QUASISPIN FORMALISM IN THE THEORY OF A STRONG CRYSTAL FIELD

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Abstract

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QUASISPIN FORMALISM IN THE THEORY OF A STRONG CRYSTAL FIELD

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In 1943 Racah ([1]) introduced, for the classification of the states of many-electron atoms, the quantum number of seniority v. The concept of seniority enabled him to establish a connection between the wave functions of n electrons and v electrons ($n > v$). Relations were found between the matrix elements of operators of various physical quantities for the corresponding states of n and v particles, and new selection rules with respect to the quantum number v were obtained. Subsequently this idea of Racah found wide application and further development in the theory of nuclear spectra ([2]-[7]). In the present work we generalize the concept of seniority to the case of a system of n electrons in a strong cubic crystal field. For this purpose we shall use a very convenient mathematical apparatus—the quasispin formalism—which makes it possible to treat equally simply both the case of n electrons in one shell (configuration l^n ([2]-[8])) and mixed configurations, for example $l_1^{n_1} l_2^{n_2}$, where the electrons fill two shells ([7]). This circumstance is essential, since, for example, a d-shell in a strong cubic field is split into two subshells γ_1 and γ_2, corresponding to the two-dimensional and three-dimensional irreducible representations of the cubic groups (E and T_2 in the case of the group T_d); we are dealing with mixed configurations $\gamma_1^{n_1} \gamma_2^{n_2}$.

Let us first consider, by analogy with ([2]-[8]), the case of the configuration γ^n. Introduce the operators $a^+_{\gamma\mu\sigma}$ and $a_{\gamma\mu\sigma}$, the creation and annihilation operators of an electron in the state $|\gamma\mu\sigma\rangle$, where μ is the row index of the irreducible representation γ of the cubic group according to which the wave function of this state transforms, and σ is the projection of the electron spin. For these operators the usual anticommutation relations hold:

$$[a^+_{\gamma\mu\sigma}, a^+_{\gamma'\mu'\sigma'}]_+ = [a_{\gamma\mu\sigma}, a_{\gamma'\mu'\sigma'}]_+ = 0, \qquad [a_{\gamma\mu\sigma}, a^+_{\gamma'\mu'\sigma'}] = \delta_{\gamma\gamma'}\delta_{\mu\mu'}\delta_{\sigma\sigma'}. \quad (1)$$

We now construct from the operators a^+ and a the operators

$$I_+ = \frac{1}{2}\sum_{\mu\sigma}(-1)^{1/2-\sigma} a^+_{\gamma\mu\sigma} a^+_{\gamma\mu-\sigma},$$

$$I_- = \frac{1}{2}\sum_{\mu\sigma}(-1)^{1/2-\sigma} a_{\gamma\mu-\sigma} a_{\gamma\mu\sigma}, \tag{2}$$

$$I_0 = \frac{1}{2}\left(\sum_{\mu\sigma} a^+_{\gamma\mu\sigma} a_{\gamma\mu\sigma} - \frac{1}{2}n_0\right) = \frac{1}{2}\left(\hat{n} - \frac{n_0}{2}\right),$$

where $\hat{n}$ is the particle-number operator; n_0 is the total number of places in the shell γ, equal to $2[\gamma]$ ($[\gamma]$ is the dimension of the representation γ). These operators satisfy the same commutation rules as the three components $I_+ = I_x + iI_y$, $I_- = I_x - iI_y$, $I_0 = I_z$ of the ordinary angular-momentum operator:

$$[I_+ I_-] = 2I_0, \qquad [I_0, I_+] = I_+, \qquad [I_0 I_-] = -I_-. \tag{3}$$

The wave functions of the configurations γ^n can be chosen so that they are eigenfunctions of the operators I^2 and I_0 and are characterized by the quantum numbers I (quasispin) and M_I (quasispin projection). We note that the operator I_+ (I_-) is proportional to the operator for creation (annihilation) of two electrons in the state $|\gamma^2\Gamma S\rangle$ with $\Gamma = 0$ and $S = 0$ ($\Gamma = 0$ corresponds to the totally symmetric representation A_1 of the cubic group). The concept of the seniority number v for the state of n electrons in a cubic field is generalized as follows. It denotes the number of electrons among n that are not coupled into pairs with $\Gamma = 0$ and $S = 0$. Since in the state $|\gamma^v v\Gamma S\rangle$ there is no such pair, we have

