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To cite this version:

Coraline Letouzé, Guillaume Radtke, Benjamin Lenz, Christian Brouder. Parametrization of the Coulomb interaction matrix with point-group symmetry. Physical Review B, 2023, 108 (11), pp.115137. 10.1103/PhysRevB.108.115137 . hal-04046322v2

HAL Id: hal-04046322

https://hal.science/hal-04046322v2

Submitted on 26 Sep 2023

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Parametrization of the Coulomb interaction matrix with point-group symmetry

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(Dated: August 1, 2023)

Coulomb integrals, i.e. matrix elements of bare or screened Coulomb interaction between one-electron orbitals, are fundamental objects in many approaches developed to tackle the challenging problem of calculating the electronic structure of strongly correlated materials. In this paper, Coulomb integrals are analyzed by considering both the point group symmetry of the site occupied by the atom in the crystal or molecule and the permutation symmetries of the orbitals in the integrals. In particular, the case where one-electron orbitals form the basis of a general (i.e. a real, complex or pseudo-real) irreducible representation is considered. Explicit formulas are provided to calculate all integrals of the interaction tensor in terms of a minimum set of independent ones. The effect of a symmetry breaking is also investigated by describing Coulomb integrals of a group in terms of those of one of its subgroups. We develope the specific example of $O(3)$ as the larger group which can therefore be used to quantify the deviation of a specific system from the spherical symmetry. Possible applications of the presented framework include the calculation of solid-state and molecular spectroscopies via multiplet techniques, dynamical mean-field theory or the GW approximation.

I. INTRODUCTION

Electronic correlations play a fundamental role in determining the properties of compounds with partially filled d- or f-shells. Strong Coulomb interactions occuring between electrons occupying these localized orbitals are indeed among the most important parameters favouring, for instance, a particular ground-state symmetry of the ions. Thus, they determine their magnetic properties [1, 2], induce metal-insulator transitions [3, 4], superconductivity or trigger long-range ordering phenomena involving either charge, orbital or spin degrees of freedom [5].

From a theoretical point of view, the explicit inclusion of local Coulomb interactions between correlated electrons beyond single-particle approaches often relies on the density-density approximation, where only dominant direct Coulomb and exchange terms are retained from the full tensor. These terms are then frequently averaged over the manifold of correlated orbitals, resulting in effective Hubbard U and Hund's exchange J_{H} parameters [6]. The averaged parameters are commonly employed in standard implementations of the so-called LDA+U method, where an effective single-particle approach based on the local density approximation is corrected in the manifold of correlated orbitals by on-site Hubbard and exchange terms [7, 8]. The orbitally averaged density-density approximation is also frequently employed in Green's function based many-body techniques, such as dynamical mean-field theory (DMFT) [9–12].

While this approach might be accurate enough to approximate the ground-state properties of materials in many cases, it is clearly not sufficient to provide a good description of the full multiplet structure accessible by many solid-state or molecular spectroscopies, ranging from infrared or visible light optical absorption [13], X-ray absorption or (non) resonant inelastic X-ray scattering to electron energy loss spectroscopy [14]. In this case indeed, a full account of the Coulomb tensor within and between the correlated electronic shells involved in the excitation process is mandatory but theoretically and numerically very challenging. For decades, this problem has been tackled by assuming that transition metal or rare-earth ions retained a dominant atomic-like character in the molecular or solid state and, therefore, that Coulomb interaction could be handled within the spherical symmetry [15]. A great advantage of this approximation lies in the fact that only a very limited number of numerical parameters, known as Slater integrals or Slater-Condon parameters [16, 17], need to be introduced to parametrize the full tensor. For example, if one considers the case of d electrons, the $5^4 = 625$ elements of the spin-independent Coulomb tensor can be expressed in terms of only three Slater integrals, F^0, F^2 and F^4 and simple expressions such as $U = F^0$ and $J_{\mathrm{H}} = (F^2 + F^4)/14$ are obtained. Also when considering d electrons within a perfectly cubic symmetry represented by real wavefunctions, effective descriptions like the Kanamori form [18], which goes beyond density-density interactions, can be expressed in terms of these three Slater integrals [19].

The validity of this approximation is, however, questionable for ions in solids or molecules where the local symmetry of the atomic site is reduced and a covalent interaction with the surrounding ligand atoms always occurs to a certain degree. In this case, the inclusion of the resulting anisotropy of the interaction can lead to important corrections, for instance for the Fermi surface [20, 21]. Recent progresses in the first-principle calculation of screened Coulomb interactions within the constrained random phase approximation in solids [22] indeed show numerically that, whereas Slater parametrization is fairly accurate for ions with very localized states

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and in highly symmetric environments, larger deviations are expected when increasing the spatial extension of the orbitals, the covalent character of the interaction with the ligands or reducing the local site symmetry [23–25]. In such cases, a proper analysis of the effective interaction tensor should be carried out by accounting explicitly for the local point group symmetry of the atomic site. In particular, the central question of the number of independent parameters required to describe exactly the entire tensor immediately arises. This is indeed of primary importance in the analysis of spectroscopic data, since this number is the maximum number of independent parameters to fit, but also when investigating numerically the properties of realistic model Hamiltonians accounting for the exact spatial symmetry of the system.

This problem was pioneered by Tanabe, Sugano and Kamimura [26] in the early 1970's for the specific case of d-shell electrons in octahedral O_h symmetry. It was recently extended by Bünemann and Gebhard to the case of d- and f-shell electrons in O_h, O, T_d, T_h, D_{6h} and D_{4h} symmetries [27]. Iimura, Hirayama and Hoshino followed a different route and expressed the anisotropic Coulomb tensor in terms of multipole operators [28]. A general theory dealing with any orbital in any group is, however, still missing and is therefore the main focus of the present paper. In particular, we consider here all types of irreducible representations (irreps) whereas previous works only focussed on real wavefunctions. Moreover, we provide general expressions for the independent Coulomb parameters as well as for any Coulomb integral on the interaction tensor in terms of these parameters. Finally, we study the effect of a symmetry breaking by comparing Coulomb integrals of a group with those of one of its subgroups.

We would like to underline the broad applicability of our approach. Indeed, we make only two assumptions: (i) the (possibly screened) electron-electron interaction $U(\mathbf{r},\mathbf{r}')$ is symmetric (i.e. $U(\mathbf{r},\mathbf{r}') = U(\mathbf{r}',\mathbf{r})$) and invariant under the operations of a crystal point group G; (ii) the basis functions $\phi_a^{(\alpha)}(\mathbf{r})$ transform as the basis elements of an irrep α of G [29]. In particular, we do not assume that the wave functions $\varphi_a^{(\alpha)}(\mathbf{r})$ entering the Coulomb integrals are built from spherical harmonics of a specific ℓ, nor do they need to have the same radial part. In addition, $U(\mathbf{r},\mathbf{r}')$ can also be frequency-dependent (corresponding to a dynamical interaction) since the frequency ω does not enter in the following derivations. This renders the framework applicable to dynamical interactions, which are for instance used in the context of the GW approximation [30, 31], extended DMFT [32] or techniques combining both [33, 34].

The paper is organized as follows. Section II starts with a discussion of the various symmetries of Coulomb integrals for complex and real one-electron orbitals. More specifically, we consider the case of one-electron orbitals forming bases for irreducible representations of a crystal point group G. In section III, we use the Clebsch-Gordan coefficients of G to define linear combinations of Coulomb integrals (called G-invariants) that are invariant under the action of the operations of G and we show that all Coulomb integrals can be written in terms of these G-invariants. Section IV describes how permutation symmetries can be taken into account to further reduce the number of independent integrals, which are now called (permutation)-symmetrized G-invariants. In this section, we give an explicit formula for calculating any Coulomb integral in terms of these symmetrized G-invariants and we show, conversely, that symmetrized G-invariants can be calculated from the same number of well-chosen Coulomb integrals. Section V explores the important case of symmetry breaking by considering that G is the subgroup of a larger group $\mathcal{G}$ and presents the expression of the G-invariants in terms of $\mathcal{G}$ invariants. The example where $\mathcal{G}$ is the infinite group $O(3)$ is detailed to illustrate the calculations. In this case, the relation between $O(3)$-invariants (related to Slater integrals) and G-invariants can be used to quantify the deviation of the system from spherical symmetry. In section VI finally, we present our conclusions as well as possible extensions of our work.

II. INVARIANCE OF COULOMB INTEGRALS

In solid-state and molecular physics the electron-electron interaction between orbitals φ_a, φ_b, φ_c, φ_d is described by Coulomb integrals defined as

$$\begin{aligned} U_{abcd} &= \langle \varphi_a \varphi_b | U | \varphi_c \varphi_d \rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \varphi_a(\mathbf{r})^* \varphi_b(\mathbf{r}')^* U(\mathbf{r},\mathbf{r}') \varphi_d(\mathbf{r}') \varphi_c(\mathbf{r}), \quad (1) \end{aligned}$$

where $U(\mathbf{r},\mathbf{r}')$ is proportional to $1/|\mathbf{r}-\mathbf{r}'|$ for the bare electron-electron interaction but can be much more complicated if we consider screened Coulomb interactions as we do here. We assume $U(\mathbf{r},\mathbf{r}')$ to be real (otherwise consider its real and imaginary parts separately) and permutation symmetric in the sense $U(\mathbf{r}',\mathbf{r}) = U(\mathbf{r},\mathbf{r}')$. Note that the spin degree of freedom is not considered in the present work.

In this paper we focus on two kinds of symmetries of U_{abcd}: (i) the on-site symmetry represented by a crystal point group G (section II A) and (ii) the permutation of the orbitals (section II B).

A. Invariance under point symmetry operations

a. Action of a group. In an abstract way, the action of a group G on a vector space X is a linear operation that associates to each pair $(R,x) \in G \times X$ an element of X denoted by $R \triangleright x$. This operation satisfies

(i) $1 \triangleright x = x \quad \forall x \in X$, where 1 is the identity element of the group;

(ii) $\forall R, S \in G$ and $\forall x \in X$, $R \triangleright (S \triangleright x) = (RS) \triangleright x$.

