

Multiplet Structure of Core-Level Spectrum of Solids and Phenomenological Full-Multiplet Calculation

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In the core-level photoemission and photoabsorption spectra of transition metal and rare earth elements, multiplet structures (MS) are often seen. MS reflect the local electronic states of partially filled valence orbitals and therefore have been heavily studied in investigations of rare earth (RE) and transition metal (TM) compounds. Typical examples are RE elements with partially filled $4f$ orbital and TM elements with partially filled $3d$ orbitals. MS is usually seen when total spin (S) and/or orbital angular momentum (L) is not zero in the local orbital. Since partially filled $4f$ orbital of RE always carries nonzero S , MS is always seen in RE elements. On the other hand, S and L of partially filled $3d$ orbital of TM atom are both zero in some compounds, for which MS can vanish.

For RE elements, MS are seen not only in core-level photoemission (XPS) and photoabsorption (XAS) but also in valence band photoemission (VB-PES). MS in VB-PES that strongly reflect the excitation of a $4f$ electron have widely been studied both experimentally and theoretically [1-3]. Core-level spectroscopies such as $3d$ and $4d$ XAS [4-6] and $3d$ and $4d$ XPS [3, 7-10], have intensively been studied. For ferromagnetic RE compounds, magnetic linear and circular dichroism (MLD and MCD) in XAS have been noticed [11, 12], where MS play central roles, and especially MCD have heavily been used [13-16]. Linear dichroism (LD) in $3d$ XAS has been utilized to study the anisotropy in $4f$ state of RE [17]. More recently, LD in angle-resolved $3d$ XPS of RE is attracting strong interest because anisotropy of higher order, in other words higher order multipoles, can be investigated by measuring how the intensity ratios among MS depend upon polarization of the incident photon and the orientation of the single crystal sample [18-22].

In the case of TM elements, MS are typically seen in TM $2p$ XAS of ionic crystals as oxides and of complexes, where MS is sensitive to the environment of the TM ions as crystal field [14, 23-25]. MS are also seen in metallic systems if the TM atom carries magnetic moment, which has been confirmed through spin-polarized $3s$ XPS and MCD of $2p$ XAS [26, 27]. On the other hand, MS is essentially absent when TM atom is

nonmagnetic as in the case of Fe $2p$ XPS of the superconductor LaFePO [28].

MS is essentially the same thing as the spectral terms of atoms, and its origin is the same as that of Hund's rule [29]. It is very important to understand that the main origin common to these phenomena is that, depending upon the mutual relationship between spins and orbital angular momenta of the electrons in the atom, the radial wave function changes, and therefore the electric attraction potential energy between the nucleus and the electrons changes [30]. Most typically, when spins of electrons align parallel, in other words when total spin S is larger, the radial wave function approaches the nucleus leading to lower energy. The traditional explanation that the decrease of repulsive potential energy between electrons with parallel spins is the main origin for the term dependence of total energy has been shown to be wrong in most cases [29].

If we tentatively omit the spin-orbit interaction, the Hamiltonian of many electrons in an atom of atomic number Z is written as follows, where the MKSA system is used.

$$\mathcal{H} = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] + \sum_i \left[-\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i|} \right] + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The first two terms are one-body interaction acting on each electron and the last term is the two-body interaction between electrons.

In the Hartree-Fock (HF) approximation, the many electrons state is written as a single Slater determinant of N electronic states ψ_i ($i = 1, \dots, N$) and the energy of the state is written as

$$\begin{aligned} \langle \Psi | \mathcal{H} | \Psi \rangle &= \sum_i \left\langle \psi_i(\mathbf{r}) \left| \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}|} \right) \right| \psi_i(\mathbf{r}) \right\rangle + \sum_{i<j} J_{ij} - \sum_{i<j(//)} K_{ij} \\ J_{ij} &= \left\langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \right\rangle \\ K_{ij} &= \left\langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \right\rangle \end{aligned}$$

where J_{ij} and K_{ij} are called Coulomb and exchange integrals, respectively. The exchange integral consists only of interaction between pairs of electrons with parallel spins, as is indicated by the sign $//$ in the sum.

First order perturbation theory and variational method lead to qualitatively different interpretations. In the first order perturbation [31], the wave function is fixed. The radial wave function hence does not depend on whether spins of electrons are parallel or antiparallel. Therefore, the one-body energy is force to be the same for all states and only the repulsive interaction between electrons can differ between different states. The

Coulomb and exchange interactions themselves are positive in many cases. Therefore, when spins of electrons are parallel, exchange interaction is larger and the total energy is lower. In short, in first order perturbation theory, parallel spins lead to smaller electron-electron repulsive energy. This is usually interpreted that, when the spins of electrons are parallel, the Pauli principle make the distance between electrons larger and therefore make the repulsive energy between electrons smaller.

In the variational method based on HF approximation [30], the wave function is self-consistently determined by solving the HF equation. Therefore, the radial wave function is different for different states, which is the largest difference from the first order perturbation theory. Particularly, when spins of electrons align parallel (larger S), radial wave function gets closer to the nucleus, leading to larger attractive potential between the nucleus and the electrons, which lowers the energy. At the same time, the repulsive potential between electrons becomes *larger*. The total energy becomes lower for larger S because the amount of the lowering due to the nucleus-electron potential exceeds the raising due to the electron-electron potential [30]. It is interpreted that, because the Pauli principle makes the distance of electrons with parallel spins larger, the electron-electron potential more weakly screens the nucleus-electron potential, leading to a stronger attractive central force and a radial wave function closer to the nucleus [32].

It has been shown that the variational method based on HF approximation is more accurate than the first order perturbation theory. Therefore, based on the conclusion of the variational method that the electron-electron repulsive potential is larger in the larger S state with lower energy, it has been concluded that the interpretation based on the first order perturbation, namely the interpretation that the decrease of repulsive potential energy between electrons with parallel spins is the main origin for the term dependence of energy, is wrong [29, 30, 32].

Although the interpretation of MS based on the first order perturbation is wrong as described above, phenomenological theoretical calculations of MS based on the first order perturbation theory have succeeded in many cases [2, 4, 6, 11, 12, 16-25]. In such calculations, the secular equation of the first order perturbation acts as a good model Hamiltonian when the Coulomb and exchange integrals are replaced by proper values, which enables full-multiplet calculation, namely evaluation of initial and final states as sum of many Slater determinants. However, one should carefully note that the term dependence of the radial wave function plays a crucial role in some cases [33]. Moreover, it is expected that realistic calculation of MS of core-level and valence spectra of RE and TM elements incorporated with calculation of term dependent radial wave function will soon be possible.

References

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