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Generating functions for effective Hamiltonians via the symmetrized Hadamard product

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Abstract

We present a method which enables one to calculate generating functions counting the number of linearly independent tensor operators of different degrees which should be included in phenomenological effective Hamiltonians constructed from boson creation and annihilation operators for several degrees of freedom in the presence of resonances and symmetry. The method is based on the application of the Molien generating function technique and the Hadamard product of rational functions. The latter leads to the representation of the answer in a form of a rational function. The technique is illustrated by the example of effective Hamiltonians for vibrational polyads in a methane-type molecule, which is a dynamical system with nine degrees of freedom formed by one non-degenerate, one doubly degenerate and two triply degenerate modes in resonance 2:1:1:2:2:2:1:1:1.

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1. Introduction

Phenomenological description of many different physical problems is based on approximate models constructed in terms of harmonic oscillator creation and annihilation operators (bosonic operators). The number of degrees of freedom being finite, the most essential feature of the model which should be properly taken into account is the symmetry and resonance conditions, which impose the existence of additional exact or approximate integrals of motion and good quantum numbers. A typical example which we had in mind when preparing this paper is the vibrational structure of molecules. In the simplest approximation, molecular vibrations are described by a system of nonlinearly coupled anharmonic oscillators. In the presence of symmetry, different vibrational degrees of freedom can be classified by the irreducible representations of the symmetry group. For sufficiently high symmetry (cubic, for example) this leads to the formation of degenerate vibrational harmonic modes. An additional resonance condition between vibrational modes which also typically exists in many molecular systems results in the formation of the so-called vibrational polyads formed by a group of vibrational states [5, 20]. Rather complicated internal organization of such polyads can be qualitatively understood through the topological analysis of corresponding classical dynamical systems [5]. In turn, the global topology of a single or multiple reduced classical phase space is reflected in the generating function giving the number of invariants for the associated quantum problem [7, 16, 28]. This explains, in particular, more fundamental interest in the generating function approach rather than in simple enumeration applications.

A nontrivial example of resonances and polyads is given by the methane molecule, CH_4. This molecule has equilibrium configuration with tetrahedral symmetry (point group T_d, which is isomorph to permutation group of four identical objects). As a consequence, its nine vibrational degrees of freedom are classified by the symmetry group as one non-degenerate mode, ν_1, one doubly degenerate mode ν_2, and two triply degenerate modes ν_3, ν_4. Moreover the ratio between corresponding harmonic frequencies can be relatively well approximated by simple integers as $\nu_1{:}\nu_2{:}\nu_3{:}\nu_4 = 2{:}1{:}2{:}1$ with the corresponding classical reduced phase space being the complex eight-dimensional weighted projective space. Due to this resonance condition the vibrational states form so-called polyads. The polyad number N is defined as a weighted total number of quanta on all modes which takes into account the resonance condition, i.e. $N = 2n_1 + 2n_3 + n_2 + n_4$, where n_i is the number of quanta on ith mode.

In order to construct the effective Hamiltonian describing the internal structure of vibrational polyads in an AB_4 molecule of T_d symmetry in terms of creation and annihilation operators for different harmonic vibrational modes, it is necessary to take all invariant operators written schematically in the form of tensor products in the T_d group as

$$\left\{\left[\left(a_1^+\right)^{s_1} \times \left(a_2^+\right)^{s_2} \times \left(a_3^+\right)^{s_3} \times \left(a_4^+\right)^{s_4}\right]^{\Gamma} \times [(a_1)^{t_1} \times (a_2)^{t_2} \times (a_3)^{t_3} \times (a_4)^{t_4}]^{\Gamma}\right\}^{A_1},$$