For example, if $X = \mathbb{R}^3$ and G is a point symmetry group defined by matrices R, then $R \triangleright \mathbf{r} = R\mathbf{r}$.

b. Action of a group on functions. In molecular or solid-state physics, we deal with orbitals or (wave)functions φ, which are functions of $\mathbf{r}$. The action of the symmetry operation S on φ is a new function φ_S of $\mathbf{r}$ defined by

$$(S \triangleright \varphi)(\mathbf{r}) = \varphi_S(\mathbf{r}) = \varphi(S^{-1}\mathbf{r}),$$

where the argument of φ (originally denoted by $\mathbf{r}$) is replaced by $S^{-1}\mathbf{r}$ in φ. The presence of $S^{-1}\mathbf{r}$ instead of $S\mathbf{r}$ is required by the axioms of an action. Indeed

$$\begin{aligned}\big(R \triangleright (S \triangleright \varphi)\big)(\mathbf{r}) &= (R \triangleright \varphi_S)(\mathbf{r}) = \varphi_S(R^{-1}\mathbf{r}) \\ &= \varphi\big(S^{-1}(R^{-1}\mathbf{r})\big) = \varphi((RS)^{-1}\mathbf{r}) \\ &= \big((RS) \triangleright \varphi\big)(\mathbf{r}) = \varphi_{RS}(\mathbf{r}).\end{aligned}$$

We can now describe the action of a symmetry operation on a Coulomb integral by its action on the orbitals (Schrödinger representation)

$$\begin{aligned}R \triangleright U_{abcd} = \int d\mathbf{r}d\mathbf{r}' \varphi_a(R^{-1}\mathbf{r})^* \varphi_b(R^{-1}\mathbf{r}')^* U(\mathbf{r},\mathbf{r}') \\ \times \varphi_d(R^{-1}\mathbf{r}')\varphi_c(R^{-1}\mathbf{r}),\end{aligned}$$

which can be transformed into an action on $U(\mathbf{r},\mathbf{r}')$ (Heisenberg representation) by a change of variable

$$R \triangleright U_{abcd} = \int d\mathbf{r}d\mathbf{r}' \varphi_a(\mathbf{r})^* \varphi_b(\mathbf{r}')^* U(R\mathbf{r}, R\mathbf{r}')\varphi_d(\mathbf{r}')\varphi_c(\mathbf{r}),$$

where we used the fact that symmetry operations preserve volumes (i.e. $d(R\mathbf{r}) = d\mathbf{r}$). Thus, Coulomb integrals are invariant under the operations of the group G if U is invariant under the operations of G: $U(R\mathbf{r}, R\mathbf{r}') = U(\mathbf{r},\mathbf{r}')$ for all R of G. *We assume this to hold in the present paper.* As a consequence, the symmetry of the system is expressed by the property of the Coulomb integrals

$$R \triangleright U_{abcd} = U_{abcd}, \tag{2}$$

for all R of G.

c. Group representation. A group representation is a set of unitary matrices $\Gamma(R)$, one for each element R of the group, which satisfies $\Gamma(R)\Gamma(S) = \Gamma(RS)$ for any two elements R and S in G. If d is the dimension of the matrices, a basis of the carrier space of this representation is a set of d orbitals $\varphi_a, \varphi_b, \ldots$ such that

$$R \triangleright \varphi_a = \sum_b \Gamma_{ba}(R)\varphi_b. \tag{3}$$

The order of the indices of Γ might appear surprising at first glance, but is actually required [35] to satisfy the second property of the action

$$\begin{aligned}R \triangleright (S \triangleright \varphi_a) &= R \triangleright \big(\sum_b \Gamma_{ba}(S)\varphi_b\big) = \sum_b \Gamma_{ba}(S)(R \triangleright \varphi_b) \\ &= \sum_{bc} \Gamma_{ba}(S)\Gamma_{cb}(R)\varphi_c = \sum_c (\Gamma(R)\Gamma(S))_{ca}\varphi_c \\ &= \sum_c (\Gamma(RS))_{ca}\varphi_c = (RS) \triangleright \varphi_a,\end{aligned}$$

where we used the linearity of the action in the first line, then that $\Gamma(R)\Gamma(S) = \Gamma(RS)$ between the second and third lines.

d. Irreducible representations. We are particulary interested in irreducible representations (irreps) which are representations that cannot be decomposed into smaller representations. In this paper, we assume that the orbitals transform as irreps (denoted by α, β, γ and δ) of G. For each of these representations, for instance α, let $\{\varphi_a^{(\alpha)}\}$, $a = 1, \ldots, \dim\alpha$, be a basis of this representation and $\{\Gamma^{(\alpha)}(R),\ \forall R \in G\}$ be its representation matrices. We denote the Coulomb integral on the basis of the irreps as

$$U_{abcd}^{(\alpha\beta\gamma\delta)} = \langle \varphi_a^{(\alpha)}\varphi_b^{(\beta)}|U|\varphi_c^{(\gamma)}\varphi_d^{(\delta)}\rangle.$$

The action of R on $U_{abcd}^{(\alpha\beta\gamma\delta)}$ can now be described by representation matrices

$$\begin{aligned}R \triangleright U_{abcd}^{(\alpha\beta\gamma\delta)} = \sum_{a'b'c'd'} \Gamma_{a'a}^{(\alpha)}(R)^* \Gamma_{b'b}^{(\beta)}(R)^* \Gamma_{c'c}^{(\gamma)}(R)\Gamma_{d'd}^{(\delta)}(R) \\ \times U_{a'b'c'd'}^{(\alpha\beta\gamma\delta)}.\end{aligned} \tag{4}$$

There are three types of irreps, in the sense of the Frobenius-Schur criterion [36]:

(a) real irreps, for which we can find real representation matrices;

(b) pseudo-real (or quaternionic) irreps, for which $\Gamma(R)$ and $\Gamma(R)^*$ are equivalent in the sense that they are related by a similarity transformation, but they are not all equivalent to real representation matrices;

(c) complex irreps, for which $\Gamma(R)$ and $\Gamma(R)^*$ are not equivalent, meaning that they are associated to different irreps; an example of which is given by $e^{\pm i\mathbf{k}\cdot\mathbf{r}}$ for the translation group.

The distinction between real and non-real (i.e. pseudo-real or complex) irreps is crucial. Indeed, in the case of real representations, we can choose real representation matrices and also real-valued basis functions $\{\varphi_a^{(\alpha)}\}$ of the carrier space of the irrep. Please note that even real representations can be represented by complex-valued matrices, as it is the case for instance of the real representation E_g for the group O_h in Altmann and Herzig's tables [37]. However, in the case of non-real representations, the representation matrices and the basis functions cannot be chosen real-valued.

For the groups O_h, O, T_d, D_{6h} and D_{4h} investigated by Bünemann and Gebhard [27], all irreps are real. For the last group T_h studied in that article, there are four complex one-dimensional representations $({}^1E_g, {}^2E_g, {}^1E_u, {}^2E_u)$. They can be grouped into pairs to become two-dimensional real representations, which are however no longer irreducible.

B. Invariance under some permutations

We now describe additional symmetries of the Coulomb integrals, related to the permutation of $\mathbf{r}$ and $\mathbf{r}'$ and the complex conjugation in Eq. (1). The permutation symmetries differ between real- and complex-valued orbitals.

a. Non-real representations. In the (more general) case of non-real representations, we assume complex-valued orbitals φ_a. Interchanging $\mathbf{r}$ and $\mathbf{r}'$ in the integral definition of U_{abcd} (Eq. (1)) gives $U_{abcd} = U_{badc}$, and taking its complex conjugate yields $U^*_{abcd} = U_{cdab}$. As a consequence, we obtain an equality between four Coulomb integrals

$$U_{abcd} = U_{badc} = U^*_{cdab} = U^*_{dcba}. \tag{5}$$

This can be seen as the invariance of the Coulomb integrals under the action of an additional group G_P of four elements $\{p_1, p_2, p_3, p_4\}$. Its action on U_{abcd} is defined by

$$\begin{aligned} p_1 \triangleright U_{abcd} &= U_{abcd}, \quad & p_2 \triangleright U_{abcd} &= U_{badc}, \\ p_3 \triangleright U_{abcd} &= U^*_{cdab}, \quad & p_4 \triangleright U_{abcd} &= U^*_{dcba}. \end{aligned}$$

and is represented graphically on Fig. (1a).

Due to the complex conjugation in its action, G_P is a magnetic group, of which the Coulomb integrals form a corepresentation, as defined by Wigner [38].

More precisely, the permutation group G_P is isomorphic to the Shubnikov group of the third kind $m'm2'$. It has two unitary operations E and σ_y, and two anti-unitary operations C_{2z} and σ_x [56].

b. Real representations. In the case of real representations, we assume real-valued orbitals. The previous equality (Eq. (5)) still holds with $U_{abcd} = U_{cdba} = U_{badc} = U_{dcba}$. In addition, the two orbitals $\varphi_a(\mathbf{r})$ and $\varphi_c(\mathbf{r})$, as well as $\varphi_b(\mathbf{r}')$ and $\varphi_d(\mathbf{r}')$, now play an equivalent role and can be interchanged, yielding equalities like $U_{abcd} = U_{cbad}$. We therefore get equalities between eight Coulomb integrals [27]

$$\begin{aligned} U_{abcd} &= U_{cdba} = U_{badc} = U_{dcba} \\ &= U_{adcb} = U_{cbad} = U_{bcda} = U_{dabc}. \end{aligned} \tag{6}$$

Again, these equalities can be interpreted as the invariance of the Coulomb integral under the action of a group $G_P = D_4$ of eight permutations (see Fig. (1b)).

III. GROUP INVARIANTS

We now introduce the central objects of the present paper. Since they are built to be invariant under the action of the considered group, we call them group invariants and denote them I. As we shall see, they correspond to the eigenvalues of the interaction matrix, on the basis of the irreps of the group.

As a starting point, we consider the point group only, leaving the permutation groups to the next section.

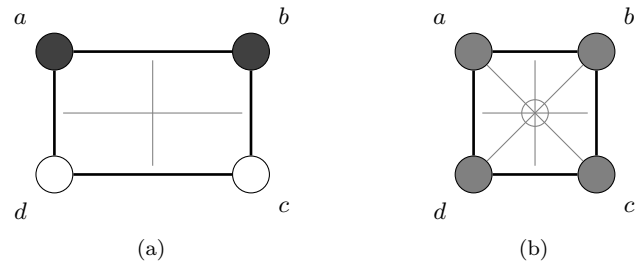

FIG. 1. Geometric representation of the permutation symmetries of U_{abcd}. The vertices are labelled clockwise with the orbital indices a, b, c and d. (a) The complex conjugation of non-real orbitals is graphically represented as a transformation of black vertices into white ones (and vice versa). The permutations form the group $m'm2'$ which describes the symmetries of a rectangle with 2 white and 2 black vertices. (b) The permutations of real orbitals form the group D_4 which describes the symmetries of a square.

