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Polarization dependence of multiphoton transitions

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In order to determine the polarization dependence of multiphoton transitions to excitonic states in solids, we develop a symmetry analysis of the transition-rate formula that includes the study of its transformation properties under permutation of the photon indices. These properties play an important role when some or all of the photons have equal frequency or polarization. The way permutation invariance affects the transition rate depends on the symmetry of the excited state. We show how the number of dynamical parameters in the polarization dependence is reduced when some of the photons are of equal frequency and how this effect can lead to more stringent selection rules. We apply the theory to the case of two-, three-, and four-photon transitions. We describe a procedure that gives the polarization dependence for any crystal point group. In particular, we point out that the more stringent selection rules that are found in the case of photons of equal frequency are the same as in the case of photons of equal polarization. This property is related to the invariance of the transition rate under permutations of all the photon indices.

I. INTRODUCTION

In recent decades multiphoton spectroscopy has become a powerful tool to investigate electronic properties in solids. Spectroscopic techniques that differ because of the number of photons participating in the interaction process generally provide alternative and complementary information. The selection rules are different according to the number of participating photons. For instance, in solids with inversion symmetry, two-photon spectroscopy allows us to detect transitions to states of even parity, which are forbidden for one-photon transitions. With the increase in the number of photons involved, generally more transitions become allowed. For example, in solids of O_h symmetry, more states can be excited in three-photon spectroscopy than in one-photon spectroscopy.[1-5] Another aspect of multiphoton spectroscopy is the increased flexibility of the technique. By changing independently the polarizations of the photons, it is possible to determine the symmetry of the excited state.[6-9] Moreover, the possibility of varying the total $\mathbf{k}$ vector by changing the relative direction of the photons can be used in order to study the $\mathbf{k}$ dispersion of the polariton and even excite the longitudinal excitons.[10-12]

In multiphoton absorption processes from the crystal ground state, the polarization dependence for transitions to states of a given symmetry can be determined, i.e., all transitions to states of that symmetry have the same polarization dependence. In this case the transition rate can be separated into a geometrical factor that contains the polarization dependence and a dynamical factor that contains the transition-matrix elements.[13] Only the latter is dependent on the photon frequencies. However, this is not generally the case: the transition rate is then no longer separable and the polarization dependence contains dynamical parameters that have different values for different excited states of the same symmetry.[14,4,15] Only the number of dynamical parameters that appear in the transition rate is determined by the symmetry of the excited state. The number of dynamical parameters in the case of small point groups is generally larger than in the case of point groups of higher symmetry.[14] When the number of absorbed photons increases, generally the number of dynamical parameters increases as well.[14,4] These parameters, which are usually unknown, are taken as free parameters and therefore a precise symmetry identification of the excited state from polarization measurements alone is often difficult in multiphoton transitions. We will show that with the use of permutation symmetry it is possible to reduce the number of nonvanishing dynamical parameters. In some cases it is even possible that additional selection rules occur.[4,5] The possibility of varying the number of nonvanishing dynamical parameters is an extremely valuable tool for symmetry assignments of excited states.

In this paper we present a general procedure that gives the polarization dependence of multiphoton transitions, with a particular emphasis on the cases in which the absorbed photons are of equal polarization or frequency. We show that the dynamical factors in the n-photon transition rate transform under permutation of the photon frequencies like basis-functions of irreducible representations of the permutation group on n elements.[16] This implies that if some or all of the involved photons are of

equal frequency, some of the dynamical factors may vanish. If, for transitions to states of a particular symmetry, all the dynamical factors vanish, additional selection rules occur. For example, in the case of two-photon absorption, it is known that the dynamical parameters are either symmetric or antisymmetric for exchange of the photon frequencies.[13] Antisymmetric dynamical factors vanish when the absorbed photons have equal frequencies. In this case, excited states of a particular symmetry whose transition rate contains only antisymmetric dynamical factors are forbidden. In this paper we show that this additional selection rule found in the case of two-photon transitions is related to the permutation symmetry of the photon frequencies, and we develop a general framework that allows us to deduce similar rules for cases in which more photons are absorbed. In general, permutation symmetry reduces the number of nonvanishing dynamical factors and therefore simplifies the polarization dependence. The polarization dependence turns out to be the same for all excited states of the same given symmetry if all dynamical factors but one vanish. The symmetry analysis shows that particular irreducible representations of the permutation group are associated to the allowed irreducible representations of the point group. Thus it is possible to study the symmetry of the excited states by analyzing how the number of dynamical parameters in the polarization dependence varies when some or eventually all the absorbed photons are of equal frequency.

In particular, we show that when the photons are taken of equal frequency *or* of equal polarization, the dipole selection rules are affected in the *same* way. The relation between the transformation properties for separate permutations of the photon frequencies and polarizations is given by the condition that the transition rate is invariant if frequencies *and* polarizations are permuted simultaneously. The invariance under permutation of all the photon quantum numbers of the electron-photon interaction is a consequence of the bosonic character of the photons.

In Sec. II, we present a symmetry analysis of the n-photon transition rate that emphasizes the transformation properties of the geometrical and dynamical factors under permutations of the photon indices. In Sec. III, the theory is applied to the case of two-, three-, and four-photon transitions. A general procedure is presented that yields the polarization dependence for any crystal point group. Concluding remarks can be found in Sec. IV.

II. SYMMETRY ANALYSIS OF THE MULTIPHOTON TRANSITION RATE

The n-photon transition rate can be obtained from time-dependent perturbation theory. We are interested in the transition rate from the ground state of the system $|0\rangle$ to a final state f_ν^α which belongs to the νth row of the representation α of the point group. In the dipole approximation, the transition rate is proportional to

$$\sum_\nu \left| \sum_\sigma O_\sigma \langle f_\nu^\alpha \mid \epsilon_1^* \cdot \mathbf{P}\, \Lambda(\omega_2 + \cdots + \omega_n) \cdots \epsilon_{n-1}^* \cdot \mathbf{P}\, \Lambda(\omega_n)\, \epsilon_n^* \cdot \mathbf{P} \mid 0 \rangle \right|^2 , \tag{1}$$

where the Λ are symmetry invariant operators

$$\Lambda(\omega) = \sum_k \frac{|\psi_k\rangle\langle\psi_k|}{E_k - E_0 - \hbar\omega}, \tag{2}$$

the total momentum operator $\mathbf{P}$ is given by $\mathbf{P} = \sum_i \mathbf{p}_i$, and ϵ_j and ω_j $(j = 1, 2, \cdots, n)$ represent the polarization vector and the frequency of the jth photon, respectively. The operator O_σ permutes all the indices of the polarizations and frequencies. The sum over σ in (1) stands for the sum over all the $n!$ permutations of n indices. Because of this sum the expression is symmetric for a permutation of the photon indices.