with additional restriction $2s_1 + s_2 + 2s_3 + s_4 = 2t_1 + t_2 + 2t_3 + t_4$, which follows directly from the resonance conditions. Along with T_d geometrical invariance imposed on the Hamiltonian by physical requirements, the invariance with respect to time reversal should typically be imposed as well. The difference between spatial symmetry and time-reversal invariance is technically important, because elementary creation (annihilation) operators in most cases could be chosen as transforming according to irreducible representations of the symmetry group, whereas time-reversal operation transforms creation operators into annihilation and vice versa. From the other side, the resolution of the ambiguity problem for effective operators (well known in molecular rotational spectroscopy as Watson reduction [26]) should be done for phenomenological vibrational Hamiltonians as well, and to realize this transformation the generators of the corresponding unitary transformations should be invariant with respect to the symmetry group, but should change the sign under time reversal. The number and the type of these generators can also be predicted with generating functions in any order.

The step-by-step construction of invariant operators from elementary tensors is well known and is not difficult. Systematic application of the tensor coupling procedure based on the Clebsh–Gordan coefficients is the standard tool of group theoretical method applications in physics. Irreducible tensor methods [6] are well adapted to finite groups [9]. Practically, for all point groups and typical chains of groups of interest in molecular applications, the coupling coefficients and, naturally, characters are well described and easily calculable [2].

Less known are more global methods of invariant theory based on the generating function technique, which allow us to give the symbolic description of the whole algebra of invariants and in particular to give formulae for the number of invariants which can be constructed in any degree starting from a given set of elementary tensors [3, 10, 16, 18, 22–24]. Relatively popular now, the application of continuous symmetry groups to molecular models originated mainly from atomic [14] and nuclear [13] problems can also be successfully treated within the geometric invariant theory [21] by the generating function symbolic approach, but we leave these problems outside the scope of the present paper. We show below what kind of results can be obtained by applying the generating function method using as an example one concrete problem of molecular physics.

2. Molien function

The crucial initial point is the Molien theorem [1, 16, 17, 22–24] which in its simplest form enables one to construct the generating function for a number of irreducible representations of the given type in the decomposition of the Nth symmetric power of one irreducible representation. More exactly, for the finite group G, for the initial representation Γ_i and for the final representation Γ_f the generating function,

$$M^G(\Gamma_f \leftarrow \Gamma_i; \lambda) = |G|^{-1} \sum_{g \in G} \tilde{\chi}^{\Gamma_f}(g) \det(I_n - \lambda \Gamma_i(g))^{-1} = \sum_{N=0}^{\infty} C_N \lambda^N, \tag{1}$$

gives the numbers C_N indicating how many times the final representation Γ_f presents in the decomposition of the Nth symmetric power of the initial Γ_i representation. In (1) $|G|$ is the order of the finite group G, χ^Γ is the character of the irreducible representation, tilde means complex conjugation, and λ is a dummy variable. This generating function can typically be written in the form of a rational function of some special form:

$$\frac{\sum_k c_k \lambda^k}{(1 - \lambda^{d_1})(1 - \lambda^{d_2}) \cdots (1 - \lambda^{d_s})},$$

which has a symbolic meaning specifying the existence of a certain number of functionally independent denominator invariants and linearly independent though algebraically dependent numerator invariants, thus giving the description of the integrity basis (or in other words, the homogeneous system of parameters [25]). Alternative symbolic interpretations of generating functions can be done in terms of a set of generators (which are typically functionally dependent) and a set of relations (syzygies) between them, a set of relations between relations etc [12].

Calculation of the generating functions for the number of invariants or covariants constructed from elementary tensors transforming according to a given irreducible or reducible representation of finite groups is just a relatively simple task as soon as the character table is known. The generating functions for invariants and covariants constructed from irreducible representations of all 3D-point groups are given, for example, in [18]. Relatively detailed application of the generating function method for the construction of potential functions for tetrahedral molecules was recently realized in [3]. Another direct physical application [27] of such an approach is the construction of a generating functions for a number of quantum states in vibrational polyads, formed by overtones of one or several degenerate or quasi-degenerate modes [20, 28].

