Problem Set 7

Due: Friday 5pm, April 1st, via Canvas upload or in envelope outside 26-255
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1 Spherical Harmony

Our goal is to be able to evaluate matrix elements like

$$\left\langle J' m_J' | Y_{Lm} | J m_J \right\rangle = \int \mathrm{d}\Omega \, Y^*_{J' m_J'} Y_{Lm} Y_{J m_J} \tag{1}$$

of which $L = 1$ is relevant for dipole transitions, $L = 2$ for quadrupole etc...

To this end, consider two particles with angular momenta $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$. The total angular momentum is $\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2$. We know that we can couple the states $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ into states of definite total angular momentum J with the help of Clebsch-Gordan coefficients:

$$|(j_1 j_2) JM\rangle = \sum_{m_1, m_2} |j_1 m_1\rangle \, |j_2 m_2\rangle \, \langle j_1 m_1 j_2 m_2 | JM \rangle \tag{2}$$

$$|j_1 m_1\rangle \, |j_2 m_2\rangle = \sum_{J, M} |(j_1 j_2) JM\rangle \, \langle JM | j_1 m_1 j_2 m_2 \rangle \tag{3}$$

The Clebsch-Gordan coefficients imply that the sum over M has just one non-zero term, $M = m_1 + m_2$, and that J runs from $|j_1 - j_2|$ to $j_1 + j_2$. The wavefunction of each particle at polar angle $(\theta_i, \phi_i) \equiv \Omega_i$ is $\langle \Omega_i | j_i m_i \rangle = Y_{j_i m_i}(\Omega_i)$ for $i = 1, 2$, and that for the state of definite total angular momentum is $\Phi_{JM}(\Omega_1, \Omega_2) = \langle \Omega_1, \Omega_2 | (j_1 j_2) JM \rangle$. Note that the latter requires two sets of polar angles. The function $F_{JM}(\Omega) \equiv \langle \Omega, \Omega | (j_1 j_2) JM \rangle$, where the two polar angles $\Omega_1 = \Omega_2 = \Omega$ are equal, is a wavefunction of an effective particle with angular momentum quantum numbers J, M. Indeed, it inherits its eigenvalues of $\boldsymbol{J}^2$ and J_z from $\Phi_{JM}(\Omega_1, \Omega_2)$. So $F_{JM}(\Omega)$ must be proportional to the spherical harmonic $Y_{JM}(\Omega)$:

$$F_{JM}(\Omega) = A_{(j_1 j_2) J} Y_{JM}(\Omega) \tag{4}$$

The factor $A_{(j_1 j_2) J}$ cannot depend on M as F_{JM} must behave in all respects like Y_{JM}, in particular when acted upon with $J_\pm$, which changes M. So we have shown a relation for the spherical harmonics:

$$A_{(j_1 j_2) J} Y_{JM}(\Omega) = \sum_{m_1, m_2} \langle j_1 m_1 j_2 m_2 | JM \rangle \, Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega) \tag{5}$$

YOUR TASKS:

a) Find $A_{(j_1 j_2) J}$.

Hint: Recall that $Y_{lm}(\theta = 0, \phi) = \sqrt{\frac{2l+1}{4\pi}} \delta_{m0}$.

The relation above should be equal for all solid angles, so it is clever (also looking at the hint) to consider a particular direction, namely with the polar angle $\Omega_0 = (\theta, \phi) = (0, \phi)$ pointing in the z-direction.

So plugging that solid angle into 2 gives

$$\begin{aligned} F_{JM}(\Omega_0) &= \langle \Omega_0, \Omega_0 | (j_1 j_2) JM \rangle & (6) \\ &= \sum_{m_1, m_2} \langle \Omega_0 | j_1, m_1 \rangle \langle \Omega_0 | j_2, m_2 \rangle \langle j_1 m_1 j_2 m_2 | JM \rangle & (7) \\ &= \sum_{m_1, m_2} Y_{j_1 m_1}(\theta = 0, \phi) Y_{j_2, m_2}(\theta = 0, \phi) \langle j_1 m_1 j_2 m_2 | JM \rangle & (8) \\ &= \sum_{m_1, m_2} \sqrt{\frac{2j_1 + 1}{4\pi}} \delta_{m_1, 0} \sqrt{\frac{2j_2 + 1}{4\pi}} \delta_{m_2, 0} \langle j_1 m_1 j_2 m_2 | JM \rangle & (9) \\ &= \frac{\sqrt{(2j_1 + 1)(2j_2 + 1)}}{4\pi} \langle j_1 0 j_2 0 | JM \rangle & (10) \\ &= \frac{\sqrt{(2j_1 + 1)(2j_2 + 1)}}{4\pi} \langle j_1 0 j_2 0 | J0 \rangle \, \delta_{M,0} & (11) \end{aligned}$$

where the last $\delta_{M,0}$ is a consequence of the Clebsch-Gordan coefficient requiring $M = m_1 + m_2 = 0$ (this is just z-angular momentum conservation). We also have

$$\begin{aligned} F_{JM}(\Omega_0) &= A_{(j_1 j_2) J} Y_{JM}(\Omega_0) & (12) \\ &= A_{(j_1 j_2) J} \sqrt{\frac{2J + 1}{4\pi}} & (13) \end{aligned}$$

