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Atoms

We present here an overview of the electronic structure of atoms. We begin with the mean-field approximation. This scheme is sometimes also called the Hartree approximation, and is the most basic starting point when discussing many-electron systems. In this approach, the atomic states are distinguished from one another by their electronic configuration. An electronic configuration is, in general, degenerate with a number of other configurations. However, when we take into account the corrections due to the deviation of the Coulomb interaction away from the mean field, the energy levels are split into a number of distinct levels, and each of these split energy levels is called a multiplet. In order to demonstrate this point, we introduce the Slater determinant. After this, we discuss the Coulomb integral and the exchange integral. In particular, because of the Pauli principle, the exchange integral exists only between electrons with the same spin orientations. This allows us to explain Hund's rule, that is, the multiplet that has the largest value of composite spin has the lowest energy.

1.1 Mean-field approximation and electronic configurations

The usual starting point for discussing the electronic structure of atoms is the mean-field approximation.

The motion of an electron is affected by attractive Coulomb interaction due to the positive charge *Ze* of the nucleus and repulsive Coulomb interaction due to the other electrons. The latter is time dependent owing to the motion of the other electrons, but we may, as an approximation, replace these electrons by an appropriate charge distribution and consider the Coulomb force due to it. This is called the mean-field approximation. In this way, we

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978-1-107-02418-2 - The Physics of Dilute Magnetic Alloys
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regard each electron as moving in the mean field, independently of the other electrons.

To determine the charge distribution which replaces the other electrons, we make use of the self-consistency condition. This point will be discussed later. Here, we consider the electronic wavefunction for a given mean field.

The potential energy of the electron in the mean field is denoted by $V(\boldsymbol{r})$. The vector $\boldsymbol{r}$ gives the spatial coordinates of the electron. The nucleus is assumed to remain stationary at the origin. Insofar as the problem concerns single atoms, we may almost always regard $V(\boldsymbol{r})$ to be a function of $r = |\boldsymbol{r}|$ only. $V(r)$ is then called the central field. When r is sufficiently large, $V(r)$ approaches $-e^2/r$. This is because when an electron is sufficiently far away from the origin, the Ze positive charge at the origin and the $Z - 1$ electrons around it exert a combined force, to the distant electron, which is asymptotically equivalent to that of a single positive charge at the origin. On the other hand, when r is sufficiently small, we see immediately that $V(r)$ approaches $-Ze^2/r$+const.

Now, in the mean-field approximation, the atomic Hamiltonian is expressed as

$$H_0 = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z} \Delta_i + \sum_{i=1}^{Z} V(r_i). \tag{1.1}$$

Δ_i is the Laplacian with respect to the spatial coordinates of the ith electron. The Schrödinger equation,

$$H_0 \Psi = E\Psi, \tag{1.2}$$

is reduced, upon the substitution

$$\Psi = \prod_i \psi_i(\boldsymbol{r}_i), \tag{1.3}$$

to Z one-electron Schrödinger equations given by

$$\left[-\frac{\hbar^2}{2m}\Delta_i + V(r_i)\right]\psi_i(\boldsymbol{r}_i) = \varepsilon_i \psi_i(\boldsymbol{r}_i), \tag{1.4}$$

$$E = \sum_i \varepsilon_i. \tag{1.5}$$

Since $V(r_i)$ is spherically symmetric, the solution to eq. (1.4) is specified by quantum numbers n, l and m.

$$\psi_{nlm}(\boldsymbol{r}_i) = R_{nl}(r_i) Y_{lm}(\theta_i, \varphi_i). \tag{1.6}$$

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Y_{lm} are the spherical harmonic functions, and $R_{nl}(r)$ satisfy the following equations:

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+U(r)+\frac{l(l+1)}{r^2}\right]R_{nl}(r)=\frac{2m\varepsilon_{nl}}{\hbar^2}R_{nl}(r), \tag{1.7}$$

$$U(r)=\frac{2m}{\hbar^2}V(r). \tag{1.7a}$$

By solving eq. (1.7) with the boundary condition $R_{nl}(r) \to 0$ as $r \to \infty$, we obtain negative eigenvalues ε_{nl}. For a given l, n is assigned the values $n = l+1, l+2, \ldots$. The eigenvalues increase in this order. The quantum number l represents the magnitude of the orbital angular momentum, and the quantum number m represents the z-component of l. Eigenvalues ε_{nl} are $(2l + 1)$-fold degenerate since they are independent of m.