A. Clebsch-Gordan coefficients

For any finite (or compact) group G, the tensor product (also known as the direct product, or the Kronecker product [35]) of two irreps can be written as a direct sum of irreps, called a Clebsch-Gordan series [50]

$$\alpha \otimes \beta = \eta_1 \oplus \cdots \oplus \eta_k, \tag{7}$$

where we assume that no irrep η_i appears more than once. In other words, we assume tensor products of irreps to be multiplicity-free. This assumption can be relaxed without conceptual complication by using methods which are now standard in the literature [42–48], but this leads to a cluttering of indices in formulas, that we prefer to avoid. Additionally, this assumption is actually justified for crystal point groups. Indeed, their product tables [37] indicate that all crystal point groups except T and T_h are multiplicity-free. Even the exceptions T and T_h satisfy the assumption in the broader sense that their doubly occuring irreps can be distinguished by their symmetric and anti-symmetric nature.

At the level of the matrix representations of the irreps, a unitary transformation brings their tensor product into a sum of the irrep matrices. The coefficients of this unitary transformation are called Clebsch-Gordan coefficients. More precisely, we define the Clebsch-Gordan coefficients to be any set of complex numbers $(\alpha a \beta b|\eta e)$ solving the equation [35]

$$\Gamma^{(\alpha)}_{a'a}(R)\Gamma^{(\beta)}_{b'b}(R) = \sum_{\eta e e'} (\alpha a' \beta b'|\eta e')\Gamma^{(\eta)}_{e'e}(R)(\alpha a \beta b|\eta e)^*. \tag{8}$$

A possible solution of this equation is given by Dirl's formula [49]

$$(\alpha a \beta b|\eta e) = \frac{\sum_R \Gamma^{(\alpha)}_{aa_0}(R)\Gamma^{(\beta)}_{bb_0}(R)\left(\Gamma^{(\eta)}_{ee_0}(R)\right)^*}{\sqrt{N(a_0, b_0, e_0)}}, \tag{9}$$

with

$$N(a_0,b_0,e_0)=\frac{|G|}{\dim\eta}\sum_R \Gamma^{(\alpha)}_{a_0a_0}(R)\Gamma^{(\beta)}_{b_0b_0}(R)\big(\Gamma^{(\eta)}_{e_0e_0}(R)\big)^*,$$

where $|G|$ is the order of G (ie. the number of its elements) and, for each triple (α,β,η), three components (a_0,b_0,e_0) are chosen so that $N(a_0,b_0,e_0)\neq 0$. Such components exist if η belongs to the tensor product of $\alpha\otimes\beta$ (see also [50]). These Clebsch-Gordan coefficients are a generalization of the ones used in angular momentum theory. They satisfy orthogonality relations

$$\sum_{ab}(\alpha a\beta b|\eta e)^*(\alpha a\beta b|\phi f)=\delta_{\eta\phi}\delta_{ef}, \tag{10}$$

$$\sum_{\eta e}(\alpha a\beta b|\eta e)^*(\alpha a'\beta b'|\eta e)=\delta_{aa'}\delta_{bb'}, \tag{11}$$

due to the fact that they are elements of a unitary matrix [35].

The definition of Clebsch-Gordan coefficients as any solution of Eq. (9) is inspired by Derome and Sharp (see note [70]). Note that this definition does not fully specify the Clebsch-Gordan coefficients, since multiplying them by a phase depending on α, β and γ transforms a solution into another one. Other approaches choose these phases carefully in order to maximize the symmetry of Clebsch-Gordan coefficients [44, 46–48, 51–53]. However, these phases depend on each group and the Clebsch-Gordan coefficients given by Dirl's formula (Eq. (9)) generally do not satisfy these symmetries. We also chose to use the Clebsch-Gordan coefficients as defined by Derome and Sharp for another, crucial but technical reason; the interested reader is invited to read the note [71].

B. Definition and properties of the point-group invariants

As a first step of the symmetry analysis of Coulomb integrals, we consider the submatrix $U^{(\alpha\beta\gamma\delta)}$ of elements $U^{(\alpha\beta\gamma\delta)}_{abcd}$ for a given quadruple of irreps $\sigma=(\alpha\beta\gamma\delta)$. We define the associated G-invariant as

$$I^{(\alpha\beta\gamma\delta,\eta)}=\sum_{abcde}\frac{(\alpha a\beta b|\eta e)^*U^{(\alpha\beta\gamma\delta)}_{abcd}(\gamma c\delta d|\eta e)}{\dim\eta}, \tag{12}$$

where η belongs to the Clebsch-Gordan series of both $\alpha\otimes\beta$ and $\gamma\otimes\delta$.

Note that $I^{(\alpha\beta\gamma\delta,\eta)}$ is basis-independent. Indeed, let $P^{(\alpha)}=\sum_a|\varphi^{(\alpha)}_a\rangle\langle\varphi^{(\alpha)}_a|$ be the projector onto a representation α. There is a way to map tensor products of states into sums of states so that

$$(\gamma c\delta d|\eta e)=(\langle\varphi^{(\gamma)}_c|\otimes\langle\varphi^{(\delta)}_d|)\ |\varphi^{(\eta)}_e\rangle,$$
$$(\alpha a\beta b|\eta e)^*=\langle\varphi^{(\eta)}_e|\ (|\varphi^{(\alpha)}_a\rangle\otimes|\varphi^{(\beta)}_b\rangle).$$

Recalling that $U^{(\alpha\beta\gamma\delta)}_{abcd}=\langle\varphi^{(\alpha)}_a\varphi^{(\beta)}_b|U|\varphi^{(\gamma)}_c\varphi^{(\delta)}_d\rangle$, we obtain

$$I^{(\alpha\beta\gamma\delta,\eta)}=\frac{1}{\dim\eta}\mathrm{Tr}\Big(P^{(\eta)}(P^{(\alpha)}\otimes P^{(\beta)})U(P^{(\gamma)}\otimes P^{(\delta)})\Big),$$

which is basis independent. This means that G-invariants can be compared even if the matrices of the irreps are different. However, if $(\gamma,\delta)\neq(\alpha,\beta)$ they can differ from one another by a phase due to the phase ambiguity of Clebsch-Gordan coefficients.

The second result is a consequence of Schur's lemma: if $U^{(\alpha\beta\gamma\delta)}_{abcd}$ is invariant under the action of G (i.e. satisfies Eq. (2)), then the matrix $U^{(\alpha\beta\gamma\delta)}_{abcd}$ is diagonalized by the Clebsch-Gordan coefficients and its eigenvalues are $I^{(\alpha\beta\gamma\delta,\eta)}$

$$\sum_{abcd}(\alpha a\beta b|\phi f)^*U^{(\alpha\beta\gamma\delta)}_{abcd}(\gamma c\delta d|\eta e)=\delta_{\phi\eta}\delta_{ef}I^{(\alpha\beta\gamma\delta,\eta)}. \tag{13}$$

As a consequence, any $U^{(\alpha\beta\gamma\delta)}_{abcd}$ can be written explicitly in terms of G-invariants

$$U^{(\alpha\beta\gamma\delta)}_{abcd}=\sum_{\eta e}(\alpha a\beta b|\eta e)I^{(\alpha\beta\gamma\delta,\eta)}(\gamma c\delta d|\eta e)^*. \tag{14}$$

This shows that, if η runs over the $n^{(\alpha\beta\gamma\delta)}$ irreps shared by $\alpha\otimes\beta$ and $\gamma\otimes\delta$, then the set of $I^{(\alpha\beta\gamma\delta,\eta)}$ forms a complete family of G-invariants generating $U^{(\alpha\beta\gamma\delta)}$.

Moreover, the number $n^{(\alpha\beta\gamma\delta)}$ of G-invariants for the set $(\alpha\beta\gamma\delta)$ can be obtained by the character formula

$$n^{(\alpha\beta\gamma\delta)}=\frac{1}{|G|}\sum_{R\in G}\chi^\alpha(R)^*\chi^\beta(R)^*\chi^\gamma(R)\chi^\delta(R), \tag{15}$$

where the character of a representation η is defined as $\chi^\eta(R)=\mathrm{Tr}\big(\Gamma^{(\eta)}(R)\big)$.

IV. PERMUTATION-SYMMETRIZED INVARIANTS

The G-invariants of Eq. (12) do not take into account the permutation symmetry as described in section II B. These additional constraints considerably decrease the number of invariants and are discussed now.

A. Real representations

In this section, we assume that all the irreps are real and that they are represented by real matrices. Consequently, the Clebsch-Gordan coefficients can be chosen real, too. The suitable permutation invariance of the integrals were given in Eq. (6).

1. *Symmetrization*

As for any group, we obtain D_4-symmetrized G-invariants by projecting $U^{(\alpha\beta\gamma\delta)}_{abcd}$ onto the fully-symmetric

irrep A_1 of the permutation group D_4

$$\langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle = \frac{1}{|D_4|}\sum_{p\in D_4} U^{p(\alpha\beta\gamma\delta)}_{p(abcd)} = \frac{1}{8}\big(U^{(\alpha\beta\gamma\delta)}_{abcd} + U^{(\gamma\delta\alpha\beta)}_{cdab} + U^{(\beta\alpha\delta\gamma)}_{badc} + U^{(\delta\gamma\beta\alpha)}_{dcba} + U^{(\alpha\delta\gamma\beta)}_{adcb} + U^{(\gamma\beta\alpha\delta)}_{cbad} + U^{(\beta\gamma\delta\alpha)}_{bcda} + U^{(\delta\alpha\beta\gamma)}_{dabc}\big). \tag{16}$$

By definition, $\langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle$ is invariant under the action of D_4. In fact, we know from Eq. (6) that Coulomb integrals satisfy $\langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle = U^{(\alpha\beta\gamma\delta)}_{abcd}$, but as for the calculation of G-invariants, we investigate the properties of D_4-symmetrized Coulomb integrals by assuming that we start from non-symmetrized ones. As a consequence, the permutation-symmetrized G-invariants are given by

$$\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle = \sum_{abcde}\frac{\langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e)}{\dim\eta}, \tag{17}$$

which is a sum of 8 terms as in Eq. (16). This is the expression of the $G\times D_4$ invariants in terms of the Coulomb integrals. We will write them in terms of the G-invariants, as detailed in the next two subsections. The goal is to transform the Clebsch-Gordan coefficients of each sum so that they match the indices of the permuted integral $U^{p(\alpha\beta\gamma\delta)}_{p(abcd)}$, in order to identify a G-invariant. Two cases must be distinguished: either the representations coupled by the Clebsch-Gordan coefficients are also coupled in the permuted integral (pair-conserving permutations), or they are reshuffled (pair-mixing permutations).

a. The first four terms: pair-conserving permutations. The terms of $\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle$ corresponding to the first two terms on the right hand side of Eq. (16) are trivial

$$\sum_{abcde} U^{(\alpha\beta\gamma\delta)}_{abcd}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) = I^{(\alpha\beta\gamma\delta,\eta)}\dim\eta,$$
$$\sum_{abcde} U^{(\gamma\delta\alpha\beta)}_{cdab}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) = I^{(\gamma\delta\alpha\beta,\eta)}\dim\eta.$$

To deal with the next two terms, we notice that, as a consequence of Schur's lemma, the Clebsch-Gordan coefficients $(\alpha a\beta b|\eta e)$ and $(\beta b\alpha a|\eta e)$ differ by at most a phase depending on α, β and η (but not on a, b and e). We denote this phase by $\{\alpha\beta,\eta\}$ [46, 52]: $(\alpha a\beta b|\eta e) = \{\alpha\beta,\eta\}(\beta b\alpha a|\eta e)$. Moreover $\{\alpha\beta,\eta\}=\pm1$ for real Clebsch-Gordan coefficients.

