E142: Ammonia molecule

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The problem:

Ammonia molecule (NH_3) has two configuration states, such that one state is a mirror reflection of the other. If transitions between the two states were impossible, each state energy would be E_0. In actual fact, the transition amplitude per unit time between the states is c.

(1) What are the possible energies of the Ammonia molecule?
(2) Assume that in $t = 0$ the molecule is found to be at the first state. What is the probability $P(t)$ that the molecule is found at the second state after time t?

Now, assume that each state of the molecule has electric dipole moment μ. When the molecule is inserted into electric field $\mathcal{E}$, the geometry does not change, however, the energy of each state changes by $\pm\mu\mathcal{E}$ for each state respectively.

(3) What are the current possible energies?
(4) What is the expectation value $\mathcal{D}$ of the electric dipole moment in the ground state?

The solution:

(1) The molecule has two possible configurations, therefore we treat it as two-site system. The Hamiltonian can be represented in a matrix form:

$$\hat{\mathcal{H}} \mapsto \begin{pmatrix} E_0 & c \\ c & E_0 \end{pmatrix}$$

from which we get the eigenenergies of the system: $E_\pm = E_0 \pm c$

(2) The eigenstates basis of the system is:

$$\left\{ |+\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle + |2\rangle \right) \ , \ |-\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle - |2\rangle \right) \right\}$$

where $\{|1\rangle, |2\rangle\}$ is the standard (site) basis.

The initial state at $t = 0$ is:

$$|\psi(t=0)\rangle = |1\rangle = \frac{1}{\sqrt{2}} \left(|+\rangle + |-\rangle \right)$$

and the time evolution of the state is generated by the Hamiltonian:

$$|\psi(t)\rangle = \hat{\mathcal{U}}(t)|\psi(0)\rangle = e^{-i\hat{\mathcal{H}}t}|\psi(0)\rangle = \frac{1}{\sqrt{2}} \left(e^{-iE_+ t}|+\rangle + e^{-iE_- t}|-\rangle \right),$$

where $\hat{\mathcal{U}}(t)$ is called the evolution operator.

The probability $P(t)$ of finding the particle in the second configuration state ($|2\rangle$) after time t is the projection:

$$P(t) = |\langle\psi(0)|\psi(t)\rangle|^2 = \left| \langle 2|\hat{\mathcal{U}}(t)|1\rangle \right|^2 = \frac{1}{4} \left| \left(\langle +| - \langle -| \right) \left(e^{-iE_+ t}|+\rangle + e^{-iE_- t}|-\rangle \right) \right|^2 = \sin^2(ct).$$

One can notice that we obtained typical 2-site oscillating system with frequency $2c$.

(3) Now, as electric field $\mathcal{E}$ is added to the system, each site gets the dipole energy $\pm\mu\mathcal{E}$ respectively. Then, the Hamiltonian is:

$$\hat{\mathcal{H}} \mapsto \begin{pmatrix} E_0 + \mu\mathcal{E} & c \\ c & E_0 - \mu\mathcal{E} \end{pmatrix}$$

which implies about the reflection symmetry.
Out of that we get the eigenenergies: $E_\pm(\mathcal{E}) = E_0 \pm \sqrt{(\mu\mathcal{E})^2 + c^2}$

(4) The dipole moment operator is defined as the change of the energy with the change of the electric field (i.e generalized force), hence we define its operator as follows:

$$\hat{\mu} = -\frac{\partial\hat{\mathcal{H}}}{\partial\mathcal{E}}$$

We are asked to calculate the dipole moment expectation value in the ground state, i.e the state which corresponds to the lower energy E_-, then we get:

$$\mathcal{D} \equiv \langle -|\hat{\mu}|-\rangle = -\frac{\partial}{\partial\mathcal{E}}\langle -|\hat{\mathcal{H}}|-\rangle = -\frac{\partial E_-}{\partial\mathcal{E}} = \frac{\mu^2\mathcal{E}}{\sqrt{(\mu\mathcal{E})^2 + c^2}}$$