A solution, given by eq. (1.6), to the one-electron Schrödinger equation is called an ‘atomic orbital’, or simply ‘orbital’. As stated earlier, an orbital is specified by the three quantum numbers n, l and m. By convention, $l = 0, 1, 2, 3, \ldots$ are assigned the letters s, p, d, f, ... For example, the ‘2p orbital’ refers to the wavefunction of eq. (1.6) with the quantum numbers $n = 2$ and $l = 1$.

For most atoms, writing the orbitals in the ascending order of the corresponding energy leads to 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, ... To obtain the ground state, we then place Z electrons into the orbitals starting from the lowest state, in a way that respects the Pauli exclusion principle. According to this principle, only one spin-up electron and one spin-down electron can enter each orbital given by eq. (1.6). Each s orbital therefore accommodates only two electrons, and the full set of p orbitals accommodates six electrons in total.

For example, in the case of Si, the ground state is denoted by $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$. This is called the electronic configuration of the atom. Orbitals that are completely filled with electrons, that is, the ‘closed shell’, are usually omitted in the notation. Si is therefore expressed as $(3p)^2$ or $(3s)^2(3p)^2$, while $(3s)^1(3p)^3$ denotes the electronic configuration of an excited state of Si.

1.2 Multiplets

Let us consider an electronic configuration. The sum of the energies of all of the orbitals contained in the configuration, given by eq. (1.5), is called the configuration energy, and is a first approximation for the value of the atomic

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energy. In general, when the shell is not closed, the configuration energy has a large degree of degeneracy.

For example, the $(2p)^2$ configuration is ${}_6C_2 = 15$-fold degenerate. This is due to the mean-field approximation and, as the approximation is improved, the level should, in principle, split into several levels. To obtain such a splitting, we take the following Hamiltonian instead of H_0:

$$H = -\frac{\hbar^2}{2m}\sum_i \varDelta_i - \sum_i \frac{Ze^2}{r_i} + \sum_{i>j}\frac{e^2}{r_{ij}}. \tag{1.8}$$

The second term here is the potential energy due to the attractive Coulomb interaction between each electron and the nucleus. The third term is the potential energy of the Coulomb interaction between electrons ($r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$). For example, in the case of $(2p)^2$, we can improve the approximation using perturbation theory if we diagonalize H, using the 15 wavefunctions that are the eigenstates of H_0. In order to do so, we have to explicitly take into account the spin-coordinate dependence of the wavefunctions, and furthermore make the wavefunctions satisfy the Pauli principle.

Spin is an intrinsically quantum mechanical concept, but as a classical analogy, we can imagine the electrons to be spinning, and the corresponding angular momentum is the spin. When we equate its magnitude with $\sqrt{s(s+1)}\hbar$, we find that $s = 1/2$ in the case of the electron. Its z-component is only allowed to take either of the two values $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.

This can be quantified by introducing the spin coordinate. In addition to the spatial coordinates, the electron has a spin coordinate which takes the value $+\frac{1}{2}$ or $-\frac{1}{2}$. The state in which the probability of the former (latter) is equal to unity is designated as the state whose z-component of spin is equal to $+\frac{1}{2}\hbar$ $(-\frac{1}{2}\hbar)$. This state is denoted as $\alpha(\zeta)$ $(\beta(\zeta))$. ζ is the spin coordinate. Let us write the spin angular momentum divided by $\hbar$ as $\boldsymbol{s} = (s_x, s_y, s_z)$. This operator acts on functions of the spin coordinate. We then have

$$s_z\alpha(\zeta) = \frac{1}{2}\alpha(\zeta), \quad s_z\beta(\zeta) = -\frac{1}{2}\beta(\zeta). \tag{1.9a}$$

We obtain the following from the generic properties of angular momentum operators:

$$s_x\alpha(\zeta) = \frac{1}{2}\beta(\zeta), \quad s_x\beta(\zeta) = \frac{1}{2}\alpha(\zeta), \tag{1.9b}$$

$$s_y\alpha(\zeta) = \frac{i}{2}\beta(\zeta), \quad s_y\beta(\zeta) = -\frac{i}{2}\alpha(\zeta). \tag{1.9c}$$

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Furthermore, because of the orthonormality between α and β, we have

$$\left.\begin{aligned} \langle\alpha|\alpha\rangle &= \sum_{\zeta=1/2,-1/2} \alpha(\zeta)^2 = 1 \\ \langle\beta|\beta\rangle &= \sum_{\zeta=1/2,-1/2} \beta(\zeta)^2 = 1 \\ \langle\alpha|\beta\rangle &= \sum \alpha(\zeta)\beta(\zeta) = 0 \\ \langle\beta|\alpha\rangle &= \sum \beta(\zeta)\alpha(\zeta) = 0 \end{aligned}\right\}. \tag{1.10}$$

