A Unitary Group Approach to Strong Icosahedral Crystal Field

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Abstract: A general treatment of f electrons in a strong icosahedral crystal field in endohedral fullerenes is given using the unitary group approach. This approach shows the convenience of unitary group approach over the conventional Racah method.

Key Words: Icosahedral Field, Unitary Group, Strong Crystal Field, F-electrons, Endohedral fullerenes.

1. INTRODUCTION

Since the discovery of the first fullerenes in 1985 [1], the fullerene, C_{60}, cages have been the focus of attention for both experimentalists and theorists. Endohedral metallofullerenes which have atoms inside the C_{60} cage have attracted wide attention due to their properties such as magnetic and possible superconducting behaviour. La was the first atom trapped in a C_{60} cage [2]. Polonium is the biggest atom which can be embed into this cage [3]. The case of polonium suggests that rare earth elements can be placed at the centre of the cage.

C_{60} molecule is a cage-like structure belonging to the icosahedral symmetry [4-5]. The unitary group approach is a well established method for the treatment of many particle systems [6-8]. The convenience of the unitary group method for analytical calculations for octahedral crystal fields has already been established [9-10].

Zeroth order many electron wave function in a strong crystal field can be written as:

$|(\gamma_1)^{N}{}_1 \ldots\ldots (\gamma_i)^{N}{}_i\ ;\ {}^{2S+1}\Gamma M\ M_S\ \alpha >$, where $(\gamma_1)^{N}{}_1 \ldots\ldots (\gamma_i)^{N}{}_i$ is a strong field configuration, M_S is the z component of the total spin, ${}^{2S+1}\Gamma M$ represents a term belonging to the M component of the irreducible representation Γ, N_i are the number of particles under consideration and α can be an additional index which fully specifies the strong crystal field state. The symmetry adapted wave functions can be expressed in terms of linear combinations of Gel'fand basis functions as represented by Young Tableau. The tableau basis was derived from the sub group chain of U(2n), where n is the number of independent single particle wave functions. For a particular symmetry group chain is given by

$$U(2n) \supset U(2) \times U(n)$$

In the unitary group method, wave functions are expanded in Gel'fand bases, the canonical bases of the infinitesimal representations for the unitary group as follows:

$$|(\gamma_1)^{N}{}_1 \ldots\ldots (\gamma_i)^{N}{}_i\ ;\ {}^{2S+1}\Gamma M\ \alpha > = |(\gamma_1)^{N}{}_1 \ldots\ldots (\gamma_i)^{N}{}_i\ ;\ [\lambda]\ \Gamma M\ \alpha >$$

$$= \Sigma_\rho\ |[\lambda]\ \rho > < [\lambda]\ \rho\ |[\lambda]\ \Gamma M\ \alpha >$$

here $[\lambda]$ labels the particular irreducible representation of U(n) and ρ is the Gel'fand tableau.

The production of symmetry adapted wave functions is the most interesting aspect of the unitary group approach. Once the wave functions are known, the evaluation of matrix elements of the Hamiltonian can be performed in a number of ways [11-13].

2. ICOSAHEDRAL CRYSTAL FIELD

In this paper, we treat the case of f electrons in a strong crystal field of icosahedral symmetry [14-15]. The seven f orbitals, $|3m>$, m = -3, -2, -1, 0, 1, 2, 3 transform under the symmetry operations of Icosahedral group according to the irreducible representations g and t_2. It is convenient to label the following linear combinations as the basis functions for g and t_2 irreducible representation

$$|A> = g_1 = (3/5)^{1/2}\, Y_{3,3} + (2/5)^{1/2}\, Y_{3,-2}$$

$$|B> = g_2 = Y_{3,-1}$$

$$|C> = g_3 = Y_{3,1}$$

$$|D> = g_4 = -(3/5)^{1/2}\, Y_{3,3} + (2/5)^{1/2}\, Y_{3,-2}$$

and for T_2 we get

$$|E> = t_{21} = -(2/5)^{1/2}\, Y3,-3 + (3/5)^{1/2}\, Y_{3,2}$$

$$|F> = t_{22} = Y_{3,0}$$

$$|G> = t_{23} = (2/5)^{1/2}\, Y_{3,3} + (3/5)^{1/2}\, Y_{3,-2}$$

It is assumed that the z axis is passing though the two vertices along which five fold axes are defined [15].The three fold axes join the centers of two opposite faces, while the two fold axes join the mid points of two opposite edges.

