8 Electron orbit in atoms

8.3 Transition selection rule

Now imagine we apply an external perturbation to the atom in order to drive a transition of the electron from one orbital to another. How does the transition rate depend on the form of the perturbation? Quantum mechanics tells us that the transition amplitude is give by

$$T_{if} = \langle \psi_i | O | \psi_f \rangle \tag{1}$$

where O is the perturbation operator and $|T_{if}|^2$ gives the transition probability.

In the study of atomic spectrum, the most common perturbation is electric dipole operator $\vec{E} \cdot \vec{r}$ (by e.g. shining a laser on the atom). Suppose that we choose the electric field in the laser to point in the z direction, can we drive the transition between two s orbitals? That is, we want to calculate the probability amplitude

$$T_{if} = \langle \psi_i^s | E_z z | \psi_f^s \rangle \tag{2}$$

What we find is that, T_{if} actually has to be zero. To see this, we insert operator $e^{-i\pi J_x} e^{i\pi J_x}$ between the operator and the initial and final states

$$T_{if} = \langle \psi_i^s | e^{-i\pi J_x} e^{i\pi J_x} E_z z e^{-i\pi J_x} e^{i\pi J_x} | \psi_f^s \rangle \tag{3}$$

We combine these operators so that the initial and final state are both acted upon by the operator $e^{i\pi J_x}$ which does a π rotation around the x direction and the dipole operator in the middle gets conjugated by $e^{i\pi J_x}$ which also does the x axis π rotation.

As the initial and final states are both s orbitals, they remain invariant under this rotation

$$e^{i\pi J_x} | \psi_f^s \rangle = | \psi_f^s \rangle, e^{i\pi J_x} | \psi_i^s \rangle = | \psi_i^s \rangle \tag{4}$$

The dipole operator on the other hand, gets a $-$ sign

$$e^{i\pi J_x} E_z z e^{-i\pi J_x} = -E_z z \tag{5}$$

Because of this extra sign

$$T_{if} = -T_{if} \tag{6}$$

and it has to be zero.

In deriving this result, we have used only the symmetry property of the initial, final state and that of the perturbation operator.

In the above discussion, we are considering a C_2 symmetry of the total rotation group (π rotation around x axis). The initial and final states both form a $(1, 1)$ representation of the C_2 group. The dipole operator, on the other hand, forms $(1, -1)$ representation of the C_2 group. The transition probability is zero because the direct product of a $(1, 1)$ representation (the initial state) with a $(1, -1)$ representation (the perturbation operator) cannot give rise to a $(1, 1)$ representation (the final state). Therefore, it is not possible to make transitions between two s orbitals with an electric dipole perturbation, hence a selection rule.

If we use the full $SO(3)$ rotation symmetry of the group, we can obtain stronger selection rules. In particular, operators can also form $j = 0$, $j = 1$, $j = 2...$ representations of $SO(3)$. The transition probability from a state with angular momentum j_1, m_1 to a state with angular momentum j_2, m_2 through an operator with angular momentum j, m is proportional to the CG coefficient of composing j_1, m_1 with j, m and obtaining j_2, m_2. This is the content of the so called Wigner-Eckart theorem.

Tensor Operator: An irreducible tensor operator T^j_m is a set of operators labelled by fixed integer j and $m = -j, -j+1, ..., j$ which transform under rotation according to

$$U(R)T^j_m U(R)^{-1} = \sum_{m'} D^{(j)}_{mm'}(R)T^j_{m'} \tag{7}$$

where $U(R) = e^{i\theta J_{\vec{n}}}$ represents rotation around axis $\vec{n}$ through angle θ and $D^{(j)}_{mm'}$ is the $2j+1$ dimensional irrep of $SO(3)$.