In this way, the wavefunction of an electron is specified by four quantum numbers *nlms*, that is, the wavefunction is given by $\psi_{nlm}(\boldsymbol{r}_i)\alpha(\zeta_i)$ or $\psi_{nlm}(\boldsymbol{r}_i)\beta(\zeta_i)$. Here, $s = 1/2$ corresponds to α and $s = -1/2$ to β. From now on, we write the set of three quantum numbers nlm as λ and the set of λ and s as k. We then write the wavefunction of an electron as $\phi_k(i)$. The argument i refers to the spatial and spin coordinates. In the general case where there are Z electrons with quantum numbers $k_1, k_2, \ldots, k_Z$, the wavefunctions are written as

$$\Psi(1,\ 2,\ \ldots, Z) = \phi_{k_1}(1)\phi_{k_2}(2)\cdots\phi_{k_Z}(Z).$$

This is eq. (1.3) modified by including the spin functions.

Before going on to diagonalizing eq. (1.8) using this result, we have to rewrite Ψ so that it satisfies the Pauli principle. According to this principle, the wavefunction $\Psi(1, 2, \ldots)$ for a many-electron system must change its sign when any pair of electrons exchange their coordinates. For example,

$$\Psi(2, 1,\ \ldots) = -\Psi(1, 2,\ \ldots). \tag{1.11}$$

All of the arguments, other than the first two, are identical on both sides.

Ψ as written above by itself does not satisfy the Pauli principle, but one can construct such a function as follows. Let us denote the operation of the permutation of coordinates as P. PΨ then refers to Ψ with the order of the coordinates rearranged according to a permutation P. It is also an eigenfunction of H_0 with the same eigenvalue as Ψ. $Z!$ such permutations are linearly combined as follows:

$$\begin{aligned} \Phi(1, 2, \ldots) &= \frac{1}{\sqrt{Z!}} \sum_{\mathrm{P}} (-)^{\mathrm{P}} \mathrm{P}\Psi \\ &= \frac{1}{\sqrt{Z!}} \begin{vmatrix} \phi_{k_1}(1) & \phi_{k_2}(1) & \cdots \\ \phi_{k_1}(2) & \phi_{k_2}(2) & \\ \vdots & & \ddots \end{vmatrix}. \end{aligned} \tag{1.12}$$

Here, $(-)^P$ is equal to 1 when P is an even permutation, and -1 when it is an odd one. This is called the Slater determinant and is easily seen to satisfy the Pauli principle. We also see that eq. (1.12) vanishes if there is a pair of identical labels, no matter which, from among $k_1, k_2, \ldots, k_Z$. This is nothing other than the exclusion principle. The overall factor $1/\sqrt{Z!}$ is needed to normalize eq. (1.12).

Now we take $(2p)^2$ as an example. As we mentioned earlier, this electronic configuration is 15-fold degenerate, which is found by counting the number of ways of choosing k_1, k_2. We list them explicitly in the following. Out of the four components of k, we omitted n and l and wrote out only m and s explicitly. We have defined $M_L = \sum m_i$ and $M_S = \sum s_i$.

	k_1		k_2		M_L	M_S
Φ_1	1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0
Φ_2	1	$\frac{1}{2}$	0	$\frac{1}{2}$	1	1
Φ_3	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	1	0
Φ_4	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	0
Φ_5	1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	1	-1
Φ_6	1	$\frac{1}{2}$	-1	$\frac{1}{2}$	0	1
Φ_7	1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0
Φ_8	1	$-\frac{1}{2}$	-1	$\frac{1}{2}$	0	0
Φ_9	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0
Φ_{10}	1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1
Φ_{11}	0	$\frac{1}{2}$	-1	$\frac{1}{2}$	-1	1
Φ_{12}	0	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0
Φ_{13}	0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	0
Φ_{14}	0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1
Φ_{15}	-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0

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In order to diagonalize H using these functions as the bases, it is convenient to classify the wavefunctions according to the total angular momentum. For the total orbital angular momentum $\boldsymbol{L} = (L_x, L_y, L_z)$ and the total spin angular momentum $\boldsymbol{S} = (S_x, S_y, S_z)$, their x-components, for example, are defined by

$$L_x = \sum_{i=1}^{Z} l_{ix}, \quad S_x = \sum_{i=1}^{Z} s_{ix}.$$

The five operators $\boldsymbol{L}^2, L_z, \boldsymbol{S}^2, S_z$ and H can be shown to commute with each other. Hence if we choose the eigenfunctions of $\boldsymbol{L}^2, L_z, \boldsymbol{S}^2$ and S_z as the bases, there are no matrix elements of H between the basis wavefunctions that have different eigenvalues.

