

## 9 Electron orbits in atoms

Now let's see how our understanding of the irreps of  $SO(3)$  ( $SU(2)$ ) can help us understand the structure of electron orbits in atoms.

### 9.1 Central potential

Consider an electron moving around a nucleus. The Hamiltonian of the electron is

$$H = \frac{P^2}{2m} + V(r) \quad (1)$$

$V(r)$  is the Coulomb potential of the electron in the field of the nucleus. The crucial property of this central potential is that it depends only on  $r$ , the distance of the electron from the nucleus, and not on the direction of the electron. Therefore, the Hamiltonian is invariant under rotation in full three dimensional space. That is

$$R_{\vec{n}}(\theta) H R_{\vec{n}}(-\theta) = H \quad (2)$$

The wave function of the electron is a (normalized) complex function over space  $\psi(x, y, z)$ . In spherical coordinates, it is written as  $\psi(r, \theta, \phi)$ , where  $r$  is the radial distance from the origin,  $\theta$  is the angle between the vector and the positive  $z$  direction,  $\phi$  is the angle between the projection on the  $xy$  plane and the positive  $x$  direction. It lives in an infinite dimensional Hilbert space. In this Hilbert space, the angular momentum operators take the form

$$J_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \quad J_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right), \quad J_z = -i\hbar \frac{\partial}{\partial \phi} \quad (3)$$

Because of this, we can conclude that the **the eigenstates of  $H$  (the electron orbitals) form irreducible representations of  $SO(3)$** . That is, the eigenstates can be grouped into subsets labelled by  $j$ ,  $j = 0, 1, 2, \dots$ . The set labeled by  $j$  contains  $2j + 1$  states, which can be further labeled by  $m = -j, -j + 1, \dots, j$ . The  $2j + 1$  states in the same irrep have the same energy (are degenerate). The irrep labeled by  $j$  corresponds to orbits with total angular momentum  $J^2 = j(j + 1)$ . In atomic physics, the usual notation for angular momentum is  $l$  instead of  $j$  and the orbits with  $l = 0, 1, 2, 3, \dots$  are called  $s, p, d, f, \dots$  orbits respectively. The state labeled by  $m$  in the  $l$  irrep corresponds to orbits with  $z$  direction angular momentum  $m$ .

$l$  and  $m$  are not sufficient to uniquely label different electron orbits in atoms, as they describe only the angular distribution of the electron wave function and does not contain any radial information. We need one more label  $n$  which describes roughly how far away the electron is from the nucleus. It turns out for each  $n$ , the possible choice of  $l$  is limited to be from 0 to  $n - 1$ . Therefore, we can have orbits  $1s, 2s, 2p, 3s, 3p, 3d$  etc.

In Hydrogen atom, the energy of the orbits depends solely on  $n$ . However, in more general atoms, the energy of the orbits depends both on  $n$  and  $j$ . Of course, the energy does not depend on  $m$

which labels different states of the same irrep, due to the rotation symmetry of the atom. The Hydrogen atom contains a lot of ‘accidental’ degeneracy if we consider only the  $SO(3)$  symmetry. In fact, it was realized that the Hydrogen atom has a higher  $SO(4)$  symmetry which guarantees the degeneracy of different orbitals with the same  $n$ . Here is an article that explains this <http://hep.uchicago.edu/rosner/p342/projs/weinberg.pdf>.

## 9.2 Spin orbit interaction

If we examine the electron orbits around the Hydrogen atom really carefully, we will find that some electron orbits (e.g.  $2p$ ) splits into two with a small energy difference. How could that happen? People realized that this is due to the interaction between the orbital and spin degrees of freedom of the electron. That is, the Hamiltonian contains an extra term of the form

$$\Delta H = f(r)\vec{S} \cdot \vec{J} = f(r)(S_x J_x + S_y J_y + S_z J_z) \quad (4)$$

where  $\vec{S}$  denotes the spin angular momentum of the electron and  $\vec{J}$  denotes the orbital angular momentum of the electron. Due to this coupling, the Hamiltonian is no longer invariant under rotation on the orbital part or the spin part alone. Instead, it is invariant if the orbital angular momentum and spin angular momentum rotates together so that their dot product remains the same.

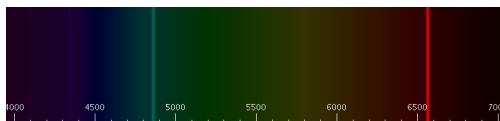
In this case, the spin angular momentum and orbital angular momentum are no longer good labels of the eigenstates of the Hamiltonian.  $\vec{S}^2 = s(s+1)$  and  $\vec{J}^2 = j(j+1)$  still commute with the Hamiltonian but  $S_z$  and  $J_z$  do not. Instead, the total angular momentum operator  $\vec{L} = \vec{S} + \vec{J}$  commute with the Hamiltonian

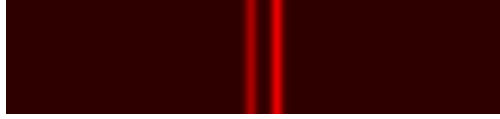
$$\vec{L}^2 = \vec{S}^2 + \vec{J}^2 + 2\vec{S} \cdot \vec{J}, L_z = S_z + J_z, [\vec{L}^2, H] = 0, [L_z, H] = 0 \quad (5)$$

and we can use their eigenvalue to label eigenstates of the Hamiltonian. That is, due to spin orbit interaction, the eigenstates of the Hamiltonian are no longer tensor product of eigenstates of spin and orbital angular momentum  $|j, m_j; s, m_s\rangle$ . Instead they are eigenstates of total angular momentum  $|(j, s) l, m_l\rangle$ , which is the result of adding spin and orbital angular momentum together.

