar}At}\right) \\
&= e^{-\frac{i}{\hbar}E_0t}\cos\left(\frac{At}{\hbar}\right).
\end{aligned}$$

$$\begin{aligned}
\langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|2\rangle &= \langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|+\rangle\langle +|2\rangle + \langle 1|e^{-\frac{i}{\hbar}\hat{H}t}|-\rangle\langle -|2\rangle \\
&= \frac{1}{2}\left(e^{-\frac{i}{\hbar}E_+t} - e^{-\frac{i}{\hbar}E_-t}\right) \\
&= \frac{1}{2}e^{-\frac{i}{\hbar}E_0t}\left(e^{-\frac{i}{\hbar}At} - e^{+\frac{i}{\hbar}At}\right) \\
&= e^{-\frac{i}{\hbar}E_0t} i\sin\left(\frac{At}{\hbar}\right).
\end{aligned}$$

and similarly for the other two matrix elements. The full matrix representation is therefore:

$$\hat{U}(t) = e^{-\frac{i}{\hbar}E_0t}\begin{pmatrix} \cos\left(\frac{At}{\hbar}\right) & i\sin\left(\frac{At}{\hbar}\right) \\ i\sin\left(\frac{At}{\hbar}\right) & \cos\left(\frac{At}{\hbar}\right) \end{pmatrix}. \tag{2.7}$$

(c) Verify that this is indeed a unitary matrix.

For a unitary operator we require $U^\dagger U = UU^\dagger = \mathbb{1}$. Considering explicitly the matrix product $\hat{U}^\dagger(t)\hat{U}(t)$, it can be verified that it is equal to the identity operator.

(d) Given an arbitrary state at time $t = 0$, $|\psi\rangle = c_1(0)\,|1\rangle + c_2(0)\,|2\rangle$, calculate the coefficients $c_1(t)$, $c_2(t)$ for the time-dependent state $|\psi(t)\rangle = c_1(t)\,|1\rangle + c_2(t)\,|2\rangle$ in the Schrödinger representation. What are the coefficients for the initial conditions $c_1(0) = 1, c_2(0) = 0$?

Now, for a generic state $|\psi(t)\rangle$, we can determine the time evolution of the amplitudes, i.e., $c_1(t)$ and $c_2(t)$, simply by applying the time-evolution matrix:

$$\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = e^{-\frac{i}{\hbar}E_0 t} \begin{pmatrix} \cos\left(\frac{At}{\hbar}\right) & i\sin\left(\frac{At}{\hbar}\right) \\ i\sin\left(\frac{At}{\hbar}\right) & \cos\left(\frac{At}{\hbar}\right) \end{pmatrix} \begin{pmatrix} c_1(0) \\ c_2(0) \end{pmatrix} \tag{2.8}$$

$$= e^{-\frac{i}{\hbar}E_0 t} \begin{pmatrix} \cos\left(\frac{At}{\hbar}\right) c_1(0) + i\sin\left(\frac{At}{\hbar}\right) c_2(0) \\ i\sin\left(\frac{At}{\hbar}\right) c_1(0) + \cos\left(\frac{At}{\hbar}\right) c_2(0) \end{pmatrix}, \tag{2.9}$$

which fully specifies the time evolution of the state. For example, if we started from a state pointing in the up direction (i.e., $c_1(0) = 1$ and $c_2(0) = 0$), we would have

$$\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = e^{-\frac{i}{\hbar}E_0 t} \begin{pmatrix} \cos\left(\frac{At}{\hbar}\right) & i\sin\left(\frac{At}{\hbar}\right) \\ i\sin\left(\frac{At}{\hbar}\right) & \cos\left(\frac{At}{\hbar}\right) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.10}$$

$$= e^{-\frac{i}{\hbar}E_0 t} \begin{pmatrix} \cos\left(\frac{At}{\hbar}\right) \\ i\sin\left(\frac{At}{\hbar}\right) \end{pmatrix}. \tag{2.11}$$

(e) Suppose that at time $t = 0$ the molecule is known to be in the configuration $|1\rangle$ (with nitrogen up). What are the probabilities of observing the configurations $|1\rangle$ (nitrogen up) and $|2\rangle$ of the Ammonia molecule as a function of time?

Using the result from the previous Question for $c_1(0) = 1, c_2(0) = 0$, the probability of flipping into the down position is:

$$P(2) = |\langle 2|\Psi(t)\rangle|^2 \tag{2.12}$$

$$= |c_2(t)|^2 \tag{2.13}$$

$$= \left[\sin\left(\frac{At}{\hbar}\right)\right]^2, \tag{2.14}$$

whereas the probability of finding the Nitrogen up is:

$$P(1) = |\langle 1|\Psi(t)\rangle|^2 \tag{2.15}$$

$$= |c_1(t)|^2 \tag{2.16}$$

$$= \left[\cos\left(\frac{At}{\hbar}\right)\right]^2. \tag{2.17}$$

B. The charge distribution in the ammonia molecule is not spatially symmetric, specifically the electronic charge tends to be closer to the nitrogen atom. As a consequence, there is en effective electric dipole moment $\vec{\mu}_E$ pointing from the nitrogen atom to the hydrogens plane.

