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Particles and Holes in the Unitary Group Method

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Based on the definition for complementary Gel'fand states, we proved the simple relationship between the matrix elements of particle states and those of hole states by unitary calculus.

Key words: Complementary theorem – Unitary group method.

1. Introduction

It is a well-known principle that a partly-filled shell of N particles can be treated either as N particles or as $\mathcal{N}$-N holes, where $\mathcal{N}$ is the total capacity of the shell. According to this principle a configuration of N particles and a configuration of N holes will produce identical multiplet terms and have the same energy interval between the various terms of both configurations. In fact this principle can be derived by means of the relations which connect Hamiltonian matrix elements between hole states with those between particle states. The latter may be called the complementary theorem [1]. In the theory of atomic spectra, for free atoms or ions Shortley [2] and Racah [3] found a complementary theorem, which can easily be generalized to weak ligand fields. For strong ligand fields a similar theorem was obtained by Griffith through a long derivation [4]. Noting that there are unitary transformations among the wavefunctions of strong, weak fields and free ions, it is a straightforward task to prove the equivalence of the complementary theorems for the previous cases, as Tang Au-chin et al. have done [1].

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In recent years some merits of the unitary group method have been manifested. The peculiarity of the method is

1) Many-particle wavefunctions with arbitrary symmetries are written as linear combinations of Gel'fand bases, the canonical bases of a unitary group.

2) Interactron operators are expressed in terms of the generators of the unitary group.

Since general, easily programmable expressions for the matrix elements of generators in the Gel'fand bases are available, this method is developing into an elegant and effective procedure for large scale CI calculations [5] as well as for ligand field theory.

The main purpose of this short note is to try to add a little more power to the unitary approach by proving a complementary theorem based on earlier work [6].

Here we will prove that

$$\langle \Psi_{R'} | \mathscr{H} | \Psi_R \rangle = K\delta_{R'R} \pm \eta \langle \Psi_{L'} | \mathscr{H} | \Psi_L \rangle, \tag{1}$$

where $\mathscr{H}$ is an interaction operator. The minus sign is taken for single particle operators and the positive sign for double particle operators. η is a phase factor which indicates the oddness or evenness of single particle operators with respect to time reversal. For an odd operator (e.g. $\hat{l}$, $\hat{s}$ etc.), $\eta = -1$, otherwise $\eta = 1$ (e.g. $\hat{l} \cdot \hat{s}$, $\hat{V}_{\text{oct}}$ etc.), but for double particle operators η is always equal to 1. In the formula (1) $\Psi_{L'}$ and Ψ_L are Gel'fand states coming from less-than-half-filled configurations (e.g. $t_2^m e^n$, $m+n \leqslant 5$) and hereafter they will be called L-Gel'fand states or L-states (see the next section); $\Psi_{R'}$ and Ψ_R are the Gel'fand states coming from the corresponding or complementary more-than-half-filled configurations (e.g. $t_2^{6-m} e^{4-n}$) and they will be called R-Gel'fand states or R-states. K is a constant for both complementary configurations. By using formula (1), we can obtain the required relations for free ions and for weak, intermediate and strong fields. Let us take the strong octahedral field as an example. In reference [6], strong field wave functions adapted with irreps of the group O are expressed as

$$\Psi(t_2^m e^n, {}^{2s+1}\Gamma M_s M a) = \sum_L a_L \Psi_L. \tag{2}$$

If we write the corresponding function in the complementary configuration as

$$\Psi(t_2^{6-m} e^{4-n}, {}^{2s+1}\Gamma M_s M a) = \sum_R a_R \Psi_R, \tag{3}$$

where

$$a_R = a_L. \tag{4}$$

From Eq. (1), then we have

$$\langle \Psi(t_2^{6-m} e^{4-n}, {}^{2s'+1}\Gamma' M_s' M' a') | \mathscr{H} | \Psi(t_2^{6-m} e^{4-n}, {}^{2s+1}\Gamma M_s M a) \rangle$$