So therefore:

$$A_{(j_1 j_2) J} = \sqrt{\frac{(2j_1 + 1)(2j_2 + 1)}{4\pi(2J + 1)}} \langle j_1 0 j_2 0 | J0 \rangle \tag{14}$$

So the relation 5 is

$$Y_{JM}(\Omega) = \sqrt{\frac{4\pi(2J + 1)}{(2j_1 + 1)(2j_2 + 1)}} \sum_{m_1, m_2} \frac{\langle j_1 m_1 j_2 m_2 | JM \rangle}{\langle j_1 0 j_2 0 | J0 \rangle} Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega) \tag{15}$$

We now have an appreciation for why sometimes one prefers to work with the modified spherical harmonics

$$C_{JM}(\Omega) \equiv \sqrt{\frac{4\pi}{2J + 1}} Y_{JM}(\Omega) \tag{16}$$

which at the north pole are simply $C_{JM}(\theta = 0, \phi) = \delta_{M,0}$. The expression is then written more simply:

$$C_{JM}(\Omega) = \sum_{m_1,m_2} \frac{\langle j_1 m_1 j_2 m_2 | JM \rangle}{\langle j_1 0 j_2 0 | J0 \rangle} C_{j_1 m_1}(\Omega) C_{j_2 m_2}(\Omega) \tag{17}$$

b) Find an expression relating $Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega)$ to a sum over the $Y_{JM}(\Omega)$.

Applying $\langle \Omega, \Omega |$ to the left of Eq. 3 gives, according to the definition of $F_{JM}(\Omega)$:

$$Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega) = \sum_{JM} F_{JM}(\Omega) \langle JM | j_1 m_1 j_2 m_2 \rangle \tag{18}$$

Using $F_{JM}(\Omega) = A_{(j_1 j_2)J} Y_{JM}(\Omega)$ yields

$$Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega) = \sum_{JM} A_{(j_1 j_2)J} \langle JM | j_1 m_1 j_2 m_2 \rangle Y_{JM}(\Omega) \tag{19}$$

$$= \sum_{JM} \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2J+1)}} \langle j_1 0 j_2 0 | J0 \rangle \langle JM | j_1 m_1 j_2 m_2 \rangle Y_{JM}(\Omega) \tag{20}$$

Again, using modified spherical harmonics turns this into the simpler

$$C_{j_1 m_1}(\Omega) C_{j_2 m_2}(\Omega) = \sum_{JM} \langle j_1 0 j_2 0 | J0 \rangle \langle JM | j_1 m_1 j_2 m_2 \rangle C_{JM}(\Omega) \tag{21}$$

It makes of course good sense that it is possible to express the product of two spherical harmonics in terms of a linear superposition of single Y_{JM}'s. Any function of the solid angle Ω can be decomposed into the spherical harmonics, since they provide a complete basis of functions on the unit sphere.

c) Find the matrix element $\langle j_3 m_3 | Y_{j_2 m_2} | j_1 m_1 \rangle$.

We would like to calculate

$$\langle j_3 m_3 | Y_{j_2 m_2} | j_1 m_1 \rangle = \int \mathrm{d}\Omega \, Y^*_{j_3 m_3}(\Omega) Y_{j_2 m_2}(\Omega) Y_{j_1 m_1}(\Omega) \tag{22}$$

We can use our result for the product of two spherical harmonics in terms of sums of individual ones for the last two factors (for example). Then we see

$$\langle j_3 m_3 | Y_{j_2 m_2} | j_1 m_1 \rangle = \sum_{JM} A_{(j_1,j_2)J} \int \mathrm{d}\Omega \, Y^*_{j_3 m_3}(\Omega) Y_{JM}(\Omega) \langle JM | j_2 m_2 j_1 m_1 \rangle \tag{23}$$

$$= A_{(j_1,j_2)j_3} \langle j_3 m_3 | j_2 m_2 j_1 m_1 \rangle \tag{24}$$

Combining this with our result for $A_{(j_1,j_2)j_3}$ gives

$$\langle j_3 m_3 | Y_{j_2 m_2} | j_1 m_1 \rangle = \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j_3+1)}} \langle j_1 0 j_2 0 | j_3 0 \rangle \langle j_3 m_3 | j_2 m_2 j_1 m_1 \rangle \tag{25}$$

This is an example of the Wigner-Eckart theorem: The $Y_{JM}(\Omega)$ are tensors of rank J, and matrix elements of tensors factorize into a directional part - the Clebsch-Gordan coefficient - and a scalar. Physically, we see that for the matrix element Eq. 22 to be non-zero, the integrand must be a scalar. So the only part of the state $Y_{j_2 m_2} |j_1 m_1\rangle$ that can contribute is that which rotates like $|j_3 m_3\rangle$. By definition, this amplitude is given by the Clebsch-Gordan coefficient, and this is the geometrical factor containing all dependence on magnetic quantum numbers.