A less trivial problem is the construction of a generating function for diagonal within polyads operators. This can be achieved by extending the geometrical symmetry group with the dynamical symmetry responsible for the resonance or by constructing the required generating function from two generating functions, one for creation operators, another for annihilation operators. The nontrivial part consists of introducing the important restriction on the numbers of creation and annihilation operators which leads to operators diagonal within polyads. Such construction was realized, for example, in [19]. In this paper, a slightly different approach is proposed which is based on the construction known as the Hadamard product of formal power series [8, 11, 15, 25]. The advantage of this approach is due to the possibility of taking into account, in a simple way, additional symmetry requirements, which imposed simultaneously on creation and annihilation operators, such as invariance with respect to time reversal, and to represent the answer again in the rational function form.

3. The rational form of generating functions

In this section, we present several simple results on the explicit form of rational generating functions constructed through the Hadamard product of rational functions. We remind readers here that the Hadamard product of two formal power series $f(z) = \sum_{n\geqslant 0} f_n z^n$ and $g(z) = \sum_{n\geqslant 0} g_n z^n$ is defined as their term-by-term product [8, 11, 15, 25]:

$$f(z) \star g(z) = \sum_{n\geqslant 0} f_n g_n z^n. \tag{2}$$

The following fact is known: the Hadamard product of two rational functions is a rational function [8, 11, 15, 25]. We use this statement below when converting the formal power series into a rational function form.

3.1. Diagonal operators for two modes in 1:1 *resonance with trivial symmetry*

We start with an extremely simple example of two A modes in 1:1 resonance with a trivial symmetry group. The generating function for creation (or equivalently for annihilation) operators takes the form depending on two dummy variables (λ, k) which count independently the degree of creation operators and the associated modifications of the polyad quantum numbers:

$$g(A \leftarrow 2A, \lambda, k) = \frac{1}{(1-\lambda k)^2} = \sum_{n=0}^{\infty} (n+1)\lambda^n k^n. \tag{3}$$

Now in order to construct the generating function for diagonal operators we need to form the power series in k with coefficients being squares of coefficients in (3). This operation is exactly the Hadamard product (square) of formal power series [8, 11, 15, 25]. We denote the Hadamard product by $\star_k$, and its application to generating function (3) gives for the Hadamard square

$$\frac{1}{(1-\lambda k)^2} \star_k \frac{1}{(1-\lambda k)^2} = \sum_{n=0}^{\infty} (n+1)^2 \lambda^{2n} k^n = \frac{1+\lambda^2 k}{(1-\lambda^2 k)^3}. \tag{4}$$

The degree of auxiliary variable λ now counts the total degree of creation and annihilation operators. At the same time the variable k counts Δn associated with only creation (or only annihilation) operators forming the diagonal operator.

Formula (4) follows directly from the identity (where t replaces the $\lambda^2 k$):

$$\frac{\mathrm{d}}{\mathrm{d}t} t \frac{\mathrm{d}}{\mathrm{d}t} (1 + t + t^2 + t^3 + \cdots) = \sum_{n=0}^{\infty} (n+1)^2 t^n, \tag{5}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} t \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{1}{(1-t)} \right) = \frac{1+t}{(1-t)^3}. \tag{6}$$

In order to take into account only time-reversal invariant operators, we need to use instead of the simple Hadamard square the symmetrized Hadamard square $[(g(\lambda) \star_k g(\lambda) + g(\lambda^2)]/2$ which is an analog of the symmetrized square of an irreducible representation. As soon as the normal Hadamard square is known, the calculation of the symmetrized square is not difficult. Thus, for the generating function (3) its symmetrized Hadamard square, counting the number of diagonal time-reversal invariant operators, becomes

$$\frac{1}{2}[(g \star_k g) + g(\lambda^2)] = \frac{1}{2}\left(\frac{1+\lambda^2 k}{(1-\lambda^2 k)^3} + \frac{1}{(1-\lambda^2 k)^2}\right) = \frac{1}{(1-\lambda^2 k)^3}.$$