$$= \sum_{R,R'} a_R a_{R'} \langle \Psi_{R'} | \mathscr{H} | \Psi_R \rangle$$

$$= \sum_{R,R'} a_R a_{R'}[K\delta_{RR'} \pm \eta \langle \Psi_{L'}|\mathcal{H}|\Psi_L\rangle]$$

$$= K\delta_{RR'} \pm \eta \langle \Psi(t_2^m\, e^n,\, {}^{2s'+1}\Gamma' M_s' M' a')|\mathcal{H}|\Psi(t_2^m\, e^n,\, {}^{2s+1}\Gamma M_s M a)\rangle, \quad (5)$$

which is the usual form of the complementary theorem for strong fields.

2. The Definitions of L- and R-Gel'fand States

It can be proved [7] that two irreps of the $U(n)$ (strictly $SU(n)$) group are equivalent if the Young shapes corresponding to them can be fitted together to form a rectangle, i.e.

$$[\lambda_1\lambda_2 \ldots \lambda_n] \equiv [\lambda_1 - \lambda_n, \lambda_1 - \lambda_{n-1}, \ldots, \lambda_1 - \lambda_2, 0]. \quad (6)$$

The rectangle is, say, $[1^n]$ if $\lambda_1 = 1$ or $[2^n]$ if $\lambda_1 = 2$. But here we are only interested in $[2^n]$, because it is $[2^n]$ that relates to a closed shell, and moreover there is another theorem[1] which ensures the equivalence of irreps $[1^n]$ and $[2^n]$.

The relationship between two irreps like (6) exactly represents that between the irreps of L- and R-Gel'fand states. For d orbitals the relationship gives, for example,

$$[21] \equiv [21000] \equiv [22210] \equiv [2221],$$

which means that if the Young shape for L-states is [21], the Young shape for R-states should be [2221].

Now we use Paldus tableaux to express Gel'fand states:

$$\Psi_L = \left| \begin{matrix} \cdots \\ a_i b_i c_i \\ \cdots \end{matrix} \right\rangle, \quad (7)$$

where a_i, b_i and c_i are integers representing the numbers of the entries m_{ji} which are equal to 2, 1 and 0. Exchanging a_i and c_i in every row of the tableau of Ψ_L, which is equivalent of replacing particles with holes or vice versa, we obtain

$$\Psi_{\tilde{L}} = \left| \begin{matrix} \cdots \\ c_i b_i a_i \\ \cdots \end{matrix} \right\rangle = \left| \begin{matrix} \cdots \\ a_i' b_i' c_i' \\ \cdots \end{matrix} \right\rangle, \quad (8)$$

where $a_i' = c_i$, $b_i' = b_i$ and $c_i' = a_i$ are the numbers of the entries m_{ji}' having value 2, 1 and 0 in $\Psi_{\tilde{L}}$. It is obvious that the single-particle orbitals in $\Psi_{\tilde{L}}$ are exactly complementary to those in Ψ_L in the sense that the totality of single particle orbitals in Ψ_L and $\Psi_{\tilde{L}}$ forms a closed shell. We define

$$\Psi_R = (-1)^{(\sum_{i\in\tilde{L}} i - \sum_{j\in L} j)/2}\Psi_{\tilde{L}}. \quad (9)$$

The summations in $(\sum_{i\in\tilde{L}} i)$ and $(\sum_{j\in L} j)$ are over the labels of orbitals in $\Psi_{\tilde{L}}$ and Ψ_L, respectively.

[1] $[\lambda_1\lambda_2 \ldots \lambda_n] \equiv [\lambda_1 - a, \lambda_2 - a, \ldots, \lambda_n - a]$, where a is any integer such that $\lambda_n - a \geqslant 0$.

