RACAH RECOUPLING MATRICES
FOR SYSTEM OF TWO FREE ELECTRONS
CONFINED TO SINGLE STAR

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Racah–Wigner type of calculus is adapted to the system of two free electrons in a cubic box, confined to a single star $p00$ of quasimomentum. Various coupling schemes (LS-like, jj-like, and transitive) have been reviewed in analogy to the case of a free atom. Racah recoupling matrices are calculated explicitly, and their quantum-mechanical meaning is exposed in terms of octahedral multipoles.

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1. Introduction

We observe recently an increasing interest in electronic properties of systems with a finite number of electrons, like nanometer-scale magnets [1], quantum dots [2], quantum Hall effect [3], or high temperature superconductivity [4]. Finite volume of such systems, and small number of electrons, justify a Racah–Wigner type of approach which has proved to be successful in the case of free atoms or ions [5]. It becomes interesting to establish conservation laws, good quantum numbers, classification of states, determination of energy level structure, selection rules etc. for various standard model systems, like free, bound, or itinerant electrons in finite cavities with different geometries. It encourages us to attempt to an adaptation of standard techniques of Racah–Wigner calculus to such extended N-electronic systems [6]. In this spirit, we examine in the present paper the particular notion of Racah recoupling matrices [7] (or their symmetrized version, usually referred to as the $3nj$-symbols), within the model of free electrons in a periodic cubic box. We restrict the considerations to a simple case of $N = 2$ electrons, which are confined to a single star $(p00)$ of quasimomentum. In due course we expose analogies with the theory of atomic spectra.

2. Electronic spaces

a) The single-electron space has the form

$$L = B \otimes W, \tag{1}$$

where

$$B = \mathrm{lc}_{\mathcal{C}}\, \varphi \tag{2}$$

is the positional space, spanned on an orthonormal basis labelled by arms of the star of quasimomentum

$$\varphi = \{|\pm p, 0, 0\rangle, |0, \pm p, 0\rangle, |0, 0, \pm p\rangle\}, \tag{3}$$

where $|n_x, n_y, n_z\rangle$, $n_x, n_y, n_z \in Z$, denotes the orbital with the quasimomentum $k = (2\pi/L)(n_x, n_y, n_z)$, Z is the ring of integers, L is the length of an edge of the cube,

$$W = \mathrm{lc}_{\mathcal{C}}\{m_s = \pm 1/2\} \tag{4}$$

is the spin space of a single electron, and the symbol $\mathrm{lc}_{\mathcal{C}}$ denotes the linear closure, i.e. the space over the field $\mathcal{C}$ of complex numbers, spanned on an appropriate set of states. The atomic counterpart of (1) consists in factorization of single-electron shell spaces to orbital and spin factors. In our case,

$$\dim L = \dim B \cdot \dim W = 6 \cdot 2 = 12. \tag{5}$$

We observe that our orbital analogue — the positional space B is 6-dimensional, which is intermediate between atomic d and f electrons (with the dimension $2l + 1 = 5$ and 7, respectively).

b) The two-electron space is determined by the Pauli exclusion principle, which yields that it is the antisymmetric square $L^{\{1^2\}}$ of the space L. Taking into account the factorization (1), we obtain

$$L^{\{1^2\}} = (B \otimes W)^{\{1^2\}} \approx B^{1^{\{2\}}} \otimes W^{\{2\}} \oplus B^{\{2\}} \otimes W^{\{1^2\}}, \tag{6}$$

where the first and the second term in the right hand side of (6) corresponds to triplet ($S = 1$) and singlet ($S = 0$) pairing, respectively. The dimensional check reads

$$\dim L^{\{1^2\}} = 15 \cdot 3 + 21 \cdot 1 = 66 = \binom{12}{2}, \tag{7}$$

i.e. the triplet and singlet manifold exhibits 15- and 21-fold orbital degeneracy, respectively. The atomic counterpart of (7) is

$$10 \cdot 3 + 15 \cdot 1 = 45 = \binom{10}{2}, \tag{8}$$

and

$$21 \cdot 3 + 28 \cdot 1 = 91 = \binom{14}{2}, \tag{9}$$

for d^2 and f^2 configurations, respectively.

3. Coupling schemes

The factorization (1) of the single-electron space L into the positional and spin factor spaces yields the same variety of possibilities of multiple couplings in construction of many-electron spaces as in the case of Wigner–Racah calculus for atoms. They involve $3j$, $6j$ and higher order symbols, coefficients of fractional parentage, etc. We demonstrate here only the simplest case of two electrons.

