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Course: **8.421 - AMO I**
Problem set: **#6**
Due: Friday, March 18, 2022.

1. Symmetries and Permanent Dipole Moments

(a) As we know, the energy eigenstates of the rotationally invariant Hamiltonian of HCl have no "permanent" electric dipole moment in the lab frame. This makes sense since the orientation of the molecule is arbitrary. More precisely, The energy eigenfunctions go like $\psi_{nlm} = R_{nl}Y_{lm}$ and have parity $(-1)^l$, which gives $\left\langle Jm_J \right| \hat{d} \left| JmJ \right\rangle = 0$. This means that the observed "permanent electric dipole" only exists in the presence of a bias electric field which breaks symmetry. The the presence of an electric field, states of difference parities connect and the molecule behaves like it has a permanent electric dipole.

(b) The observed linear Stark effect comes from the fact that the HCl molecule has permanent electric dipole moment. This is allowed when l is large, at which point there is a degeneracy of states with different parities.

(c) Naively I would think that since the orbital magnetic moments of electrons and protons in atoms do not necessarily cancel, it is possible for an atom to have a permanent magnetic dipole moment. However, this cannot be the case for electric dipole moment because this would imply that there exists a "separation of charges" in the atoms, i.e., the "centers" of the negative and positive charge distributions do not coincide. But this implies that there is a restoring force present which is possible only if the atom is polarized.

2. The Stark Effect in Hydrogen

(a) To do this problem, we must first identity the relevant two-level system. The $n = 2$ level of hydrogen has a total of 8 states when both electron charge and spin are included in the Hamiltonian. Fine structure splitting raises the four $2P_{3/2}$ states about 10 GHz above the two $2P_{1/2}$ and two $2S_{1/2}$ states. From here, plus the fact that the two levels must have different l's, we can ignore the $2P_{3/2}$ states. The Lamb shift raises $2S_{1/2}$ above $2P_{1/2}$ by about 1 GHz. This is a small splitting so we may as well treat $2S_{1/2}$ and $2P_{1/2}$ as "degenerate" in order to do degenerate perturbation theory (we'll keep the energy splitting the diagonal terms though). Both $2S_{1/2}$ and $2P_{1/2}$ have total angular momentum $J = 1/2$. The substates in each level can be assumed to be degenerate and treated as one state.

The Hamiltonian is thus

$$\mathcal{H} = \begin{pmatrix} E_0 - \Delta/2 & 3ea_0\mathcal{E} \\ 3ea_0\mathcal{E} & E_0 + \Delta/2 \end{pmatrix}$$

where we have picked the basis with $\left|g\right\rangle = \left|2P_{1/2}\right\rangle = (1,0)^\top$ and $\left|e\right\rangle = \left|2S_{1/2}\right\rangle = (0,1)^\top$. The eigenvalues are

$$\begin{aligned} E_\pm &= E_0 \pm \sqrt{\Delta^2/4 + (3ea_0\mathcal{E})^2} \\ \left|+\right\rangle &= \\ \left|-\right\rangle &= \end{aligned}$$

Here we have chosen Δ to be the Lamb shift. Since it doesn't change the dynamics, we may also just set $E_0 = 0$. Working in units of frequency and writing the off-diagonal term as V we have

$$\mathcal{H} = \begin{pmatrix} -\omega_0/2 & V \\ V & \omega_0/2 \end{pmatrix}.$$

The eigenvalues and eigenvectors are

$$\begin{aligned}
\omega^{\pm} &= \pm\sqrt{(\omega_0/2)^2 + V^2} \\
|+\rangle &= \sin\frac{\theta}{2}\left|g\right\rangle + \cos\frac{\theta}{2}\left|e\right\rangle \\
|-\rangle &= -\cos\frac{\theta}{2}\left|g\right\rangle + \sin\frac{\theta}{2}\left|e\right\rangle
\end{aligned}$$

where we have defined $\tan\theta = 2V/\omega_0$.

(b) For the Stark shift to be linear, we must have that

$$2V \approx \omega_0 \implies 2(3ea_0\mathcal{E}) \approx \omega_0\hbar \implies \mathcal{E} \approx \frac{h\nu_0}{6ea_0}$$

The numerical value of this quantity is

$$\mathcal{E}_0 \approx 13.62 \text{ kV/m} = \boxed{136.2 \text{ V/cm}}$$

In this case, the linear shift may be calculated by evaluating the limit of $d\Delta E/d\mathcal{E}$ as $\mathcal{E} \to \infty$. The value obtained is

$$\left.\frac{d\Delta\omega}{d\mathcal{E}}\right|_{\mathcal{E}\to\infty} = \frac{3ea_0}{h} = \frac{\nu_0/2}{\mathcal{E}_0}.$$

Here $\omega_0 = 1.06$ GHz is the Lamb shift. So the numerical value for this quantity is

$$\left.\frac{d\Delta\nu}{d\mathcal{E}}\right|_{\mathcal{E}\to\infty} = \frac{530}{136.2} \text{ MHz/(V/cm)} \approx \boxed{3.89 \text{ MHz/(V/cm)}}$$

Note to the grader: My apologies in advance for the sloppiness in presentation, explanation etc. in this pset. I have not had proper sleep since Sunday, March 12, 2022 thanks to my wonderfully considerate roommate and his associates. There could also be a factor of $\sqrt{3}$ missing in the final answers because of the extra spin degree of freedom. If we treat this as a rough calculation then okay maybe we could ignore this number. It's not entirely difficult to include though: We would do this by writing the $2P_{1/2}$ state as a superposition in the $|m_L m_S\rangle$ basis. The dipole operator only connect $2S_{1/2}$ with the $m_L = 0$ state in $2P_{1/2}$. Clebsch and Gordan tell us that there is a factor of $\sqrt{3}$ on top of the $3ea_0$ that comes from the wavefunction.