We consider the operator in the matrix element in (1) for one particular permutation: suppose for simplicity the identity. The transition operators in (1) transform in the same way as $P_{i_1} P_{i_2} \cdots P_{i_n}$, where i_k for $k = 1, 2, \cdots, n$ indicates the component of each momentum operator. The order in which the momentum operators appear is relevant because of the presence of the Λ operators. These transition operators transform as a 3^n-dimensional representation R of the point group as well as of the permutation group. Moreover, as permutation operators and symmetry operators of the point group commute, the transition operators also transform as a 3^n-dimensional representation of the group, which is obtained as a direct-product of the point group and the permutation group. The representation R can therefore be decomposed in the irreducible representations of this direct product group, which are direct products of the irreducible representations of the point group and the permutation group. Expression (1) can be rewritten by decomposing the transition operators in operators $T_{\nu'\lambda}^{(\alpha'\beta)}$, which transform as the ν'th row of the irreducible representation α' of the point group under space operators and as the λth row of the irreducible representation β of the permutation group under permutations of the component indices i_k. Expression (1) now reads

$$\left|\sum_{\nu}\left|\sum_{\sigma}O_{\sigma}\sum_{n,(\alpha'\beta)}\sum_{\nu'=1}^{l_{\alpha'}}\sum_{\lambda=1}^{l_{\beta}}[\phi^{n,(\alpha'\beta)}_{\nu'\lambda}(\epsilon_1,\cdots,\epsilon_n)]^*\langle f^{\alpha}_{\nu}\mid T^{n,(\alpha'\beta)}_{\nu'\lambda}(\omega_1,\cdots,\omega_n)\mid 0\rangle\right|^2, \tag{3}$$

where the index n labels identical representations $(\alpha'\beta)$, which can occur more than once, and where $l_{\alpha'}$ and l_{β} are the dimensions of the representations α' and β, respectively. The ϕ are expressions of the polarization vectors,

$$\phi^{n,(\alpha\beta)}_{\nu\lambda}(\epsilon_1,\cdots,\epsilon_n)=\sum_{i_1,\cdots,i_n}c^{n,(\alpha\beta),\nu\lambda}_{i_1\cdots i_n}\epsilon_{1i_1}\cdots\epsilon_{ni_n}, \tag{4}$$

where the $c^{n,(\alpha\beta),\nu\lambda}_{i_1\cdots i_n}$ are the analogous of the Clebsch-Gordan coefficients. With the use of the Wigner-Eckart theorem, we derive that the transition operators must have the same symmetry as the final state, and the above expression simplifies to

$$\left|\sum_{\nu}\left|\sum_{\sigma}O_{\sigma}\sum_{n,\beta}\sum_{\lambda=1}^{l_{\beta}}[\phi^{n,(\alpha\beta)}_{\nu,\lambda}(\epsilon_1,\cdots,\epsilon_n)]^*\langle f^{\alpha}\parallel T^{n,(\alpha\beta)}_{\lambda}(\omega_1,\cdots,\omega_n)\parallel 0\rangle\right|^2, \tag{5}$$

where standard notation has been used for the reduced matrix elements. Because of the scalar products in (1), the ϕ's have the same transformation properties as the T's. We note that as the different ϵ_{ki_k} are labeled by the photon index k, a permutation of the component indices i_k yields the same result as the same permutation of the photon indices k. Thus the ϕ's transform under the operators O_{σ} according to the irreducible representation β of the permutation group. On the other hand, the $T^{n,(\alpha\beta)}_{\lambda}$ do not transform as any irreducible representation when the indices of the photon frequencies are permuted. However, if the effect of the O_{σ} on the ϕ's in (5) is worked out, it can be seen that the T's are projected on the same irreducible representation β to which the ϕ's belong. A detailed derivation is given in Appendix A. We obtain

$$\sum_{\nu}\left|\sum_{n,\beta}\sum_{\lambda=1}^{l_{\beta}}[\phi^{n,(\alpha\beta)}_{\nu,\lambda}(\epsilon_1,\cdots,\epsilon_n)]^*D^{n,(\alpha\beta)}_{\lambda}(\omega_1,\cdots,\omega_n)\right|^2, \tag{6}$$

where the $D^{n,(\alpha\beta)}_{\lambda}$ are the projected T's. The explicit expression of the $D^{n,(\alpha\beta)}_{\lambda}$ as a function of the T's is given in Appendix A.

Some important remarks can be made on the result (6). First, according to the symmetry α of the excited state, not only the polarization dependence is different, as was expected,[14,4] but in general also the associated permutation symmetries β are different. In fact, in the decomposition of the transition operator into the irreducible representations of the product group, product representations are found that relate representations of the permutation group to representations of the point group.

Second, in the polarization dependence of the transition rate, a certain number of dynamical factors D can appear. These factors have different values for different excited states of a given symmetry. If more than one dynamical factor appears in (6), the polarization dependence is not dependent on symmetry alone and contains $N_{\alpha}-1$ dynamical parameters, where N_{α} is the number of dynamical factors in (6). The number N_{α} corresponds to the number of times the representation α appears in the decomposition of the representation R of the transition operators into the irreducible representations of the point group. If $N_{\alpha}=1$, the transition rate is a simple product of geometrical and dynamical factors and the polarization dependence of the transition rate is the same for all final states of symmetry α.

Third, expression (6) shows that the dynamical factors transform under permutations of the frequencies according to irreducible representations of the permutation group on n elements. This result is very useful in order to determine which dynamical factors vanish when some or all the photons have the same frequency. This aspect is analyzed in detail in the next section for the cases of two-, three-, and four-photon transitions.