For example,

$$\Psi_L = \begin{array}{|c|c|}\hline \xi & \eta \\ \hline \zeta & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} = \left| \begin{array}{ccc} 1 & 1 & 3 \\ 1 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{array} \right\rangle$$

$$\Psi_{\tilde{L}} = \begin{array}{|c|c|}\hline \xi & \eta \\ \hline \zeta & \theta \\ \hline \theta & \varepsilon \\ \hline \varepsilon & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} = \left| \begin{array}{ccc} 3 & 1 & 1 \\ 2 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{array} \right\rangle$$

thus

$$\begin{aligned} \Psi_R &= (-1)^{(\xi+\eta+\zeta+2\theta+2\varepsilon-\xi-\eta-\zeta)/2}\Psi_{\tilde{L}} \\ &= -\Psi_{\tilde{L}}, \end{aligned}$$

in the last step we used the convention in reference [6].

3. Lemma

$$\langle \Psi_{\tilde{L}'} | E_{ij} | \Psi_{\tilde{L}} \rangle = (-1)^{i-j+1} \langle \Psi_{L'} | E_{ji} | \Psi_L \rangle \tag{10}$$

where i and j are labels of the single particle orbitals, and E_{ij} are the generators of $U(n)$.

Proof: Let us assume that $j > i$. it can easily be verified from appendix B of reference [6] that

$$\langle \Psi_{\tilde{L}'} | E_{i,i+1} | \Psi_{\tilde{L}} \rangle = \langle \Psi_{L'} | E_{i+1,i} | \Psi_L \rangle. \tag{11}$$

Using the commutation rules for the generators of unitary group,

$$\begin{aligned} E_{i,i+2} &= [E_{i,i+1}, E_{i+1,i+2}] \\ &= [E_{i,i+1}E_{i+1,i+2} - E_{i+1,i+2}E_{i,i+1}) \end{aligned}$$

and

$$\begin{aligned} E_{i+2,i} &= [E_{i+2,i+1}, E_{i+1,i}] \\ &= -[E_{i+1,i}E_{i+2,i+1} - E_{i+2,i+1}E_{i+1,i}] \end{aligned}$$

We get

$$\begin{aligned} \langle \Psi_{\tilde{L}'} | E_{i,i+2} | \Psi_{\tilde{L}} \rangle &= \langle \Psi_{\tilde{L}'} | (E_{i,i+1}E_{i+1,i+2} - E_{i+1,i+2}E_{i,i+1}) | \Psi_{\tilde{L}} \rangle \\ &= \langle \Psi_{L'} | (E_{i+1,i}E_{i+2,i+1} - E_{i+2,i+1}E_{i+1,i}) | \Psi_L \rangle \\ &= -\langle \Psi_{L'} | E_{i+2,i} | \Psi_L \rangle. \end{aligned}$$

As a result lemma (10) is obtained by induction up to j.

4. The Proof of the Complementary Theorem

a. Single particle operators:

$$\mathscr{H}_1 = \sum_{t=1}^{N} h_t = \sum_{i,j}^{n} \langle i|h_1|j\rangle E_{ij}. \tag{12}$$

The matrix element between L-Gelfand states is

$$\langle \Psi_{L'}|\mathscr{H}_1|\Psi_L\rangle = \sum_{i,j} \langle i|h_1|j\rangle\langle \Psi_{L'}|E_{ij}|\Psi_L\rangle \tag{13}$$

it is proved in appendix A of Ref. [6] that the matrix elements of single particle operators between the Gel'fand states will vanish except when one of the states differs from the other by at most one orbital. Suppose that $\phi_i \in \Psi_L$ and $\phi_j \in \Psi_{L'}$ are the different orbitals, from the definition of complementary states and the lemma we have

$$\left\langle \underset{i\in R'}{\Psi_{R'}} \middle| E_{ij} \middle| \underset{j\in R}{\Psi_R} \right\rangle = (-1)^{-(\Sigma_{i'\in \tilde{L}'}i' - \Sigma_{j'\in L'}j' - \Sigma_{i\in \tilde{L}'}i + \Sigma_{j\in L}j)/2} \left\langle \underset{i\in \tilde{L}'}{\Psi_{\tilde{L}'}} \middle| E_{ij} \middle| \underset{j\in \tilde{L}}{\Psi_{\tilde{L}}} \right\rangle \tag{14}$$

