Atomic Magnetism by Yao Wang

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1 Magnetism of a single atom

Note that both the total spin magnetic moment and the orbital magnetic moment of a closed shell are zero, and the magnetism shown in an atom solely comes from open shells. We use the following Hamiltonian to describe open shells:

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m} + \sum_i V(\boldsymbol{r}_i) + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_{ij}|} + \sum_i \xi \boldsymbol{l}_i \cdot \boldsymbol{s}_i. \tag{1}$$

The (pseudo)potential $V(\boldsymbol{r})$ is assumed to only be dependent to $|\boldsymbol{r}|_i$, and in this case symmetry guarantees it is spherical. This is not the case when we do *ab initio* calculation and make quantitative comparison between computational and experimental results.

The Coulomb interaction between electrons means that there is no rotational invariance for a single electron, but the atom as a whole still has rotational invariance. Therefore, if we just consider the Coulomb interaction, then the good quantum numbers of the system include the total orbital angular momentum $\boldsymbol{L}$ and the total spin momentum $\boldsymbol{S}$. Taking the spin-orbital coupling into account, only $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is a good quantum number.

The relative magnitudes of the two interaction term decide whether we should use *L-S* **coupling** or *J-J* **coupling**. For elements that are usually encountered in condensed matter physics, *L-S* coupling is the correct choice, where Coulomb repulsion is much stronger than spin-orbital coupling. In this way we have the **Hund's rule**: due to Coulomb repulsion the total spin should be maximized in the ground state, and then due to spin-orbital coupling the total orbital angular momentum can be determined, and finally we obtain J and can then derive the Landé g-factor.

Adding a megnetic field $\boldsymbol{B} = (0, 0, B_0)$, we have

$$\sum_i \frac{(\boldsymbol{p}_i + e\boldsymbol{A})^2}{2m} = \sum_i \frac{\boldsymbol{p}_i^2}{2m} - \frac{eB_0}{2m} \sum_i \boldsymbol{l}_i \cdot \hat{\boldsymbol{e}}_z + \frac{e^2 B_0^2}{4m} \sum_i (x_i^2 + y_i^2). \tag{2}$$

The magnetic moment of the atom is therefore

$$\boldsymbol{\mu} = \boldsymbol{L}+ \tag{3}$$

and the atom-magnetic field coupling Hamiltonian is $-\boldsymbol{\mu} \cdot \boldsymbol{B}$. We can see that if the atom has a total orbital angular momentum, then it shows **paramagnetism**, otherwise it shows **diamagnetism**.

2 Crystal field theory

The magnetic moment derived for isolated atoms often does not work well for atoms in a crystal. The reason is clear, since an electron is actually surrounded by other atoms in the crystal. We call this correction of $V(\boldsymbol{r})$ the **crystal field**. Usually for a L-S coupling atom, we have

energy gap between different l > exchange energy > crystal field > spin-orbital coupling,

and therefore the crystal field can be seen as a perturbation acting on orbitals that have no spin-orbital coupling and mixing only orbitals with the same l.

Group representation theory can be used to see the structure of energy splitting: We are actually splitting a irreducible representation of $SO(3)$ (with a definite l) into several irreducible representations of the point group G after introducing the crystal field. Orbitals in the same irreducible representation of G share the same energy. We use the symbols for irreducible

representation of point groups to label the orbitals after energy splitting. For example, orbitals that are in a T_2 representation are called t_{2g} orbitals, where g means "inversion even" (on the contrary, subscript u means "inversion odd").

The energy splitting caused by the crystal field is the underlying reason why crystals have colors. Hopping between split energy levels from orbitals with the same l usually corresponds to a photon within the visible light spectrum, and hence the crystal absorbs visible light and therefore has the complementary color of the absorbed frequency.

We already have automated tools for determining the structure of energy splitting from the crystal structure. With pesudopotentials, the energy levels can also be found. `PyCrystalField`, for example, is such a tool in Python.