Fourth, the transformation properties of the dynamical factors D under permutation of the photon frequencies are exactly the same as those of the corresponding geometrical factors ϕ under permutations of the photon polarizations. In fact, because of this property the whole expression (6) is still invariant for permutation of all the photon indices, although the projector $\sum_{\sigma}O_{\sigma}$ does not appear explicitly any more. The fact that the transition rate is symmetric under permutation of the photon indices follows directly from the bosonic character of the photons. The formulation in Eq. (6) is useful because it emphasizes the transformation properties of geometrical and dynamical factors separately. For instance, in two-photon transitions, if the dynamical factor vanishes for equal frequencies, we know that the corresponding geometrical factor vanishes for equal polarizations.

We conclude this section with some remarks on the n-photon transition rate (1). This formula is obtained by supposing that the absorption occurs taking one photon from each of the n beams that are focused on the sample. The total energy that is needed to reach the final state corresponds to the sum of all the photon energies. If some of the beams have equal energy (but not necessarily equal polarization), it is also possible to reach the final state by taking two photons from the same beam. Be-

cause of this possibility, additional terms appear within the square modulus of formula (1) for the transition rate. These other terms, which are omitted in (1), can be analyzed in the same way. When this occurs, the polarization dependence of the transition rate can be dependent on the relative intensities and phases of the electromagnetic fields of the radiation beams.

We have analyzed explicitly the case of n-photon absorption processes. If a photon is emitted, as occurs, for example, in hyper-Raman scattering[17] or in difference-frequency generation,[12] the polarization vector of the emitted photon has to be replaced by its complex conjugate and its frequency ω by $-\omega$.

We note that all the conclusions of this paper are based on an analysis of the transition rate (1) in the dipole approximation. In this approximation, the only relevant quantum numbers of the photons are their frequencies and polarization vectors, as their wave vectors do not appear in formula (1). Nevertheless, the analysis can be applied to derive selection rules for longitudinal and transversal excitations, e.g., the longitudinal exciton (LE) and the transverse polaritons (TP). In this case the interaction with the electromagnetic radiation yields a symmetry reduction with respect to the symmetry of the point group. The polarization dependence can be found analogously by decomposing the excited state in components that are parallel (for LE) or perpendicular (for TP) to the total wave vector.[18]

III. APPLICATION TO TWO-, THREE-, AND FOUR-PHOTON TRANSITIONS

In this section we apply the theory to the cases of two-, three-, and four-photon transitions with a particular emphasis on the effects due to permutation symmetry. We will first take as a symmetry group of the system the full spherical group O(3), which includes all proper and improper rotations in three dimensions. As O(3) contains all the crystal point groups, the results for a particular point group follow easily, making use of compatibility relations. For the point groups we will use the notation of Koster *et al.*[19] We will study in detail the point groups O_h, T_d, and C_{6v}, which correspond to the cubic, zinc-blende, and wurtzite structure, respectively. We will limit ourselves to the case of n-photon absorption processes from the crystal ground state.

A. Two-photon transitions

The polarization dependence of two-photon transitions has been studied for all the crystal point groups. It is well known that dynamical factors can either be symmetric or antisymmetric for the exchange of the photon frequencies.[13] A tabulation of all possible cases can be found in the paper by Inoue and Toyozawa.[14] In this subsection, we apply our formulation in order to recover these results and to illustrate the procedure in a simple case. As we will show, our procedure is particularly useful in the more complicated cases in which three or more photons are absorbed.

The transition operators transform as $P_{i_1}P_{i_2}$ and form a 9-dimensional representation R of the group O(3), of the permutation group on two elements S_2, and of the product group $\mathrm{O}(3)\otimes S_2$. We decompose the representation R into irreducible representations of these three groups:

$$\mathrm{O}(3): \quad R \rightarrow D_0^+ \oplus D_1^+ \oplus D_2^+, \tag{7}$$

$$S_2: \quad R \rightarrow 6\tilde{\Gamma}_1^+ \oplus 3\tilde{\Gamma}_1^-, \tag{8}$$

$$\mathrm{O}(3)\otimes S_2: \quad R \rightarrow D_0^+ \cdot \tilde{\Gamma}_1^+ \oplus D_1^+ \cdot \tilde{\Gamma}_1^- \oplus D_2^+ \cdot \tilde{\Gamma}_1^+, \tag{9}$$

where the $D_j^{\pm}$'s represent the well known irreducible representations of O(3) and $\tilde{\Gamma}_1^+$ and $\tilde{\Gamma}_1^-$ are the one-dimensional symmetric and antisymmetric representations of S_2, respectively. We will denote the representations of the permutation groups by $\tilde{\Gamma}_k^{\pm}$, where k is the dimensionality of the representation and the sign indicates whether the representation has a positive or negative character for the exchange of two elements. The representations of $\mathrm{O}(3)\otimes S_2$ have been indicated as products of representations of its subgroups. We note that the representation of the highest angular momentum transforms necessarily as the total symmetric representation of the permutation group.

Let us consider, for example, the case of the point group O_h. By use of compatibility tables, we deduce from Eqs. (7) and (9)

$$O_h: \quad R \rightarrow \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+, \tag{10}$$

$$O_h\otimes S_2: \quad R \rightarrow \Gamma_1^+ \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_3^+ \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_4^+ \cdot \tilde{\Gamma}_1^- \oplus \Gamma_5^+ \cdot \tilde{\Gamma}_1^+. \tag{11}$$

All symmetries of the point group appear just once in the decomposition of R into the irreducible representations of O_h and therefore the polarization dependence is the same for all transitions to states of a given symmetry. Only the dynamical factors of transitions to Γ_4^+ states are antisymmetric with respect to the exchange of the frequencies. In the case of two radiation beams of equal frequency, transitions to Γ_4^+ states are forbidden. We note that the additional terms, which appear in the transition rate because of the possibility of absorbing two photons of the same beam, vanish for the same reason. Another important remark is that also the geometrical factor of Γ_4^+ transitions is antisymmetric for the exchange of the two polarization vectors. Hence, in the case of two beams of different frequency but equal polarization, Γ_4^+ states cannot be detected. Of course, in the case of one-beam two-photon spectroscopy (equal frequency and equal polarization) the transition rate vanishes as well.