We can directly read off selection rules:

i) We have $m_3 = m_1 + m_2$, which we can interpret this as conservation of z angular momentum. It is directly obvious by considering the ϕ-integral, which is $\int_0^{2\pi} \mathrm{d}\phi\, e^{i(m_1+m_2-m_3)\phi} = \delta_{0,m_1+m_2-m_3}$.

ii) We must be able to form a triangle of lengths j_1, j_2 and j_3 (so j_3 must lie between $|j_2 - j_1|$ and $j_1 + j_2$).

iii) In addition, the prefactor $\langle j_1 0 j_2 0 | j_3 0 \rangle$ implies an additional rule: $j_1 + j_2 - j_3$ must be even. This is just expressing the parity rule: For the integral over the unit sphere to be non-zero, the product of the three spherical harmonics must be an even function under parity.

2 Dipole operator

A symmetric top molecule has a Hamiltonian $H = B\boldsymbol{J}^2$, with B the rotational constant. The dipole moment operator is $\hat{\boldsymbol{d}} = d\hat{\boldsymbol{r}}$, with d the value of the "permanent dipole moment" (in the molecular frame)

a) Show that the unit vector $\hat{\boldsymbol{r}}$ can be written in terms of the modified spherical harmonics $C_{1m}(\theta,\phi) = \sqrt{\frac{4\pi}{3}}\, Y_{1m}(\theta,\phi)$, the unit vector $\hat{\boldsymbol{e}}_z \equiv \hat{\boldsymbol{e}}_0$ and the vectors

$$\hat{\boldsymbol{e}}_+ \equiv \hat{\boldsymbol{e}}_{+1} \equiv -\frac{\hat{\boldsymbol{e}}_x + i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \tag{26}$$

$$\hat{\boldsymbol{e}}_- \equiv \hat{\boldsymbol{e}}_{-1} \equiv \frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \tag{27}$$

as what's called the spherical tensor decomposition:

$$\hat{\boldsymbol{r}} = \sum_m C^*_{1m}\hat{\boldsymbol{e}}_m = \sum_m C_{1m}\hat{\boldsymbol{e}}^*_m \tag{28}$$

We have

$$\hat{\boldsymbol{r}} = \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} = \begin{pmatrix} \sin\theta\,\cos\phi \\ \sin\theta\,\sin\phi \\ \cos\theta \end{pmatrix} \tag{29}$$

The spherical harmonics of order $l = 1$ are

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{30}$$

$$Y_{11} = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \tag{31}$$

$$Y_{1-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} \tag{32}$$

The modified spherical harmonics $C_{1m}(\theta,\phi) = \sqrt{\frac{4\pi}{3}}\, Y_{1m}(\theta,\phi)$ are then

$$C_{10} = \cos\theta = \hat{z} \tag{33}$$

$$C_{11} = -\frac{1}{\sqrt{2}}\sin\theta\, e^{i\phi} = -\frac{\hat{x}+i\hat{y}}{\sqrt{2}} = -C^*_{1-1} \tag{34}$$

$$C_{1-1} = \frac{1}{\sqrt{2}}\sin\theta\, e^{-i\phi} = \frac{\hat{x}-i\hat{y}}{\sqrt{2}} = -C^*_{11} \tag{35}$$

One can write

$$\hat{\boldsymbol{r}} = \hat{x}\hat{\boldsymbol{e}}_x + \hat{y}\hat{\boldsymbol{e}}_y + \hat{z}\hat{\boldsymbol{e}}_z \tag{36}$$

$$= \frac{\hat{x}+i\hat{y}}{\sqrt{2}}\frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} + \frac{\hat{x}-i\hat{y}}{\sqrt{2}}\frac{\hat{\boldsymbol{e}}_x + i\hat{\boldsymbol{e}}_y}{\sqrt{2}} + \hat{z}\hat{\boldsymbol{e}}_z \tag{37}$$

$$= -C_{11}\hat{\boldsymbol{e}}_- - C_{1-1}\hat{\boldsymbol{e}}_+ + C_{10}\hat{\boldsymbol{e}}_0 \tag{38}$$

$$= C^*_{11}\hat{\boldsymbol{e}}_+ + C^*_{1-1}\hat{\boldsymbol{e}}_- + C_{10}\hat{\boldsymbol{e}}_0 \tag{39}$$

$$= \sum_m C^*_{1m}\hat{\boldsymbol{e}}_m = \sum_m C_{1m}\hat{\boldsymbol{e}}^*_m \tag{40}$$

b) Show that

$$\hat{\boldsymbol{e}}^*_m \cdot \hat{\boldsymbol{e}}_n = \sum_p \delta_{mp}\delta_{np} = \delta_{mn} \tag{41}$$

(so in particular $\hat{\boldsymbol{e}}_+^* \cdot \hat{\boldsymbol{e}}_- = 0$, $\hat{\boldsymbol{e}}_-^* \cdot \hat{\boldsymbol{e}}_+ = 0$ and $\hat{\boldsymbol{e}}_+^* \cdot \hat{\boldsymbol{e}}_+ = \hat{\boldsymbol{e}}_-^* \cdot \hat{\boldsymbol{e}}_- = 1$).

