Ben Sauerwine
Practice for Qualifying Exams

Problem Source: **CMU August 2003 Qualifying Exam**

Consider transitions from excited states of a hydrogen atom (2S and 2P) into the ground state (1S). The 2S level is slightly higher in energy than the 2P level $\left(E_{2S} - E_{2P} = 4\times10^{-6} eV\right)$ due to a hyperfine splitting known as the Lamb shift. Denote the Hamiltonian of an isolated atom by H_0. For the sake of clarity, take as the 2S, 2P and 1S states, respectively:

$$|\alpha\rangle = \left|n=2, l=0, m=0, m_S = -\frac{1}{2}\right\rangle$$

$$|\beta\rangle = \left|n=2, l=1, m=0, m_S = \frac{1}{2}\right\rangle$$

$$|\gamma\rangle = \left|n=1, l=0, m=0, m_S = \frac{1}{2}\right\rangle$$

(a) An atomic orbital couples to electromagnetic radiation fields via $W = W_{DE} + W_{DM} + \ldots$ The relevant operators W_i are given by $W_{DE} = -eE\hat{Z}\cos\omega t$, where $\hat{Z}$ is the position operator, and $W_{DM} = -\frac{e}{2m}B\left(\hat{L}_x + 2\hat{S}_x\right)\cos\omega t$. For each W_i explain clearly why the matrix element $\langle\gamma|W_i|\alpha\rangle$ does or does not vanish. State briefly why the 2S level of hydrogen is long-lived (its lifetime is almost a second) and describe the dominant decay mechanism by which 2S decays to 1S.

The dipole transition between α and γ, or the 2S and 1S states, is not allowed due to the parity: These are in the same angular-momentum states, but the $\hat{Z}$ operator is odd parity and so must switch parity.

The magnetic transition also vanishes: Consider individually $\hat{L}_x$ and $\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right)$. Since both wave functions are spherically symmetric, $\hat{L}_x$ is zero. The spin operator will certainly swap the electron spin, but leave the still-orthogonal angular momentum portion untouched.

This is a long-lived state because the dominant means of decay would be to decay to 2P and then decaying to 1S.

(b) Repeat part (a) using the 2P level, state $|\beta\rangle$ in place of the 2S level (state $|\alpha\rangle$). State why 2P is relatively short-lived (its lifetime is about 10^{-10}

seconds) and describe the dominant decay mechanism by which 2P decays to 1S.

The dipole transition between β and γ, or the 2P and 1S states, is allowed since now the parity is correct. Further, consideration of the Clebsch-Gordan coefficient corresponding to the $\hat{Z} \approx P_0^1$ operator, I see that the coefficient $\langle 1 \quad 0 \quad 1 \quad 0 \| 0,0 \rangle$ corresponding to the angular momentum portion $\langle 0 \quad 0 | P_0^2 | 1 \quad 0 \rangle$ is not excluded by the selection rules.

In the magnetic transition, $\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right)$ certainly eliminates the spin portion. Further, the angular momentum ladder operator $\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$ has no means to switch between shells.

Thus, the electric dipole transition is the dominant decay mechanism here, and it is rather short lived due to the strong coupling of this transition.

(c) The wave function

$$\psi(t) = b_\alpha(t) e^{-\frac{iE_\alpha t}{\hbar}} |\alpha\rangle + b_\beta(t) e^{-\frac{iE_\beta t}{\hbar}} |\beta\rangle$$

represents a superposition of states $|\alpha\rangle$ and $|\beta\rangle$ and satisfies the time-dependent Schrodinger equation with a Hamiltonian H_0, with $b_\alpha(t), b_\beta(t)$ independent of time. Now apply a constant electric field E_0 to the atom so that it feels a potential $V(\vec{R}) = -eE_0\hat{Z}$. Derive equations for $\dot{b}_\alpha = \frac{db_\alpha}{dt}, \dot{b}_\beta = \frac{db_\beta}{dt}$ assuming $\psi(t)$ has the form given above, with E_α and E_β the energies when $E_0 = 0$. Introduce a suitable notation for any nonzero matrix elements you may need, but do NOT attempt to evaluate them.

Write the perturbation as

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \left[H_0 + W_{DE}\right]\psi(t)\rangle$$

for an exact solution, then, I will simplify a bit:

$$i\hbar\left[\dot{b}_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle - \frac{iE_\alpha}{\hbar} b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle + \dot{b}_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle - \frac{iE_\beta}{\hbar} b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle\right] =$$

$$E_\alpha b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle + E_\beta b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle + b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle\left\langle\alpha\right|W_{DE}\left|\alpha\right\rangle$$

$$+ b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\beta\right\rangle\left\langle\beta\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\alpha\right\rangle\left\langle\alpha\right|W_{DE}\left|\beta\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle\left\langle\beta\right|W_{DE}\left|\beta\right\rangle$$

