Quenching of Orbital Angular Momentum

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1 OAM with Spherical Symmetrical Potential

Consider a spinless particle bound by a spherical symmetrical potential $V(\mathbf{x}) = V(r)$. For example, an electron of an isolated atom bounded by the Coulomb interaction (if we temporarily forget about the spin for now). In the language of group theory, this potential features an SO(3) symmetry.

Since the Hamiltonian is rotationally invariant, $\widehat{H}$ commutes with $\widehat{L_z}$ and $\widehat{\mathbf{L}^2}$, therefore the energy eigenstates can be labeled by three quantum numbers n, l, m:

$$\psi(\mathbf{x}) = \langle \mathbf{x}|n, l, m\rangle = R_{nl}(r)Y_l^m(\theta, \phi) \tag{1}$$

where $Y_l^m(\theta, \phi)$ is the spherical harmonics. These eigenstates of $\widehat{H}$ are also the eigenstates of $\widehat{L_z}$ and $\widehat{\mathbf{L}^2}$:

$$\widehat{\mathbf{L}^2}|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle \tag{2}$$

$$\widehat{L_z}|l, m\rangle = \hbar m|l, m\rangle \tag{3}$$

where $m = -l, -l+1, \cdots, l-1, l$.

2 OAM with Spherical Asymmetrical Potential

Now let's consider a spinless particle bound by a potential $V(\mathbf{x})$ so asymmetrical that no energy level is degenerate.[1] Since the Hamiltonian is invariant under time reversal, we have

$$\widehat{H}\widehat{\mathcal{T}}|n\rangle = \widehat{\mathcal{T}}\widehat{H}|n\rangle = E_n\widehat{\mathcal{T}}|n\rangle \tag{4}$$

where $\widehat{\mathcal{T}}$ is the time reversal operator and $|n\rangle$ is the eigenstate of $\widehat{H}$ with eigenvalue E_n. Notice that l & m are no longer good quantum numbers.

Since there is no degeneracy, $|n\rangle$ and $\widehat{\mathcal{T}}|n\rangle$ can differ at most by a phase factor:

$$|\tilde{n}\rangle \equiv \widehat{\mathcal{T}}|n\rangle = e^{i\delta}|n\rangle \tag{5}$$

Notice that the time reversal operator $\widehat{\mathcal{T}}$ is an anti-unitary operator[2], and the orbital angular momentum changes sign under time reversal, we have

$$\langle \mathbf{L}\rangle = \langle n|\mathbf{L}|n\rangle = -\langle \tilde{n}|\mathbf{L}|\tilde{n}\rangle = -\langle n|\mathbf{L}|n\rangle = 0 \tag{6}$$

where the third equivalent comes from Eq.(5). This result indicates that as if the orbital angular momentum vanishes with spherical asymmetrical potential, which is also known as *quenching of orbital angular momentum*.

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[1]See J. J. Sakurai & J. Napolitano, *Modern Quantum Mechanics (2nd Edition)*, Pearson (2014), Chapter 4 Problem 11.

[2]The operator $\hat{A} : |\alpha\rangle \mapsto \hat{A}|\alpha\rangle \equiv |\tilde{\alpha}\rangle$ is anti-unitary if $\langle \tilde{\beta}|\tilde{\alpha}\rangle = \langle \beta|\alpha\rangle^*$ and $\hat{A}(c_1|\alpha\rangle + c_2|\beta\rangle) = c_1^*\hat{A}|\alpha\rangle + c_2^*\hat{A}|\beta\rangle$. The latter requirement defines an anti-linear operator.

3   OAM with Crystal Potential

Crystal potential is somewhere between the previous two examples — it do have some symmetries, but not the spherical symmetry. This symmetry is known as the point group symmetry.

The crystal potential can be expanded in the spherical harmonics basis, namely

$$V(\mathbf{x}) = \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} A_{lm}(r) Y_l^m(\theta, \phi) \tag{7}$$

where $A_{lm}(r)$ is the expansion coefficient. If the crystal has q-fold symmetry for a given site, the potential at that site will be in the following form

$$V(\mathbf{x}) = \sum_{l=0}^{+\infty} \sum_{m=nq} A_{lm}(r) Y_l^m(\theta, \phi) \tag{8}$$

where n is some integer. This can be easily checked by orthogonality theorem. Here I present several examples to demonstrate how this special crystal field affects the electron orbitals and the orbital angular momentum.