A few steps of algebra gives the result.

c) As a by-product of this formalism, by taking two unit vectors $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{r}}'$, pointing in the direction of solid angle (θ, ϕ) and (θ', ϕ'), derive a known fact from geometry, namely

$$\cos(\Theta) = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi') \tag{42}$$

where Θ is the angle between $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{r}}'$, so between (θ, ϕ) and (θ', ϕ').

This is a very fancy way to write simply $\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{r}}' = \cos(\Theta)$. The result is of course immediate if we use the components of $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{r}}'$, as we get $\cos\theta\ \cos\theta' + \sin\theta\sin\theta'(\cos\phi\cos\phi' + \sin\phi\sin\phi')$ and, using a trig identity, the desired result. Instead, here we are tasked to make use of the spherical tensor decomposition $\hat{\boldsymbol{r}} = \sum_m C_{1m}^* \hat{\boldsymbol{e}}_m$ and $\hat{\boldsymbol{r}}' = \sum_m C_{1m}'^* \hat{\boldsymbol{e}}_m$. We have

$$\begin{aligned}
\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{r}}' &= \sum_{m,m'} C_{1m} C_{1m'}'^* \hat{\boldsymbol{e}}_m^* \cdot \hat{\boldsymbol{e}}_{m'} && (43)\\
&= \sum_{m,m'} C_{1m} C_{1m'}'^* \delta_{m,m'} && (44)\\
&= \sum_{m} C_{1m} C_{1m}'^* && (45)\\
&= \cos\theta\cos\theta' + \frac{\sin\theta}{\sqrt{2}} e^{i\phi} \frac{\sin\theta'}{\sqrt{2}} e^{-i\phi'} + \frac{\sin\theta}{\sqrt{2}} e^{-i\phi} \frac{\sin\theta'}{\sqrt{2}} e^{i\phi'} && (46)\\
&= \cos\theta\cos\theta' + \sin\theta\ \sin\theta' \frac{1}{2}\left(e^{i(\phi-\phi')} + e^{-i(\phi-\phi')}\right) && (47)\\
&= \cos\theta\cos\theta' + \sin\theta\ \sin\theta' \cos(\phi - \phi') && (48)
\end{aligned}$$

Additional information for general knowledge: In fact, the equation is the $l = 1$ version of the general

$$P_l(\cos\Theta) = \sum_m C_{lm}^*(\theta, \phi) C_{lm}(\theta', \phi') \tag{49}$$

with $C_{lm}(\theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}$. This fact we used in multipole decomposition of the Coulomb interaction between electrons and nucleus.

The proof for general l is as follows. The scalar product $\boldsymbol{C}_l \cdot \boldsymbol{C}_l' \equiv \sum_m C_{lm}^*(\theta, \phi) C_{lm}(\theta', \phi')$ is invariant under rotations of axes. It can thus only be a function of the angle Θ between the directions (θ, ϕ) and (θ', ϕ'), this angle being the only quantity independent of the choice of axes. Choosing axes so that (θ', ϕ') becomes the new z-axis we have $C_{lm}(\theta', \phi') \to C_{lm}(0, 0) = \delta_{m0}$. And $C_{l0}(\theta, \phi) \to P_l(\cos\theta) = P_l(\cos\Theta)$.

d) The electric field can be written

$$\begin{aligned} \boldsymbol{E} &= E_z \hat{\boldsymbol{e}}_z + E_x \hat{\boldsymbol{e}}_x + E_y \hat{\boldsymbol{e}}_y && (50)\\ &= E_0 \hat{\boldsymbol{e}}_0 + E_-^* \hat{\boldsymbol{e}}_- + E_+^* \hat{\boldsymbol{e}}_+ && (51)\\ &= \sum_m E_m^* \hat{\boldsymbol{e}}_m = \sum_m E_m \hat{\boldsymbol{e}}_m^* && (52) \end{aligned}$$

with $E_0 = E_z$, $E_+ = -\frac{1}{\sqrt{2}}(E_x + iE_y)$, $E_- = \frac{1}{\sqrt{2}}(E_x - iE_y)$. Show that the dipole operator can be written

$$-\hat{\boldsymbol{d}} \cdot \boldsymbol{E} = -d \sum_m C_{1m}^* E_m = -d \sum_m C_{1m} E_m^* \tag{53}$$