Examples:

(1) $j = 0$

The operator J^2 commute with all $J_{\vec{n}}$, therefore it remains invariant under the above transformation

$$U(R)J^2U(R)^{-1} = J^2 \tag{8}$$

We say that J^2 is a scalar operator. In particular, if we regard the commutation relation $[J_{\vec{n}}, J^2] = 0 = 0 \cdot J^2$ as the action of $J_{\vec{n}}$ on J^2, we see that J^2 forms a one dimensional vector space where all the generators of $SO(3)$ acts as 0. Therefore, all the group elements of $SO(3)$ acts as 1 and J^2 forms the $j = 0$ singlet representation of $SO(3)$.

Similarly $r^2 = x^2 + y^2 + z^2$ which measures the distance of a particle from the origin is also a scalar operator. This is easy to understand intuitively because the distance of the particle from the origin does not change if we rotate the system. To see how the math works more explicitly, notice that in quantum mechanics the angular momentum operator is given by

$$\vec{J} = \vec{r} \times \vec{p} = (yp_z - zp_y, zp_x - xp_z, xp_y - yp_x) \tag{9}$$

Using the commutation relation between position and momentum ($[x, p_x] = [y, p_y] = [z, p_z] = i$, otherwise they commute), we get

$$[r^2, J_x] = [x^2, J_x] + [y^2, J_x] + [z^2, J_x] = [y^2, -zp_y] + [z^2, yp_z] = -2iyz + 2iyz = 0 \tag{10}$$

Similarly we find $[r^2, J_y] = [r^2, J_z] = 0$. Therefore, r^2 is also a scalar operator, as expected.

(2) $j = 1$

The operators J_x, J_y, J_z transforms as a three dimensional vector under rotation and forms a $j = 1$ representation. In homework 7 problem 1, you have shown this in questions 1-4. We say that $J_{\vec{n}}$ is a vector operator.

Similarly, $\vec{r} = (x, y, z)$ is also a vector operator. Again this is true intuitively because $\vec{r}$ describes the position of the particle from the origin. To see why this is true mathematically, we need to work out the commutation relation between $\vec{r}$ and $J_{\vec{n}}$. It can be checked that $[J_a, r_b] = i\epsilon_{abc}r_c$. This is analogous to the commutation relation $[J_a, J_b] = i\epsilon_{abc}J_c$. If we think of the commutation relation as action of J_a on r_b or J_b, then we can see that $\{r_b\}$ and $\{J_b\}$ both form a three dimensional vector space on which $\{J_a\}$ acts as the generator of 3 dimensional special orthogonal matrices, which forms the $j = 1$ representation of $SO(3)$.

$$J_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad J_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad J_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{11}$$

(3) $j = 2$

We will see an example of tensor operator in homework. We will not discuss it in detail here.

Wigner-Eckart Theorem

The Wigner-Eckart theorem states that: the transition amplitude from one angular momentum state $|jm\rangle$ to another angular momentum state $|j'm'\rangle$ via the application of a tensor operator T^J_M is proportional to the CG coefficient $C(j'Jj, m'Mm)$ and the proportionality constant depends only on $j'Jj$ and not on $m'Mm$.

$$\langle j'm'|T^J_M|jm\rangle = C(j'Jj; m'Mm)\langle j'||T^J||j\rangle \tag{12}$$

We are not going to present the proof for the Wigner-Eckard theorem but only discuss its consequences. For proof, see Jones, page 114-115.

One of the most important consequence of the Wigner-Eckard theorem is the dipole selection rules, which tells us how electrons can move from one orbital $|nlm\rangle$ to another orbital $|n'l'm'\rangle$ due to the application of an external electric field. The electric field operator $E\vec{r}$ is a vector operator. From Wigner-Eckart theorem, we know that

$$\langle n'l'm'|Er_M|nlm\rangle = C(l'1l, m'Mm)\langle n'l'||\vec{r}||nl\rangle \tag{13}$$

Hence we have the selection rules: (1) $\delta_l = l' - l = -1, 0, 1$.

(2) If the electric field is pointing in the z direction, $M = 0$, $\delta_m = m' - m = 0$. If the electric field is pointing in x or y direction, $\delta_m = \pm 1$.

(Actually $\delta_l = 0$ is not allowed due to spatial inversion symmetry ($x \to -x$, $y \to -y$, $z \to -z$). Can you see why?)

