Problem Set 6

Due: Friday 5pm, Mar 18, via Canvas upload or in envelope outside 26-255
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1   Symmetries and Permanent Dipole Moments

The molecule HCl is reported to have a permanent electric dipole moment (EDM) of 0.41 ea_o. There is more than one way to answer each of the three parts.
Note on grading: this problem is graded out of 10 points: a) 3 points, b) 4 points, c) 3 points.
a) Considering electromagnetic interactions only, the Hamiltonian of HCl is rotationally invariant in the lab frame. Explain the connection between this and HCl's observed electric dipole moment. (Hint: This question can be answered by thinking about both parity and rotational invariance.)
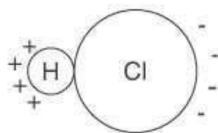

Figure 1: HCl molecule

A chlorine atom is said to be more electronegative than a hydrogen atom; in the HCl molecule, one finds that the distribution of electrons is pulled toward the chlorine atom, as indicated in the picture above. When we have a *fixed* molecule like this, we see that it makes sense to say that HCl has a permanent EDM. When chemists speak of the dipole moment of a molecule, they are referring to the dipole moment in this *rest* frame.

In the *lab* frame, however, the energy of the electromagnetic interactions of the nuclei and electrons is invariant under rotations of the whole molecule. This means that the total angular momentum J commutes with the Hamiltonian; J and m_J are thus good quantum numbers, and the corresponding eigenstates must have definite parity. Since $\mathbf{r}$ is an odd operator, we know $\langle J \ m_J | \mathbf{r} | J \ m_J \rangle = 0$, and it follows that the expectation value of the electric dipole operator is always zero. This means there is no EDM in the lab frame. Another way to think about this: in the absence of an applied electric field, the internuclear axis of the molecule is equally likely to point in any direction.

As noted above, the EDM is clearly nonzero in the frame where the molecule is at rest. In this frame, the Hamiltonian is not invariant under general rotations; one must

add extra non-invariant terms to the molecule's Hamiltonian in order to fix the orientation of its axis.The eigenstates do not have definite parity, and it is indeed possible to have a nonzero expectation value for the dipole operator. Another way to see this: to construct a state where the molecule is pointing in a definite direction, one must make a superposition of angular momentum eigenstates; such a superposition will not have definite parity.

b) The fact that a "permanent" EDM value is quoted for HCl indicates that there is an experimental regime where the observed dipole moment is independent of the electric field. This can be observed as a linear Stark effect. Given the parity considerations from part (a), where does this measured linear Stark effect come from?

To find the shifts of the energy levels in HCl as a function of an applied electric field $\mathbf{E_o}$, we treat the Stark Hamiltonian $H' = e\mathbf{E_o} \cdot \mathbf{r} = eE_o z$ as a perturbation. Suppose we want to find the shift due to H' of the eigenstate $|\psi_i\rangle$ (with corresponding energy E_i) in the lab frame. We already know that $\langle\psi_i|H'|\psi_i\rangle = 0$, so we need to apply perturbation theory of at least second order, which involves the matrix elements of H' with other eigenstates of opposite parity $\{|\psi_j\rangle\}$. As long as $|\langle\psi_i|H'|\psi_j\rangle| \ll |E_i - E_j|$ for all j, second-order perturbation theory predicts a *quadratic* Stark effect. The energy shift in this case turns out to be

$$\frac{I_o d^2}{\hbar^2} \left[\frac{J(J+1) - 3m_J^2}{J(J+1)(2J-1)(2J+3)} \right] E_o^2, \tag{1}$$

where I_o is the moment of inertia and d is the permanent EDM.

If the field is large enough such that $|\langle\psi_i|H'|\psi_j\rangle| > |E_i - E_j|$ for some j, then second-order perturbation theory is no longer valid. At still larger fields, degenerate perturbation theory applies, which amounts to diagonalizing H' in the basis of "nearly-degenerate" eigenstates. Suppose there is one state $|\psi_j\rangle$ much closer in energy to $|\psi_i\rangle$ than any other. The shifts of the energy levels turnout to be *linear*. Also, there is maximal mixing of the states $|\psi_i\rangle$ and $|\psi_j\rangle$. The new eigenstates are approximately

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}(|\psi_i\rangle \pm |\psi_j\rangle). \tag{2}$$

Because these mixed states are a superposition of opposite-parity states, they will generally exhibit an EDM. In fact, since these states are maximally mixed, they respresent the states with the largest possible EDM for a given $|\psi_i\rangle$. The linear Stark effect is, then, equivalent to inducing the largest possible *induced* EDM in a molecule. This regime can generally be reached by applying a sufficiently large electric field.