This is a similar exercise in algebra from above. Writing it this way makes it clear which combination of electric fields are coupled to which operator, and so which combination causes what change in magnetic quantum number.

e) *Extra credit:* Take $\boldsymbol{E} = E\hat{z}$. So the only interaction is $\propto C_{10}$. In Mathematica (or your preferred program) setup the Hamiltonian matrix $H = B\boldsymbol{J}^2 - \hat{\boldsymbol{d}} \cdot \boldsymbol{E}$, including states up to sufficiently high J to give the energies of the first six energy levels (up to $|2,0\rangle$) up to an electric field $E \approx 10B/d$. Plot the probability $|\langle\theta,\phi|\Psi\rangle|^2$ (using e.g. SphericalPlot3D) of the lowest state ($|0,0\rangle$ at $E = 0$) for a few values, e.g. $dE/B = 0, 1, 10$.

Additional information for general knowledge: For matrix elements of the dipole operator we have

$$\left\langle J'm_J'|C_{1m}|Jm_J\right\rangle = \int \mathrm{d}\Omega\, Y_{J'm_J'}^* C_{1m} Y_{Jm_J} \tag{54}$$

which you calculated in problem 1. From this follow the selection rules $\Delta J = \pm 1$ and $\Delta M = 0, \pm 1$. Note that $C_{11} \propto Y_{11}$ increases the magnetic quantum number by $\Delta M = +1$, while $C_{1,-1}$ lowers it by $\Delta M = -1$. $C_{1,0}$ gives $\Delta M = 0$.

The somewhat surprising choices of signs in the components E_+ and E_- are made so that the E_m transform under rotations as irreducible tensors of rank 1. If D is the operator of an arbitrary rotation (e.g. described by Euler angles), then an irreducible tensor of rank k has $2k+1$ components T_{kq} which transform as

$$T_{kq}' = DT_{kq}D^\dagger = \sum_p T_{kp}\mathcal{D}_{pq}^k(\alpha\beta\gamma).$$

with $\mathcal{D}_{pq}^k(\alpha\beta\gamma)$ the entries of the rotation (Wigner D-)matrix for given Euler angles. Writing this for an infinitesimal rotation $D = 1 - i\alpha J_\lambda$ by angle α about an axis λ yields commutation relations of T_{kq} with the angular momentum operators that each irreducible tensor must obey. In particular, for J_z and $J_\pm$ one finds

$$[J_z, T_{kq}] = qT_{kq} \tag{55}$$

$$[J_\pm, T_{kq}] = \sqrt{k(k+1) - q(q\pm 1)}\, T_{kq\pm 1} \tag{56}$$

These commutation relations can be used to find the spherical equivalents of cartesian tensors. If $\boldsymbol{A}$ is a vector, then $[J_z, A_z] = 0$ and so $A_0 = A_z$. One then finds $A_{\pm 1} = \frac{1}{\sqrt{2}}[J_\pm, A_0] = \mp\frac{1}{\sqrt{2}}(A_x \pm iA_y)$.

Writing the dipole operator as a scalar product of irreducible tensors allows to nicely separate the geometric part of the problem (dependence on magnetic quantum numbers) from the excitation (E-field: π-polarized, σ_+-polarized etc.).

For more information on the general topic of spherical tensors, irreducible representations of the rotation group, Wigner D-matrices, etc., please see:

[1] D. Brink, G. Satchler, *Angular Momentum* (Clarendon Press 1968)
Very clear, concise, thorough presentation.

[2] Julian Schwinger, *On Angular Momentum*, 1952
Builds up general angular momentum from spin 1/2 particles, in an elegant, powerful treatment. For that latter technique, also see

[3] F. Bloch, I.I. Rabi, *Atoms in Variable Magnetic Fields*, Rev. Mod. Phys. 17, 237 (1945). They cite a paper by E. Majorana, Nuovo Cimento **9**, 43 (1932) which is the first to present the so-called "Majorana star" representation of an angular momentum state.

3 The Stark Effect in Hydrogen

Episode 2: Stark Quenching

This is the second part of the "Stark Effect" question on the last problem set.

a) 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 $\Gamma_a = 8\ \mathrm{s}^{-1}$. 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 $\Gamma_b = 6.3 \times 10^8\ \mathrm{s}^{-1}$. 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 $b(t)$:

$$i\dot{a} = V^* e^{i\omega_o t} b - i\frac{\Gamma_a}{2} a, \tag{57}$$

$$i\dot{b} = V e^{-i\omega_o t} a - i\frac{\Gamma_b}{2} b. \tag{58}$$

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,

$$a(t) = a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}, \tag{59}$$

$$b(t) = b_1 e^{-(\mu_1 + i\omega_o)t} + b_2 e^{-(\mu_2 + i\omega_o)t}, \tag{60}$$

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 $\Gamma_a \ll \mu_1, \mu_2$.

