

Exercises on Quantum Mechanics II (TM1/TV)

Problem set 11, discussed January 13 - January 17, 2019

Exercise 64 (Central Tutorial)

Let's consider the hydrogen atom ignoring the spins of the electron and of the proton. In order to have non-zero transition probability from an energy state $|\psi_a\rangle$ to another one $|\psi_b\rangle$, the matrix element of the dipole moment operator $\mathbf{D}_{ba} \equiv e \langle \psi_b | \hat{\mathbf{r}} | \psi_a \rangle$ must be non-zero too ($\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$). The conditions to have non-zero transition probabilities are called *selection rules*.

- (i) Which are good quantum numbers that characterize the state $|\psi\rangle$ of the hydrogen atom? To what do they physically correspond?
- (ii) Which values can those quantum numbers have? What is the degeneracy of the state for a given energy level?
- (iii) Recalling the definition of the angular momentum operator $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$, calculate

$$[\hat{L}_z, \hat{x}] \quad , \quad [\hat{L}_z, \hat{y}] \quad , \quad [\hat{L}_z, \hat{z}] \quad (1)$$

- (iv) Using the results of the previous point and taking the expectation values of those between two different states $|\psi_a\rangle$ and $|\psi_b\rangle$, derive the selection rules to have $\mathbf{D}_{ab} \neq 0$.
- (v) These are not the only selection rules. Recall the definition of the Casimir operator \hat{L}^2 ; what is the action of this operator on an eigenstate $|\psi\rangle$? Prove that

$$[\hat{L}^2, [\hat{L}^2, \hat{\mathbf{r}}]] = 2\hbar^2(\hat{\mathbf{r}}\hat{L}^2 + \hat{L}^2\hat{\mathbf{r}}) \quad (2)$$

- (vi) Use the previous results to find other selection rules for the transition between $|\psi_a\rangle$ and $|\psi_b\rangle$.
- (vii) What do these selection rules correspond physically to?

Solution

- (i) From the course of QMI we know that a state of the hydrogen atom (ignoring spins) is characterized by three quantum numbers: n for the energy level, l for the total angular momentum and m for the projection of the angular momentum on the \hat{z} -axis. Therefore, not considering super-positions of states, we can write the state as

$$|\psi\rangle = |n, l, m\rangle \quad (3)$$

- (ii) The quantum number for the energy n can take all positive integer values, i.e. $n \in \mathbb{N}$; l can take integer values in $[0, n-1]$; lastly, m can take integer values in $[-l, +l]$. For a fixed l , m has $2l+1$ possibilities. In the same way, for a fixed n , l takes values from 0 to $n-1$. Therefore the degeneracy for a given energy level specified by n is

$$\sum_{l=0}^{n-1} (2l+1) = 2 \sum_{l=0}^{n-1} (l) + n = 2 \frac{(n-1)n}{2} + n = n^2 \quad (4)$$

(iii) The angular momentum operators for each component are

$$\begin{aligned}\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\end{aligned}\quad \text{with} \quad \hat{\mathbf{L}} = \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix}$$

Using Heisenberg commutation relations

$$[\hat{r}_j, \hat{p}_k] = i\hbar\delta_{jk}\mathbb{1} \quad , \quad \hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z}) \quad , \quad \hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) \quad (5)$$

it follows that:

$$[\hat{L}_z, \hat{z}] = 0 \quad (6)$$

since \hat{L}_z does not depend on \hat{z} or \hat{p}_z .

$$\begin{aligned}[\hat{L}_z, \hat{x}] &= [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = 0 - [\hat{y}\hat{p}_x, \hat{x}] = i\hbar\hat{y} \\ [\hat{L}_z, \hat{y}] &= [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}] = [\hat{x}\hat{p}_y, \hat{y}] - 0 = -i\hbar\hat{x}\end{aligned} \quad (7)$$

(iv) Let's calculate the matrix element of $\hat{\mathbf{r}}$ with these information. As we know the action of \hat{L}_z on $|n, l, m\rangle$ is given by

$$\hat{L}_z |n, l, m\rangle = \hbar m |n, l, m\rangle \quad (8)$$

$$\begin{aligned}0 &= \left\langle \underbrace{n', l', m'}_{\psi_b} \left| [\hat{L}_z, \hat{z}] \right| \underbrace{n, l, m}_{\psi_a} \right\rangle = \left\langle n', l', m' \left| [\hat{L}_z, \hat{z}] \right| n, l, m \right\rangle = \left\langle n', l', m' \left| \hat{L}_z \hat{z} - \hat{z} \hat{L}_z \right| n, l, m \right\rangle = \\ &= \hbar(m' - m) \langle n', l', m' | \hat{z} | n, l, m \rangle\end{aligned} \quad (9)$$

Therefore $\langle n', l', m' | \hat{z} | n, l, m \rangle$ can be different from 0 only if $m = m'$.

