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.

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.)

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?

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

2) The Stark Effect in Hydrogen

a) The Stark splitting of the 2S and 2P levels

(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 ?)

b) Stark quenching of the 2S state

Since the dipole selection rules forbid single photon radiation from the 2S state ($\equiv |a\rangle$) to the 1S ground state, the 2S state is metastable. In the absence of external fields, its lifetime is about 1/8 of a second, corresponding to a decay rate $\Gamma_a = 8 \text{ s}^{-1}$. When an electric field is applied, the 2S state becomes mixed with the 2P state (again, predominantly with the $2P_{1/2} \equiv |b\rangle$ state), which is strongly coupled to the ground state by the Lyman-alpha transition. The 2P state lifetime is only 1.6 ns, and it decays at a rate $\Gamma_b = 6.3 \times 10^8 \text{ s}^{-1}$. Depending on the strength of the electric field, then, the lifetime of the 2S state can be shortened by many orders of magnitude. This process is known as "quenching." To get a better idea of how this works, let's examine how the amplitude a(t) of $|a\rangle$ evolves over time in the presence of a DC Stark perturbation with matrix element $\hbar V = \langle b| e \mathbf{E} \cdot \mathbf{r} |a\rangle$.

Find an expression for a(t) assuming that the atom is initially in the 2S state. Discuss the large V and small V limits, and give an expression for the 2S decay rate in each case. How do your results relate to the perturbation theory results for Stark shift energies?

Detailed Hints: Working in the interaction picture (see, for example, section 5.5 of Sakurai, *Modern Quantum Mechanics*), one can derive the following coupled differential equations for a(t) and b(t):

$$i\dot{a} = V^* e^{i\omega_o t} b - i \frac{\Gamma_a}{2} a, \qquad (1)$$

$$i\dot{b} = Ve^{-i\omega_o t}a - i\frac{\Gamma_b}{2}b.$$
 (2)

Here, $\hbar\omega_o$ is the energy difference $E_a - E_b$. The terms involving V describe the coupling between the states, while the rightmost terms are included to describe the decay of each state. The easy way to solve these equations is to make the ansatz,

$$a(t) = a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}, \tag{3}$$

$$b(t) = b_1 e^{-(\mu_1 + i\omega_o)t} + b_2 e^{-(\mu_2 + i\omega_o)t},$$
(4)

where $a_{1,2}$ are constants. The real parts of $\mu_{1,2}$ will provide the decay rate of the 2S state, and the imaginary parts tell about the level shifts. You can make use of $\Gamma_a \ll \Gamma_b$, and you may also assume $\Gamma_a \ll \mu_1, \mu_2$.

c) Effect of the Lamb shift on quenching

Find the electric field in V/cm for which the 2S state lifetime is equal to 1 μ s, for the following two cases.

First, calculate the electric field in the weak coupling limit (i.e. $V^2 \ll \omega_o^2$) assuming that ω_o is much smaller than the actual 2P linewidth Γ_b .

Second, perform the calculation in the weak field limit as above but with the actual Lamb shift splitting.

What effect does inclusion of the splitting have on the necessary electric field for quenching on this time scale?

Comment: Such calculations are relevant to a fruitful method for high-resolution spectroscopy of the 1S-2S transition. Hydrogen atoms in either an atomic beam or a magnetic trap are excited by a laser pulse into the 2S state via two-photon absorption. These metastable atoms can be detected by quenching with an electric field some hundreds of microseconds or even milliseconds later. The resulting burst of Lyman-alpha photons can thus be counted by a detector with minimal background from the excitation laser. (C. L. Cesar *et al.*, Phys. Rev. Lett. **77**, 225 (1996), for example.)

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