For the point group T_d, the conclusions are identical

to the case of O_h apart from the fact that parity is no longer a good quantum number. In fact, in two-photon spectroscopy it is possible to excite states that are also excited in one-photon spectroscopy (states of Γ_5 symmetry):

$$T_d: \quad R \rightarrow \Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5, \tag{12}$$

$$T_d \otimes S_2: \quad R \rightarrow \Gamma_1 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_3 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_4 \cdot \tilde{\Gamma}_1^- \oplus \Gamma_5 \cdot \tilde{\Gamma}_1^+. \tag{13}$$

As another example we consider the group C_{6v}, which is the point group of the wurtzite structure. We find

$$C_{6v}: \quad R \rightarrow 2\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_5 \oplus \Gamma_6, \tag{14}$$

$$C_{6v} \otimes S_2: \quad R \rightarrow 2\Gamma_1 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_2 \cdot \tilde{\Gamma}_1^- \oplus \Gamma_5 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_5 \cdot \tilde{\Gamma}_1^- \oplus \Gamma_6 \cdot \tilde{\Gamma}_1^+. \tag{15}$$

For this point group it is not always possible to express the transition rate as a simple product of dynamical and geometrical factors. In the case of excited states of Γ_1 or Γ_5 symmetry, there are two dynamical factors, and therefore one dynamical parameter appears in the polarization dependence. The transition rates of Γ_2 and Γ_6 contain just one dynamical factor and their polarization dependence is thus independent of dynamical parameters. In the case of photons of equal frequency, transitions to Γ_2 states are forbidden analogously to the case of transitions to Γ_4^+ states in O_h. For Γ_1 transitions the two dynamical factors are both symmetric for the exchange of frequencies, whereas for Γ_5 transitions one is symmetric and the other is antisymmetric. In the case of photons of equal frequency, the polarization dependence of transitions to Γ_1 states will therefore still contain one dynamical parameter. On the other hand, for Γ_5 transitions, the antisymmetric dynamical factor vanishes and the polarization dependence will thus be identical for all Γ_5 states. Care must be taken in the transition rate of Γ_5 states in the case of two beams of equal frequency. Now the symmetric geometric and dynamical factors that correspond to the case of two photons being absorbed from the same beam do not vanish and must be accounted for in the polarization dependence.

In order to use a handy formulation we introduce Young diagrams that represent projectors on the rows of the representations of the permutation group.[16] In the case of two-photon transitions the representations are one dimensional and can be represented as in Fig. 1. The projectors associated to the diagrams act by first taking the symmetric part with respect to the indices that are contained in the horizontal boxes and then the antisymmetric part with respect to those that appear in the same vertical column. It is evident that the result will vanish if the Young projector is applied on expressions that are invariant for exchanges of indices that appear in the same column.

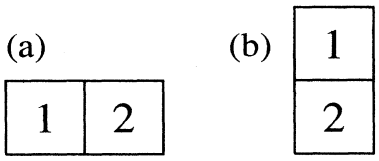

FIG. 1. Young diagrams for the projectors on the rows of the irreducible representations of the permutation group on two elements S_2: (a) $\tilde{\Gamma}_1^+$, the symmetric representation; and (b) $\tilde{\Gamma}_1^-$, the antisymmetric representation.

B. Three-photon transitions

Recently there has been increased interest in the use of three-photon spectroscopy to investigate electronic states in crystals.[3] Since there are many allowed states, the understanding of the polarization dependence of the transitions is particularly useful. For the case of absorption processes of three photons of equal frequency and polarization, the polarization dependence has been tabulated for all crystal point groups.[4] In the case of O_h symmetry, the polarization dependence has also been given for photons of equal frequency but for all possible polarizations.[5] As already pointed out,[5] Ref. 20 contains incorrect statements.

We start our analysis as in the case of two-photon transitions with the full spherical group O(3). The transition operators transform as a 27-dimensional representation of O(3), of S_3, and of O(3) $\otimes$ S_3:

$$\mathrm{O}(3): \quad R \rightarrow D_0^- \oplus 3D_1^- \oplus 2D_2^- \oplus D_3^-, \tag{16}$$

$$S_3: \quad R \rightarrow 10\tilde{\Gamma}_1^+ \oplus 8\tilde{\Gamma}_2 \oplus \tilde{\Gamma}_1^-, \tag{17}$$

$$\mathrm{O}(3) \otimes S_3: \quad R \rightarrow D_0^- \cdot \tilde{\Gamma}_1^- \oplus D_1^- \cdot \tilde{\Gamma}_1^+ \oplus D_1^- \cdot \tilde{\Gamma}_2 \oplus D_2^- \cdot \tilde{\Gamma}_2 \oplus D_3^- \cdot \tilde{\Gamma}_1^+. \tag{18}$$

The permutation group on three elements S_3 has three kinds of irreducible representations: the symmetric representation $\tilde{\Gamma}_1^+$, the antisymmetric representation $\tilde{\Gamma}_1^-$, and a two-dimensional representation $\tilde{\Gamma}_2$. The associated Young diagrams are given in Fig. 2. Dynamical or geometrical factors that transform as $\tilde{\Gamma}_1^+$ do not vanish even if the three absorbed photons are equal. On the other hand, dynamical (geometrical) factors that transform as $\tilde{\Gamma}_1^-$ vanish unless the three photons have three different frequencies (polarizations). In the case of the $\tilde{\Gamma}_2$ representation, there are two dynamical factors that appear together and transform according to the two rows of the representation. The rows that are defined by the projectors in Fig. 2 represent one possible choice. If the frequencies of the three involved photons are taken to be equal, both of the $\tilde{\Gamma}_2$ dynamical factors vanish. In fact, if the dynamical factors are chosen to transform as defined by the projectors in Fig. 2, the first is antisymmetric for the exchange of the frequencies of photon 1

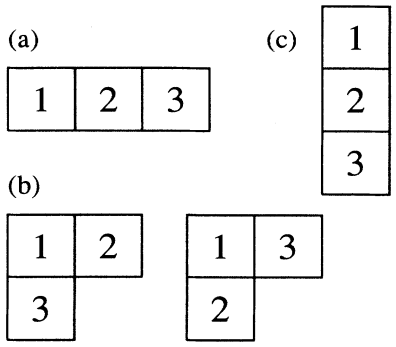

FIG. 2. Young diagrams for the projectors on the rows of the irreducible representations of the permutation group on three elements S_3: (a) $\tilde{\Gamma}_1^+$, the symmetric representation; (b) $\tilde{\Gamma}_2$, the two-dimensional representation; and (c) $\tilde{\Gamma}_1^-$, the antisymmetric representation.

and photon 3, whereas the second is antisymmetric for the exchange of the frequencies of photon 1 and photon 2. If only two frequencies are equal, for instance those of photon 1 and photon 2, the first dynamical factor contributes, whereas the second vanishes. The same reasoning applies for the geometrical factors in the case of equal polarizations. From Eq. (18), we see how the dynamical factors in the transition rates of states of a given symmetry transform under permutations. In particular the transition rate of states of D_1^- symmetry contains three dynamical factors; one that transforms as $\tilde{\Gamma}_1^+$ and two that transform as $\tilde{\Gamma}_2$. In the case of photons of equal frequency, the nonvanishing dynamical factors are deduced as discussed above.