Let's start by keeping everything very general. We consider a two-level system split by $\hbar\omega_0$. The unperturbed Hamiltonian H_0 is essentially the same as from previous homework, if we use the $|a\rangle$ and $|b\rangle$. This time however we want the levels to have a finite width in energy. In other words, they will have finite lifetimes. We introduce phenomenologically imaginary parts to the eigenvalues of H_0.

$$H_0 = \begin{pmatrix} \omega_0 - i\frac{\Gamma_a}{2} & 0 \\ 0 & -i\frac{\Gamma_b}{2} \end{pmatrix} \tag{61}$$

Thus in the absence of a perturbation the amplitude of state $|a\rangle$ evolves as $e^{-i\omega_0 t} e^{-\Gamma_a/2t}$, and its population given by $|a|^2$ decays according to $e^{-\Gamma_a t}$.

To make use of the interactino picture we write the time dependence of the amplitudes due to H_0 as an explicit separate factor

$$|\psi\rangle = a(t)e^{-i\omega_0 t}|a\rangle + b(t)|b\rangle \tag{62}$$

Including now the perturbation, the Schrodinger equation in matrix form is

$$\begin{pmatrix} \omega_0 - i\frac{\Gamma_a}{2} & V^* \\ V & -i\frac{\Gamma_b}{2} \end{pmatrix} \begin{pmatrix} a(t)e^{-i\omega_0 t} \\ b(t) \end{pmatrix} = i\frac{\partial}{\partial t} \begin{pmatrix} a(t)e^{-i\omega_0 t} \\ b(t) \end{pmatrix} \tag{63}$$

Multiplying this matrix equation out leads to the coupled differential equations of the interaction picture, as given in the hint for the problem

$$i\dot{a} = V^* e^{i\omega_0 t} b - i\frac{\Gamma_a}{2} a \tag{64}$$

$$i\dot{b} = V e^{-i\omega_0 t} a - i\frac{\Gamma_b}{2} b \tag{65}$$

The hint also suggests the following ansatz

$$a(t) = a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t} \tag{66}$$

$$b(t) = b_1 e^{-(\mu_1 + i\omega_0)t} + b_2 e^{-(\mu_2 + i\omega_0)t} \tag{67}$$

To see why this is a reasonable choice for an ansatz substitute $a(t)$, $b(t)$ back into $|\psi\rangle$.

$$|\psi\rangle = \left(\sum_{i=1,2} a_i e^{-\mu_i t}\right) e^{-i\omega_0 t} |a\rangle + \left(\sum_{i=1,2} b_i e^{-\mu_i t}\right) e^{-i\omega_0 t} |b\rangle \tag{68}$$

$$|\psi\rangle = e^{-\mu_1 t} \left(a_1 |a\rangle + b_1 |b\rangle\right) + e^{-\mu_2 t} \left(a_2 |a\rangle + b_2 |b\rangle\right) \tag{69}$$

Thus the ansatz gives us a convenient way of solving for the eigenstates and eigenvalues of the perturbed system. (These are not really eigenstates because they are decaying away in time). The constants μ_1 and μ_2 will in general have both real and imaginary parts. By analogy to solutions of the time dependent Schrodinger equation, we interpret $\mathrm{Im}(\mu_1)$, $\mathrm{Im}(\mu_2)$ as giving the energies of the eigenstates, and $\mathrm{Re}(\mu_1)$, $\mathrm{Re}(\mu_2)$ will give us the respective decay constants.

To solve the problem we start by substituting the ansatz, giving us

$$-i\mu_1 a_1 e^{-\mu_1 t} - i\mu_2 a_2 e^{-\mu_2 t} = V^*(b_1 e^{-\mu_1 t} + b_2 e^{-\mu_2 t}) - i\frac{\Gamma_a}{2}(a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}) \tag{70}$$

$$\begin{aligned} -i(\mu_1 + i\omega_0) b_1 e^{-(\mu_1 + i\omega_0)t} - i(\mu_2 + i\omega_0) b_2 e^{-(\mu_2 + i\omega_0)t} &= \\ V e^{-i\omega_0 t}(a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}) - i\frac{\Gamma_b}{2}&(b_1 e^{-(\mu_1 + i\omega_0)t} + b_2 e^{-(\mu_2 + i\omega_0)t}) \end{aligned} \tag{71}$$

Equating the coefficients of $e^{\mu_1 t}$ leads to the following pairs of time-independent equations

$$\mu_1 a_1 = iV^* b_1 + \frac{\Gamma_a}{2} a_1 \tag{72}$$

$$(\mu_1 + i\omega_0) b_1 = iV a_1 + \frac{\Gamma_b}{2} b_1 \tag{73}$$

Written as a matrix equation for a_1, b_1 we obtain

$$\begin{pmatrix} i(\mu_1 - \frac{\Gamma_a}{2}) & V^* \\ V & i(\mu_1 - \frac{\Gamma_b}{2} + i\omega_0) \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = 0 \tag{74}$$