It can be seen that the R(3) based symmetry operations of the icosahedral group manifest themselves in U(n) as a set of permutation operators expressible in terms of the generators of the group U(n). The creation (a_A)* and annihilation (a_A)

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0250-5363/08

operators can be treated through unitary group algebra and the young tableaux.

3. THE F^2 CONFIGURATION

When an atom or ion with two electrons in the f-orbital is placed in a crystal field of icosahedral symmetry, the expected crystal field configurations are: g^2, $g^1 t_2^1$ and t_2^2. It is expected that the ground state configuration will be g^2 with two electrons in the orbital g with lower energy. The total number of states for all three states is 91. The unitary group approach in crystal field theory depends on the sub group chain of U(2n), where n is the number of independent single particle states. For f shell electrons, n = 7, so the group chain will be

$$U(14) \supset U(2) \otimes U(7)$$

Above equation implies a set of 14 single particle spin orbitals. The final subgroup chain for the system of two f electrons in a strong icosahedral crystal field will look like

$$U(14) \supset U(2) \otimes U(7) \supset U(2) \otimes [\, U(4) \oplus U(3) \supset R(4) \oplus R(3) \supset I \,]$$

The spin orbital and creation operators transform like covariant tensor of rank one under unitary transformation. If $|\, i >$ are degenerate, g or t_2 type, orbitals and $|\, \sigma >$ ($\sigma = \pm$ ½) denotes spin part of the wave function, then it can be proved that $E_{i,\sigma}^{j\upsilon} = (a_{A,\sigma})^* (a^{j,\upsilon})$ satisfy the commutation relations

$$[\, E_{i,\sigma}^{j,\upsilon} , E_{k,\sigma'}^{l,\upsilon'} \,] = \delta_{jk}\, \delta_{\upsilon,\sigma'} E_{i,\sigma}^{l,\upsilon'} - \delta_{il}\, \delta_{\sigma,\upsilon'} E_{k,\sigma'}^{j,\upsilon}$$

On contraction, one gets the following

$$E_i^j = \Sigma_\sigma E_{i,\sigma}^{j,\sigma} \text{ and } E_\sigma^{\ \upsilon} = \Sigma_i E_{i,\sigma}^{i,\upsilon}$$

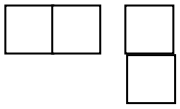
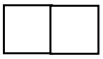
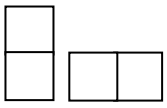
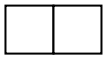
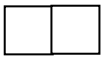
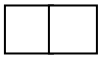
Which finally satisfy the relation given below

$$[\, E_i^j , E_k^{\ l} \,] = \delta_{jk} E_i^{\ l} - \delta_{il} E_k^{\ j} \text{ and } [\, E_\sigma^{\ \upsilon} , E_{\sigma'}^{\ \upsilon'} \,] = \delta_{\upsilon\sigma'} E_\sigma^{\ \upsilon'} - \delta_{\sigma\upsilon'} E_{\sigma'}^{\ \upsilon}$$

$E_{i,\sigma}^{j\upsilon}$, E_i^j and $E_\sigma^{\ \upsilon}$ are the infinitesimal operators for U(14), U(7) and U(2). All possible wave functions and their labeling for strong icosahedral crystal field are given in Table **1**. The numbers below the irreducible representations are the dimensions.

It is known that each point group is isomorphic to a subgroup of permutation group. It has been established that the icosahedral point group, I_h , is isomorphic to an