In the following part of this subsection we will illustrate our analysis in the case of the O_h, T_d, and C_{6v} point groups. The polarization dependence for these groups is given in Appendix B. An analogue analysis can be carried out for any point group.

For the O_h point group the transition operator transforms as

$$O_h: \quad R \rightarrow \Gamma_1^- \oplus \Gamma_2^- \oplus 2\Gamma_3^- \oplus 4\Gamma_4^- \oplus 3\Gamma_5^-, \tag{19}$$

$$O_h \otimes S_3: \quad R \rightarrow \Gamma_1^- \cdot \tilde{\Gamma}_1^- \oplus \Gamma_2^- \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_3^- \cdot \tilde{\Gamma}_2 \oplus 2\Gamma_4^- \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_4^- \cdot \tilde{\Gamma}_2 \oplus \Gamma_5^- \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_5^- \cdot \tilde{\Gamma}_2. \tag{20}$$

If only one radiation beam is used, only states of Γ_2^-, Γ_4^-, and Γ_5^- symmetry can be excited. The polarization dependence of Γ_2^- and Γ_5^- states have only one dynamical factor and thus contain no dynamical parameters. In the case of Γ_4^- transitions, there is one dynamical parameter as the representation $\Gamma_4^- \cdot \tilde{\Gamma}_1^+$ appears twice in the decomposition of R. If two beams are used, also Γ_3^- states are observable. The polarization dependence of Γ_2^- transitions still has no dynamical parameters, whereas those of Γ_4^- and Γ_5^- acquire one parameter more. Finally, with three photons of different frequency and polarization it is also possible to observe the Γ_1^- states. In the latter case the number of dynamical factors that occurs in the polarization dependence of transitions to states of a given symmetry is given by the number of times that symmetry appears in the decomposition of R: 1 for Γ_1^- and Γ_2^-, 2 for Γ_3^-, 4 for Γ_4^-, and 3 for Γ_5^-.

The representation R of transition operators decomposes as follows in irreducible representations of T_d and $T_d \otimes S_3$:

$$T_d: \quad R \rightarrow \Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3 \oplus 3\Gamma_4 \oplus 4\Gamma_5, \tag{21}$$

$$T_d \otimes S_3: \quad R \rightarrow \Gamma_1 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_2 \cdot \tilde{\Gamma}_1^- \oplus \Gamma_3 \cdot \tilde{\Gamma}_2 \oplus \Gamma_4 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_4 \cdot \tilde{\Gamma}_2 \oplus 2\Gamma_5 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_5 \cdot \tilde{\Gamma}_2. \tag{22}$$

Knowing the relation between permutation symmetry and point-group symmetry, it is now simple to deduce as above the number of nonvanishing dynamical factors for each possible configuration of the photons. In particular, we note that for three photons of equal frequency, Γ_1, Γ_4, and Γ_5 states can be excited. We note that Γ_5 states are observable in *one*-beam spectroscopy either absorbing one, two, or three photons.

As a final example, we give the decomposition of R for the C_{6v} point group:

$$C_{6v}: \quad R \rightarrow 4\Gamma_1 \oplus 3\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus 6\Gamma_5 \oplus 3\Gamma_6, \tag{23}$$

$$C_{6v} \otimes S_3: \quad R \rightarrow 2\Gamma_1 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_1 \cdot \tilde{\Gamma}_2 \oplus \Gamma_2 \cdot \tilde{\Gamma}_1^- \oplus \Gamma_2 \cdot \tilde{\Gamma}_2 \oplus \Gamma_3 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_4 \cdot \tilde{\Gamma}_1^+ \oplus 2\Gamma_5 \cdot \tilde{\Gamma}_1^+ \oplus 2\Gamma_5 \cdot \tilde{\Gamma}_2 \oplus \Gamma_6 \cdot \tilde{\Gamma}_1^+ \oplus \Gamma_6 \cdot \tilde{\Gamma}_2. \tag{24}$$

Representations of C_{6v} are either one-dimensional, such as Γ_1, Γ_2, Γ_3, and Γ_4, or two-dimensional, such as Γ_5 and Γ_6. Because of the lower symmetry of C_{6v} with respect to the cubic groups, there are now many dynamical parameters, as much as five for Γ_5 transitions. If the absorbed photons are all of equal frequency (or polarization), all states but those of Γ_2 symmetry are observable. In this case, Γ_3, Γ_4, and Γ_6 transitions have a polarization dependence with no dynamical parameters, whereas Γ_1 and Γ_5 transitions have a polarization dependence with one dynamical parameter.

C. Four-photon transitions

In this subsection we present the results of our symmetry analysis for four-photon transitions. We only discuss the case of the O(3) point group. The transition operators transform as an 81-dimensional representation of O(3), of S_4, and of O(3) $\otimes$ S_4:

$$\mathrm{O}(3): \quad R \rightarrow 3D_0^+ \oplus 6D_1^+ \oplus 6D_2^+ \oplus 3D_3^- \oplus D_4^-, \tag{25}$$

$$S_4: \quad R \rightarrow 15\tilde{\Gamma}_1^+ \oplus 15\tilde{\Gamma}_3^+ \oplus 6\tilde{\Gamma}_2 \oplus 3\tilde{\Gamma}_3^-, \tag{26}$$

$$\mathrm{O}(3)\otimes S_4: \quad R \rightarrow D_0^+\cdot\tilde{\Gamma}_1^+ \oplus D_0^+\cdot\tilde{\Gamma}_2 \oplus D_1^+\cdot\tilde{\Gamma}_3^+ \oplus D_1^+\cdot\tilde{\Gamma}_3^- \oplus D_2^+\cdot\tilde{\Gamma}_1^+ \oplus D_2^+\cdot\tilde{\Gamma}_2 \oplus D_2^+\cdot\tilde{\Gamma}_3^+ \oplus D_3^+\cdot\tilde{\Gamma}_3^+ \oplus D_4^+\cdot\tilde{\Gamma}_1^+. \tag{27}$$

The Young diagrams for S_4 are given in Fig. 3. From Fig. 3 we can deduce the transformation properties of the dynamical factors and identify the nonvanishing ones in the case of photons of equal frequency. Only the $\tilde{\Gamma}_1^+$ representation is nonvanishing if all the frequencies are equal. We thus deduce that in the case of one-beam spectroscopy, only states of D_0^+, D_2^+, and D_4^+ symmetry can be detected. As another example, if we take the frequencies of photons 1 and 2 to be equal and at the same time the frequencies of photons 3 and 4 to be equal to each other but different with respect to those of photons 1 and 2, we see that only the dynamical factors that transform as $\tilde{\Gamma}_1^+$ and one of the two that transform as $\tilde{\Gamma}_2$ do not vanish.