This only has a non-trivial solution if the determinant of the 2 by 2 matrix is zero

$$\left(\mu_1 - \frac{\Gamma_a}{2}\right)\left(\mu_1 - \frac{\Gamma_b}{2} + i\omega_0\right) + |V|^2 = 0 \tag{75}$$

$$\mu_1^2 - \left(\frac{\Gamma_a + \Gamma_b}{2} - i\omega_0\right)\mu_1 + \frac{\Gamma_a}{2}\left(\frac{\Gamma_b}{2} - i\omega_0\right) + |V|^2 = 0 \tag{76}$$

If we equate the coefficients of $e^{-\mu_2 t}$ in Eqs. (70) and (71), we arrive at the same equation for μ_2. Thus,

$$\mu_{1,2} = \frac{1}{2}\left\{\frac{\Gamma_a + \Gamma_b}{2} - i\omega_0 \pm \left[\left(\frac{\Gamma_a + \Gamma_b}{2} - i\omega_0\right)^2 - 2\Gamma_a\left(\frac{\Gamma_b}{2} - i\omega_0\right) - 4|V|^2\right]^{1/2}\right\} \tag{77}$$

Using the fact that

$$\left(\frac{\Gamma_a + \Gamma_b}{2} - i\omega_0\right)^2 - 2\Gamma_a\left(\frac{\Gamma_b}{2} - i\omega_0\right) = \left(\frac{\Gamma_b - \Gamma_a}{2} - i\omega_0\right)^2 \tag{78}$$

we can write our expression for $\mu_{1,2}$ more simply

$$\mu_{1,2} = \frac{1}{2}\left\{\frac{\Gamma_b + \Gamma_a}{2} - i\omega_0 \pm \left[\left(\frac{\Gamma_b - \Gamma_a}{2} - i\omega_0\right)^2 - 4|V|^2\right]^{1/2}\right\} \tag{79}$$

We can arbitrarily assign μ_1 to correspond to μ_+ and μ_2 to μ_-.

Now let's make our solutions specific to the problem at hand: Stark quenching of the 2S state in Hydrogen $|a\rangle = 2S_{1/2}$, $|b\rangle = 2P_{1/2}$, $\hbar V = \langle b|\, e\boldsymbol{E}\cdot\boldsymbol{r}\,|a\rangle = 3ea_0E = \hbar V^*$, $\Gamma_a = 8\mathrm{s}^{-1}$, $\Gamma_b = 6.3\cdot 10^8\mathrm{s}^{-1}$.

Since Γ_a is negligible compared to Γ_b,

$$\mu_{1,2} = \frac{1}{2}\left\{\frac{\Gamma_b}{2} - i\omega_0 \pm \left[\left(\frac{\Gamma_b}{2} - i\omega_0\right)^2 - 4|V|^2\right]^{1/2}\right\} \tag{80}$$

We are told to find an expression for $a(t)$ assuming the atom is initially in the $2S$ state

$$a(0) = a_1 + a_2 = 1 \tag{81}$$
$$b(0) = b_1 + b_2 = 0 \tag{82}$$

If now we assume $\Gamma_a \ll |\mu_1|$ (which as we will see is a good assumption when there is any mixing of $|a\rangle$ and $\langle a|$, equation (72) yields

$$b_1 = \frac{-ia_1\mu_1}{V} \tag{83}$$

The analogous equation for μ_2 is

$$b_2 = \frac{-ia_2\mu_2}{V} \tag{84}$$

Thus,

$$a_1\mu_1 + a_2\mu_2 = 0 \tag{85}$$

together with $(a_1 + a_2)\mu_1 = \mu_1$, we have enough constraints to express $a_{1,2}$ in terms of $\mu_{1,2}$.

$$a_1 = -\frac{\mu_2}{\mu_1 - \mu_2} \tag{86}$$

$$a_2 = \frac{\mu_1}{\mu_1 - \mu_2} \tag{87}$$

And thus quite generally

$$a(t) = -\frac{\mu_2}{\mu_1 - \mu_2}e^{-\mu_1 t} + \frac{\mu_1}{\mu_1 - \mu_2}e^{-\mu_2 t} \tag{88}$$

Strong field case. $V^2 \gg \omega_0^2$ In this case Eq. (80) becomes

$$\mu_{1,2} = \frac{1}{2}\left[\frac{\Gamma_b}{2} - i\omega_0 \pm 2iV\right] \tag{89}$$

It follows that

$$a_1 = -\left(\frac{\frac{\Gamma_b}{2} - i\omega_0 - i2V}{i4V}\right) \approx \frac{1}{2} \tag{90}$$

$$a_2 = \left(\frac{\frac{\Gamma_b}{2} - i\omega_0 + i2V}{i4V}\right) \approx \frac{1}{2} \tag{91}$$

and therefore

$$b_1 = \frac{-ia_1\mu_1}{V} \approx \frac{1}{2} \tag{92}$$

$$b_2 = \frac{-ia_2\mu_2}{V} \approx -\frac{1}{2} \tag{93}$$

Leading to

$$|\psi\rangle = \frac{1}{2}e^{-\mu_1 t}\left(|a\rangle + |b\rangle\right) + \frac{1}{2}e^{-\mu_2 t}\left(|a\rangle - |b\rangle\right) \tag{94}$$

Since $\mathrm{Re}(\mu_1) = \mathrm{Re}(\mu_2)$, we see that for all times the decaying $2S$ state can be decomposed into equal amplitudes of the Stark shifted states $(|a\rangle \pm |b\rangle)/2$.