and from this

$$i\hbar\left[\dot{b}_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle - \frac{iE_\alpha}{\hbar} b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle\right] = E_\alpha b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle + b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\alpha\right\rangle\left\langle\alpha\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\alpha\right\rangle\left\langle\alpha\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\alpha e^{-\frac{iE_\alpha t}{\hbar}} = i\hbar\frac{iE_\alpha}{\hbar} b_\alpha e^{-\frac{iE_\alpha t}{\hbar}} + E_\alpha b_\alpha e^{-\frac{iE_\alpha t}{\hbar}} + b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left\langle\alpha\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left\langle\alpha\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\alpha = i\hbar\frac{iE_\alpha}{\hbar} b_\alpha + E_\alpha b_\alpha + b_\alpha\left\langle\alpha\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{i(E_\beta - E_\alpha)t}{\hbar}}\left\langle\alpha\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\alpha = b_\alpha\left\langle\alpha\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{i(E_\beta - E_\alpha)t}{\hbar}}\left\langle\alpha\right|W_{DE}\left|\beta\right\rangle$$

and also

$$i\hbar\left[\dot{b}_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle - \frac{iE_\beta}{\hbar} b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle\right] = E_\beta b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle + b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left|\beta\right\rangle\left\langle\beta\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left|\beta\right\rangle\left\langle\beta\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\beta e^{-\frac{iE_\beta t}{\hbar}} = i\hbar\frac{iE_\beta}{\hbar} b_\beta e^{-\frac{iE_\beta t}{\hbar}} + E_\beta b_\beta e^{-\frac{iE_\beta t}{\hbar}} + b_\alpha e^{-\frac{iE_\alpha t}{\hbar}}\left\langle\beta\right|W_{DE}\left|\alpha\right\rangle + b_\beta e^{-\frac{iE_\beta t}{\hbar}}\left\langle\beta\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\beta = i\hbar\frac{iE_\beta}{\hbar} b_\beta + E_\beta b_\beta + b_\alpha e^{-\frac{i(E_\alpha - E_\beta)t}{\hbar}}\left\langle\beta\right|W_{DE}\left|\alpha\right\rangle + b_\beta\left\langle\beta\right|W_{DE}\left|\beta\right\rangle$$

$$i\hbar\dot{b}_\beta = b_\alpha e^{-\frac{i(E_\alpha - E_\beta)t}{\hbar}}\left\langle\beta\right|W_{DE}\left|\alpha\right\rangle + b_\beta\left\langle\beta\right|W_{DE}\left|\beta\right\rangle$$

Solving these coupled differential equations exactly would give the exact perturbed time dependence.

(d) The application of a constant electric field reduces the lifetime of the 2S state $\left|\alpha\right\rangle$. To estimate what happens, add to your equation for $\dot{b}_\beta$ a term $\frac{-b_\beta}{\tau}$ to represent the decay of the 2P state caused by its coupling to the radiation field. For simplicity use the approximation $E_\alpha = E_\beta$. Show by using the modified differential equations that if the applied electric field E_0 is small, there are two decay constants τ_1 and τ_2, one much larger than τ, for each of which you should obtain an explicit expression to lowest order in the applied field. What happens when the applied field is large?

Under the approximation $E_\alpha = E_\beta$, I have

$$i\hbar\dot{b}_\alpha = b_\alpha\langle\alpha|W_{DE}|\alpha\rangle + b_\beta\langle\alpha|W_{DE}|\beta\rangle$$

and

$$i\hbar\dot{b}_\beta = b_\alpha\langle\beta|W_{DE}|\alpha\rangle + b_\beta\langle\beta|W_{DE}|\beta\rangle - \frac{b_\beta}{\tau}$$

To solve these differential equations, one writes this in matrix form:

$$\vec{b} = \begin{bmatrix} b_\alpha \\ b_\beta \end{bmatrix}$$

$$\dot{\vec{b}} = -\frac{i}{\hbar}\begin{bmatrix} \langle\alpha|W_{DE}|\alpha\rangle & \langle\alpha|W_{DE}|\beta\rangle \\ \langle\beta|W_{DE}|\alpha\rangle & \langle\beta|W_{DE}|\beta\rangle - \frac{1}{\tau} \end{bmatrix}\vec{b}$$

Now briefly consider these coefficients: none are forbidden explicitly by the Clebsch-Gordan coefficients, but parity forbids the electric dipole transition from occurring between the same state. Thus, I have:

$$W = \langle\alpha|W|\beta\rangle$$

$$\dot{\vec{b}} = -\frac{i}{\hbar}\begin{bmatrix} 0 & W \\ W^* & -\frac{1}{\tau} \end{bmatrix}\vec{b}$$

Certainly, the general solution to this is

$$\vec{b} = e^{-\frac{i}{\hbar}\begin{bmatrix} 0 & W \\ W^* & -\frac{1}{\tau} \end{bmatrix}t}$$

The eigenvalues of this matrix are clearly

$$\lambda^2 + \frac{1}{\tau}\lambda - WW^* = 0$$

$$\lambda = \frac{\frac{1}{\tau} \pm \sqrt{\frac{1}{\tau^2} - 4|W|^2}}{2}$$

A matrix M composed of the eigenvectors will then give

$$\vec{b} \approx [M]\begin{bmatrix} e^{-\frac{i}{\hbar}\lambda_1 t} & 0 \\ 0 & e^{-\frac{i}{\hbar}\lambda_2 t} \end{bmatrix}[M^+]$$

Something here can only have gone wrong. I see that the "decay time" of this state, dominated by the imaginary parts of the eigenvealues, will leave an amplitude that goes to zero and an amplitude that grows to infinity over time! I believe I've misinterpreted this problem.