It is worthwhile to note that all the results presented here can also be applied to atomic and molecular gases. The same analysis can be carried out considering the point group of a molecular system. Finally, the transition rate is obtained by averaging the directions of the polarization vectors over the whole solid angle. In this way, only expressions of the polarization vectors that are spherically invariant are maintained. Operatively this can be done by expressing the ϕ that appear in Eq. (6) for a particular molecular point group as linear combinations of expressions R_{lm} that transform in the same way as the spherical harmonics Y_{lm}. The products $R^*_{l'm'}R_{lm}$, which occur after the square modulus has been taken, can again be decomposed into linear combinations of R'_{lm} that also transform as spherical harmonics. When the spherical average is taken, all the R'_{lm} vanish except those transforming as Y_{00}. In this way a procedure is provided that produces analogue results as alternative methods in which the average over the whole solid angle is taken in the beginning of the analysis.[21–23] In particular our procedure can be useful if for some reason a full spherical average is not required.

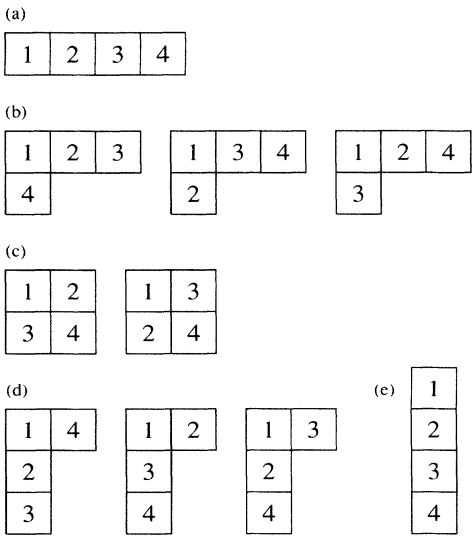

FIG. 3. Young diagrams for the projectors on the rows of the irreducible representations of the permutation group on four elements S_4: (a) $\tilde{\Gamma}_1^+$, (b) $\tilde{\Gamma}_3^+$, (c) $\tilde{\Gamma}_2$, (d) $\tilde{\Gamma}_3^-$, and (e) $\tilde{\Gamma}_1^-$.

Before concluding this section we want to make some remarks on the polarization dependence. The polarization dependence that has been described here is complete, i.e., it gives the full dependence on the polarization vectors for a given point group. However, it is often possible to go beyond the most general polarization dependence because of additional physical information. For example, if it is known that only particular intermediate states are important in the absorption process, a more detailed description of the polarization dependence can be given using two-band[24] or three-band[25] models. As another example, if the final states are well described in a spherical model, the polarization dependence will rather be as for the O(3) group instead of as for the crystal point group, i.e., because of additional information we know that some of the crystal dynamical parameters are very small.

For certain point groups, final states of different spatial symmetry can be degenerate because of time-reversal symmetry. In this case, the absorption rate is given by the sum of the transition rates of each of the states that are degenerate. The dynamical parameters that appear in the single expressions can be related to each other because of time-reversal symmetry. Sometimes, for example in the case of Wannier exciton states, different states of different symmetry turn out to be almost degenerate.[13] Analogously as for the time-reversal degeneracy the transition rate is obtained as a sum of different contributions. In this respect, Refs. 18 and 13 are particularly interesting.

Additional selection rules can occur because of the fact that the electromagnetic radiation can only excite the singlet component of exciton states. This property is independent of the number of photons participating in the process. Although the spin is not a good quantum number, the mixing because of the spin-orbit interaction between singlet and triplet is often very weak. The mixing can be increased by external magnetic fields.[2]

IV. CONCLUSIONS

We have presented a symmetry analysis of the multiphoton transition rate of exciton states in crystals. Particular emphasis is given to the transformation properties of the rate under permutation of the photon indices. The transition rate is expressed as the square modulus of a sum of products of geometrical factors, which depend on the polarizations of the photons, and dynamical factors, which depend on the frequencies. We show that the geometrical as well as the dynamical factors of the n-photon transition rate transform as irreducible representations of

the permutation group on n elements under permutations of the photon polarizations and frequencies, respectively. Our formulation turns out to be particularly useful to determine the number of nonvanishing dynamical factors in the case of absorbed photons of equal frequency. When all the dynamical factors vanish, a new selection rule occurs in addition to the usual dipole and geometrical selection rules. We have pointed out that because of the fact that corresponding dynamical and geometrical factors belong to the same irreducible representation of the permutation group, for permutations of frequencies and polarizations, respectively, the same additonal selection rules are found if the photons are taken of equal frequency *or* of equal polarization. This property is related to the fact that the transition rate is invariant under simultaneous permutations of all the photon indices.

The theory can be applied to any point group and for any number of absorbed photons. We have considered in detail the case of two-, three-, and four-photon transitions and we have analyzed as examples the point groups O_h, T_d, and C_{6v}, which correspond to the cubic, zincblende, and wurtzite structure, respectively. For these point groups we have given the polarization dependence explicitly in the case of three-photon transitions.

We have considered multiphoton absorption processes from the crystal ground state. The same analysis can be extended to cope with transitions between states of all possible symmetries, as has been done in the case of two-photon transitions by Bader and Gold.[15] If initial and final state transform as Γ_i and Γ_f of the point group, respectively, the transition operators that transform as one of the representations in the product $\Gamma_f^* \otimes \Gamma_i$ will be active. The number of nonvanishing dynamical factors depends on the number of photons of equal frequency and can be determined as for transitions from the ground state. Other processes, related to higher-order susceptibilities $\chi^{(n)}$, such as sum-frequency or difference-frequency generation,[17] can also be described by formulas that are similar to that of Eq. (1). In this case, the final and initial state are the crystal ground state. In order to have nonvanishing $\chi^{(n)}$, there must be a transition operator that transforms as the representation Γ_1. Moreover, if some of the involved photons are of equal frequency, at least one of the Γ_1 dynamical factors should not be vanishing.