This is just a time-dependent extension of the result obtained in Pset 6 for $V \gg \omega_0$. We have again the maximally mixed states of degenerate perturbation theory. The decay of the $2S$ state is described by

$$a(t) = \frac{1}{2} e^{-(\mu_1+\mu_2)t} = e^{-\Gamma_b t/4} e^{-i_0 t/2} \cos(Vt) \tag{95}$$

we get damped Rabi oscillations with decay rate $\Gamma_{2S} = \frac{\Gamma_b}{2}$. Finally, note that the energies of the Stark shifted states are

$$-\hbar\,\mathrm{Im}(\mu_1) = \hbar\,(\omega_0/2 + V) \tag{96}$$

$$-\hbar\,\mathrm{Im}(\mu_2) = \hbar\,(\omega_0/2 - V) \tag{97}$$

Weak field case. $V^2 \ll \omega_0^2$

Expand the square root of Eq. (80)

$$\mu_{1,2} \approx \frac{1}{2}\left\{\left(\frac{\Gamma_b}{2} - i\omega_0\right)\left[1 \pm \left(1 - \frac{2V^2}{(\Gamma_b/2 - i\omega_0)^2}\right)\right]\right\} \tag{98}$$

$$\mu_1 = \frac{\Gamma_b}{2} - i\omega_0 - \frac{V^2}{\Gamma_b/2 - i\omega_0} = \frac{\Gamma_b}{2}\left(1 - \frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right) - i\omega_0\left(1 + \frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right) \tag{99}$$

and

$$\mu_2 = \frac{V^2(\Gamma_b/2 + i\omega_0)}{(\Gamma_b/2)^2 + \omega_0^2} = \frac{\Gamma_b}{2}\left(\frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right) + i\omega_0\left(\frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right) \tag{100}$$

The level shifts in terms of frequency

$$\pm\,\omega_0\left(\frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right) \tag{101}$$

with the upper sign corresponding to $2S1/2$ and the lower sign to $2P1/2$, this is quadratic Stark shift. In the limit of an infinite $2P$ lifetime $\Gamma_b = 0$, we get the same expression as obtained in Pset 6 for weak field drive.

Note that the finite width of the $2P$ state does make a small correction to the level shifts in this limit. Now, since $\mathrm{Re}(\mu_1) \gg \mathrm{Re}(\mu_2)$, the $e^{-\mu_1 t}$ term in $a(t)$ damps out very quickly. Also, $|a_1| = \left|\frac{\mu_2}{\mu_1-\mu_2}\right| \ll 1$, but $a_2 = \frac{\mu_1}{\mu_1-\mu_2} \sim 1$.

Thus we only need to keep the $e^{-\mu_2 t}$ term: $a(t) \sim e^{-\mu_2 t}$ and $|a(t)|^2 \sim e^{-2\mu_2 t}$. The $2S$ decay rate in this case is

$$\Gamma_{2S} = \mathrm{Re}(2\mu_2) = \Gamma_b\left[\frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2}\right] \tag{102}$$

b) Effect of the Lamb shift on quenching

Find the electric field in V/cm for which the $2S$ state lifetime is equal to 1 μs, 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 meta-stable 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.)

The purpose of this question is basically to see how much different $2S$ quenching would be if the Lamb shift were much smaller that it actually is. If the Lamb shift were exactly zero, then the $2S$ and $2P$ states are completely mixed by any electric field, and the decay rate is just $\Gamma_b/2$ for any $|\boldsymbol{E}| > 0$. If $V^2 \ll \omega_0^2$ then we can use the decay rate expression for the weak field limit

$$\Gamma_{2S} = \Gamma_b \left[\frac{V^2}{(\Gamma_b/2)^2 + \omega_0^2} \right] \approx \frac{4V^2}{\Gamma_b} \tag{103}$$

$$V = \sqrt{\Gamma_b \Gamma_{2S}}/2 = 1.25 \cdot 10^7 \text{rad/s} \tag{104}$$

We showed that $\hbar V = 3ea_0E$, using this we obtain

$$E = 0.52 \text{V/cm} \tag{105}$$

Finally plugging in the actual Lamb shift splitting $\omega_0 = 2\pi \cdot 1.06\text{GHz}$ we obtain modified electric field

$$E = 11\,\text{V/cm} \tag{106}$$