Doing the same with the other two commutators we find that:

$$\begin{cases} i\hbar \langle n', l', m' | \hat{y} | n, l, m \rangle = \hbar(m' - m) \langle n', l', m' | \hat{x} | n, l, m \rangle \\ -i\hbar \langle n', l', m' | \hat{x} | n, l, m \rangle = \hbar(m' - m) \langle n', l', m' | \hat{y} | n, l, m \rangle \end{cases} \quad (10)$$

The solution found before $m' = m$ would lead to $\langle n', l', m' | \hat{x} | n, l, m \rangle = \langle n', l', m' | \hat{y} | n, l, m \rangle = 0$. Solving this system with $m' \neq m$ we find that:

$$\hbar^2 \langle n', l', m' | \hat{y} | n, l, m \rangle = \hbar^2(m' - m)^2 \langle n', l', m' | \hat{y} | n, l, m \rangle \quad (11)$$

It is true only if:

$$\hbar^2 = \hbar^2(m' - m)^2 \quad \iff \quad m' - m = \pm 1 \quad (12)$$

Therefore the conditions to have a non-zero dipole moment expectation value are

$$m' - m \equiv \Delta m = 0, \pm 1 \quad (13)$$

(v) The casimir operator is defined as:

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (14)$$

Its action on a state $\psi \equiv |n, l, m\rangle$ is given by

$$\hat{\mathbf{L}}^2 |n, l, m\rangle = \hbar^2 l(l+1) |n, l, m\rangle \quad (15)$$

To prove the relation we first prove other useful relations. In the following we are going to use Einstein's convention with Euclidean metric.

$$[\hat{\mathbf{L}}^2, \hat{L}_j] = [\hat{L}_i \hat{L}_i, \hat{L}_j] = \hat{L}_i [\hat{L}_i, \hat{L}_j] + [\hat{L}_i, \hat{L}_j] \hat{L}_i = i\hbar \epsilon_{ijk} (\hat{L}_i \hat{L}_k + \hat{L}_k \hat{L}_i) \stackrel{\text{symm.}}{=} 0 \quad (16)$$

where the commutation relation between angular momentum operators has been used:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \quad (17)$$

Lastly:

$$[\hat{L}_i, \hat{x}_j] = \epsilon_{inm}[\hat{x}_n\hat{p}_m, \hat{x}_j] = \epsilon_{inm}\hat{x}_n[\hat{p}_m, \hat{x}_j] = -i\hbar\epsilon_{inm}\hat{x}_n\delta_{mj} = i\hbar\epsilon_{ijk}\hat{x}_k \quad (18)$$

We can now start the computation.

$$\begin{aligned} [\hat{\mathbf{L}}^2, \hat{x}_n] &= \hat{L}_i [\hat{L}_i, \hat{x}_n] + [\hat{L}_i, \hat{x}_n] \hat{L}_i = i\hbar\epsilon_{inj}(\hat{L}_i\hat{x}_j + \hat{x}_j\hat{L}_i) \stackrel{Eq.18}{=} i\hbar\epsilon_{inj}(\epsilon_{ijk}\hat{x}_k + 2\hat{x}_j\hat{L}_i) = \\ &= 2i\hbar(\epsilon_{ijn}\hat{x}_i\hat{L}_j - i\hbar\hat{x}_n) \end{aligned} \quad (19)$$

Therefore:

$$\begin{aligned} [\hat{\mathbf{L}}^2, \hat{x}] &= 2i\hbar(\hat{y}\hat{L}_z - \hat{z}\hat{L}_y - i\hbar\hat{x}) \\ [\hat{\mathbf{L}}^2, \hat{y}] &= 2i\hbar(\hat{z}\hat{L}_x - \hat{x}\hat{L}_z - i\hbar\hat{y}) \\ [\hat{\mathbf{L}}^2, \hat{z}] &= 2i\hbar(\hat{x}\hat{L}_y - \hat{y}\hat{L}_x - i\hbar\hat{z}) \end{aligned} \quad (20)$$

We now calculate the commutator $[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{z}]]$:

$$[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{z}]] = [\hat{\mathbf{L}}^2, 2i\hbar(\hat{x}\hat{L}_y - \hat{y}\hat{L}_x - i\hbar\hat{z})] \stackrel{Eq.16}{=} 2i\hbar([\hat{\mathbf{L}}^2, \hat{x}]\hat{L}_y - [\hat{\mathbf{L}}^2, \hat{y}]\hat{L}_x - i\hbar[\hat{\mathbf{L}}^2, \hat{z}]) \quad (21)$$