The fact that a "permanent" EDM value for HCl is quoted indicates that there is an experimental regime where the observed dipole moment is independent of the electric field. In this regime, HCl has a linear Stark effect. As it turns out, it doesn't require a very strong electric field to reach this regime, since the "ground state" of HCl consists of two nearly-degenerate states of opposite parity. Because of this, some would say HCl effectively has a permanent EDM even in the lab frame: as soon as an external field is turned on, one

observes the characteristic dipole moment, $0.41ea_o$.

c) Justify why atoms can have permanent magnetic dipole moments, but not EDM's. A clearly explained diagram will suffice.

For an atom, there is no difference in the Hamiltonian between lab frame and rest frame. An atomic eigenstatehas definite parity, and it cannot exhibit an EDM. Another way tolook at this is to consider what happens when an atom is subjected to a parity reversal operation: the atom's angular momentum is unchanged, but any EDM would be reversed in direction (see diagram below). Thus, the existence of an EDM constitutes a parity violation. On the other hand, the magnetic moment of an atom is always proportional to its angular momentum. A magnetic moment does not reverse direction under a parity operation, and it is consistent with parity symmetry; it is reasonable to expect atoms to have permanent magnetic moments.
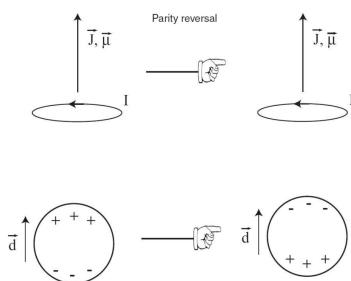

Figure 2: Magnetic and electric dipoles under parity reversal.

Vector quantities which transform to their inverse under a parity operation are known as *polar vectors*. And vectors which remain unchanged under a parity operation are called *axial vectors*. Thus, an EDM is a polar vector, and a magnetic dipole moment is an axial vector. For a more precise discussion of polar vectors, axial vectors, and the parity operation (spatial inversion), take a look at Jackson's *Classical Electrodynamics*, 2nd Ed., pp. 247–249.

Finally, it is interesting to note that some extensions to the Standard Model allow for a permanent EDM of the electron which could lead to tiny $(< 10^{-16}ea_o)$ permanent atomic EDM's. A number of impressive experiments have been undertaken in the past two decades to look for an electron EDM in atoms and molecules. The latest of these experiments are stringent enough to test the predictions of Standard Model extensions. So far, all experimental results are consistent with zero permanent EDM in atomic systems.

2   The Stark Effect in Hydrogen

Episode 1 - The Stark splitting of the $2S$ and $2P$ levels

Note on grading: this problem is graded out of 10 points. i) 6 points, ii) 4 points.

(i) Find the energies and eigenfunctions of the $n = 2$ states of hydrogen in an applied electric field $\mathbf{E} = E\hat{\mathbf{z}}$. You should simplify the problem to a two level system by considering only the essential physics of the two closest interacting states. In order to do this you must justify what assumptions you have made and why they are reasonable.

(ii)   How large (in V/cm) must the electric field be for the Stark shift to be linear? Calculate the linear shift in the lab units of MHz/(V/cm).

Suggestions:

- The $n = 2$ level of hydrogen has a total of 8 states when both electron charge and spin are included in the Hamiltonian.

- The 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.

- The Lamb shift raises $2S_{1/2}$ above $2P_{1/2}$ by 1.06 GHz.

- Both $2S_{1/2}$ and $2P_{1/2}$ have total angular momentum J = 1/2. Your answer to 1c will be useful in arguing that the two substates for each level remain degenerate and can be treated as one state for this problem.

- The electric dipole moment between the $2S$ and $2P$ states is $3ea_o$. Use this to construct your interaction hamiltonian.