This enables us to write

$$\sum_{abcde} U^{(\beta\alpha\delta\gamma)}_{badc}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) = \{\alpha\beta,\eta\}\{\gamma\delta,\eta\}\sum_{abcde} U^{(\beta\alpha\delta\gamma)}_{badc}(\beta b\alpha a|\eta e)(\delta d\gamma c|\eta e) = \{\alpha\beta,\eta\}\{\gamma\delta,\eta\}I^{(\beta\alpha\delta\gamma,\eta)}\dim\eta,$$

and similarly

$$\sum_{abcde} U^{(\delta\gamma\beta\alpha)}_{dcba}(\beta b\alpha a|\eta e)(\delta d\gamma c|\eta e) = \{\alpha\beta,\eta\}\{\gamma\delta,\eta\}\times I^{(\delta\gamma\beta\alpha,\eta)}\dim\eta.$$

b. The last four terms: pair-mixing permutations. The last four terms are more cumbersome, because their Clebsch-Gordan coefficients couple the first and third, and the second and fourth representations of the integrals, thus breaking the "bra" and "ket" pairs.

In order to reshuffle these Clebsch-Gordan coefficients into new pairs, we need to use a recoupling formula. Precisely, we use the one proposed by Derome and Sharp (theorem 3 of [42], and see notes [71, 72]) for their general Clebsch-Gordan coefficients. For real representation matrices (and multiplicity-free point groups), the recoupling formula takes the form

$$\sum_e(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) = \dim\eta\sum_{\phi f}(-1)^{\phi+\eta}\begin{Bmatrix}\alpha & \beta & \eta\\ \gamma & \delta & \phi\end{Bmatrix}\times(\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f), \tag{18}$$

where the $6j$-symbols are defined by

$$\begin{Bmatrix}\alpha & \beta & \eta\\ \gamma & \delta & \phi\end{Bmatrix} = \frac{(-1)^{\alpha+\beta+\eta+\gamma+\delta+\phi}}{\dim\eta\dim\phi}\times\sum_{abcdef}(\gamma c\delta d|\eta e)(\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f)(\alpha a\beta b|\eta e). \tag{19}$$

In Eqs. (18) and (19), the symbols $(-1)^\alpha$, $(-1)^\beta,\ldots$ are defined as follows. According to Derome and Sharp, we first define $1j$-symbols by $(\alpha)_{aa'} = (\alpha a00|\alpha a')$, where 0 is the fully-symmetric irrep. By Schur's lemma, it can be shown that $(\alpha)_{aa'} = \pm\delta_{aa'}$ and we denote the sign $\pm$ by $(-1)^\alpha$. In particular, if Clebsch-Gordan coefficients are calculated from Dirl's formula in Eq. (9), then $(-1)^\alpha = 1$ for every irrep α. We also use the obvious notation $(-1)^{\phi+\eta} = (-1)^\phi(-1)^\eta$.

In the literature, other $6j$-symbols were defined which display interesting symmetry properties [46, 52]. However, these symmetries require to adjust the phases of the Clebsch-Gordan coefficients. Instead, we follow Derome's approach again and work with general Clebsch-Gordan coefficients [42, 43, 55]. We are now ready to apply the remaining permutations of D_4 to $I^{(\alpha\beta\gamma\delta,\eta)}$. For example

$$\sum_{abcde} U^{(\gamma\beta\alpha\delta)}_{cbad}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) = \dim\eta\sum_\phi(-1)^{\phi+\eta}\begin{Bmatrix}\alpha & \beta & \eta\\ \gamma & \delta & \phi\end{Bmatrix}\times\sum_{abcdf}U^{(\gamma\beta\alpha\delta)}_{cbad}(\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f) = \dim\eta\sum_\phi(-1)^{\phi+\eta}\dim\phi\begin{Bmatrix}\alpha & \beta & \eta\\ \gamma & \delta & \phi\end{Bmatrix}I^{(\gamma\beta\alpha\delta,\phi)}.$$

c. D_4-symmetrized invariant. By treating the three remaining terms in the same manner, the D_4-symmetrization of $I^{(\alpha\beta\gamma\delta,\eta)}$ yields

$$\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle = \frac{1}{8}\Big(I_{pc} + \sum_\phi(-1)^{\eta+\phi}\dim\phi\begin{Bmatrix}\alpha & \beta & \eta\\ \gamma & \delta & \phi\end{Bmatrix}I_{npc}\Big), \tag{20}$$

where the pair-conserving terms I_{pc} and the pair-non-conserving terms I_{npc} are

$$I_{pc} = I^{(\alpha\beta\gamma\delta,\eta)} + I^{(\gamma\delta\alpha\beta,\eta)} + \{\alpha\beta,\eta\}\{\gamma\delta,\eta\}\big(I^{(\beta\alpha\delta\gamma,\eta)} + I^{(\delta\gamma\beta\alpha,\eta)}\big),$$

$$I_{npc} = I^{(\alpha\delta\gamma\beta,\phi)} + I^{(\gamma\beta\alpha\delta,\phi)} + \{\alpha\delta,\phi\}\{\beta\gamma,\phi\}\big(I^{(\beta\gamma\delta\alpha,\phi)} + I^{(\delta\alpha\beta\gamma,\phi)}\big).$$

2. Enumeration of $G \times D_4$-invariants

A permutation p of D_4 transforms a quadruple of irreps $\sigma = (\alpha,\beta,\gamma,\delta)$ into another quadruple $p(\sigma)$. Let S be the set of quadruples obtained from σ by the action of D_4 (this is called the *orbit* of σ). The number of elements of S depends on the irreps in σ. For instance, if $\sigma = (\alpha,\alpha,\alpha,\alpha)$, then S has only one element $S = \{\sigma\}$. If all irreps are different, then S has 8 elements. We shall see that there are five different types of S.

As noticed in Ref. [27], the number of independent permutation-symmetrized $G \times D_4$-invariants for a given set S can again be obtained from the character formula

$$n^S = \frac{1}{|G \times D_4|} \sum_{(R,p)\in G\times D_4} \chi^S(R,p), \tag{21}$$

where the character $\chi^S(R,p)$ of the element (R,p) in $G\times D_4$ in the orbit S is defined by

$$\chi^S(R,p) = \sum_{(\alpha\beta\gamma\delta)\in S} \delta_{(\alpha\beta\gamma\delta),p(\alpha\beta\gamma\delta)} \times \sum_{abcd} \Gamma^{(\alpha)}_{a'a}(R)\Gamma^{(\beta)}_{b'b}(R)\Gamma^{(\gamma)}_{c'c}(R)\Gamma^{(\delta)}_{d'd}(R)\Big|_{(a'b'c'd')=p^{-1}(abcd)}.$$

We give the formula for $\sum_p \chi^S(R,p)$ in terms of the characters $\chi^\alpha(R)$ of G for every possible set S.

- $S_1 = \{(\alpha,\alpha,\alpha,\alpha)\}$

$$\sum_p \chi^{S_1}(R,p) = \chi^\alpha(R)^4 + 3\chi^\alpha(R^2)^2 + 2\chi^\alpha(R^2)\chi^\alpha(R)^2 + 2\chi^\alpha(R^4);$$

- $S_2 = \{(\alpha,\beta,\alpha,\beta),(\beta,\alpha,\beta,\alpha)\}$ with $\beta \neq \alpha$

$$\sum_p \chi^{S_2}(R,p) = 2\big(\chi^\alpha(R)^2 + \chi^\alpha(R^2)\big) \times \big(\chi^\beta(R)^2 + \chi^\beta(R^2)\big);$$

- $S_3 = \{(\alpha,\alpha,\beta,\beta),(\alpha,\beta,\beta,\alpha),(\beta,\beta,\alpha,\alpha),(\beta,\alpha,\alpha,\beta)\}$ with $\beta \neq \alpha$

$$\sum_p \chi^{S_3}(R,p) = 4\chi^\alpha(R)^2\chi^\beta(R)^2 + 4\chi^\alpha(R^2)\chi^\beta(R^2);$$

- $S_4 = \{(\alpha,\beta,\alpha,\gamma),(\alpha,\gamma,\alpha,\beta),(\beta,\alpha,\gamma,\alpha),(\gamma,\alpha,\beta,\alpha)\}$ where $\beta \neq \alpha$ and $\beta \neq \gamma$, but $\gamma = \alpha$ is allowed

$$\sum_p \chi^{S_4}(R,p) = 4\big(\chi^\alpha(R)^2 + \chi^\alpha(R^2)\big)\chi^\beta(R)\chi^\gamma(R);$$

- For all the other cases

$$\sum_p \chi^{S_5}(R,p) = 8\chi^\alpha(R)\chi^\beta(R)\chi^\gamma(R)\chi^\delta(R).$$

3. Independent components of Coulomb integrals

For convenience, we write Eq. (20) in matrix form: $\langle I^p\rangle = M_{pq}I^q$, where p and q are compound indexes (σ,η) and were $M^2 = M$ is a projection matrix. As such, it is diagonalizable, but since M is not an orthogonal projection, its eigenspaces are not orthogonal. To solve this problem, we define the matrix $Q_{(\sigma,\eta)(\tau,\phi)} = \delta_{\sigma\tau}\delta_{\eta\phi}\sqrt{\dim\eta}$ and the modified projection matrix $N = QMQ^{-1}$, which is symmetric (i.e. $N^T = N$) because of the symmetries of $6j$ symbols [42]. The eigenvalues of N are 0 and 1 and its orthonormal eigenvectors are denoted by $\mathbf{v}^p$.