3.1   t$_{2g}$-e$_g$ Splitting in Octahedral Crystal Field

For d-electrons in an isolated atom, there are 5 eigenstates $|l, m\rangle$:

$$|2, 0\rangle, |2, \pm 1\rangle, |2, \pm 2\rangle. \tag{9}$$

These are notations that been used frequently by us. However if you want to know the wavefunctions (i.e. compute $\psi_{lm}(\mathbf{x}) = \langle \mathbf{x}|l, m\rangle$), you may find that only $\langle \mathbf{x}|2, 0\rangle$ gives out a real function in the above 5 states (recall that the spherical harmonics has a term $e^{im\theta}$, which is a complex function). Therefore we can make superposition of these eigenstates to get 5 new eigenstates whose wavefunctions are totally real:

$$d_{z^2} = |2, 0\rangle \tag{10a}$$

$$d_{x^2-y^2} = \frac{1}{i\sqrt{2}} (|2, 2\rangle - |2, -2\rangle) \tag{10b}$$

$$d_{xy} = \frac{1}{\sqrt{2}} (|2, 2\rangle + |2, -2\rangle) \tag{10c}$$

$$d_{xz} = \frac{1}{\sqrt{2}} (|2, 1\rangle + |2, -1\rangle) \tag{10d}$$

$$d_{yz} = \frac{1}{i\sqrt{2}} (|2, 1\rangle - |2, -1\rangle) \tag{10e}$$

These recombined eigenstates with real wavefunctions are also called *orbitals* (see Tab.1). However when this atom is inside of an octahedral crystal field, let's say at a site with O$_h$ symmetry, these 5 degenerated eigenstates will no longer form basis for an irreducible representation, since O$_h$ group does not have a 5-dimensional irreducible representation. With the character table for O$_h$ group, d-electron orbitals are found to split into two irreducible representations of O$_h$ group, namely T$_{2g}$ and E$_g$, known as the famous t$_{2g}$-e$_g$ splitting:

$$\mathrm{R_{d-orbitals} = T_{2g} \oplus E_g}. \tag{11}$$

Using first order degenerate perturbation theory, it can be easily shown that in addition to an overall energy shift of the *d*-electron orbitals (which does not lift the degeneracy), the 2-fold degenerate e_g orbitals' energy is raised by $\frac{3}{5}\Delta$, and the 3-fold degenerate t_{2g} orbitals' energy is lowered by $\frac{2}{5}\Delta$, where Δ is the energy difference between these two energy levels (see Fig.1).

Table 1: 3*d*-electron orbitals in O_h crystal field

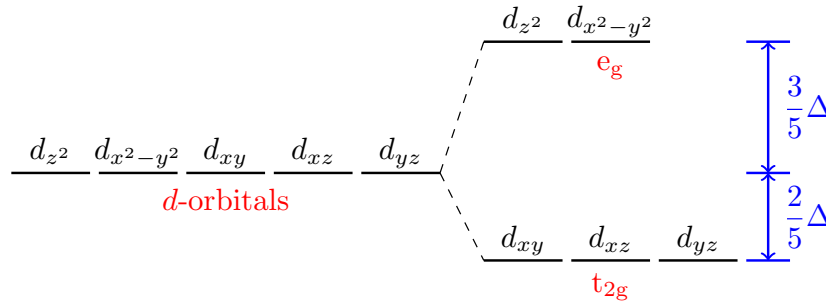| e_g		t_{2g}		
d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}

Figure 1: t_{2g}-e_g splitting in O_h crystal field.

By the way, this d-orbital splitting is also the origin of color in some transition metal complexes. It is due to an electron being excited from one d-orbital to another d-orbital with higher energy. In the octahedral field case, this process is excitation from t_{2g} to e_g, while in the tetrahedral field case (e.g. T_d point group), the excitation is from e to t_2.[3] As an example, in $[Ti(H_2O)_6]^{3+}$ an excitation from t_{2g} to e_g corresponds to 520 nm. Here I also want to point out that this absorption of light (or photon) is very special. Using the selection rule, one can easily prove that such an absorption which excites electron from t_{2g} to e_g is forbidden since these two orbitals have the same parity (note the $_g$ subscript). However, this process can still happen with the assistance of phonons (e.g. a phonon with odd parity).

Now let's reconsider the orbital angular momentum. Apparently the original orbital angular momentum is no longer a good description since the former 5-fold degeneracy are now partially lifted. Briefly speaking, with the O_h crystal field, we end up with a 3-fold degenerate energy state and another 2-fold degenerate energy state. So what is the orbital angular momentum now if it still exists?

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[3]Note that the crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For a given ligand at the same M-L distances, the relationship may be represented as $\Delta_t = 4/9\Delta_o$.

With careful observation, one may find the similarity between t_{2g} orbitals and p-electron orbitals in isolated atoms. Actually this relation is described by the so called t_2-p *isomorphism*:

$$d_{xy} \leftrightarrow p_z, \ d_{xz} \leftrightarrow p_y, \ d_{yz} \leftrightarrow p_x, \tag{12}$$

which as if indicates t_{2g} orbitals have an effective orbital angular momentum of $l = 1$! This somewhat a little bit surprising result brings us to this essential question: what to the ground is orbital angular momentum?