From here we can understand how the atomic spectrum changes with spin orbit interaction. On an  $s$  orbital, spin orbital interaction corresponds to the addition of  $j = 0$  with  $s = 1/2$  which results in a single irrep  $l = 1/2$ . Therefore, spin orbit interaction does not split the degeneracy of the  $j = 0$  orbital. On a  $p$  orbital, on the other hand, spin orbital interaction corresponds to the addition of  $j = 1$  with  $s = 1/2$  which results in two irreps, one with  $l = 1/2$  one with  $l = 3/2$ . These two irreps have different energy (states within each irrep have the same energy). Therefore, spin orbit interaction splits the energy of a  $p$  orbital.

If we now look at the spectral line generated by the transition of an electron between a  $p$  orbital and an  $s$  orbital, a single line will split into a doublet. This is the fine structure of Hydrogen spectrum.





### 9.3 Transition selection rule

Now imagine we apply an external perturbation to the atom in order to drive 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

$$T_{if} = \langle \psi_i | O | \psi_f \rangle \quad (6)$$

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

$$T_{if} = \langle \psi_i^s | E_z z | \psi_f^s \rangle \quad (7)$$

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

$$T_{if} = \langle \psi_i^s | e^{-i\pi J_x} e^{i\pi J_x} E_z z e^{-i\pi J_x} e^{i\pi J_x} | \psi_f^s \rangle \quad (8)$$

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  $\pi$  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  $\pi$  rotation.

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

$$e^{i\pi J_x} | \psi_f^s \rangle = | \psi_f^s \rangle, e^{i\pi J_x} | \psi_i^s \rangle = | \psi_i^s \rangle \quad (9)$$

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

$$e^{i\pi J_x} E_z z e^{-i\pi J_x} = -E_z z \quad (10)$$

Because of this extra sign

$$T_{if} = -T_{if} \quad (11)$$

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.

Here we encounter an important concept. That is, operators, just like states, can transform under symmetry and form representations. The way symmetry acts on operators is by conjugation

$$O \rightarrow D(g) O D^{-1}(g) \quad (12)$$

Under this conjugation, an operator, represented as an  $n \times n$  matrix, is mapped to a different operator, represented as another  $n \times n$  matrix. If we find a basis for the set of operators which

transform into each other under symmetry conjugation, we can decompose the initial and final operator in this basis and find the representation of the symmetry in this basis.

In the above discussion, we are considering a  $C_2$  symmetry of the total rotation group ( $\pi$  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 a 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  $j = 0, j = 1, j = 2 \dots$  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  $T_m^j$  is a set of operators labelled by fixed integer  $j$  and  $m = -j, -j + 1, \dots, j$  which transform under rotation according to

$$U(R)T_m^jU(R)^{-1} = \sum_{m'} D_{mm'}^j(R)T_{m'}^j \quad (13)$$

where  $U(R) = e^{i\theta J_{\vec{n}}}$  represents rotation around axis  $\vec{n}$  through angle  $\theta$  and  $D_{mm'}^j$  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

$$U(R)J^2U(R)^{-1} = J^2 \quad (14)$$

We say that  $J^2$  is a **scalar** operator. In particular, if we regard the commutation relation  $[J_{\vec{n}}, J^2] = 0$  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

$$\vec{J} = \vec{r} \times \vec{p} = (yp_z - zp_y, zp_x - xp_z, xp_y - yp_x) \quad (15)$$

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

$$[r^2, J_x] = [x^2, J_x] + [y^2, J_x] + [z^2, J_x] = [y^2, -zp_y] + [z^2, yp_z] = -2iyz + 2iyz = 0 \quad (16)$$

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  $SO(3)$ .

(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  $T_M^J$  is proportional to the CG coefficient  $C(j'Jj, m'Mm)$  and the proportionality constant depends only on  $j'Jj$  and not on  $m'Mm$ .

$$\langle j'm'|T_M^J|jm\rangle = C(j'Jj, m'Mm)\langle j'||T^J||j\rangle \quad (17)$$

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

One of the most important consequence of the Wigner-Eckart 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

$$\langle n'l'm'|Er_M|nlm\rangle = C(l'l, m'Mm)\langle n'l'||\vec{r}||nl\rangle \quad (18)$$

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 ( $x \rightarrow -x, y \rightarrow -y, z \rightarrow -z$ ). Can you see why?)