In general, when a matrix N is diagonalizable with eigenvalues λ_p and eigenvectors $\mathbf{v}^p$, we can define the matrix $B_{qp} = v^p_q$, where v^p_q is the qth component of $\mathbf{v}^p$ and N is recovered by $N_{pr} = \sum_q B_{pq}\lambda_q(B^{-1})_{qr}$. The eigenvalue $\lambda_q = 0$ does obviously not contribute and we are left with $N_{pr} = \sum_{q,\lambda_q=1} B_{pq}(B^{-1})_{qr}$. We can now define the *independent components* u^q of symmetrized G-invariants to be

$$u^q = \sum_r (B^{-1}Q)_{qr}I^r, \tag{22}$$

where q is such as $\lambda_q = 1$. These independent components are the minimal information required to compute all Coulomb integrals. Indeed

$$\sum_{q,\lambda_q=1} (Q^{-1}B)_{pq}u^q = \sum_r M_{pr}I^r = \langle I^p\rangle. \tag{23}$$

4. The norm of Coulomb integrals

In order to analyze the screening of electron-electron interaction in the solid-state, evaluate the effect of an external parameter such as pressure on Coulomb integrals, or simply fit Coulomb integrals in a crystal with a spherical model, we need to evaluate the distance between Coulomb integrals. Since Coulomb integrals are matrix elements of an operator, the natural distance is given by the Hilbert-Schmidt (or Frobenius) norm defined by

$$||U^{(\alpha\beta\gamma\delta)}||^2 = \sum_{abcd} |U^{(\alpha\beta\gamma\delta)}_{abcd}|^2.$$

This norm is natural because it is invariant under unitary transformations and it is perfectly suited to least square minimization. The mixing of irreps due to permutations leads us to consider also the distance between Coulomb integrals for a given set S of quadruples $\sigma = (\alpha\beta\gamma\delta)$

$$||U^S||^2 = \sum_{\sigma\in S} ||U^\sigma||^2.$$

Since we express Coulomb integrals in terms of G-invariants, we need to define a distance between G-invariants which is compatible with the distance between Coulomb integrals. By using Eq. (14) and the orthogonality of Clebsch-Gordan coefficients we obtain

$$||U^S||^2 = \sum_{\sigma\in S}\sum_{\eta} \dim\eta |I^{(\sigma,\eta)}|^2. \tag{24}$$

We are now ready to compute the norm of Coulomb integrals in terms of the independent components. Since matrix Q^{-1} in Eq. (23) removes the coefficient $\dim\eta$ in Eq. (24) and the columns of B are orthonormal, we find

$$||U^S||^2 = \sum_{q,\lambda_q=1} |u^q|^2, \tag{25}$$

where, in Eq. (24), we used $I^p = \langle I^p\rangle$, which is a consequence of definition (17) of $\langle I^p\rangle$ when Coulomb integrals satisfy the D_4-permutation symmetry (i.e. $U^{(\alpha\beta\gamma\delta)}_{abcd} = \langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle$).

In summary, it is possible to evaluate the total distance between two sets of Coulomb integrals from the distance between the independent components u^q. An example of this calculation is given in section V A 2.

5. Minimizing Coulomb integral calculations

In this section, we determine the minimal number of Coulomb integrals $U^{(\alpha\beta\gamma\delta)}_{abcd}$ that we have to calculate to be able to determine all Coulomb integrals. This is obviously useful to mimize the computational cost of electronic structure calculations. We recall Eq. (14)

$$U^{(\alpha\beta\gamma\delta)}_{abcd} = \sum_{\eta e} (\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e) I^{(\alpha\beta\gamma\delta,\eta)},$$

which can be used to calculate $n = \dim\alpha\dim\beta\dim\gamma\dim\delta$ Coulomb integrals in terms of $n^{(\alpha\beta\gamma\delta)}$ G-invariants (see Eq. (15)). If S denotes the type of set described in section IV B 2 to which $(\alpha\beta\gamma\delta)$ belongs, symmetrization mixes now $|S|n$ Coulomb integrals, where $|S|$ is the number of elements of S, and these $|S|n$ Coulomb integrals can be determined in terms of n^S permutation-symmetrized G-invariants, as explained in section IV B 2. More precisely, we have shown in the previous section that there are n^S quantities u^q such that $\langle I^p\rangle = \sum_q (Q^{-1}B)_{pq} u^q$. Combining these two relations, we see that there is an $(|S|n)\times n^S$ matrix $A^{\alpha\beta\gamma\delta,q}_{abcd}$, where $(\alpha\beta\gamma\delta)$ is in S, such that

$$U^{(\alpha\beta\gamma\delta)}_{abcd} = \sum_q A^{\alpha\beta\gamma\delta,q}_{abcd} u^q.$$

The rank r of A is the length of the longest list of independent columns of A [57]. The case $r < n^S$ is possible, but it means that the Coulomb integrals are linear combinations of a number of parameters smaller than n^S. This can happen when the true symmetry group is larger than the one considered in the calculation. However the most common case is $r = n^S$ and we only consider this case. By definition of the rank of A, we can choose n^S independent columns of A. Each column corresponds to a specific Coulomb integral $U^{(\alpha_p\beta_p\gamma_p\delta_p)}_{a_pb_pc_pd_p}$. We take such a set of independent columns to build an $n^S\times n^S$ matrix P relating the $U^{(\alpha_p\beta_p\gamma_p\delta_p)}_{a_pb_pc_pd_p}$ to u^q. The matrix P is invertible since the columns are independent. Therefore, P^{-1} allows us to express the n^S independent components u^q in terms of the n^S selected Coulomb integrals. Since the independent components generate all Coulomb integrals, we can compute all Coulomb integrals from n^S of them.

An example of this selection of a minimum of Coulomb integrals is given in section V A 2.

B. Non-real representations

In this section, the representation matrices, the orbital wavefunctions and the Clebsch-Gordan coefficients are assumed to be complex. The suitable permutation invariance of the integrals were given in Eq. (5).

1. Symmetrization

It is clear that

$$\langle U^{(\alpha\beta\gamma\delta)}_{abcd}\rangle = \frac{1}{4}\Big(U^{(\alpha\beta\gamma\delta)}_{abcd} + U^{(\beta\alpha\delta\gamma)}_{badc} + (U^{(\gamma\delta\alpha\beta)}_{cdab})^* + (U^{(\delta\gamma\beta\alpha)}_{dcba})^*\Big),$$

is invariant under the operations of $m'm2'$. Therefore, the relation between symmetrized and non-symmetrized components for non-real representations is

$$\begin{aligned}
4\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle &= \sum_{abcde} U^{(\alpha\beta\gamma\delta)}_{abcd}(\alpha a\beta b|\eta e)^*(\gamma c\delta d|\eta e) \\
&\quad + \sum_{abcde} U^{(\beta\alpha\delta\gamma)}_{badc}(\alpha a\beta b|\eta e)^*(\gamma c\delta d|\eta e) \\
&\quad + \sum_{abcde} (U^{(\gamma\delta\alpha\beta)}_{cdab})^*(\alpha a\beta b|\eta e)^*(\gamma c\delta d|\eta e) \\
&\quad + \sum_{abcde} (U^{(\delta\gamma\beta\alpha)}_{dcba})^*(\alpha a\beta b|\eta e)^*(\gamma c\delta d|\eta e) \\
&= I^{(\alpha\beta\gamma\delta,\eta)} + \{\alpha\beta\eta\}\{\gamma\delta\eta\} I^{(\beta\alpha\delta\gamma,\eta)} \\
&\quad + (I^{(\gamma\delta\alpha\beta,\eta)})^* + \{\alpha\beta\eta\}\{\gamma\delta\eta\}(I^{(\delta\gamma\beta\alpha,\eta)})^*.
\end{aligned}$$

By similarly calculating $\langle I^{(\beta\alpha\delta\gamma,\eta)}\rangle$, $\langle I^{(\gamma\delta\alpha\beta,\eta)}\rangle$ and $\langle I^{(\delta\gamma\beta\alpha,\eta)}\rangle$, we obtain the following relations between symmetrized components

$$\begin{aligned}\langle I^{(\beta\alpha\delta\gamma,\eta)}\rangle &= \{\alpha\beta\eta\}^*\{\gamma\delta\eta\}\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle,\\ \langle I^{(\gamma\delta\alpha\beta,\eta)}\rangle &= \langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle^*,\\ \langle I^{(\delta\gamma\beta\alpha,\eta)}\rangle &= \{\alpha\beta\eta\}^*\{\gamma\delta\eta\}\langle I^{(\alpha\beta\gamma\delta,\eta)}\rangle^*.\end{aligned}$$

2. Enumeration of symmetrized G-components

Irreducible corepresentations are not as familiar as irreps but there is also a character formula for counting the number of times a given irreducible corepresentation appears in a general corepresentation [58]. In Newmarch's language, we consider the fully symmetric irreducible corepresentation, which is of type (a), corresponding to an intertwining number $I = 1$.

A particularity of the character theory of corepresentations is that it takes into account only unitary operations (in our case the unit permutation $(\alpha\beta\gamma\delta)$ and the permutation $(\beta\alpha\delta\gamma)$). The character of the representation corresponding to permutation p is

$$\chi^S(R,p) = \sum_{(\alpha\beta\gamma\delta)\in S} \delta_{(\alpha\beta\gamma\delta),p(\alpha\beta\gamma\delta)} \times \sum_{abcd} \Gamma^{(\alpha)}_{a'a}(R)^*\Gamma^{(\beta)}_{b'b}(R)^*\Gamma^{(\gamma)}_{c'c}(R)\Gamma^{(\delta)}_{d'd}(R)\Big|_{(a'b'c'd')=p^{-1}(abcd)},$$

and the number of symmetrized G-components is

$$n^S = \frac{1}{2|G|}\sum_p{}' \sum_R \chi^S(R,p),$$

where $\sum'$ runs only over the two permutations corresponding to unitary operations. We have only two cases to consider

- $S = \{(\alpha,\alpha,\beta,\beta)\}$, where α and β can be equal

$$n^S = \frac{1}{2|G|}\sum_R \Big(\big(\chi^\alpha(R)^*\big)^2\chi^\beta(R)^2 + \chi^\alpha(R^2)^*\chi^\beta(R^2)\Big); \tag{26}$$

- For all other cases

$$n^S = \frac{1}{|G|}\sum_R \chi^\alpha(R)^*\chi^\beta(R)^*\chi^\gamma(R)\chi^\delta(R). \tag{27}$$

3. Minimizing Coulomb integral calculations

Exactly as in the case of real representation matrices treated in section IV A 5, Coulomb integrals can be calculated from a minimum number n^S of them.

V. SUBDUCTION

In this section, we consider the point group G, which is a subgroup of a larger group $\mathcal{G}$ (symmetry breaking) in order to compare the invariants of both groups. To do so, we will give the expression of the G-invariants on the basis of the $\mathcal{G}$-invariants.

A typical application consists in taking the continuous rotation group $SO(3)$ as the larger group. Therefore, we first show that the $SO(3)$ invariants are related to the well-known Slater integrals, which parametrize Coulomb interaction in spherical symmetry.