The positional space B is the carrier of a representation R of the symmetry group G of the box, which we assume hereafter to be the octahedral group O_h. In the case of a single star φ, this is the transitive representation $R^{O_h:C_{4v}}$, with C_{4v} being the stabilizer of a single arm of the star (3). The corresponding decomposition

$$B = \sum_{\lambda \in \tilde{O}_h, t \in \tilde{m}(R,\Lambda)} \oplus B^{\Lambda t} \tag{10}$$

of the positional space B into irreducible subspaces $B^{\Lambda t}$ points out the role of irreducible representations (irreps) $\Lambda \in \tilde{O}_h$ as analogs of the single-electron orbital angular momentum quantum number l. Here $\tilde{O}_h$ denotes the set of equivalence classes of irreps of O_h, which in the Mulliken notation reads

$$\tilde{O}_h = \{A_{1g}, A_{1u}, A_{2g}, A_{2u}, E_g, E_u, T_{1g}, T_{1u}, T_{2g}, T_{2u}\}, \tag{11}$$

and $\tilde{m}(R, \Lambda) = \{t = 1, \ldots m(R, \Lambda)\}$ is the set of repetition labels for multiplicity $m(R, \Lambda)$ of Λ in R. In our case

$$R^{O_h:C_{4v}} \approx A_{1g} \oplus E_g \oplus T_{1u}, \tag{12}$$

so that the repetition label t is redundant. The scheme defined by the basis

$$|\Lambda_1 \Lambda_2 \Lambda \lambda, S, \Gamma\gamma\rangle \tag{13}$$

corresponds to atomic LS coupling for two electrons. The irrep Λ, which emerges from the Clebsch–Gordan decomposition

$$\Lambda_1 \otimes \Lambda_2 = \sum_{\Lambda \in \tilde{O}_h} \oplus m(\lambda_1 \otimes \Lambda_2, \Lambda)\Lambda \tag{14}$$

of single-electron orbitals Λ_1 and Λ_2, is the analogue of atomic orbital quantum number L, S is the same as for atoms ($S = 1$ and 0 for spin triplets and singlets, respectively), Γ corresponds to the total angular momentum J and arises from

$$\Lambda_1 \otimes \Delta = \sum_{\Gamma \in \tilde{O}_h} \oplus m(\Lambda_1 \otimes \Delta, \Gamma)\Gamma, \tag{15}$$

where Δ is an irrep of O_h corresponding to S ($\Delta = A_{1g}$ and T_{1g} for $S = 0$ and 1, respectively), and $\gamma \in \tilde{\Gamma}$ is the degenerate basis of Γ, i.e. the counterpart of the z-projection M_J of the total angular momentum J. Equation (12) can be also interpreted in terms of multipole expansion of plane waves. Six plane waves, labelled by arms of the star φ can be rearranged into cubic partial waves, labelled by irreps Λ entering (12). $\Lambda = A_{1g}, E_g$, and T_{1u} is the cubic counterpart of a monopole ($l = 0$), quadrupole ($l = 2$) and dipole ($l = 1$), with l denoting the rank of the parent spherical multipole. Correspondingly, Eq. (14) describes a superposition

of single-electron cubic partial waves Λ_1 and Λ_2 into the resultant cubic multipole Λ. Another scheme, namely

$$|\Lambda_1 \Gamma_1, \Lambda_2 \Gamma_2, \Gamma w \gamma\rangle \tag{16}$$

corresponds to atomic j-j coupling. Here, the octahedral group O_h should be replaced by its double group O'_h. We have

$$\tilde{O}'_h = \tilde{O}_h \cup \{E'_g, E'_u, E''_g, E''_u, U'_g, U'_u\}, \tag{17}$$

where the last set in the right-hand side of (17) corresponds to spinor irreps. The label w distinguishes repeated irreps in the Clebsh–Gordan series for O'_h.

A distinctive feature of our approach consists in a fact that the symmetry group O_h acts in the positional space B essentially as a permutation representation on the set φ of arms of a star. An explanation of this fact in the midst of Racah–Wigner calculus relies on the Mackey theorem for transitive representations [8]. It allows a new coupling, called the transitive scheme, which is not present in the atomic case.