- You may find it helpful to express the eigenvectors in terms of an angle θ defined by $\tan\theta = 2V/\omega_0$, where V is the off-diagonal matrix element in the interaction Hamiltonian. (Do you recognize the geometric interpretation of θ?)

Stay tuned for episode 2 - Stark Quenching!

As suggested by the hints

- The four $2P_{3/2}$ states can be ignored for Stark energies less then about 10 GHz.

- Using the result from 1c, the two J=1/2 states are equivalent under a parity reversal, so the electric field will not distinguish between them. This will not be the case for all states if J=3/2. The $m_J = \pm 1/2$ states will be distinguishable from the $m_J = \pm 3/2$ states.
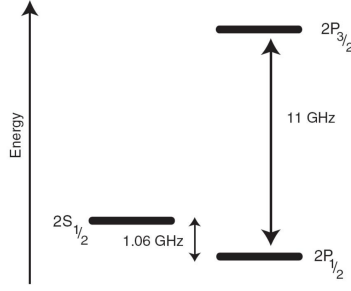
Figure 3: Energies of Hydrogen $n = 2$

These two assumptions allow us to reduce our problem to the two level system with basis $\{|2S_{1/2}\rangle, |2P_{1/2}\rangle\}$. If we define the zero of energy at the $2P_{1/2}$ state, the matrix representation of the unperturbed Hamiltonian H_o in this subspace is

$$H_o = \hbar \begin{pmatrix} \omega_o & 0 \\ 0 & 0 \end{pmatrix}, \tag{3}$$

where $\omega_o/2\pi$ is the Lamb shift frequency. The perturbation $H' = eEz$ can be written

$$H' = \hbar \begin{pmatrix} 0 & V^* \\ V & 0 \end{pmatrix}, \tag{4}$$

where $V = \sqrt{3}ea_oE/\hbar$, making use of the dipole moment given in the problem. Note that the value $3ea_o$ given in the problem is the dipole moment between the electron orbital wavefunctions $\langle 200|ez|210\rangle$. This dipole moment squared gets distributed between $P_{3/2}$ and $P_{1/2}$ by $2/3$ and $1/3$.

The total Hamiltonian is

$$H = H_o + H' = \hbar \begin{pmatrix} \omega_o & V^* \\ V & 0 \end{pmatrix}. \tag{5}$$

Now, we could use perturbation theory to find the eigenvalues and eigenstates accurately in the limiting cases $|V| \ll \omega_o$ and $|V| \gg \omega_o$, but since this is just a 2×2 matrix, it's pretty easy to diagonalize it exactly for all V. To get the energies $\hbar\lambda_\pm$, we solve the characteristic equation

$$\begin{vmatrix} \omega_o - \lambda & V^* \\ V & -\lambda \end{vmatrix} = 0, \tag{6}$$

or

$$\lambda^2 - \lambda\omega_o - |V|^2 = 0. \tag{7}$$

The solutions are

$$\lambda_\pm = \frac{1}{2}\left[\omega_o \pm \omega_o\left(1 + \frac{4|V|^2}{\omega_o^2}\right)^{1/2}\right]. \tag{8}$$

Let's check the limiting cases.

i) $|V| \ll \omega_o$:

$$\lambda_\pm \simeq \frac{1}{2}\left[\omega_o \pm \omega_o\left(1 + \frac{2|V|^2}{\omega_o^2}\right)\right] \tag{9}$$

$$\Rightarrow \lambda_+ = \omega_o + \frac{|V|^2}{\omega_o}, \quad \lambda_- = -\frac{|V|^2}{\omega_o} \tag{10}$$

This is the quadratic Stark shift which we would obtain using second-order perturbation theory.

ii) $|V| \gg \omega_o$:

$$\lambda_\pm = \frac{\omega_0}{2} \pm |V|\sqrt{1 + \frac{\omega_0^2}{4|V|^2}} \simeq \frac{\omega_0}{2} \pm |V|\left(1 + \frac{\omega_0^2}{8|V|^2}\right) \tag{11}$$

$$\Rightarrow \lambda_\pm = \frac{\omega_o}{2} \pm |V| \tag{12}$$

And this is the linear Stark shift which we can also obtain by degenerate perturbation theory, which we must use when the spacing between unperturbed levels is small compared to the perturbation.
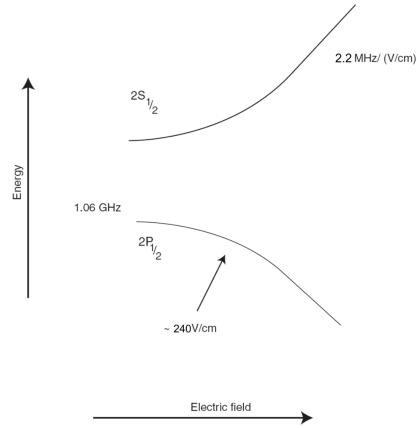