All point symmetry groups are subgroups of $O(3)$ rather than $SO(3)$, but since $O(3)$ is the direct product of $SO(3)$ and $C_i\{1,\mathcal{I}\}$, where $\mathcal{I}$ is the inversion, the irreps of $O(3)$ are direct products of irreps of $SO(3)$ and of C_i. To simplify notations, we first concentrate on $SO(3)$ and use the results to describe subduction from $O(3)$.

A. $SO(3)$-invariants

1. $SO(3)$-invariants for spherically-symmetric potentials

The theory presented in the previous section does not directly apply to $SO(3)$ because, although irreps ℓ are real (in the sense of Frobenius-Schur), they are usually represented by Wigner matrices $D^\ell(R)$ which can be complex. The usual basis of spherical harmonics Y^m_ℓ is also generally not real. This, however, has only a benign effect and we only indicate the results. We follow the notation used in Cowan's book [59], where Coulomb integrals are given (for a Coulomb potential) by

$$\begin{aligned}U^{(\ell_1\ell_2\ell_3\ell_4)}_{m_1m_2m_3m_4} &= \langle \ell_1m_1\ell_2m_2|\frac{2}{r_{ij}}|\ell_3m_3\ell_4m_4\rangle\\ &= \sum_k R^k(\ell_1\ell_2,\ell_3\ell_4)\delta_{m_3-m_1,m_2-m_4}(-1)^{m_2+m_3}\\ &\quad\times\sqrt{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)(2\ell_4+1)}\\ &\quad\times\begin{pmatrix}\ell_1 & k & \ell_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & k & \ell_4\\ 0 & 0 & 0\end{pmatrix}\\ &\quad\times\begin{pmatrix}\ell_1 & k & \ell_3\\ -m_1 & m_1-m_3 & m_3\end{pmatrix}\begin{pmatrix}\ell_2 & k & \ell_4\\ -m_2 & m_2-m_4 & m_4\end{pmatrix},\end{aligned}$$

where [59]

$$\begin{aligned}R^k(\ell_1\ell_2,\ell_3\ell_4) = \int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\frac{2r_<^k}{r_>^{k+1}}\\ \times R_{\ell_1}(r_1)R_{\ell_2}(r_2)R_{\ell_3}(r_1)R_{\ell_4}(r_2),\end{aligned}$$

are radial integrals and we assumed real radial wavefunctions R_ℓ. The $3j$-symbols involving a row of zeros can only be non zero if $\ell_1+\ell_3+k$ and $\ell_2+\ell_4+k$ are even. As a consequence, $\ell_1+\ell_3+\ell_2+\ell_4$ is even and $(-1)^{\ell_1+\ell_3+\ell_2+\ell_4} = 1$.

Our $SO(3)$-invariants $I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}$ were calculated by Cowan (Eq. (10.17) and (10.20), [59])

$$\begin{aligned} I^{(\ell_1\ell_2\ell_3\ell_4,\ell)} &= \langle(\ell_1\otimes\ell_2)^\ell_m|\frac{2}{r_{ij}}|(\ell_3\otimes\ell_4)^\ell_m\rangle \\ &= (-1)^{\ell_1-\ell_3+\ell} \\ &\quad\times\sqrt{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)(2\ell_4+1)} \\ &\quad\times\sum_k \begin{pmatrix}\ell_1 & k & \ell_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & k & \ell_4\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}\ell_1 & \ell_2 & \ell\\ \ell_4 & \ell_3 & k\end{Bmatrix} \\ &\quad\times R^k(\ell_1\ell_2,\ell_3\ell_4), \end{aligned}$$

where the right hand side is known to be independent of m. Cowan's result relates to the present work through

$$|(\ell_1\otimes\ell_2)^\ell_m\rangle = \sum_{m_1m_2}(\ell_1m_1\ell_2m_2|\ell m)\varphi^{\ell_1}_{m_1}(\mathbf{r}_i)\varphi^{\ell_2}_{m_2}(\mathbf{r}_j).$$

Moreover, since the right hand side of the equation for $I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}$ is independent of m, it can be replaced by its average over m. Thus, we obtain

$$\begin{aligned} I^{(\ell_1\ell_2\ell_3\ell_4,\ell)} = \frac{1}{2\ell+1}\sum_{m_1m_2m_3m_4m}&(\ell_1m_1\ell_2m_2|\ell m) \\ &\times(\ell_3m_3\ell_4m_4|\ell m)\,U^{(\ell_1\ell_2\ell_3\ell_4)}_{m_1m_2m_3m_4}, \end{aligned}$$

which is indeed a $SO(3)$-invariant in the sense of Eq. (12).

In the case of d electrons for which $\ell_1=\ell_2=\ell_3=\ell_4=2$, we write $F^k=R^k(22,22)$ for the standard d-shell Slater integrals and we obtain

$$\begin{aligned} I^{(2^4,0)} &= F^0+\frac{2}{7}F^2+\frac{2}{7}F^4, \\ I^{(2^4,1)} &= F^0+\frac{1}{7}F^2-\frac{4}{21}F^4, \\ I^{(2^4,2)} &= F^0-\frac{3}{49}F^2+\frac{4}{49}F^4, \\ I^{(2^4,3)} &= F^0-\frac{8}{49}F^2-\frac{1}{49}F^4, \\ I^{(2^4,4)} &= F^0+\frac{4}{49}F^2+\frac{1}{441}F^4. \end{aligned}$$

The expressions of this section were obtained by explicitly assuming that the interaction potential is the Coulomb potential. In the following, we only assume that the potential is spherically symmetric (so that the invariants remain $SO(3)$-invariants) and symmetric under the exchange of particles (so that the D_4 permutation symmetry is still valid.) This enables us to consider more general effective potentials.

2. *Permutation-symmetrized $SO(3)$-invariants*

As in the case of the general group G, we can build permutation-symmetrized $SO(3)$-invariants. The D_4 permutation symmetry can only be applied if the complex spherical harmonics are transformed into real (or cubic or tesseral) harmonics, but the corresponding Clebsch-Gordan coefficients are not the usual ones. We prefer to work with spherical harmonics, but the action of D_4 permutations is now different

$$\begin{aligned} U^{(\ell_1\ell_2\ell_3\ell_4)}_{m_1m_2m_3m_4} &= U^{(\ell_2\ell_1\ell_4\ell_3)}_{m_2m_1m_4m_3} = (-1)^{m_1+m_3}U^{(\ell_2\ell_3\ell_4\ell_1)}_{m_2-m_3m_4-m_1} \\ &= (-1)^{m_1+m_2+m_3+m_4}U^{(\ell_3\ell_4\ell_1\ell_2)}_{-m_3-m_4-m_1-m_2} \\ &= (-1)^{m_1+m_2+m_3+m_4}U^{(\ell_4\ell_3\ell_2\ell_1)}_{-m_4-m_3-m_2-m_1} \\ &= (-1)^{m_1+m_3}U^{(\ell_3\ell_2\ell_1\ell_4)}_{-m_3m_2-m_1m_4} \\ &= (-1)^{m_2+m_4}U^{(\ell_4\ell_1\ell_2\ell_3)}_{-m_4m_1-m_2m_3} \\ &= (-1)^{m_2+m_4}U^{(\ell_1\ell_4\ell_3\ell_2)}_{m_1-m_4m_3-m_2}. \end{aligned}$$

Still, the result $\langle I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}\rangle$ of permutation symmetrization has the same form as the one for real representation matrices given by Eq. (20), if we substitute $\alpha=\ell_1$, $\beta=\ell_2$, $\gamma=\ell_3$, $\delta=\ell_4$, $\eta=\ell$, $\phi=\ell'$, all permutation factors $\{\ell_i\ell_j,\ell_k\}=(-1)^{\ell_i+\ell_j-\ell_k}$ and $(-1)^{\eta+\phi}$ is replaced by $(-1)^{\ell_1+\ell_3}$. Note that, because of the last substitution, the formula for $SO(3)$ is not a special case of the general formula given in Eq. (20) because, for all irreps $\alpha(=\ell)$ of $SO(3)$, $(-1)^\alpha=1$ in the sense of the definition given in section IV A 1 b. The additional factor $(-1)^{\ell_1+\ell_3}$ comes from the fact that the action of D_4 involves signs due to the complex nature of the representation matrices.

In particular, if $\ell_1=\ell_2=\ell_3=\ell_4$, then

$$\langle I^{(\ell_1^4,\ell)}\rangle = \frac{1}{2}I^{(\ell_1^4,\ell)}+\frac{1}{2}\sum_{\ell'}(2\ell'+1)\begin{Bmatrix}\ell_1 & \ell_1 & \ell'\\ \ell_1 & \ell_1 & \ell\end{Bmatrix}I^{(\ell_1^4,\ell')}.$$

For $\ell_1=\ell_2=\ell_3=\ell_4=2$, this formula gives us

$$\langle I^{(2^4,\ell)}\rangle = \sum_{\ell'=0}^{4}M_{\ell\ell'}I^{(2^4,\ell')},$$

where

$$M=\frac{1}{140}\begin{pmatrix}84 & -42 & 70 & -98 & 126\\ -14 & 105 & -35 & 0 & 84\\ 14 & -21 & 55 & 56 & 36\\ -14 & 0 & 40 & 105 & 9\\ 14 & 28 & 20 & 7 & 71\end{pmatrix}. \tag{28}$$

As expected M is a (non-orthogonal) projector (i.e. $M^2=M$) with eigenvalues $(1,1,1,0,0)$. Therefore, there are three independent components that can be related to the three Slater integrals. The reader can check that $\langle I^{(2^4,\ell)}\rangle = I^{(2^4,\ell)}$ when $I^{(2^4,\ell)}$ is expressed in terms of Slater integrals F^k as in the end of the previous section.