The Mackey theorem consists in the decomposition of the direct product of two constituent transitive representations into resultant transitive representations. The general formula is

$$R^{G:H} \otimes R^{G:D} = \sum_{\omega \in \Omega} R^{G:L_\omega}, \tag{18}$$

where H, D and L_ω are stabilizers of the first and second constituent, and resultant representation, respectively, Ω is the set of double cosets of the group G with respect to its subgroups D and H, defined by the decomposition

$$G = \bigcup_{\omega \in \Omega} D g_\omega H \tag{19}$$

with representatives g_ω, and the stabilizer L_ω is given by the intersection

$$L_\omega = D \bigcap g_\omega H g_\omega^{-1}. \tag{20}$$

Mackey theorem is a transitive analogue of coupling of two angular momenta. In our case the Mackey theorem reads

$$R^{O_h:C_{4v}} \otimes R^{O_h:C_{4v}} = 2R^{O_h:C_{4v}} + R^{O_h:C_{1h}}, \tag{21}$$

which corresponds to the direct product of the action of O_h on the star φ. Pairs of arms of the form $(k, k), (k, k')$ with $k' \neq \pm k$, and $(k, -k)$, $k, k' \in \varphi$, correspond respectively to the orbit $\omega = 0, 1$, and 2 of the resultant transitive representation in the right-hand side of Eq. (21). The orbits $\omega = 0$ and $\omega = 2$ are characterized by the stabilizer C_{4v}, whereas the orbit $\omega = 1$ corresponds to C_{1h}. The transitive scheme is of the form

$$|\omega \Lambda a \lambda, SM\rangle, \tag{22}$$

where $\Lambda \in \tilde{O}_h$ is an irrep entering the resultant transitive representation $R^{O_h:L_\omega}$, and $a \in \tilde{m}(\omega, \Lambda)$ is the corresponding repetition label.

The label ω of the resultant transitive representations in Eq. (21) has a clear kinematical meaning: orbits $\omega = 0, 1$, and 2 gather pairs of momenta which are mutually parallel, perpendicular, and antiparallel, respectively. Each orbit ω gives rise to some irreps Λ corresponding to appropriate octahedral partial waves.

In order to complete the classification scheme, we need to point out restrictions imposed on each coupling scheme by the Pauli exclusion principle. It requires that the two-electron basis states should be antisymmetric under the transposition of electrons, i.e. they should be characterised by the irrep $\{1^2\}$ of the symmetric group Σ_2 acting on electrons. This restriction can be incorporated within each of the coupling schemes (13), (16), and (22).

The statistics y_S of the spin part is

$$y_S = \begin{cases} \{2\} & \text{for } S = 1, \\ \{1^2\} & \text{for } S = 0. \end{cases} \tag{23}$$

To determine the statistics y_0 of the orbital part in schemes (13) and (16), we have to consider two cases: (i) $\Lambda_1 \neq \Lambda_2$, and (ii) $\Lambda_1 = \Lambda_2$. In the former case the definite orbital statistics is established by putting

$$|y_0 \Lambda_1 \Lambda_2 \alpha\rangle = 2^{-1/2}(|\Lambda_1 \Lambda_2 \alpha\rangle \pm |\Lambda_2 \Lambda_1 \alpha\rangle), \tag{24}$$

which yields $y_0 = \{2\}$ and $\{1^2\}$ for the upper and lower sign in (24), respectively. In the latter case the statistics y_0 is given by the unique decomposition

$$\Lambda_1 \otimes \Lambda_1 = \Lambda_1^{\{2\}} \oplus \Lambda^{\{1^2\}} \tag{25}$$

of the square of the irrep Λ_1 into the symmetric and antisymmetric parts, e.g.

$$T_{2u} \otimes T_{2u} = T_{2u}{}^{\{2\}} \oplus T_{2u}^{\{1^2\}} \tag{26}$$

with

$$T_{2u}^{\{2\}} = A_{1g} \oplus E_g \oplus T_{2u}, \quad T_{2u}^{\{1^2\}} = T_{1g}. \tag{27}$$

The total statistics y is given by

$$y = y_0 y_S = \begin{cases} \{2\} & \text{for } y_0 = y_{S'}, \\ \{1^2\} & \text{for } y_0 \neq y_{S'}. \end{cases} \tag{28}$$