We analyze the first two terms separately:

$$\begin{aligned} [\hat{\mathbf{L}}^2, \hat{x}]\hat{L}_y &= 2i\hbar(\hat{y}\hat{L}_z - \hat{z}\hat{L}_y - i\hbar\hat{x})\hat{L}_y = 2i\hbar(\hat{y}\hat{L}_z - i\hbar\hat{x})\hat{L}_y - 2i\hbar\hat{z}\hat{L}_y^2 = \\ &\stackrel{Eq.18}{=} 2i\hbar(\hat{L}_z\hat{y}\hat{L}_y - \hat{z}\hat{L}_y^2) \end{aligned} \quad (22)$$

For the second one:

$$\begin{aligned} -[\hat{\mathbf{L}}^2, \hat{y}]\hat{L}_x &= -2i\hbar(\hat{z}\hat{L}_x - \hat{x}\hat{L}_z - i\hbar\hat{y})\hat{L}_x = 2i\hbar(-\hat{z}\hat{L}_x^2 + \hat{x}\hat{L}_z\hat{L}_x + i\hbar\hat{y}\hat{L}_x) = \\ &\stackrel{Eq.18}{=} 2i\hbar(\hat{L}_z\hat{x}\hat{L}_x - \hat{z}\hat{L}_x^2) \end{aligned} \quad (23)$$

Adding them:

$$[\hat{\mathbf{L}}^2, \hat{x}]\hat{L}_y - [\hat{\mathbf{L}}^2, \hat{y}]\hat{L}_x = 2i\hbar(\hat{L}_z(\hat{x}\hat{L}_x + \hat{y}\hat{L}_y) - \hat{z}(\hat{L}_x^2 + \hat{L}_y^2)) = 2i\hbar(\hat{L}_z\hat{\mathbf{r}} \cdot \hat{\mathbf{L}} - \hat{z}\hat{L}_z^2 - \hat{z}\hat{\mathbf{L}}^2 + \hat{z}\hat{L}_z^2) \quad (24)$$

But we have that:

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{L}} = \hat{x}_i\hat{L}_i = \epsilon_{ijk}\hat{x}_i\hat{x}_j\hat{p}_k = 0 \quad (25)$$

Therefore

$$[\hat{\mathbf{L}}^2, \hat{x}]\hat{L}_y - [\hat{\mathbf{L}}^2, \hat{y}]\hat{L}_x = -2i\hbar\hat{z}\hat{\mathbf{L}}^2 \quad (26)$$

Combining this result with

$$-i\hbar[\hat{\mathbf{L}}^2, \hat{z}] = -i\hbar(\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2) \quad (27)$$

we get from Equation 21 the final result:

$$[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{z}]] = 2\hbar^2(\hat{z}\hat{\mathbf{L}}^2 + \hat{\mathbf{L}}^2\hat{z}) \quad (28)$$

Therefore we can conclude in general that:

$$[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{\mathbf{r}}]] = 2\hbar^2(\hat{\mathbf{r}}\hat{\mathbf{L}}^2 + \hat{\mathbf{L}}^2\hat{\mathbf{r}}) \quad (29)$$

Note: If we consider instead of \hat{r} an operator \hat{v} such that

$$[\hat{L}_i, \hat{v}_j] = i\hbar\epsilon_{ijk}\hat{v}_k \quad (30)$$

then the proof is almost identical: the only difference is that in general Equation 25 is not true anymore. This would lead to an extra term proportional to $\hat{L}(\hat{v} \cdot \hat{L})$. Keeping into account the coefficient, the result reads

$$[\hat{L}^2, [\hat{L}^2, \hat{v}]] = 2\hbar^2(\hat{v}\hat{L}^2 + \hat{L}^2\hat{v}) - 4\hbar^2\hat{L}(\hat{v} \cdot \hat{L}) \quad (31)$$

(vi) We can now use this result to derive the other selection rules.

$$\begin{aligned} \left\langle \underbrace{n', l', m'}_{\psi_b} \left| [\hat{L}^2, [\hat{L}^2, \hat{r}]] \right| \underbrace{n, l, m}_{\psi_a} \right\rangle &= 2\hbar^2 \langle n', l', m' | \hat{r}\hat{L}^2 + \hat{L}^2\hat{r} | n, l, m \rangle = \\ &= 2\hbar^4 [l'(l'+1) + l(l+1)] \langle n', l', m' | \hat{r} | n, l, m \rangle \end{aligned} \quad (32)$$