$$= (-1)^{j-i} \left\langle \underset{i\in \tilde{L}'}{\Psi_{\tilde{L}'}} \middle| E_{ij} \middle| \underset{j\in \tilde{L}}{\Psi_{\tilde{L}}} \right\rangle$$

$$= -\left\langle \underset{j\in L'}{\Psi_{L'}} \middle| E_{ji} \middle| \underset{i\in L}{\Psi_L} \right\rangle. \tag{15}$$

Thus the non-diagonal matrix elements are

$$\langle \Psi_{R'}|\mathscr{H}_1|\Psi_R\rangle = \sum_{i,j} \langle i|h_1|j\rangle\langle \Psi_{R'}|E_{ij}|\Psi_R\rangle$$

$$= -\eta \sum_{i,j} \langle j|h_1|i\rangle\langle \Psi_{L'}|E_{ji}|\Psi_L\rangle$$

$$= -\eta\langle \Psi_{L'}|\mathscr{H}_1|\Psi_L\rangle. \tag{16}$$

to find the diagonal elements we consider

$$\langle \Psi_R|\mathscr{H}_1|\Psi_R\rangle + \langle \Psi_L|\mathscr{H}_1|\Psi_L\rangle$$

$$= \sum_i \langle i|h_1|i\rangle\langle \Psi_R|E_{ii}|\Psi_R\rangle + \sum_i \langle i|h_1|i\rangle\langle \Psi_L|E_{ii}|\Psi_L\rangle$$

$$= \sum_i \langle i|h_1|i\rangle(n_i' + n_i)$$

$$= 2\sum_i \langle i|h_1|i\rangle$$

$$= \langle [2^n]|\mathscr{H}_1|[2^n]\rangle$$

$$= K_1,$$

where n_i is the occupation number of ϕ_i in Ψ_L, $n_i'=2-n_i$ is the occupation number of ϕ_i in Ψ_R, $K_1=2\sum_i\langle i|h_1|i\rangle$ is a constant for a definite single particle operator and closed shell. The diagonal elements, therefore, become

$$\langle\Psi_R|\mathscr{H}_1|\Psi_R\rangle=K_1-\langle\Psi_L|\mathscr{H}_1|\Psi_L\rangle. \tag{17}$$

for example, for the octahedral crystal field,

$$\mathscr{H}_1=\hat{V}_{oct},\ \eta=1$$

$$K_1=2[3\times(-4Dq)+2\times 6Dq]=0,$$

$$\langle\Psi_{R'}|\hat{V}_{oct}|\Psi_R\rangle=-\langle\Psi_{L'}|\hat{V}_{oct}|\Psi_L\rangle.$$

b. Double particle operators:

$$\mathscr{H}_2=\sum_{t,u=1}^{N}h_{tu}=\tfrac{1}{2}\sum_{i,j,k,l}^{n}\langle ik|h_{12}|jl\rangle(E_{ij}E_{kl}-\delta_{kj}E_{il}). \tag{18}$$

Using the results for single particle operators discussed above it is straightforward to prove that

$$\langle\Psi_{R'}|\mathscr{H}_2|\Psi_R\rangle=\langle\Psi_{L'}|\mathscr{H}_2|\Psi_L\rangle, \tag{19}$$

which is the complementary relation for non-diagonal matrix elements between Gel'fand states. Here we only give the proof for the case in which two Gelfand states are different from each other by two orbitals. From formula (A.6) of Ref. [6], it follows that