The diagonalization therefore needs to be carried out only among the sets of wavefunctions with identical $\boldsymbol{L}^2, L_z, \boldsymbol{S}^2$ and S_z eigenvalues. Let us take $L(L+1)$, $M_L, S(S+1)$ and M_S as the eigenvalues of $\boldsymbol{L}^2, L_z, \boldsymbol{S}^2$ and S_z. The 15 Φs tabulated above are already eigenfunctions of L_z and S_z, and the values of M_L and M_S are written therein. They are the sums of the corresponding values for individual electrons. Let us first consider Φ_1. Since it has $M_L = 2$ and $M_S = 0$, and no other states have the same set of eigenvalues, Φ_1 is already an eigenfunction of $\boldsymbol{L}^2$ and $\boldsymbol{S}^2$ at the same time. In fact, since we can easily show that $\boldsymbol{L}^2\Phi_1 = 2(2+1)\Phi_1$ and $\boldsymbol{S}^2\Phi_1 = 0$, we conclude that $L = 2$ and $S = 0$. On the other hand, since, in general, an eigenfunction of the angular momentum has the following property:

$$(L_x - iL_y)\Phi(L, M_L) = \sqrt{L(L+1) - M_L(M_L-1)}\,\Phi(L, M_L - 1), \qquad (1.13)$$

we obtain another eigenfunction, with M_L reduced by 1, by applying $L_x - iL_y = (l_{1x} - il_{1y}) + (l_{2x} - il_{2y})$ to Φ_1 and expressing the result as a linear combination of the states Φ_1 to Φ_{15}. Repeating this procedure, we obtain the following five functions for $L = 2$ and $M_L = 2, 1, \ldots, -2$:

^{1}D($L = 2 \quad S = 0$)	M_L	M_S
Φ_1	2	0
$\frac{1}{\sqrt{2}}(\Phi_3 - \Phi_4)$	1	0
$\frac{1}{\sqrt{6}}(\Phi_7 - \Phi_8 + 2\Phi_9)$	0	0
$\frac{1}{\sqrt{2}}(\Phi_{12} - \Phi_{13})$	−1	0
Φ_{15}	−2	0

Next, we examine Φ_2. Since it has eigenvalues $M_L = 1$ and $M_S = 1$, and no other state has the same set of eigenvalues, it must be an eigenfunction of $\boldsymbol{L}^2$ and $\boldsymbol{S}^2$. We find that it has $L = 1$ and $S = 1$. By applying $L_x - iL_y$ and $S_x - iS_y$, respectively, we obtain functions that have M_L and M_S reduced by unity:

$^3\mathrm{P}(L = 1 \quad S = 1)$	M_L	M_S
Φ_2	1	1
$\frac{1}{\sqrt{2}}(\Phi_3 + \Phi_4)$	1	0
Φ_5	1	-1
Φ_6	0	1
$\frac{1}{\sqrt{2}}(\Phi_7 + \Phi_8)$	0	0
Φ_{10}	0	-1
Φ_{11}	-1	1
$\frac{1}{\sqrt{2}}(\Phi_{12} + \Phi_{13})$	-1	0
Φ_{14}	-1	-1

We have now obtained 14 functions. The one remaining function should be a linear combination of Φ_7, Φ_8 and Φ_9, because these three have appeared only in two eigenfunctions. From the orthogonalization condition involving these two, the remaining function is determined as

$$\frac{1}{\sqrt{3}}(-\Phi_7 + \Phi_8 + \Phi_9). \tag{1.14}$$

This is found to have $L = 0$ and $S = 0$, and we label it as ^{1}S. In general, $L = 0, 1, 2, \ldots$ are labeled S, P, D, ... and the value of $2S + 1$ is written as the superfix on the left shoulder. The $L = 1, S = 1$ state is denoted as ^{3}P.