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APPENDIX A: EXPLICIT EXPRESSIONS OF THE DYNAMICAL FACTORS

The $\phi_{\nu,\lambda}^{n,(\alpha\beta)}$ in Eq. (5) transform as partner functions of the irreducible representation β of the permutation group on n elements:

$$O_\sigma \phi_{\nu,\lambda}^{n,(\alpha\beta)} = \sum_{\lambda'=1}^{l_\beta} M_{\lambda'\lambda}^{\beta}(\sigma) \phi_{\nu,\lambda'}^{n,(\alpha\beta)}, \tag{A1}$$

where $M_{\lambda'\lambda}^{\beta}$ is a matrix representation of β. By inserting Eq. (A1) in expression (5) we obtain expression (6), where

$$\begin{aligned} D_\lambda^{n,(\alpha\beta)}(\omega_1,\cdots,\omega_n) &= \sum_{\lambda'=1}^{l_\beta} \sum_\sigma [M_{\lambda\lambda'}^{\beta}(\sigma)]^* O_\sigma \langle f^\alpha || T_{\lambda'}^{n,(\alpha\beta)}(\omega_1,\cdots,\omega_n) || 0 \rangle \\ &= \frac{n!}{l_\beta} \sum_{\lambda'=1}^{l_\beta} \mathcal{P}_{\lambda\lambda'}^{\beta} \langle f^\alpha || T_{\lambda'}^{n,(\alpha\beta)}(\omega_1,\cdots,\omega_n) || 0 \rangle, \end{aligned} \tag{A2}$$

where $\mathcal{P}_{\lambda\lambda'}^{\beta}$ are projectors on the λth row of the irreducible representation β. Hence the $D_\lambda^{n,(\alpha\beta)}$ transform under permutations of the frequencies in the same way as the corresponding $\phi_{\nu,\lambda}^{n,(\alpha\beta)}$ under permutations of the polarizations.

APPENDIX B: POLARIZATION DEPENDENCE OF THREE-PHOTON TRANSITIONS

In this appendix we give the polarization dependence of three-photon transitions for the point groups O_h, T_d, and C_{6v} explicitly. We give the $\phi_{\nu,\lambda}^{n,(\alpha\beta)}$ of Eq. (6). The ϕ transform as rows of the irreducible representations of S_3, which are given in Fig. 2. We note that the geometrical factors of a given symmetry of the point group that transform as $\tilde{\Gamma}_2$ appear always in pairs as they correspond to the two rows of the $\tilde{\Gamma}_2$ representation.

For the O_h point group we use the shorthand notation (ijk) for $\epsilon_{1i}\epsilon_{2j}\epsilon_{3k}$ and $\phi_{\alpha\nu}^{(n)}$ for the geometrical factors, dropping the indices that refer to the permutation symmetry. The basis for the polarization vectors has been chosen along the cubic axes. The geometrical factors that transform as the symmetric representation $\tilde{\Gamma}_1^+$ are given by[5]

$$\phi_2 = \frac{1}{\sqrt{6}}[\,(xyz)+(zxy)+(yzx) +(zyx)+(yxz)+(xzy)], \tag{B1}$$

$$\begin{aligned}\phi_{4x}^{(1)} &= (xxx),\\ \phi_{4y}^{(1)} &= (yyy),\\ \phi_{4z}^{(1)} &= (zzz),\end{aligned} \tag{B2}$$

$$\phi_{4x}^{(2)} = \frac{1}{\sqrt{6}}[\,(xyy)+(yxy)+(yyx) +(xzz)+(zxz)+(zzx)],$$

$$\phi_{4y}^{(2)} = \frac{1}{\sqrt{6}}[\,(yzz)+(zyz)+(zzy) +(yxx)+(xyx)+(xxy)], \tag{B3}$$

$$\phi_{4z}^{(2)} = \frac{1}{\sqrt{6}}[\,(zxx)+(xzx)+(xxz) +(zyy)+(yzy)+(yyz)],$$

$$\phi_{5yz}^{(1)} = \frac{1}{\sqrt{6}}[\,(xyy)+(yxy)+(yyx) -(xzz)-(zxz)-(zzx)],$$

$$\phi_{5zx}^{(1)} = \frac{1}{\sqrt{6}}[\,(yzz)+(zyz)+(zzy) -(yxx)-(xyx)-(xxy)], \tag{B4}$$

$$\phi_{5xy}^{(1)} = \frac{1}{\sqrt{6}}[\,(zxx)+(xzx)+(xxz) -(zyy)-(yzy)-(yyz)].$$

The geometrical factors that transform as the two-dimensional representation $\tilde{\Gamma}_2$ are

$$\begin{aligned}\phi_{31}^{(1)} &= \frac{1}{2\sqrt{3}}[(zxy)+(xyz)-(yxz)-(zyx)] +\frac{1}{\sqrt{3}}[(xzy)-(yzx)],\\ \phi_{32}^{(1)} &= \tfrac{1}{2}[(yxz)-(zxy)-(zyx)+(xyz)],\end{aligned} \tag{B5}$$

$$\begin{aligned}\phi_{31}^{(2)} &= \frac{1}{2\sqrt{3}}[(zyx)+(xzy)-(yzx)-(zxy)] +\frac{1}{\sqrt{3}}[(xyz)-(yxz)],\\ \phi_{32}^{(2)} &= \tfrac{1}{2}[(yzx)-(zyx)-(zxy)+(xzy)],\end{aligned} \tag{B6}$$

$$\begin{aligned}\phi_{4x}^{(3)} &= \tfrac{1}{2}[(xyy)-(yyx)-(zzx)+(xzz)],\\ \phi_{4y}^{(3)} &= \tfrac{1}{2}[(yzz)-(zzy)-(xxy)+(yxx)],\\ \phi_{4z}^{(3)} &= \tfrac{1}{2}[(zxx)-(xxz)-(yyz)+(zyy)],\end{aligned} \tag{B7}$$