$$I_-|\gamma^v v\Gamma S\rangle = 0.$$

Moreover, from (2) it follows that

$$M_I = \frac{1}{2}\left(v - \frac{1}{2}n_0\right).$$

These equalities mean that in the given state $M_I = -I$, and the function $|\gamma^v v\Gamma S\rangle$ is characterized by the quasispin $\frac{1}{2}\left(\frac{1}{2}n_0 - v\right)$

$$|\gamma^v v\Gamma S\rangle \equiv \left|\gamma^v I = \frac{1}{2}\left(\frac{1}{2}n_0 - v\right) M_I = \frac{1}{2}\left(v - \frac{1}{2}n_0\right)\Gamma S\right\rangle. \tag{4}$$

States with other values of M_I for a given I are obtained from the functions (4) by the action of the raising operator I_+

$$
\begin{aligned}
|\gamma^n v\Gamma S\rangle &\equiv \left|\gamma^n I = \frac{1}{2}\left(\frac{1}{2}n_0 - v\right) M_I = \frac{1}{2}\left(n - \frac{1}{2}n_0\right)\Gamma S\right\rangle \\
&= \sqrt{\frac{[\frac{1}{2}(n_0 - n - v)]!}{(\frac{n-v}{2})!\,(\frac{1}{2}n_0 - v)!}}\, I_+^{(n-v)/2}|\gamma^v v\Gamma S\rangle.
\end{aligned} \tag{5}
$$

Relation (5) shows that between the functions of states with different numbers of particles and the same seniority (quasispin) there exists a simple connection, which makes it possible to find a number of relations for matrix elements of operators over these states.

Let us consider, for example, the reduced matrix element [(4)] of the operator a^+

$$
\langle\gamma^n v\Gamma S\|a^+\|\gamma^{n-1}v'\Gamma' S'\rangle = -\sqrt{\frac{n}{[\Gamma](2S+1)}}\,\langle\gamma^n v\Gamma S|\gamma^{n-1}v'\Gamma' S'\rangle \tag{6}
$$

From the commutation relations $[I_0, a^+_{\mu\sigma}] = \frac{1}{2}a^+_{\mu\sigma}$, $[I_+, a^+_{\mu\sigma}] = 0$, $[I_-, a^+_{\mu\sigma}] = (-1)^{1/2-\sigma}a_{\mu-\sigma}$, it follows that $a^+_{\mu\sigma}$ and $(-1)^{1/2-\sigma}a_{\mu-\sigma}$ are two components of the tensor operator $t^{1/2}$ of rank $\frac{1}{2}$ in quasispin space. Introducing into (6) the quantum numbers IM_I and using the Wigner–Eckart theorem in quasispin space, we obtain

$$
\begin{aligned}
-\sqrt{\frac{n}{[\Gamma](2S+1)}}\,\langle\gamma^n v\Gamma S|\gamma^{n-1}v\Gamma' S'\rangle &= \langle\gamma^n IM_I\Gamma S|t^{1/2}_{1/2}|\gamma^{n-1}I'M_I'\Gamma' S'\rangle = \\
&= -\frac{(I'M_I'\ 1/2\ 1/2|IM_I)}{\sqrt{2I+1}}\,\langle\gamma^v I\Gamma S\|t^{1/2}\|\gamma^{v'}I'\Gamma' S'\rangle.
\end{aligned} \tag{7}
$$

Here the matrix element with three bars is the matrix element of the operator $t^{1/2}$, reduced in the orbital, spin, and quasispin spaces; $(I'M_I'\,1/2\,1/2|IM_I)$ is the usual Clebsch–Gordan coefficient. With the aid of formula (7), for example, for $v' = v-1$ we readily find