To illustrate the construction described in section IV A 4, we consider the matrix $Q_{\ell\ell'}=\delta_{\ell\ell'}\sqrt{2\ell+1}$ and we choose three orthonormal eigenvectors $\mathbf{v}^{1,p}$ of $N=QMQ^{-1}$ for eigenvalue 1 and two eigenvectors $\mathbf{v}^{0,p}$ for eigenvalue 0 (that we did not orthonormalize to sim-

plify its form) to build the matrix

$$B = \begin{pmatrix} \frac{1}{5} & \frac{1}{\sqrt{5}} & \frac{3}{5} & -\frac{1}{2} & \frac{5}{2\sqrt{7}} \\ \frac{\sqrt{3}}{5} & \frac{\sqrt{\frac{3}{5}}}{2} & -\frac{2\sqrt{3}}{5} & -\frac{5}{4\sqrt{3}} & -\frac{\sqrt{\frac{3}{7}}}{4} \\ \frac{1}{\sqrt{5}} & -\frac{3}{14} & \frac{6}{7\sqrt{5}} & -\frac{\sqrt{5}}{4} & -\frac{\sqrt{35}}{4} \\ \frac{\sqrt{7}}{5} & -\frac{4}{\sqrt{35}} & -\frac{3}{10\sqrt{7}} & 0 & 1 \\ \frac{3}{5} & \frac{6}{7\sqrt{5}} & \frac{1}{70} & 1 & 0 \end{pmatrix},$$

giving us the three independent components

$$u^1 = 5F^0, \quad u^2 = \frac{2\sqrt{5}}{7}F^2, \quad u^3 = \frac{10}{21}F^4. \tag{29}$$

Eigenvectors $\mathbf{v}^{1,p}$ were chosen to get this simple relation between independent components and Slater integrals. By using Eq. (25), we can now easily calculate the norm of the set of 625 Coulomb integrals for $S = \{2,2,2,2\}$ in terms of Slater integrals

$$\begin{aligned} ||U^S||^2 &= \sum_{m_1m_2m_3m_4} |U^{(2^4)}_{m_1m_2m_3m_4}|^2 \\ &= 25(F^0)^2 + \frac{20}{49}(F^2)^2 + \frac{100}{441}(F^4)^2. \end{aligned}$$

Incidentally, we recover the fact, often used in practice [23–25] that spherically symmetric potentials can be described by the usual three Slater integrals F^0, F^2 and F^4 for d orbitals. Indeed, Slater integrals were originally derived under the assumption that the interaction potential is of Coulomb type but the conclusion that there are only 3 symmetrized $SO(3)$ invariants are obtained here for more general potentials. We just assumed that the potential is real, spherically symmetric and invariant under the exchange of $\mathbf{x}$ and $\mathbf{y}$, so that the D_4 symmetry holds. Any real potential of the form $V(|\mathbf{x}|, |\mathbf{y}|, \mathbf{x}\cdot\mathbf{y}) = V(|\mathbf{y}|, |\mathbf{x}|, \mathbf{x}\cdot\mathbf{y})$ satisfies these assumptions.

We can also take advantage of this example to show how the method described in section IV A 5 minimizes the calculation of Coulomb integrals. Cowan's formula gives 625 Coulomb integrals $U^{(2^4)}_{m_1m_2m_3m_4}$ as a linear combination of three Slater integrals, which are simply related to our independent components in Eq. (29). Therefore, the matrix A relating Coulomb integrals to independent components has 3 lines and 625 columns. From this matrix we extract three columns corresponding to $U^{(2^4)}_{0000}$, $U^{(2^4)}_{001-1}$ and $U^{(2^4)}_{002-2}$ to build the 3×3 matrix

$$P = \begin{pmatrix} \frac{1}{5} & \frac{2}{7\sqrt{5}} & \frac{6}{35} \\ 0 & -\frac{1}{14\sqrt{5}} & -\frac{1}{7} \\ 0 & \frac{2}{7\sqrt{5}} & \frac{1}{14} \end{pmatrix}.$$

Since $\det P \neq 0$, P is invertible and we can compute the independent components u^1, u^2 and u^3 from the Coulomb integrals $U^{(2^4)}_{0000}$, $U^{(2^4)}_{001-1}$ and $U^{(2^4)}_{002-2}$. Once we know the independent components, we can calculate all 625 Coulomb integrals.

3. Enumeration of symmetrized $SO(3)$-invariants

The number of symmetrized $SO(3)$-invariants is expressed by formulas similar to the one given for G. For example, if $\ell_1 = \ell_2 = \ell_3 = \ell_4 = \ell$, and if the rotations are defined by an axis $\mathbf{n}$ and an angle ω, then the character of the rotation is $\chi_\ell(\omega) = \sin\big((2\ell+1)\omega/2\big)/\sin(\omega/2)$ and [60]

$$\begin{aligned} n^{S_1} = \frac{1}{8\pi}\int_0^{2\pi} d\omega\, \sin^2(\omega/2)\big(\chi_\ell(\omega)^4 + 3\chi_\ell(2\omega)^2 \\ +2\chi_\ell(2\omega)\chi_\ell(\omega)^2 + 2\chi_\ell(4\omega)\big) = \ell+1. \end{aligned}$$

Similarly

$$\begin{aligned} n^{S_2} &= \min(\ell_\alpha+1, \ell_\beta+1), \\ n^{S_3} &= \min(2\ell_\alpha+1, 2\ell_\beta+1), \\ n^{S_4} &= \frac{1}{2}a^{\ell_\beta\ell_\gamma}(0) - \frac{1}{2}a^{\ell_\beta\ell_\gamma}(2\ell_\alpha+1) + \frac{1}{2}b^{\ell_\beta\ell_\gamma}(2\ell_\alpha), \\ n^{S_5} &= a^{\ell_\alpha\ell_\beta}(|\ell_\gamma-\ell_\delta|) - a^{\ell_\alpha\ell_\beta}(\ell_\gamma+\ell_\delta+1), \end{aligned}$$

where

$$a^{\ell\ell'}(m) = \begin{cases} 2\min(\ell,\ell')+1 & \text{if } |m| \le |\ell-\ell'|, \\ \ell+\ell'-|m|+1 & \text{if } |\ell-\ell'| \le |m| \le \ell+\ell', \\ 0 & \text{if } |m| > \ell+\ell', \end{cases}$$

and

$$b^{\ell\ell'}(m) = \begin{cases} 1 & \text{if } \ell+\ell' \text{ is even and } |m| \ge |\ell-\ell'|, \\ -1 & \text{if } \ell+\ell' \text{ is odd and } |m| > \ell+\ell', \\ 0 & \text{otherwise.} \end{cases}$$

B. Subduction from $\mathcal{G}$ to G

We now come back to a general point group G, but for notational convenience we keep labeling the irreps of the larger group $\mathcal{G}$ by $\ell_1, \ell_2, \ldots$, as for $SO(3)$. However, we insist that the following formulas do not require $\mathcal{G} = SO(3)$.

When lowering the symmetry, each irrep of the larger group branches into several irreps of the subgroup. For instance, the $\ell = 2$ representation of $\mathcal{G} = SO(3)$ splits into the representations E_g and T_{2g} of $G = O_h$. Let us denote $\ell_1\alpha$ the irrep α of G that comes from ℓ_1 of $\mathcal{G}$, and idem for $\ell_2\beta$, $\ell_3\gamma$, $\ell_4\delta$ and $\ell\eta$. The basis of the irreps of $\mathcal{G}$, $\{|\ell m\rangle\}$ with $1 \le m \le \dim\ell$, spans the same space as $\{|\ell\alpha a\rangle\}$, where α runs over all the irreps subduced from ℓ and $1 \le a \le \dim\alpha$. As a consequence, the interaction elements can be labelled by $U^{(\ell_1\ell_2\ell_3\ell_4)}_{\alpha a\beta b\gamma c\delta d}$ or $U^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta)}_{abcd}$ indiscriminately.

1. Isoscalar factors

We showed in Sec. III B that the group invariants are basis-independent, but they depend on the point

group. In a $\mathcal{G}$-symmetric point group, the interaction elements can be expressed either in terms of $\mathcal{G}$-invariants $I^{(\ell_1\ell_2\ell_3\ell_4,l)}$

$$U^{(\ell_1\ell_2\ell_3\ell_4)}_{\alpha a\beta b\gamma c\delta d} = \sum_{\ell\eta e}(\ell_1\alpha a\ell_2\beta b|\ell\eta e)(\ell_3\gamma c\ell_4\delta d|\ell\eta e)^* I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}, \tag{30}$$

or in terms of the subduced G invariants $I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta,\eta)}$

$$U^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta)}_{abcd} = \sum_{\eta e}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e)^* I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta,\eta)}. \tag{31}$$

Now, the Racah factorization lemma [46] states that the Clebsch-Gordan coefficients of $\mathcal{G}$, $(\ell_1\alpha a\ell_2\beta b|\ell\eta e)$, and those of G, $(\alpha a\beta b|\eta e)$, are related via complex numbers $\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)$ called isoscalar factors

$$(\ell_1\alpha a\ell_2\beta b|\ell\eta e) = \left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)(\alpha a\beta b|\eta e). \tag{32}$$

Isoscalar factors are fundamental ingredients of group-subgroup symmetry calculations [44, 46, 52, 61–63]. They satisfy orthogonality relations [46]

$$\sum_{\ell}\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha' & \beta' & \eta\end{array}\right)^* = \delta_{\alpha\alpha'}\delta_{\beta\beta'},$$

$$\sum_{\alpha\beta}\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell'\\ \alpha & \beta & \eta\end{array}\right)^* = \delta_{\ell\ell'}.$$

We implicitly assumed that $\alpha, \beta, \eta, \ldots$ appear in the subduction of $\ell_1, \ell_2, \ell, \ldots$, respectively, and that η belongs to the Clebsch-Gordan expansion of $\alpha\otimes\beta$ and $\alpha'\otimes\beta'$. Isoscalar factors are usually calculated from Clebsch-Gordan coefficients, but their squares can be calculated from characters [62, 64].

By comparing the right-hand side of Eqs. (30) and (31) and using the usual orthogonality relations of Clebsch-Gordan coefficients, we get

$$I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta,\eta)} = \sum_{\ell}\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)\left(\begin{array}{cc|c}\ell_3 & \ell_4 & \ell\\ \gamma & \delta & \eta\end{array}\right)^* \times I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}, \tag{33}$$

$$I^{(\ell_1\ell_2\ell_3\ell_4,\ell)} = \sum_{\alpha\beta\gamma\delta\eta}\frac{\dim\eta}{\dim\ell}\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ \alpha & \beta & \eta\end{array}\right)^*\left(\begin{array}{cc|c}\ell_3 & \ell_4 & \ell\\ \gamma & \delta & \eta\end{array}\right) \times I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta,\eta)}. \tag{34}$$

To summarize the result of this section, $I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta,\eta)}$ are G-invariants obtained for a system with a symmetry group $\mathcal{G}\supset G$. They can be directly compared to the G-invariants of a system with the actual G symmetry group. Equation (34) can also be used to calculate a set of (approximate) $\mathcal{G}$-invariants $I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}$ from the G-invariants $I^{(\alpha\beta\gamma\delta,\eta)}$; the mean squared error of the fit would measure the deviation of the lower-symmetry system from the one with the higher symmetry.