The Pauli exclusion principle admits only those states for which

$$y = \{1^2\}. \tag{29}$$

Statistics of the orbital part in the transitive scheme is determined as follows (cf. [9] for details of the orbit structure of the groups O_h and Σ_2)

$$(R^{O_h:C_{4v}})_{\omega=0} = (R^{O_h:C_{4v}})_{\omega=0}^{\{2\}} \approx A_{1g} \oplus E_g \oplus T_{1u}, \tag{30}$$

$$(R^{O_h:C_{1h}})_{\omega=1}^{\{2\}} \approx A_{1g} \oplus E_g \oplus T_{1u} \oplus T_{2u} \oplus T_{2g}, \tag{31}$$

$$(R^{O_h:C_{1h}})_{\omega=1}^{\{1^2\}} \approx A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{1u} \oplus T_{2u}, \tag{32}$$

$$(R^{O_h:C_{4v}})_{\omega=2}^{\{2\}} \approx A_{1g} \oplus E_g, \tag{33}$$

$$(R^{O_h:C_{4v}})_{\omega=2}^{\{1^2\}} \approx T_{1u}. \tag{34}$$

It is worthwhile to observe that for repeated irreps entering $R^{O_h:C_{1h}}$ (i.e. for $\Lambda = E_g, T_{1u}$ and T_{2u}) the definite statistics y_0 is achieved by an appropriate choice of the repetition label $a \in \tilde{m}(\omega, \Lambda)$. Note also that the transitive representations $(R^{O_h:C_{4v}})_\omega$ for $\omega = 0$ and 2 are isomorphic with respect to the geometric symmetry group O_h, but are inequivalent with respect to the Pauli group Σ_2 (cf. Eq. (30) with (33), (34)). The source of this difference is the fact that the orbits $\omega = 0$ and $\omega = 2$ consist of pairs of arms (k, k) and $(k, -k)$, respectively, which yields the same geometric symmetry and distinction in statistics.

4. Racah recoupling matrices

Each of coupling schemes introduced in the previous section, namely LS-like scheme (13), jj-like (16), and transitive (22), provides a complete orthonormal basis for the space of two-electron states of the considered model. Racah recoupling matrices provide an appropriate unitary transformation between any pair of these bases. We consider here only transformations between orbital parts of the two-electron wave functions in the LS-like and transitive schemes, and choose each basis as adopted to the Pauli group Σ_2 (i.e. each basis vector has a definite orbital statistics y_0). The Racah recoupling matrix is defined by the formula

$$\langle y_0 \omega \Lambda a \lambda | y_0' \Lambda_1 \Lambda_2 \Lambda' \lambda' \rangle = \delta_{y_0 y_0'} \delta_{\Lambda \Lambda'} \delta_{\lambda \lambda'} [\omega a \| \Lambda y_0 \| \Lambda_1 \Lambda_2], \qquad (35)$$

which results from an elementary representation theory of groups (the Schur lemma for the geometric symmetry group O_h and the Pauli group Σ_2). This formula states that elements of the transformation matrix are diagonal with respect to irreps y_0 and Λ of the Pauli Σ_2 and geometric symmetry O_h group, respectively, and is independent of a choice of basis states λ for the irrep Λ. The symbols $[\omega a \| \Lambda y_0 \| \Lambda_1 \Lambda_2]$ form a unitary matrix labelled by Λy_0, with rows and columns

TABLE

Racah matrices $[\omega_a \| \Lambda y_0 \| \Lambda_1 \Lambda_2]$ for the system of two electrons on a single star $p00$. One-dimensional matrices are omitted here — they are given by Eq. (36).

a) spin singlets ($y_0 = \{2\}$):

A_{1g}	$\{2\}$	$A_{1g}A_{1g}$	$E_g E_g$	$T_{1u}T_{1u}$
0	–	$2/\sqrt{6}$	$-1/\sqrt{3}$	0
1	–	$1/\sqrt{6}$	$1/\sqrt{3}$	$-1/\sqrt{2}$
2	–	$1/\sqrt{6}$	$1/\sqrt{3}$	$1/\sqrt{2}$

E_g	$\{2\}$	$A_{1g}E_{1g}$	$E_g E_g$	$T_{1u}T_{1u}$
0	–	$-1/\sqrt{3}$	$-2/\sqrt{6}$	0
1	1	$1/\sqrt{3}$	$-1/\sqrt{6}$	$1/\sqrt{2}$
2	–	$1/\sqrt{3}$	$-1/\sqrt{6}$	$-1/\sqrt{2}$

T_{1u}	$\{2\}$	$A_{1g}T_{1u}$	$E_g T_{1u}$
0	–	$2/\sqrt{6}$	$-1/\sqrt{3}$
1	1	$1/\sqrt{3}$	$2/\sqrt{6}$

b) spin triplet ($y_0 = \{1^2\}$):

T_{1u}	$\{1^2\}$	$A_{1g}T_{1u}$	$E_g T_{1u}$
1	2	$-2/\sqrt{6}$	$1/\sqrt{3}$
2	–	$-1/\sqrt{3}$	$-2/\sqrt{6}$

labelled by ωa (the transitive scheme), and $\Lambda_1 \Lambda_2$ (the LS-like scheme), respectively.