Recall the result we derived in Sec.2, spinless systems with non-degenerate states seems have no orbital angular momentum. This is a necessary condition for orbital angular momentum to be non-zero since $|l, m\rangle$ states must have a $2l + 1$ degeneracy. Moreover, if we observe the t_{2g} orbitals in Tab.1, it's easy to find that d_{xy}, d_{xz} and d_{yz} have exactly the same shape and can be rotated onto each other with proper rotations. Electrons' hopping among these 3 orbitals seems to bring something like orbital angular momentum. However, electrons obey the Pauli exclusion principle since they are fermions, therefore such hopping manners may not be allowed to happen in certain cases, e.g. when the t_{2g} orbitals are occupied with 0 (empty), 3 (half-filled) or 6 (fully filled) electrons.

In conclusion, orbital angular momentum is present when the following conditions are satisfied:

- A set of orbitals are degenerate;

- These orbitals can be transformed to each other by proper rotations;

- This set of orbitals is not empty, half-filled or fully filled. Otherwise the orbital angular momentum is said to be *totally quenched.*

The case where some of the d-orbitals behave like p-orbitals (t_2-p isomorphism) is sometimes referred to as orbital angular momentum being *partially quenched* (l becomes smaller than before). The quenching effect has a huge influence on transition metals, which will be demonstrated in the next several examples.

3.2   Spin-Only Formula for Magnetic Moment

It is well known that both orbital angular momentum and spin angular momentum of electron contribute to the magnetic moment:

$$\mu = g_J \mu_B \sqrt{J(J + 1)} \tag{13}$$

where μ_B is the Bohr magneton and g_J is the Landé g-factor:

$$g_J = g_L \frac{J(J + 1) - S(S + 1) + L(L + 1)}{2J(J + 1)} + g_S \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \tag{14}$$

Since $g_L = 1$ and $g_S \approx 2$, we have

$$g_J \approx \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}. \tag{15}$$

If the orbital angular momentum is totally quenched (i.e. $L = 0$), one should only consider the spin angular momentum's contribution to the magnetic moment, thus leads to the following spin-only formula:

$$\mu = g_S \mu_B \sqrt{S(S + 1)}. \tag{16}$$

The following table gives a comparison of calculated spin-only magnetic moments with experimentally observed data for some octahedral complexes.[4] It can be easily checked that for the totally quenched case (e.g. Cr^{3+} and Mn^{2+}/Fe^{3+} with high spin configuration) the spin-only formula is usually good enough to describe the atomic magnetic momentum.

Here the high spin configuration and low spin configuration are the results of two competing energies — energy gap between two levels (Δ) and the energy coming from Coulomb repulsion between electrons. The former one favors a low spin configuration (fill t_{2g} first) while the latter one favors a high spin configuration (fill e_g first after t_{2g} is half-filled). Since the energy gap is determined by the strength of the crystal field, low spin configuration is often formed with a high field while high spin configuration is often formed with a low field.

Table 2: spin-only formula vs. observed result

ion	configuration	μ_{SO}/μ_B	μ_{obs}/μ_B
Ti^{3+}	d^1 (t_{2g}^1)	$\sqrt{3} = 1.73$	1.6 - 1.7
V^{3+}	d^2 (t_{2g}^2)	$\sqrt{8} = 2.83$	2.7 - 2.9
Cr^{3+}	d^3 (t_{2g}^3)	$\sqrt{15} = 3.88$	3.7 - 3.9
Cr^{2+}	d^4 high spin ($t_{2g}^3 e_g^1$)	$\sqrt{24} = 4.90$	4.7 - 4.9
Cr^{2+}	d^4 low spin (t_{2g}^4)	$\sqrt{8} = 2.83$	3.2 - 3.3
Mn^{2+}/Fe^{3+}	d^5 high spin ($t_{2g}^3 e_g^2$)	$\sqrt{35} = 5.92$	5.6 - 6.1
Mn^{2+}/Fe^{3+}	d^5 low spin (t_{2g}^5)	$\sqrt{3} = 1.73$	1.8 - 2.1
Co^{3+}	d^6 low spin (t_{2g}^6)	0	0
Co^{2+}	d^7 high spin ($t_{2g}^5 e_g^2$)	$\sqrt{15} = 3.88$	4.3 - 5.2
Co^{2+}	d^7 low spin ($t_{2g}^6 e_g^1$)	$\sqrt{3} = 1.73$	1.8
Ni^{2+}	d^8 ($t_{2g}^6 e_g^2$)	$\sqrt{8} = 2.83$	2.9 - 3.3
Cu^{2+}	d^9 ($t_{2g}^6 e_g^3$)	$\sqrt{3} = 1.73$	1.7 - 2.2

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[4]Data from http://wwwchem.uwimona.edu.jm/spectra/MagMom.html.