For notational convenience, we assumed that each irrep α of G appears only once in the subduction of the irrep ℓ of $\mathcal{G}$. However, if the order of G is small or if the dimension of ℓ is large, it usually happens that some irrep α appears more than once in the subduction from ℓ. For example, the irrep $\ell = 5$ of $SO(3)$ generates two independent irreps T_{1g} of the octahedral group O. To take this multiplicity into account, we add a new index k and a general subduction is now described by $\ell k\alpha$. For example

$$\ell = 5 \to 1T_{1g}\oplus 2T_{1g}\oplus 1E_g\oplus 1T_{2g}.$$

The Clebsch-Gordan coefficients use this additional index and the Racah factorization lemma becomes

$$(\ell_1 k_\alpha\alpha a\ell_2 k_\beta\beta b|\ell k\eta e) = \left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ k_\alpha\alpha & k_\beta\beta & k\eta\end{array}\right)(\alpha a\beta b|\eta e),$$

where the additional indices are restricted to the isoscalar factor. The Coulomb integrals can be written in terms of the subduced G invariants as

$$U^{(\ell_1 k_\alpha\alpha\ell_2 k_\beta\beta\ell_3 k_\gamma\gamma\ell_4 k_\delta\delta)}_{abcd} = \sum_{\eta e}(\alpha a\beta b|\eta e)(\gamma c\delta d|\eta e)^* I^{(\ell_1 k_\alpha\alpha\ell_2 k_\beta\beta\ell_3 k_\gamma\gamma\ell_4 k_\delta\delta,\eta)},$$

where

$$I^{(\ell_1 k_\alpha\alpha\ell_2 k_\beta\beta\ell_3 k_\gamma\gamma\ell_4 k_\delta\delta,\eta)} = \sum_{\ell k}\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ k_\alpha\alpha & k_\beta\beta & k\eta\end{array}\right)\left(\begin{array}{cc|c}\ell_3 & \ell_4 & \ell\\ k_\gamma\gamma & k_\delta\delta & k\eta\end{array}\right)^* I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}.$$

This is the generalization of Eq. (33), whereas Eq. (34) becomes

$$I^{(\ell_1\ell_2\ell_3\ell_4,\ell)} = \sum_{\substack{k_\alpha\alpha k_\beta\beta\\ k_\gamma\gamma k_\delta\delta k\eta}}\frac{\dim\eta}{\dim\ell}I^{(\ell_1 k_\alpha\alpha\ell_2 k_\beta\beta\ell_3 k_\gamma\gamma\ell_4 k_\delta\delta,\eta)} \times\left(\begin{array}{cc|c}\ell_1 & \ell_2 & \ell\\ k_\alpha\alpha & k_\beta\beta & k\eta\end{array}\right)^*\left(\begin{array}{cc|c}\ell_3 & \ell_4 & \ell\\ k_\gamma\gamma & k_\delta\delta & k\eta\end{array}\right).$$

C. Subduction from $O(3)$

As explained in the introduction of this section, the irreps of $O(3)$ are the direct product $L = (\ell, \epsilon_L)$ of an irrep ℓ of $SO(3)$ and an irrep $\epsilon_L = \pm 1$ of C_i [35]. The commutative group C_i is of order 2 with two irreps denoted by $\epsilon_L = \pm 1$ that are one-dimensional and satisfy $\mathcal{I}\triangleright\varphi_L = \epsilon_L\varphi_L$. Moreover, $\mathcal{I}$ commutes with $SO(3)$. In general, the action of $\mathcal{I}$ on a tensor product of irreps of $O(3)$ is

$$\mathcal{I}\triangleright(\varphi_{L_1}\otimes\varphi_{L_2}) = \epsilon_{L_1}\epsilon_{L_2}(\varphi_{L_1}\otimes\varphi_{L_2}).$$

The Clebsch-Gordan coefficients for $O(3)$ are

$$(L_1 m_1 L_2 m_2 | L_3 m_3) = \delta_{\epsilon_{L_1}\epsilon_{L_2},\epsilon_{L_3}} (\ell_1 m_1 \ell_2 m_2 | \ell_3 m_3).$$

The $O(3)$ invariants are

$$I^{(L_1 L_2 L_3 L_4, L)} = \delta_{\epsilon_{L_1}\epsilon_{L_2},\epsilon_L} \delta_{\epsilon_{L_3}\epsilon_{L_4},\epsilon_L} I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}.$$

The condition $\epsilon_{L_1}\epsilon_{L_2} = \epsilon_L = \epsilon_{L_3}\epsilon_{L_4}$ implies $\epsilon_{L_1}\epsilon_{L_2}\epsilon_{L_3}\epsilon_{L_4} = 1$, which is symmetric under permutation of L_1, L_2, L_3, L_4 and also implies $\epsilon_{L_i}\epsilon_{L_j} = \epsilon_{L_k}\epsilon_{L_l}$, where (i, j, k, l) is any permutation of $(1, 2, 3, 4)$. Therefore, $\langle I^{L_1 L_2 L_3 L_4, L}\rangle$ is obtained from the same formula as $\langle I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}\rangle$ up to the fact that the pair-conserving term gets the factor $\delta_{\epsilon_{L_1}\epsilon_{L_2},\epsilon_L}\delta_{\epsilon_{L_3}\epsilon_{L_4},\epsilon_L}$ while the pair-non-conserving term gets the factor $\delta_{\epsilon_{L_1}\epsilon_{L_4},\epsilon_{L'}}\delta_{\epsilon_{L_2}\epsilon_{L_3},\epsilon_{L'}}$.

In the calculations of the previous sections, we used spherical harmonics, for which $L = (\ell, \epsilon_L)$ with $\epsilon_L = (-1)^\ell$. Thus, in the following we denote by ℓ the $O(3)$ irrep $(\ell, (-1)^\ell)$. Then

$$\mathcal{I} \triangleright U^{(\ell_1\ell_2\ell_3\ell_4)}_{m_1 m_2 m_3 m_4} = U^{(\ell_1\ell_2\ell_3\ell_4)}_{m_1 m_2 m_3 m_4},$$

because the selection rules for $3j$-symbols imply $(-1)^{\ell_1+\ell_3} = (-1)^{\ell_2+\ell_4}$. Similarly $I^{(L_1 L_2 L_3 L_4, L)}$ becomes $I^{(\ell_1\ell_2\ell_3\ell_4, L)}$ where $\epsilon_L = (-1)^{\ell_1+\ell_2} = (-1)^{\ell_3+\ell_4}$ because the L in $I^{(\ell_1\ell_2\ell_3\ell_4, L)}$ does not correspond to a spherical harmonics, for the same reason as the cross product of two vectors is a pseudovector (i.e. a "vector" which is even under inversion). Hence

$$\mathcal{I} \triangleright I^{(\ell_1\ell_2\ell_3\ell_4, L)} = I^{(\ell_1\ell_2\ell_3\ell_4, L)}.$$

Finally, since the condition $(-1)^{\ell_1+\ell_3+\ell_2+\ell_4} = 1$ is invariant under permutation of L_1, L_2, L_3, L_4, we also obtain

$$\mathcal{I} \triangleright \langle I^{(\ell_1\ell_2\ell_3\ell_4, L)}\rangle = \langle I^{(\ell_1\ell_2\ell_3\ell_4, L)}\rangle,$$

and $\langle I^{(\ell_1\ell_2\ell_3\ell_4, L)}\rangle$ is obtained from the same formula as $\langle I^{(\ell_1\ell_2\ell_3\ell_4,\ell)}\rangle$, except for the fact that the sum over ℓ' becomes a sum over $L' = (\ell', \epsilon_{L'})$, with $\epsilon_{L'} = (-1)^{\ell_1+\ell_4} = (-1)^{\ell_2+\ell_3}$, the $6j$-symbols involving only ℓ and ℓ'.

The subduction formulas are the same, provided we notice that, if G contains $\mathcal{I}$, then *gerade* irreps of G can only arise from even ℓ_i and *ungerade* irreps from odd ℓ_i.

VI. CONCLUSION

Starting from the simple and familiar problem of calculating Coulomb integrals in the most efficient way, we came to use surprisingly sophisticated tools of group theory, such as Clebsch-Gordan coefficients, $6j$-symbols, corepresentation theory or Racah factorization theorem, and had to recall the remarkable work by Derome and Sharp, which was unjustly forgotten. These tools enabled us to provide explicit expressions for the Coulomb integrals in the most general case, i.e. for any orbital in any crystal point group symmetry. Moreover, instead of providing tables which would depend on the exact basis used for each irrep and on the phase choice of Clebsch-Gordan coefficients, we give here general and self-contained formulas.

Although the spin degree of freedom was neglected in the present work, it is possible to take it into account as was done by Sugano and coauthors [26], who considered Coulomb integrals between spin-1 and spin-0 states. This implies adding the action of permutations (12) and (34), for which the Coulomb integrals are odd for spin-1 and even for spin-0. In other words, the full symmetric group S_4 should be considered instead of D_4. The methods used in this paper can handle such a case, but the formula for the permutation-symmetrized G-invariants would involve 24 terms instead of 8.

It would also be tempting to refine the present treatment of complex irreps, for example by considering their real and imaginary parts and reducing the problem to the case of real representations. However, this would be a non-trivial extension of the present work, because the resulting real representations would not be irreducible and many of our proofs made a crucial use of Schur's lemma, which holds only for irreps. Pseudo-real irreps could possibly be dealt with by using the fact that a representation and its complex conjugate are related by a similarity transformation, generalizing what we did for $SO(3)$.

Finally, another fruitful extension would be to deal with magnetic groups and their corepresentations, which are used to describe the transport and response properties of magnetic and multiferroic materials [65–69]. Although we dealt with corepresentations in the present work, the theory of corepresentations is not as developed as the theory of representations, and this extension would also be non-trivial.

ACKNOWLEDGMENTS

C.L. acknowledges funding by the "Fondation CFM pour la Recherche" via a *Jean-Pierre Aguilar* PhD scholarship. We thank Shintaro Hoshino for explaining certain technical aspects of his paper [28]. We are very grateful to Jean-Robert Derome for sending us a copy of his 1965 PhD thesis [55], without which the present work could not have been carried out.

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[70] The relation between our Clebsch-Gordan coefficients and the $3j$-symbols of Ref. [42] is $(\alpha a \beta b|\eta e) = \sqrt{\dim \eta} \sum_{e'} (\alpha\beta\eta^*)^*_{abe'} (\eta)_{ee'}$, where $(\eta)_{ee'}$ is the so-called $1j$-symbol.

[71] The crucial point is the recoupling formula which we need in section IV A. In Butler's approach the recoupling formula involves $2jm$-symbols $\left(\begin{smallmatrix} \alpha & \alpha^* \\ a & a' \end{smallmatrix}\right)$ which may depend nontrivially on a. As a result, we cannot use them to identify recoupled G-invariants. On the contrary, Derome's recoupling formula makes use of $1j$-symbols $(\alpha)_{aa'}$, which are multiple of the identity for real and complex representations. Hence they simply add prefactors to the recoupled G-invariants.

[72] Note that the formulas given in Ref. 42 generalize the work by Sharp for quasi-ambivalent and multiplicity-free groups [54]. All crystal point groups are quasi-ambivalent, see Ref. [46].