But on the other side:

$$\begin{aligned} \langle n', l', m' | [\hat{L}^2, [\hat{L}^2, \hat{r}]] | n, l, m \rangle &= \langle n', l', m' | \hat{L}^2 [\hat{L}^2, \hat{r}] - [\hat{L}^2, \hat{r}] \hat{L}^2 | n, l, m \rangle = \\ &= \hbar^2 [l'(l'+1) - l(l+1)] \langle n', l', m' | [\hat{L}^2, \hat{r}] | n, l, m \rangle = \\ &= \hbar^4 [l'(l'+1) - l(l+1)]^2 \langle n', l', m' | \hat{r} | n, l, m \rangle \end{aligned} \quad (33)$$

Therefore the condition to have a non-zero dipole moment is:

$$2[l'(l'+1) + l(l+1)] = [l'(l'+1) - l(l+1)]^2 \quad (34)$$

The term in the bracket on the right can be written as

$$l'(l'+1) - l(l+1) = (l'+l+1)(l'-l) \quad (35)$$

The one on the left instead:

$$2[l'(l'+1) + l(l+1)] = (l'+l+1)^2 + (l'-l)^2 - 1 \quad (36)$$

Therefore the condition in Equation 34 can be written as:

$$[(l'+l+1)^2 - 1] [(l'-l)^2 - 1] = 0 \quad (37)$$

The second term of the product is 0 only if:

$$l' - l = \pm 1 \quad (38)$$

The first term is 0 only if $l' = l = 0$; the corresponding matrix element is in principle not zero but direct computation of $\langle n', 0, 0 | \hat{r} | n, 0, 0 \rangle$ shows that this matrix element is indeed vanishing. In fact, the radial part of the associated wave function does not depend on the angle, while the spherical harmonics $Y_0^0(\theta, \phi)$ is constant: therefore the integration of \mathbf{r} on the solid angle gives a vanishing result.

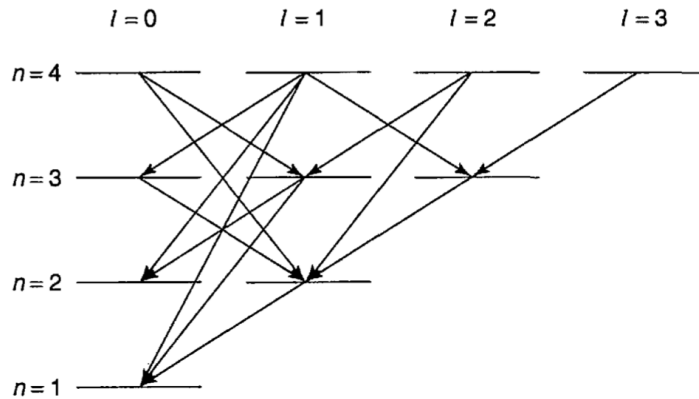


Abbildung 1: Possible transitions.

(vii) The selection rules are

$$\begin{cases} \Delta m = 0, \pm 1 \\ \Delta l = \pm 1 \end{cases} \quad (39)$$

The condition on Δl has an important physical reason. The transition between two energy level happens through the absorption/emission of a photon which is a spin-1 particle. Therefore the selection rule on l just reflects angular momentum conservation.

Exercise 65

Show that the life time τ of an atom in an excited state is inversely proportional to the Einstein-coefficient A of spontaneous emission.

Solution The definition of Einstein coefficient is

$$\frac{dN_2}{dt} = -A_{21}N_2 \quad (40)$$

where N_2 is the number of atoms in the excited level and A_{21} is the related Einstein coefficient. The solution is

$$N_2(t) = N_2(0)e^{-A_{21}t} \quad (41)$$

Therefore the lifetime is

$$\tau = \frac{1}{A_{21}} \quad (42)$$

Exercise 66

Consider a two-level system as in the lecture. Write the equations for the occupation number of the lower level, $\frac{dN_a}{dt}$, and upper level, $\frac{dN_b}{dt}$. Using these, show that $N_a + N_b = \text{const.}$

Solution The equations for the occupation numbers of the two levels are given by

$$\begin{aligned} \frac{dN_b}{dt} &= -N_b B_{ba}\rho + N_a B_{ab}\rho - N_b A_{ab} \\ \frac{dN_a}{dt} &= N_b B_{ba}\rho - N_a B_{ab}\rho + N_b A_{ab} \end{aligned} \quad (43)$$