$$\left\langle \underset{i,k\in R'}{\Psi_{R'}}\middle|\mathscr{H}_2\middle|\underset{j,l\in R}{\Psi_R}\right\rangle=\frac{1}{n_in_j}\left[\langle ik|h_{12}|jl\rangle\left\langle\underset{i,k\in R'}{\Psi_{R'}}\middle|E_{ij}E_{kl}\middle|\underset{j,l\in R}{\Psi_R}\right\rangle\right.$$
$$\left.+\langle ik|h_{12}|lj\rangle\left\langle\underset{i,k\in R'}{\Psi_{R'}}\middle|E_{il}E_{kj}\middle|\underset{j,l\in R}{\Psi_R}\right\rangle\right], \tag{20}$$

where n_i is the number of ϕ_i in $\Psi_{R'}$ and nj is the number of ϕ_j in Ψ_R. To prove formula (19), it is necessary to prove the following formulae:

$$\left\langle\underset{i,k\in R'}{\Psi_{R'}}\middle|E_{ij}E_{kl}\middle|\underset{j,l\in R}{\Psi_R}\right\rangle=\left\langle\underset{j,l\in L'}{\Psi_{L'}}\middle|E_{ji}E_{lk}\middle|\underset{i,k\in L}{\Psi_L}\right\rangle, \tag{21}$$

and

$$\left\langle\underset{i,k\in R'}{\Psi_{R'}}\middle|E_{il}E_{kj}\middle|\underset{j,l\in R}{\Psi_R}\right\rangle=\left\langle\underset{j,l\in L'}{\Psi_{L'}}\middle|E_{li}E_{jk}\middle|\underset{i,k\in L}{\Psi_L}\right\rangle. \tag{22}$$

Using Eq. (15), we have

$$\left\langle\underset{i,k\in R'}{\Psi_{R'}}\middle|E_{ij}E_{kl}\middle|\underset{j,l\in R}{\Psi_R}\right\rangle=\sum_{R''}\left\langle\underset{i\in R'}{\Psi_{R'}}\middle|E_{ij}\middle|\underset{j\in R''}{\Psi_{R''}}\right\rangle\left\langle\underset{k\in R''}{\Psi_{R''}}\middle|E_{kl}\middle|\underset{l\in R}{\Psi_R}\right\rangle$$
$$=\sum_{L''}\left\langle\underset{j\in L'}{\Psi_{L'}}\middle|E_{ji}\middle|\underset{i\in L''}{\Psi_{L''}}\right\rangle\left\langle\underset{l\in L''}{\Psi_{L''}}\middle|E_{lk}\middle|\underset{k\in L}{\Psi_L}\right\rangle$$
$$=\left\langle\underset{j,l\in L'}{\Psi_{L'}}\middle|E_{ji}E_{lk}\middle|\underset{i,k\in L}{\Psi_L}\right\rangle.$$

This is the proof for Eq. (21), and similarly for Eq. (22). Formula (19) is then proved.

Next we determine the relation between diagonal elements. We consider the difference

$$\Delta=\langle\Psi_R|\mathcal{H}_2|\Psi_R\rangle-\langle\Psi_L|\mathcal{H}_2|\Psi_L\rangle$$

$$=\frac{1}{2}\Big[\sum_{i,j}\langle ij|h_{12}|ij\rangle\langle\Psi_R|E_{ii}E_{jj}|\Psi_R\rangle$$

$$+\sum_{i,j}\langle ij|h_{12}|ji\rangle\langle\Psi_R\rangle\langle E_{ij}E_{ji}-E_{ii})|\Psi_R\rangle\Big]$$

$$-\frac{1}{2}\Big[\sum_{i,j}\langle ij|h_{12}|ij\rangle\langle\Psi_L|E_{ii}E_{jj}|\Psi_L\rangle$$

$$+\sum_{i,j}\langle ij|h_{12}|ji\rangle\langle\Psi_L|(E_{ij}E_{ji}-E_{ii})|\Psi_L\rangle\Big]$$