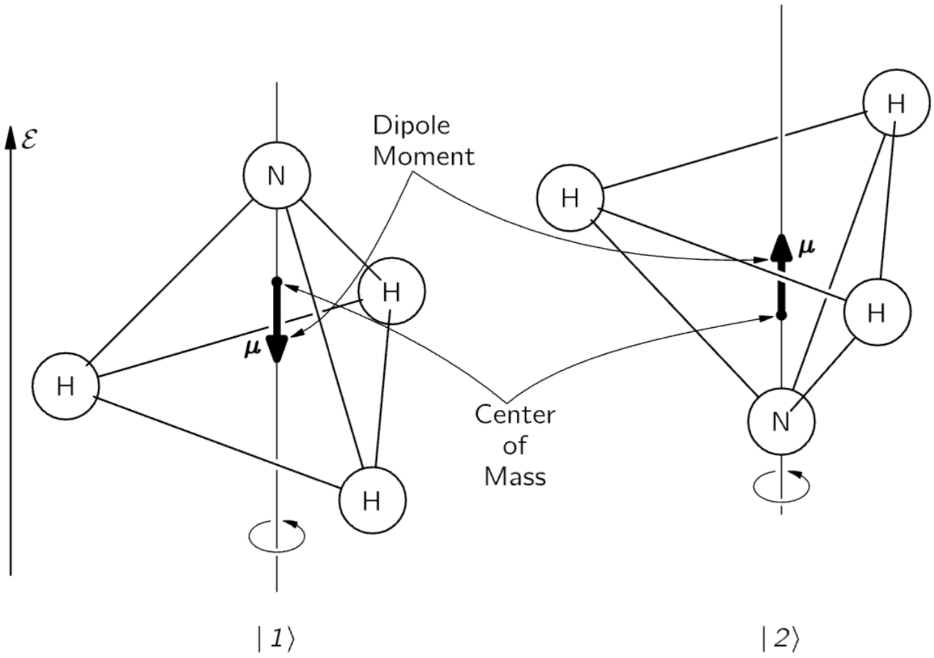

Figure 2: The ammonia molecule in the presence of an electric field in the z direction. The figure also shows that the dipole moment has two opposite directions in the states $|1\rangle$ and $|2\rangle$.

The interaction energy is:

$$U_E = -\vec{\mu}_E \cdot \vec{\mathcal{E}}. \tag{2.18}$$

We consider an electric field in the z direction, i.e. $\vec{\mathcal{E}} = \mathcal{E}_z \hat{z}$.

(a) What is the new Hamiltonian of the system?

For an electric field in the z direction we have that the two states $|1\rangle$ and $|2\rangle$ must have different energies (in one case the electric dipole is aligned with the electric field, in the other case it is anti-aligned). The Hamiltonian then becomes

$$\hat{H} = \begin{pmatrix} E_0 + \mu_E \mathcal{E}_z & -A \\ -A & E_0 - \mu_E \mathcal{E}_z \end{pmatrix}. \tag{2.19}$$

(b) What are the eigenvalues of the Hamiltonian H'? Consider the case of weak electric field $\mu_E \mathcal{E}_z \ll E_0$. Hint: You may use $\sqrt{1+\epsilon} \simeq 1 + \epsilon/2$.

The energy eigenvalues of this modified Hamiltonian can be found by solving

$$\det \begin{pmatrix} E_0 + \mu_E \mathcal{E}_z - E & -A \\ -A & E_0 - \mu_E \mathcal{E}_z - E \end{pmatrix} = (E_0 - E + \mu_E \mathcal{E}_z)(E_0 - E - \mu_E \mathcal{E}_z) - A^2 = 0, \tag{2.20}$$

which has solutions

$$E_\pm = E_0 \pm \sqrt{(\mu_E \mathcal{E}_z)^2 + A^2}. \tag{2.21}$$

In the interesting case in which the electric field is small (i.e., $\mu_E \mathcal{E}_z \ll E_0$), we can approximate the eigenvalues as

$$E_\pm \simeq E_0 \pm \left(A + \frac{(\mu_E \mathcal{E}_z)^2}{2A} \right), \tag{2.22}$$

where we have used the expansion $\sqrt{1+\epsilon} \simeq 1 + \frac{\epsilon}{2}$.

(c) An interesting consequence of the presence of the electric field is that we can use it to separate the two states $|1\rangle$ and $|2\rangle$ with a device similar to the Stern and Gerlach device (with the important difference that here we are using the electric field rather than the magnetic field to perform the separation). We consider a spatially inhomogeneous electric field. Find the force acting on the molecule, when the latter is in one of the two states we found earlier.

By considering a spatially inhomogeneous electric field, the force acting on the two states is

$$\begin{aligned} F_z &\simeq -\frac{\partial}{\partial z} E_\pm, \\ &= \mp \frac{(\mu_E)^2}{A} \frac{\partial}{\partial z} \mathcal{E}_z, \end{aligned} \tag{2.23}$$

thus at the output of the analyzer we measure the two states going in the lower and upper sides of the detector, respectively.

This selection mechanism is used, for example, in the Ammonia maser, where the molecules with the higher energy are filtered out thanks to an external electric field.