By summing these two equations we obtain

$$\frac{d}{dt}(N_a + N_b) = 0 \implies N_a + N_b = \text{const.} \quad (44)$$

Exercise 67

Consider the general Schrödinger equation

$$i\hbar \frac{\partial \psi(q, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(q, t)}{\partial q^2} + V(q)\psi(q, t) \quad (45)$$

where V is at most quadratic in q . Validate that the Ansatz

$$\psi(q, t) = \frac{1}{N} \exp \left[\alpha(t) + \frac{i}{\hbar} p_{cl}(t)(q - q_{cl}(t)) - \frac{(q - q_{cl}(t))^2}{2\sigma^2(t)} \right] \quad (46)$$

where $p_{cl} = m \frac{dq_{cl}}{dt}$ leads to an equation of the form

$$F_1(t) + F_2(t)(q - q_{cl}(t)) + F_3(t)(q - q_{cl}(t))^2 = 0 \quad (47)$$

Show that

$$\begin{aligned} F_1 = 0 &\equiv \frac{d\alpha}{dt} = \frac{i}{\hbar} \left(\frac{p_{cl}^2}{2m} - V(q_{cl}) \right) - \frac{i\hbar}{2m\sigma^2(t)} \\ F_2 = 0 &\equiv \frac{dp_{cl}}{dt} = -\frac{\partial V}{\partial q}(q_{cl}) \\ F_3 = 0 &\equiv \frac{d\sigma^2}{dt} = \frac{i\hbar}{m} - \frac{i}{\hbar} \frac{\partial^2 V}{\partial q^2} \sigma^4 \end{aligned} \quad (48)$$

Solution Substituting the ansatz for $\psi(q, t)$ into (43) and using $p_{cl} \frac{dq_{cl}}{dt} = \frac{p_{cl}}{m}$ one obtains

$$0 = \frac{\psi(q, t)}{2m\sigma^4} \left[-\hbar^2 \sigma^2 + p_{cl}^2 \sigma^4 - 2mV(q)\sigma^4 + 2i\hbar m \frac{d\alpha}{dt} \sigma^4 - 2m\sigma^4 \frac{dp_{cl}}{dt} (q - q_{cl}) + (\hbar^2 + 2i\hbar m \sigma \frac{d\sigma}{dt})(q - q_{cl})^2 \right] \quad (49)$$

Since $\frac{\psi(q, t)}{2m\sigma^4} \neq 0$, it follows

$$-\hbar^2 \sigma^2 + p_{cl}^2 \sigma^4 - 2mV(q)\sigma^4 + 2i\hbar m \frac{d\alpha}{dt} \sigma^4 - 2m\sigma^4 \frac{dp_{cl}}{dt} (q - q_{cl}) + (\hbar^2 + 2i\hbar m \sigma \frac{d\sigma}{dt})(q - q_{cl})^2 = 0 \quad (50)$$

Expanding $V(q)$ around q_{cl} we obtain

$$V(q) = V(q_{cl}) + \frac{dV}{dq}(q - q_{cl}) + \frac{1}{2} \frac{d^2V}{dq^2}(q - q_{cl})^2 \quad (51)$$

Note that all higher derivatives of V vanish since V is at most quadratic in q . Following this, let's collect all the terms

$$\begin{aligned} F_1(t) &= -\hbar^2 \sigma^2 + p_{cl}^2 \sigma^4 - 2mV(q_{cl})\sigma^4 + 2i\hbar m \frac{d\alpha}{dt} \sigma^4 \\ F_2(t) &= -2m\sigma^4 \frac{dp_{cl}}{dt} - 2m\sigma^4 \frac{dV}{dq} \\ F_3(t) &= \hbar^2 + 2i\hbar m \sigma \frac{d\sigma}{dt} - m\sigma^4 \frac{d^2V}{dq^2} \end{aligned} \quad (52)$$

Then, the equation (50) becomes

$$F_1(t) + F_2(t)(q - q_{cl}(t)) + F_3(t)(q - q_{cl}(t))^2 = 0 \quad (53)$$

Now from the condition $F_1 = F_2 = F_3 = 0$ the proposition given by (48) follows.

General information

The *lecture* takes place on:

Monday at 10:00 - 12:00 c.t. in B 052 (Theresienstraße 37)

Friday at 10:00 - 12:00 c.t. in B 052 (Theresienstraße 37)

The *central tutorial* takes place on Monday at 12:00 - 14:00 c.t. in B 139 (Theresienstraße 37)

The *webpage* for the lecture and exercises can be found at

https://www.physik.uni-muenchen.de/lehre/vorlesungen/wise_19_20/T_M1_TV_-Quantum-Mechanics-II