$$
\begin{aligned}
&\frac{\langle\gamma^n v\Gamma S|\gamma^{n-1}v-1\Gamma S\rangle}{\langle\gamma^v v\Gamma S|\gamma^{v-1}v-1\Gamma S\rangle} = \\
&= \sqrt{\frac{v}{n}}\,\frac{\left(\frac{1}{2}\left(\frac{1}{2}n_0 - v + 1\right)\ \frac{1}{2}\left(n - 1 - \frac{1}{2}n_0\right);\ \frac{1}{2}\ \frac{1}{2}\left|\frac{1}{2}\left(\frac{1}{2}n_0 - v\right)\ \frac{1}{2}\left(n - \frac{1}{2}n_0\right)\right.\right)}{\left(\frac{1}{2}\left(\frac{1}{2}n_0 - v + 1\right)\ \frac{1}{2}\left(v - 1 - \frac{1}{2}n_0\right);\ \frac{1}{2}\ \frac{1}{2}\left|\frac{1}{2}\left(\frac{1}{2}n_0 - v\right)\ \frac{1}{2}\left(v - \frac{1}{2}n_0\right)\right.\right)} = \\
&= \sqrt{\frac{v(n_0 - v - n + 2)}{n(n_0 - 2v + 2)}}.
\end{aligned} \tag{8}
$$

This relation is a generalization, to the case of electrons in a cubic field, of formula (58h) obtained by Racah [1] for free atoms and ions. It is not difficult to generalize, by an analogous method, other results of Racah' s work as well.

Let us turn to the case of mixed configurations. In this case one can introduce two quasispin operators: I_1 for the shell γ_1 and I_2 for the shell γ_2, which will commute with one another. We then deal with antisymmetric wave functions of the form

$$|\gamma_1^{n_1}\nu_1\Gamma_1 S_1,\ \gamma_2^{n_2}\nu_2\Gamma_2 S_2 : \Gamma S\rangle \equiv |\gamma_1^{n_1} I_1 M_{I_1}\Gamma_1 S_1,\ \gamma_2^{n_2} I_2 M_{I_2}\Gamma_2 S_2 : \Gamma S\rangle. \quad (9)$$

The procedure for calculating matrix elements with such functions and the calculation of genealogical coefficients for them were described in [9–15]. Using a relation of type (7) for each of the shells γ_1, γ_2, one can obtain a number of new relations between matrix elements in the case of mixed configurations. However, in considering certain questions it is more convenient to pass from the functions (9) to other functions, for which the total quasispin $I = I_1 + I_2$ is specified; we shall denote it in the following way:

$$|(\gamma_1,\gamma_2)^n I_1\Gamma_1 S_1,\ I_2\Gamma_2 S_2 : IM_I\Gamma S\rangle \equiv$$

$$\equiv |(\gamma_1,\gamma_2)^n \nu_1\Gamma_1 S_1,\ \nu_2\Gamma_2 S_2 : \nu\Gamma S\rangle. \quad (10)$$

Here $n = n_1 + n_2$, $I = \frac{1}{2}\left(\frac{1}{2}(n_{01}+n_{02}) - \nu\right)$, $M_I = \frac{1}{2}\left(n - \frac{1}{2}(n_{01}+n_{02})\right)$, $I_1 = \frac{1}{2}\left(\frac{1}{2}n_{01} - \nu_1\right)$, $I_2 = \frac{1}{2}\left(\frac{1}{2}n_{02} - \nu_2\right)$, n_{0i} is the number of places in the shell γ_i.

Obviously, the functions (10) are obtained from (9) by ordinary vector addition of the quasispins I_1 and I_2 into the total quasispin I

$$|(\gamma_1,\gamma_2)^n \nu_1\Gamma_1 S_1,\ \nu_2\Gamma_2 S_2 : \nu\Gamma S\rangle =$$

$$= \sum_{M_{I_1}+M_{I_2}=M_I} (I_1 M_{I_1} I_2 M_{I_2} | I M_I) |\gamma_1^{n_1}\nu_1\Gamma_1 S_1,\ \gamma_2^{n_2}\nu_2\Gamma_2 S_2 : \Gamma S\rangle. \quad (11)$$

The sum over M_{I_1}, M_{I_2} includes terms with different n_1 and n_2 satisfying the condition $n_1 = \nu_1, \nu_1+2, \ldots;\ n_2 = \nu_2, \nu_2+2, \ldots;\ n_1+n_2 = n$.

It is important to note that, since $|I_1 - I_2| \le I \le I_1 + I_2$, the total seniority number ν for a mixed configuration is not the arithmetic sum of ν_1 and ν_2, but assumes several values for given ν_1 and ν_2.

