Problem Set 7

Due: Friday 5pm, April 1st, via Canvas upload or in envelope outside 26-255
TA: Evgenii Kniazev, knyazev@mit.edu

1 Spherical Harmony

Our goal is to be able to evaluate matrix elements like

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

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

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

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

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

$$\hat{\boldsymbol{e}}_+ \equiv \hat{\boldsymbol{e}}_{+1} \equiv -\frac{\hat{\boldsymbol{e}}_x + i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \tag{6}$$

$$\hat{\boldsymbol{e}}_- \equiv \hat{\boldsymbol{e}}_{-1} \equiv \frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \tag{7}$$

as what's called the spherical tensor decomposition:

$$\hat{\boldsymbol{r}} = \sum_m C^*_{1m} \hat{\boldsymbol{e}}_m = \sum_m C_{1m} \hat{\boldsymbol{e}}^*_m \tag{8}$$

b) Show that

$$\hat{\boldsymbol{e}}^*_m \cdot \hat{\boldsymbol{e}}_n = \sum_p \delta_{mp}\delta_{np} = \delta_{mn} \tag{9}$$

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

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

$$\cos(\Theta) = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi') \tag{10}$$

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

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

$$P_l(\cos\Theta) = \sum_m C^*_{lm}(\theta, \phi) C_{lm}(\theta', \phi') \tag{11}$$

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

$$\begin{aligned}\boldsymbol{E} &= E_z\hat{\boldsymbol{e}}_z + E_x\hat{\boldsymbol{e}}_x + E_y\hat{\boldsymbol{e}}_y &(12)\\ &= E_0\hat{\boldsymbol{e}}_0 + E_-^*\hat{\boldsymbol{e}}_- + E_+^*\hat{\boldsymbol{e}}_+ &(13)\\ &= \sum_m E_m^*\hat{\boldsymbol{e}}_m = \sum_m E_m\hat{\boldsymbol{e}}_m^* &(14)\end{aligned}$$

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

$$-\hat{\boldsymbol{d}}\cdot\boldsymbol{E} = -d\sum_m C_{1m}^*E_m = -d\sum_m C_{1m}E_m^* \tag{15}$$

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

$$\left\langle J'm_J'|C_{1m}|Jm_J\right\rangle = \int \mathrm{d}\Omega\, Y_{J'm_J'}^* C_{1m} Y_{Jm_J} \tag{16}$$

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 $\mathcal{D}^k_{pq}(\alpha\beta\gamma)$ 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

$$[J_z, T_{kq}] = qT_{kq} \tag{17}$$

$$[J_\pm, T_{kq}] = \sqrt{k(k+1) - q(q \pm 1)}\, T_{kq\pm 1} \tag{18}$$

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 $\Gamma_b = 6.3 \times 10^8$ 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 $b(t)$:

$$i\dot{a} = V^* e^{i\omega_o t} b - i\frac{\Gamma_a}{2} a, \tag{19}$$

$$i\dot{b} = V e^{-i\omega_o t} a - i\frac{\Gamma_b}{2} b. \tag{20}$$

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,

$$a(t) = a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}, \tag{21}$$

$$b(t) = b_1 e^{-(\mu_1 + i\omega_o)t} + b_2 e^{-(\mu_2 + i\omega_o)t}, \tag{22}$$

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

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 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.)