In the above examples, each function has a different set of L, S, M_L, M_S values, and each of the 15 functions diagonalizes H. However, the 15 eigenvalues of H do not split into 15 levels. All functions with the same L and S but different values of M_L and M_S have the same eigenvalue. In order to demonstrate this point, we use eq. (1.13) to obtain

$$\begin{aligned}
&\int \Phi(L, M_L-1)^* H \Phi(L, M_L-1) d\tau \\
&\quad = [L(L+1) - M_L(M_L-1)]^{-1} \\
&\qquad \times \int \left[(L_x - iL_y)\Phi(L, M_L)\right]^* H (L_x - iL_y)\Phi(L, M_L) d\tau \\
&\quad = [L(L+1) - M_L(M_L-1)]^{-1} \\
&\qquad \times \int \Phi(L, M_L)^* H (L_x + iL_y)(L_x - iL_y)\Phi(L, M_L) d\tau .
\end{aligned}$$

Here, we made use of the fact that H commutes with L_x and L_y. Furthermore, using

$$\begin{aligned}
(L_x + iL_y)(L_x - iL_y)\Phi(L, M_L) &= (\boldsymbol{L}^2 - L_z^2 + L_z)\Phi(L, M_L) \\
&= [L(L+1) - M_L(M_L-1)]\Phi(L, M_L),
\end{aligned}$$

we find that the above integral is independent of M_L. We can derive a similar result for M_S. Therefore, in the above example, the eigenvalues split into three levels: ^{1}D (quintet or fivefold), ^{3}P (ninefold) and ^{1}S (singlet). Each level is called a multiplet. In general, the configuration energies obtained in the mean-field approximation split into several multiplets when we take into account the deviation of the Coulomb energy from the mean value. Each multiplet is $(2L+1)(2S+1)$-fold degenerate.

The degeneracy of the multiplet is broken further when we take into account the magnetic interaction between the electrons. Dirac's relativistic equation of the electron leads to a term in the Hamiltonian that is proportional to $\sum \boldsymbol{l}_i \cdot \boldsymbol{s}_i$, where $\boldsymbol{l}_i$ is the orbital angular momentum of the ith electron. This term is proportional to $\boldsymbol{L} \cdot \boldsymbol{S}$ in a particular multiplet, and is therefore called the *LS* coupling term. It gives rise to an energy that depends on the angle between L and S. The vector sum of $\boldsymbol{L}$ and $\boldsymbol{S}$ is the total angular momentum $\boldsymbol{J}$, and we obtain

$$J(J+1) = \boldsymbol{J}^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\boldsymbol{L} \cdot \boldsymbol{S} = L(L+1) + S(S+1) + 2\boldsymbol{L} \cdot \boldsymbol{S},$$

so that the energy depends on the value of J. J takes a value between $L+S$ and $|L-S|$ inclusive, and each level is $(2J+1)$-fold degenerate corresponding to $J_z = J, \ldots, -J$.

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Coming back to the problem of $(np)^2$, we obtain, from the above discussion,

$$E(^1\text{D}) = \int \Phi_1^* H \Phi_1 d\tau = H_{11}, \tag{1.15}$$

$$E(^3\text{P}) = \int \Phi_2^* H \Phi_2 d\tau = H_{22}. \tag{1.16}$$

$E(^1\text{S})$ can be derived using eq. (1.14). However, we can derive it more simply as follows. If we diagonalize the matrix elements between the states Φ_7, Φ_8 and Φ_9, that is:

$$\begin{pmatrix} H_{77} & H_{78} & H_{79} \\ H_{87} & H_{88} & H_{89} \\ H_{97} & H_{98} & H_{99} \end{pmatrix},$$

one solution should coincide with eq. (1.14), and the other two should be the $M_L = 0$ and $M_S = 0$ components of the ^{3}P and ^{1}D states. The sum of the eigenvalues of this matrix is therefore equal to $E(^1\text{S}) + E(^3\text{P}) + E(^1\text{D})$. On the other hand, since the sum of the eigenvalues is equal to the sum of the diagonal elements, we obtain

$$E(^1\text{S}) = H_{77} + H_{88} + H_{99} - H_{11} - H_{22}. \tag{1.17}$$

Thus, in the present example, all of the energy levels of the multiplets can be expressed in terms of the diagonal elements of H.

1.3 Coulomb and exchange integrals

Next, we need to calculate the matrix elements of H such as that given by eq. (1.15). In general, let us write

$$H = \sum_i h(i) + \sum_{i>j} V(i,j). \tag{1.18}$$

Here, $h(i)$ includes only the ith coordinates (which may include the spin coordinate) and, in general, the derivatives with respect to them. $V(i,j)$ is the interaction term between the ith and jth electrons. When Φ is a Slater determinant consisting of $\phi_{k_i}(i = 1, \ldots, Z)$ as shown in eq. (1.12) (ϕ_{k_i}s being orthonormal), we obtain, according to Appendix A,

$$\int \Phi^* H \Phi d\tau = \sum_i h(k_i, k_i) + \sum_{i>j} [V(k_i, k_j; k_i, k_j) - V(k_i, k_j; k_j, k_i)], \tag{1.19}$$