$$\begin{aligned}\phi_{4x}^{(4)} &= \tfrac{1}{2}[(xyy)-(yxy)-(zxz)+(xzz)],\\ \phi_{4y}^{(4)} &= \tfrac{1}{2}[(yzz)-(zyz)-(xyx)+(yxx)],\\ \phi_{4z}^{(4)} &= \tfrac{1}{2}[(zxx)-(xzx)-(yzy)+(zyy)],\end{aligned} \tag{B8}$$

$$\begin{aligned}\phi_{5yz}^{(2)} &= \tfrac{1}{2}[(xyy)-(yyx)+(zzx)-(xzz)],\\ \phi_{5zx}^{(2)} &= \tfrac{1}{2}[(yzz)-(zzy)+(xxy)-(yxx)],\\ \phi_{5xy}^{(2)} &= \tfrac{1}{2}[(zxx)-(xxz)+(yyz)-(zyy)],\end{aligned} \tag{B9}$$

$$\begin{aligned}\phi_{5yz}^{(3)} &= \tfrac{1}{2}[(xyy)-(yxy)+(zxz)-(xzz)],\\ \phi_{5zx}^{(3)} &= \tfrac{1}{2}[(yzz)-(zyz)+(xyx)-(yxx)],\\ \phi_{5xy}^{(3)} &= \tfrac{1}{2}[(zxx)-(xzx)+(yzy)-(zyy)].\end{aligned} \tag{B10}$$

The only geometrical factor that transforms as the antisymmetric representation $\tilde{\Gamma}_1^-$ is

$$\phi_1 = \frac{1}{\sqrt{6}}[\,(xyz)+(zxy)+(yzx) -(zyx)-(yxz)-(xzy)]. \tag{B11}$$

In the case of the T_d point group the polarization dependence is the same as for the O_h group, only the nomenclature is different: the Γ_1^-, Γ_2^-, Γ_3^-, Γ_4^-, and Γ_5^- of O_h correspond to the Γ_2, Γ_1, Γ_3, Γ_5, and Γ_4 of T_d, respectively.

For the point group C_{6v}, we use the shorthand notation, for example, $(0+-)$ for $\epsilon_z\sigma_+\sigma_-$, where $\sigma_\pm$ correspond to the circular polarizations $\mp(1/\sqrt{2})(\epsilon_x \pm i\epsilon_y)$. The components of the polarization vectors are taken as in Ref. 19. The symmetric geometrical factors are given by

$$\phi_1^{(1)} = (000), \tag{B12}$$

$$\phi_1^{(2)} = \frac{1}{\sqrt{6}}[\,(0+-)+(+0-)+(+-0) +(0-+)+(-0+)+(-+0)], \tag{B13}$$

$$\phi_3 = \frac{1}{\sqrt{2}}[(---)+(+++)], \tag{B14}$$

$$\phi_4 = \frac{1}{\sqrt{2}}[(---)-(+++)], \tag{B15}$$

$$\begin{aligned}\phi_{5-}^{(1)} &= \frac{1}{\sqrt{3}}[(+--)+(-+-)+(--+)],\\ \phi_{5+}^{(1)} &= \frac{1}{\sqrt{3}}[(-++)+(+-+)+(++-)],\end{aligned} \tag{B16}$$

$$\begin{aligned}\phi_{5-}^{(2)} &= \frac{1}{\sqrt{3}}[(-00)+(0-0)+(00-)],\\ \phi_{5+}^{(2)} &= \frac{1}{\sqrt{3}}[(+00)+(0+0)+(00+)],\end{aligned} \tag{B17}$$

$$\phi_{6-}^{(2)} = \frac{1}{\sqrt{3}}[(0++)+(+0+)+(++0)],$$
$$\phi_{6+}^{(2)} = \frac{1}{\sqrt{3}}[(0--)+(-0-)+(--0)]. \quad \text{(B18)}$$

The geometrical factors that transform as the $\tilde{\Gamma}_2$ representation are

$$\phi_1^{(3)} = \tfrac{1}{2}[(+-0)-(0-+)+(-+0)-(0+-)], \quad \text{(B19)}$$
$$\phi_1^{(4)} = \tfrac{1}{2}[(+0-)-(0+-)+(-0+)-(0-+)], \quad \text{(B20)}$$

$$\phi_2^{(1)} = \tfrac{1}{2}[(+-0)-(0-+)-(-+0)+(0+-)], \quad \text{(B21)}$$
$$\phi_2^{(2)} = \tfrac{1}{2}[(+0-)-(0+-)-(-0+)+(0-+)], \quad \text{(B22)}$$

$$\phi_{5-}^{(3)} = \frac{1}{\sqrt{2}}[(-00)-(00-)],$$
$$\phi_{5+}^{(3)} = \frac{1}{\sqrt{2}}[(+00)-(00+)], \quad \text{(B23)}$$

$$\phi_{5-}^{(4)} = \frac{1}{\sqrt{2}}[(-00)-(0-0)],$$
$$\phi_{5+}^{(4)} = \frac{1}{\sqrt{2}}[(+00)-(0+0)], \quad \text{(B24)}$$

$$\phi_{5-}^{(5)} = \frac{1}{\sqrt{2}}[(--+)-(+--)],$$
$$\phi_{5+}^{(5)} = \frac{1}{\sqrt{2}}[(-++)-(++-)], \quad \text{(B25)}$$

$$\phi_{5-}^{(6)} = \frac{1}{\sqrt{2}}[(-+-)-(+--)],$$
$$\phi_{5+}^{(6)} = \frac{1}{\sqrt{2}}[(-++)-(+-+)], \quad \text{(B26)}$$

$$\phi_{6-}^{(2)} = \frac{1}{\sqrt{2}}[(++0)-(0++)],$$
$$\phi_{6+}^{(2)} = \frac{1}{\sqrt{2}}[(--0)-(0--)], \quad \text{(B27)}$$

$$\phi_{6-}^{(3)} = \frac{1}{\sqrt{2}}[(+0+)-(0++)],$$
$$\phi_{6+}^{(3)} = \frac{1}{\sqrt{2}}[(-0-)-(0--)]. \quad \text{(B28)}$$

The only antisymmetric geometrical factor is given by

$$\phi_2^{(3)} = \frac{1}{\sqrt{6}}[(0+-)-(+0-)+(+-0) - (0-+)+(-0+)-(-+0)]. \quad \text{(B29)}$$

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