$$=\frac{1}{2}\Big[\sum_{i,j}\langle ij|h_{12}|ij\rangle(n_i'n_j'-n_in_j)$$

$$+\sum_{i,j}\langle ij|h_{12}|ji\rangle(-n_i'+n_j)\Big]$$

Substituting $n_i'=2-n_i$, $n_j'=2-n_j$ into the previous equation, the difference becomes

$$\Delta=\sum_{i,j}[2\langle ij|h_{12}|ij\rangle-\langle ij|h_{12}|ji\rangle]$$

$$-\sum_{i,j}(n_i+n_j)[\langle ij|h_{12}|ij\rangle-\tfrac{1}{2}\langle ij|h_{12}|ji\rangle]$$

$$=\langle[2^n]|\mathcal{H}_2|[2^n]\rangle-\sum_{i,j}n_i[2\langle ij|h_{12}|ij\rangle-\langle ij|h_{12}|ji\rangle]$$

where the first summation $\langle[2^n]|\mathcal{H}_2|[2^n]\rangle=\Sigma_{i,j}[2\langle ij|h_{12}|ij\rangle-\langle ij|h_{12}|ji\rangle]$ is the matrix element for the closed shell and is a constant, the second summation only depends on the orbitals in the L-state and is also a constant for a pair of complementary configurations. Hence the difference is a constant for a definite configuration, i.e.

$$\Delta=\langle\Psi_R|\mathcal{H}_2|\Psi_R\rangle-\langle\Psi_L|\mathcal{H}_2|\Psi_L\rangle=K_2, \tag{23}$$

or

$$\langle\Psi_R|\mathcal{H}_2|\Psi_R\rangle=K_2+\langle\Psi_L|\mathcal{H}_2|\Psi_L\rangle. \tag{24}$$

For example, if $\mathcal{H}_2=\Sigma_{t,u}1/r_{tu}$ is the electrostatic interaction, then for a strong octahedral field we find that

$$\langle[2^n]|\sum_{t,u}\frac{1}{r}|[2^n]\rangle=45A-70B+35C, \tag{25}$$

where A, B and C are the well-known Racah parameters. In deriving formula (25) we have used the reduced matrix elements given in table A26 of Ref. [4]. Furthermore, since t_2 and e electrons contribute the same to a closed shell, we find for any ϕ_i that

$$\sum_j{}' 2\langle ij|\frac{1}{r_{12}}|ij\rangle - \sum_j{}'\langle ij|\frac{1}{r_{12}}|ji\rangle + \sum\langle ii|\frac{1}{r_{12}}|ii\rangle$$
$$= 9A - 14B + 7C, \tag{26}$$

where dashes mean that in the sum $j = i$ is ruled out. Replacing K_2 in Eq. (24) with Eqs. (25) and (26), we get

$$\langle\Psi_{R'}|\sum_{t,u}\frac{1}{r_{tu}}|\Psi_R\rangle = (5-N)(9A - 14B + 7C)\delta_{R'R}$$
$$+\langle\Psi_{L'}|\sum_{t,u}\frac{1}{r_{tu}}|\Psi_L\rangle. \tag{27}$$

where N = the electron number in Ψ_L.

Finally combining Eqs. (16), (17), (19) and (24), we obtain formula (1), completing the proof.

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References

1. Tang Au-chin et al.: Scientianium Naturalium (Kirin University) **1**, 59 (1965)
2. Condon, E. U., Shortley, G. H.: The Theory of atomic spectra. Cambridge: University Press 1951
3. Racah, G.: Phys. Rev. **63**, 367 (1943)
4. Griffith, J. S.: The theory of transition–metal ions. Cambridge: University Press 1961
5. Paldus, J.: J. Chem. Phys. **61**, 5321 (1974); Int. J. Quantum Chem. **S9**, 165 (1975); Sarma, C. R., Rettrup, S.: Theoret. Chim. Acta (Berl.) **46**, 63 (1977)
6. Wen Zhen-yi: Acta Physica Sinica **28**, 88 (1979)
7. Judd, B. R.: Operator techniques in atomic spectroscopy. New York: McGraw-Hill 1962

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