We present here the complete set of Racah matrices for the system of two electrons on a single star $p00$. The one-dimensional Racah matrices are given by the formula

$$-[1 \| T_{2g}, \{2\} \| T_{1u} T_{1u}] = [1 \| T_{2u}, \{2\} \| E_g T_{1u}] = [1 \| A_{2g}, \{1^2\} \| E_g E_g]$$

$$= -[1, 2 \| E_g, \{1^2\} \| A_{1g} E_g] = -[1 \| T_{1g}, \{1^2\} \| T_{1u} T_{1u}]$$

$$= [1, 2 \| T_{2u}, \{1^2\} \| E_g T_{1u}] = 1, \tag{36}$$

where all redundant a labels are omitted. The multidimensional Racah matrices are collected in Table.

5. Discussion

We have presented here various coupling schemes and recoupling transformations for the system of two electrons confined to a single star $(p00)$, in a way similar to Racah–Wigner calculus for multielectron atoms. In particular, we calculated a complete set of Racah recoupling matrices between the LS-like and transitive schemes of two-electron basis states. We pointed out natural interpretations of both schemes in terms of multipole expansions and corresponding octahedral counterparts of partial waves. It follows that our model with the star $(p00)$ involves the monopole $\Lambda = A_{1g}$, the quadrupole $\Lambda = E_g$ and the dipole $\Lambda = T_{1u}$ at the single-electron level, and extends to another quadrupole $\Lambda = T_{2g}$ and octupoles $\Lambda = A_{2g}$ and $\Lambda = T_{2u}$ for the case of two electrons. Clearly, Wigner spherical multipoles become undistinguishable after subduction to the octahedral symmetry O_h, e.g. the same label $\Lambda = T_{1u}$ corresponds to cubic dipoles (from $l = 1$) and octupoles (from $l = 3$).

The tables of Racah matrices provide a transparent way of comparison of basis states within the LS and transitive coupling schemes. Each table corresponds to adequate octahedral harmonic (partial wave) Λ for the two-electron system, with an appropriate orbital statistics $y_0 = \{2\}$ or $\{1^2\}$ (for spin singlets $S = 0$ and triplets $S = 1$, respectively). For example, generic quadrupole $\Lambda = E_g$ for spin singlets is a superposition of 3 basis states $\Lambda_1 \Lambda_2 = A_{1g} E_g, E_g E_g, T_{1u} T_{1u}$ for the LS case, and $\omega = 1, 2, 3$ for the transitive scheme, the same quadrupole for spin triplets is uniquely determined by a single basis state ($\Lambda_1 \Lambda_2 = A_{1g} E_g$, or $\omega = 1$, both cases restricted to the antisymmetric basis $y_0 = \{1^2\}$), the octupole $\Lambda = T_{2u}$ is uniquely defined for both the singlet and triplet cases, the quadrupole $\Lambda = T_{2g}$ exists (and is unique) for singlets only, whereas the octupole $\Lambda = A_{2g}$ arises only for triplets, etc. Racah matrices allow us also to draw some conclusions on motion of the system in a state with definite resultant octahedral harmonic Λ. E.g. $\Lambda = A_{1g}$, i.e. the octahedral counterpart of completely symmetric spherical s-wave is in general a superposition of three LS basis states $\Lambda_1 \Lambda_2 = A_{1g} A_{1g}, E_g E_g$, and $T_{1u} T_{1u}$. In turn, the states $\Lambda_1 \Lambda_2$ are superpositions of orbits $\omega = 0, 1$, and 2 of the transitive scheme, thus the LS state $A_{1g} A_{1g}$ is dominated by the orbit $\omega = 0$ (with the probability 2/3), the state $E_g E_g$ is characterised by equal probabilities 1/3 from each orbit, whereas the state $T_{1u} T_{1u}$ is composed only from orbits $\omega = 1$ and

$\omega = 2$, with the exclusion of the diagonal orbit $\omega = 0$. Similarly, octahedral harmonics $\Lambda = T_{2g}, T_{2u}$ for $y_0 = \{2\}$ and $A_{2g}, E_g, T_{1g}, T_{2u}$ for $y_0 = \{1^2\}$ emerge from the single orbit $\omega = 1$ and thus correspond to a motion in which momenta of each electron are mutually perpendicular, whereas all other harmonics admit a superposition of states with single-electron momenta being parallel or antiparallel.

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