9 Lorentz Group and Special Relativity

Reference: Jones, "Groups, Representations, and Physics", Chapter 10.

Special relativity says, physics laws should look the same for different observers in different inertial reference frames.

In the non-relativistic setting, the coordinates of different reference frames are related by the Euclidean transformation. In particular, if two reference frames S and S' coincide at $t = 0$ and are moving with relative velocity $\vec{v} = (v, 0, 0)$, then the relation between the coordinates of an event in the two reference frames is

$$t' = t, \vec{r}' = \vec{r} - \vec{v}t \left(x' = x - vt, y' = y, z' = z\right) \tag{14}$$

Under such a transformation the spatial distance between two points (at the same time) remains invariant

$$(\vec{r}_1' - \vec{r}_2')^2 = (\vec{r}_1 - \vec{r}_2)^2 \tag{15}$$

In special relativity however, we need to use the Lorentz transformation and replace the above relation with

$$t' = \gamma(t - xv/c^2), x' = \gamma(x - vt), y' = y, z' = z \tag{16}$$

where $\gamma = \frac{c}{\sqrt{c^2 - \vec{v}^2}}$. This particular transformation induced by a relative velocity is called a boost.

The transformation may look complicated, but it is designed so that the velocity of light remains invariant in all inertial reference frames. Suppose that we send out a light signal from the origin at $t = 0$ in the x direction. In reference frame S, at a later time t, the signal has travelled to point $x = ct, y = 0, z = 0$. Transformed to the reference frame of S', we find that the coordinate of the corresponding signal is

$$t' = t\sqrt{\frac{c - v}{c + v}}, x' = ct\sqrt{\frac{c - v}{c + v}}, y' = 0, z' = 0 \tag{17}$$

Therefore the velocity of light in the frame of S' is also c.

This is just one particular example of the whole group of Lorentz transformation, which we are going to study in detail below.

9.1 Coordinate four vector

The fact that time and space gets mixed together under Lorentz transformation motivates the definition of the space-time four vector $\tilde{x}_\mu$, $\mu = 0, 1, 2, 3$ for the Minkowski space

$$\tilde{x}_0 = ct, \tilde{x}_1 = x, \tilde{x}_2 = y, \tilde{x}_3 = z \tag{18}$$

Notice that the components of the four vector all have the dimension of length.

Lorentz transformation leaves the 'interval'

$$|\tilde{x}|^2 = c^2t^2 - x^2 - y^2 - z^2 \tag{19}$$

invariant. (This ensures that the speed of light remains invariant in all reference frames.)

We define a metric tensor, $g^{\mu\nu}$ such that $g^{\mu\nu} = 0$ if $\mu \neq \nu$ and $g^{00} = -g^{11} = -g^{22} = -g^{33} = 1$. That is,

$$g = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{20}$$

Then we can define the 'length' of the four vector as

$$|\tilde{x}|^2 = \tilde{x}^T g \tilde{x} \tag{21}$$

This is very different from the metric we are used to. In the usual Euclidean space, $g = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ is positive definite. The metric for the Minkowski space is not positive definite and will result in some special properties of the Lorentz group.

Suppose that under a Lorentz transformation, the four vector transforms as

$$\tilde{x}' = \Lambda \tilde{x} \tag{22}$$

Then the invariance of the length of the vector requires that

$$|\tilde{x}'|^2 = \tilde{x}'^T g \tilde{x}' = \tilde{x} \Lambda^T g \Lambda \tilde{x} = \tilde{x}^T g \tilde{x} = |\tilde{x}|^2 \tag{23}$$

Because this is true for all $\tilde{x}$, we have $\Lambda^T g \Lambda = g$.

Notice that if $g = I_3$, this condition reduces to the orthogonality condition of three dimensional rotation transformations which form the group $SO(3)$. The Lorentz group can be thought of as the group of 'orthogonal' transformations on a space with metric $g = \text{diag}(1, -1, -1, -1)$ and it is denoted as $SO(3,1)$.