Figure 4: Stark shift diagram for $2S_{1/2}$ and $2P_{1/2}$

The "crossover" field strength, above which the shift behavior quickly becomes linear, is given by $V \sim \omega_o/2$. Thus,

$$
\begin{aligned}
E \;\sim\;& \frac{\hbar\omega_o}{2\sqrt{3}ea_o} \\
=\;& \frac{(6.63 \times 10^{-34}\text{J s})(1.06 \times 10^9 \text{ s}^{-1})}{2\sqrt{3}(1.6 \times 10^{-19}\text{C})(5.29 \times 10^{-9}\text{cm})} \\
\simeq\;& 240 \text{ V/cm}.
\end{aligned}
$$

For fields much stronger than this, the Stark shift is linear, and its "slope" (in Hz per unit electric field) is given by

$$
\frac{1}{2\pi}\frac{d|V|}{dE} = \frac{\sqrt{3}ea_o}{h} = \frac{\sqrt{3}(1.6 \times 10^{-19}\text{C})(5.29 \times 10^{-9}\text{cm})}{6.63 \times 10^{-34} \text{ J s}} \simeq 2.2 \text{ MHz/(V/cm)}. \tag{13}
$$

It still remains to give an explicit expression for the new eigenstates for an arbitrary electric field strength. The algebra required to find the eigenvectors of a 2×2 matrix is carried out in many books. See, for example, *Quantum Mechanics*, Vol. 1, Complement B_{IV} by Cohen-Tannoudji *et al.* Making use of the very general expression from Cohen-Tannoudji, we can write down relatively simple expressions for the eigenvectors of Eq. 5:

$$
\begin{aligned}
|\psi_+\rangle \;=\;& \cos\frac{\theta}{2}|2S_{1/2}\rangle + \sin\frac{\theta}{2}|2P_{1/2}\rangle \\
|\psi_-\rangle \;=\;& -\sin\frac{\theta}{2}|2S_{1/2}\rangle + \cos\frac{\theta}{2}|2P_{1/2}\rangle,
\end{aligned}
$$

where $\tan\theta = 2V/\omega_o$. (We are now making use of the fact that V is real.) The angle θ has a geometric interpretation. If we represent the two-level system of this problem by a fictitious spin-1/2 system in a magnetic field, θ is the angle between the effective magnetic field vector in the presence of the perturbation and the "unperturbed" magnetic field direction. In other words, θ gives the direction of the axis about which the Bloch vector of the system precesses. In the limiting cases, we again find the same results as given by perturbation theory.

i) $|V| \ll \omega_o$:

$$
\tan\theta \simeq \sin\theta \simeq \theta \;\Rightarrow\; \frac{\theta}{2} \simeq \frac{V}{\omega_o}, \tag{14}
$$

$$
\begin{aligned}
\Rightarrow |\psi_+\rangle \;=\;& |2S_{1/2}\rangle + \frac{V}{\omega_o}|2P_{1/2}\rangle \\
|\psi_-\rangle \;=\;& |2P_{1/2}\rangle - \frac{V}{\omega_o}|2S_{1/2}\rangle,
\end{aligned}
$$

to first order in V/ω_o. Each state is mostly one of the unperturbed eigenstates with a small "contamination" from the other unperturbed eigenstate.

ii) $|V| \gg \omega_o$:

$$\tan \theta \gg 1 \quad \Rightarrow \quad \theta \simeq \frac{\pi}{2}, \tag{15}$$

$$\Rightarrow |\psi_\pm\rangle = \frac{1}{\sqrt{2}}(|2P_{1/2}\rangle \pm |2S_{1/2}\rangle). \tag{16}$$

These are again the completely mixed eigenstates of degenerate perturbation theory.