Phys 402: Applications of Quantum Mechanics

Homework II (due 930am, Thursday, Jan 21, 2016)

Ammonia molecules

Two states for ammonia molecules: |u>, one with Nitrogen atom above the hydrogen plane and |d>, one with Nitrogen atom below the plane (see handouts on ammonia molecules). These two states have opposite permanent dipole moments (plus-minus \mu) so that when an electric field E is applied along the z-direction, state |u> will be shifted upward by an amount \mu E and state |d> will be shifted downward by an amount -\mu E. |u> state is coupled with |d> via quantum tunneling.

In this problem, you need to construct a Hamiltonian matrix for these molecules. What basis would you like to work with? how does the matrix look like?

\mu = μ – dipole moment; E ~ external electric field

1) When there is no external field, what is the ground state and excited state? Is there a dipole moment in either of the states?

What is the operector for dipole moment in the matrix form?

Sol:

$$H_t = -t\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \qquad |g.s.\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = |s\rangle, \quad |e.s.\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = |A\rangle$$

$$\mu_z = \begin{pmatrix}-\mu & 0\\ 0 & \mu\end{pmatrix} = \mu\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}, \qquad \langle s|\mu_z|s\rangle = \langle A|\mu_z|A\rangle = 0$$

No dipole moment in either symmetric or Anti symmetric states.

Note $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}(|u\rangle + |d\rangle), \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}(|u\rangle - |d\rangle)$

2) Assume the field is weak and can be treated as a perturbation. Calculate the polarizability of the ammonia molecules for both the ground state and the excited state using the non-degenerate second order perturbation. Discuss qualitatively the difference between the polarizability here and the polarizability of a hydrogen atom that you worked on in HW set I.

Hint: for state n, the second order correction can be written as $E_n^2 = -\frac{1}{2}\alpha_n E^2$, α_n - polarizability.

α_n is a function of state index n. For the ground state, $\alpha_n > 0$. One can also show the induced dipole moment $d_n = \alpha_n E$.

Sol: $n=0,1$ for $|g.s\rangle$ and $|e.s.\rangle$ Respectively.

$\langle 0|H'|1\rangle^0 = \mu E$. $\quad H' = \mu E \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$E_0^2 = -\frac{(\mu E)^2}{2t}$, $\quad E_1^2 = +\frac{(\mu E)^2}{2t}$ so $\alpha_0 = \frac{\mu^2}{t}$, $\alpha_1 = -\frac{\mu^2}{t}$.

Note that the polarizability for $n=0,1$ are opposite in signs.

3) When the field is very strong, find the approximate ground state and excited state.

Sol. $E >> t$,

$$|g.s.\rangle = |d\rangle \text{ or } \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \qquad |e.s.\rangle = |u\rangle \text{ or } \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

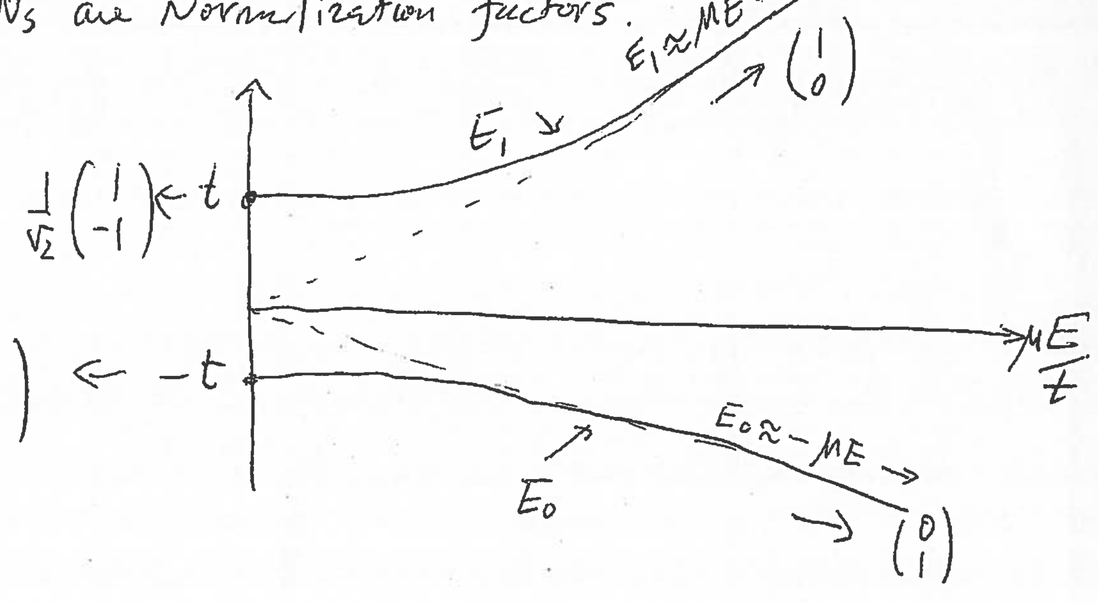
4) Using the degenerate perturbation theory to find the eigen values and eigen states for ammonia molecues as a function of external field E. Plot schematically two eigen values as a function of electric field.

Sol.

$$E_0 = -\sqrt{(\mu E)^2 + t^2}, \qquad E_1 = +\sqrt{(\mu E)^2 + t^2}$$

$$|g.s.\rangle = N_g \begin{pmatrix} t \\ \mu E + \sqrt{(\mu E)^2 + t^2} \end{pmatrix}, \qquad |e.s.\rangle = N_s \begin{pmatrix} t \\ \mu E - \sqrt{(\mu E)^2 + t^2} \end{pmatrix}$$

N_g. N_s are Normalization factors.



5) Assume an ammonia molecule is prepared in state |u> at t=0. Find out the probability of find the molecule in state |d> at an arbitrary later time t=T. At what T, the probability of finding molecules in state |u> is zero. No external field for this part.

Sol: $$|\psi(t=0)\rangle = \begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1\\1\end{pmatrix} + \frac{1}{2}\begin{pmatrix}1\\-1\end{pmatrix}$$

$$|\psi(t=T)\rangle = \frac{1}{2}\begin{pmatrix}1\\1\end{pmatrix} e^{-i\frac{tT}{\hbar}} + \frac{1}{2}\begin{pmatrix}1\\-1\end{pmatrix} e^{i\frac{tT}{\hbar}}$$

$$P_u = |\langle u|\psi(t=T)\rangle|^2 = \cos^2\frac{tT}{\hbar}$$ (t – tunneling matrix element)

$$P_d = |\langle d|\psi(t=T)\rangle|^2 = \sin^2\frac{tT}{\hbar}$$

So $\underline{P_u + P_d = 1}$,

$P_u = 0$ when $\frac{tT}{\hbar} = \frac{\pi}{2} n$, $n = 1, 3, 5 \ldots$

or $\frac{tT}{\hbar} = \pi\left(m + \frac{1}{2}\right)$, $m = 0, 1, 2 \ldots$