Table 1. Classification of f^2 *Strong Field States*

U(14)	U(2) × U(7)	U(4) ⊕ U(3)	R(4) + R(3)	R(4) → R(3)	R(3)	*I*
			(2) × (0) 5 1	(2) → (1),(1)	(1),(1)	$^3T_1$, $^3T_2$
$[1^2]$ 91	$[2] \times [1^2]$ 3 21	$[1^2] \times [0]$ 6 1	(0) × (0) 1 1	———	———	———
		$[1] \times [1]$ 4 3	(3/2) × (1) 4 3	(3/2) → (1),(1/2),(0)	(2),(3/2),(1)	^3H, ^3G, $^3T_2$
		$[0] \times [1^2]$ 1 3	(0) × (1) 1 3	———	(1)	$^3T_2$
			(3) × (0) 7 1	(3) → (2),(3/2)	(2),(3/2)	^1G, ^1H
		$[1] \times [0]$ 10 1	(1) × (0) 3 1	(1) → (0)	(0)	^1A
	$[1^2] \times [2]$ 1 28		(3/2) × (1) 4 3	(3/2) → (1),(1/2),(0)	(2),(3/2),(1)	^1H, ^1G, $^1T_2$
			(0) × (2) 1 5	———	(2)	^1H
		$[0] \times [2]$ 1 6	(0) × (0) 1 1	———	(1)	^1A

alternating group A_5, which is a sub group of S_{12}. The wave functions adapted to the chain mentioned above should be concisely denoted by $\left| g^{N1}\, t_2^{N2}; [\,\lambda\,]\, \Gamma\, M\, \alpha \right>$ in the Gel'fand basis of U(7), here N1 and N2 are the number of electrons in strong crystal field states g and t_2 of icosahedral group.

In general, a strong crystal field Hamiltonian contains crystal field perturbation, H_{cr}, the electrostatic interaction, H_{el} and the spin orbit interaction, H_{so}. The matrices for strong crystal field Hamiltonian are diagonal and they can be treated directly

$$< g^{N1}\, t_2^{N2} ; [\,\lambda\,]'\, M'\, \Gamma'\, \alpha' \mid H_{cr} \mid g^{N1}\, t_2^{N2} ; [\,\lambda\,]\, \Gamma\, M\, \alpha >$$

$$= \delta_{ij}\, \delta_{[\lambda][\lambda]'}\, \delta_{\Gamma\Gamma'}\, \delta_{MM'}\, \Sigma_{i,j}\, \Sigma_{\rho\rho'} < [\lambda]'\, \Gamma'\, M'\, \rho \mid [\lambda]\rho' > x$$

$$< [\lambda]\, \rho \mid [\lambda]\, \Gamma\, M\, \alpha > < i \mid V_{icosahedral} \mid j > < [\lambda]'\, \rho' \mid E_{ij} \mid [\lambda]\, \rho >$$

$$= \Sigma_i\, \Sigma_\rho \{ < [\lambda]\, \Gamma\, M\, \alpha \mid [\lambda]\, \rho > \}^2 < i \mid V_{icosahedral} \mid i > < [\lambda]\, \rho \mid E_{ii} \mid [\lambda]\, \rho >$$

The electrostatic interaction matrix elements are given by

$$< g^{N1}\, t_2^{N2} ; [\,\lambda\,]'\, M'\, \Gamma'\, \alpha' \mid H_{cr} \mid g^{N1}\, t_2^{N2} ; [\,\lambda\,]\, \Gamma\, M\, \alpha >$$

$$= (1/2)\, \Sigma_{\rho,\rho'}\, \Sigma_{i,j,k,l} ; [\lambda]\, \Gamma'\, M'\, \alpha' \mid [\lambda]\, \rho' > < [\lambda]\, \rho \mid [\lambda]\, \Gamma\, M\, \alpha > x$$

$$< ij \mid 1/r_{12} \mid kl > < [\lambda]\, \rho' \mid (E_{ik} - E_{jl} - \delta_{jk}\, E_{il}) \mid [\lambda]\, \rho >$$

Here i, j, k and l are single electron orbitals.

Spin orbit coupling matrix elements can be calculated in terms of the Gel'fand states of U(14). The calculation of these matrix elements has been discussed by many authors [16-17]

4. SUMMARY

Classification of symmetrized wave functions in a many electron system is the most important step towards the understanding of atomic and molecular properties. The unitary group approach to many body systems proved to be particularly useful for electronic and molecular systems, in which case at most two column representations of the unitary group U(n) are required.

We have presented an elegant way of treating the strong crystal field of icosahedral symmetry though unitary group approach. Endohedral fullerenes doped with f electron ions are obvious candidates for magnetic and superconducting properties. It requires the calculation of matrix elements of product of operators and work related to this matter is in progress.

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