It is not hard to verify that the total seniority number ν for n d-electrons in a cubic field coincides with the seniority number ν for the configuration d^n in a spherically symmetric field. Indeed, taking into account the relation between cubic and spherical harmonics [11], we find

$$a^{+}_{\gamma\mu\sigma} = \sum_{m} \alpha^{\gamma\mu}_{lm} a^{+}_{lm\sigma}, \tag{12}$$

where $a^{+}_{lm\sigma}$ is the creation operator of an electron in the state with orbital angular momentum l and with its projection on the z-axis equal to m. Since

$$\sum_{\gamma\mu} \alpha^{\gamma\mu *}_{lm} \alpha^{\gamma\mu}_{lm'} = \delta_{mm'}, \qquad \alpha^{\gamma\mu *}_{lm} = (-1)^{m} \alpha^{\gamma\mu}_{l-m},$$

then, substituting expression (12) for a^{+} into formula (2), we can write $I_{+} = I_{+1} + I_{+2}$ in the form

$$I_{+} = \frac{1}{2} \sum_{\gamma\mu\sigma} (-1)^{\frac{1}{2}-\sigma} a^{+}_{\gamma\mu\sigma} a^{+}_{\gamma\mu-\sigma} = \frac{1}{2} \sum_{\gamma\mu\sigma m m'} \alpha^{\gamma\mu}_{lm} \alpha^{\gamma\mu}_{lm'} (-1)^{\frac{1}{2}-\sigma} a^{+}_{lm\sigma} a^{+}_{lm'\sigma} =$$

$$= \frac{1}{2} \sum_{\sigma m} (-1)^{\frac{1}{2}-\sigma+m} a^{+}_{lm\sigma} a^{+}_{l-m\cdot}.$$

The right-hand side of this equality coincides with the component of the quasispin I_{+} in the case of a free atom or ion [8]. The coincidence of the total ν in the case of n

d-electrons in cubic and spherically symmetric fields makes it possible, in particular, to obtain a number of simplifications in considering the question of the relation between the wave functions of n d-electrons in the strong-cubic-field scheme and in the scheme of the intermediate crystal field.

The expansion coefficients of the intermediate-field functions $|d^{n} vL\Gamma S\rangle$ in terms of the functions (10) will be the overlap integrals

$$\langle d^{n} vL\Gamma S \mid (\gamma_1\gamma_2)^{n} v_1\Gamma_1 S_1,\ v_2\Gamma_2 S_2 : v\Gamma S\rangle\,. \tag{13}$$

These integrals are diagonal in the total quasispin I (the total v in both parts is the same and does not depend on the projection of the total quasispin M_I, i.e., on n for a given v). Therefore we have

$$\begin{aligned}
&\langle d^{n} vL\Gamma S \mid (\gamma_1\gamma_2)^{n} v_1\Gamma_1 S_1,\ v_2\Gamma_2 S_2 : v\Gamma S\rangle = \\
&= \langle d^{n_0-n} vL\Gamma S \mid (\gamma_1\gamma_2)^{n_0-n} v_1\Gamma_1 S_1,\ v_2\Gamma_2 S_2 : v\Gamma S\rangle = \\
&= \langle d^{v} vL\Gamma S \mid (\gamma_1\gamma_2)^{v} v_1\Gamma_1 S_1,\ v_2\Gamma_2 S_2 : v\Gamma S\rangle\,.
\end{aligned}$$

This result substantially simplifies the calculations, since in practice it is necessary to consider only the case $n \leq \frac{1}{2}n_0$ with $n = v$.

In conclusion, we give the recurrence formula for the coefficient (13) in one of the simplest cases

$$\langle d^n vL\Gamma S \mid \gamma_2^n v\Gamma S\rangle = \sum_{v'L'T'S'} \langle d^n vLS \mid d^{n-1}v'L'S'\rangle \langle \gamma_2^n v\Gamma S \mid \gamma_2^{n-1}v'T'S'\rangle \langle d^{n-1}v'L'T'S' \mid \gamma_2^{n-1}v'\Gamma'S'\rangle \times \\ \times \sum_{\substack{M_L M_L' \\ \mu\mu'}} a_{LM_L}^{\bar{\Gamma}\mu*} a_{L'M_L'}^{\Gamma'\mu'} a_{lm}^{\gamma_2\mu} (L'M_L'lm \mid LM_L)(\Gamma'\mu'\gamma_2\mu \mid \Gamma\mu). \tag{14}$$

Similar relations for the general case are more cumbersome, but in principle do not differ at all from (14).

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Note: Figure translations are in progress. See original paper for figures.