3.2. Diagonal operators for the doubly degenerate *E* mode for the T_d group

In the case of the doubly degenerate mode we need to calculate first the generating functions for operators of each symmetry type constructed from elementary creation/annihilation operators only, and then to take the sum of symmetrized Hadamard squares of these generating functions. The resulting generating function has rather a simple form (with TR standing for time-reversal invariant, and $\Delta n = 0$ indicating diagonal in polyad quantum number n operators):

$$g(A_1, \mathrm{TR}, \Delta n = 0, \leftarrow E; \lambda, k) = \frac{1}{(1-\lambda^2 k)(1-\lambda^4 k^2)(1-\lambda^6 k^3)}. \tag{7}$$

The k-dependence is not important in this example, because the mode is degenerated by the symmetry and consequently the resonance is 1:1. Curiously this generating function has the same form as the generating function for $T_d(O)$-invariant rotational operators, or for invariant operators constructed from x, y, z variables in the case of cubic O_h symmetry. Consequently, the denominator invariants have very simple tensorial form:

$$V_2 = (a^+a)^{A_1}, \qquad V_4 = [(a^+a^+)^E(aa)^E]^{A_1}, \tag{8}$$

$$V_6 = [(a^+a^+a^+)^{A_2}(aaa)^{A_2}]^{A_1}. \tag{9}$$

These three operators form the integrity basis, and an arbitrary diagonal time-reversal and T_d-invariant operator can be written as a polynomial in V_2, V_4, V_6.

3.3. Diagonal operators for the F_2 mode for the T_d group

For the triply degenerate mode the same procedure leads to a more complicated generating function:

$$g(A_1, \mathrm{TR}, \Delta N = 0; \leftarrow F_2; \lambda) = \frac{1+\lambda^6+\lambda^8+\lambda^{10}+\lambda^{12}+\lambda^{18}}{(1-\lambda^2)(1-\lambda^4)^2(1-\lambda^6)(1-\lambda^8)}. \tag{10}$$

The number of terms in the denominator now is equal to five, and the numerator includes six terms. Note that the form of the generating function for time-reversal operators is simpler than the corresponding function for all possible operators, which was calculated explicitly for the same problem about 20 years ago [19]. We have omitted the k-dependence from the generating function (10), because the presence of k gives no new information for the degenerate modes.

3.4. Diagonal operators for polyads formed by A_1 and *E* modes in 2:1 resonance

The nontrivial character of k dependence appears in the case of any k_1:k_2 resonances different form 1:1. We present as an example the 2:1:1 resonance between non-degenerate A_1 and doubly degenerate E modes of tetrahedral molecules.

The total generating function describing all diagonal time-reversal and T_d-invariant operators constructed through arbitrary intermediate representations has the following form:

$$g(A_1, \mathrm{TR}, \Delta N = 0, \leftarrow A_1 \oplus E(2{:}1); \lambda, k) = \frac{1+\lambda^7k^4+\lambda^8k^5-\lambda^{12}k^7-\lambda^{13}k^8-\lambda^{20}k^{12}}{(1-\lambda^2k)(1-\lambda^2k^2)(1-\lambda^3k^2)(1-\lambda^4k^2)(1-\lambda^6k^3)(1-\lambda^9k^6)}. \tag{11}$$

The generating function (11) is given in its simplest, most reduced form which has six terms in the denominator and both positive and negative contributions in the numerator. Naturally, there should be only five functionally independent invariants for this problem and consequently the six terms in the denominator correspond to a system of invariants related by syzygies. We do not want to discuss here the explicit construction of a system of syzygies. This example is given in order to demonstrate that even in the case of relatively simple generating functions the structure of the associated module of invariant functions can be rather complicated. To see the really complicated case we present below the generating function for time-reversal invariant diagonal operators for vibrational polyads in a CH_4 molecule taking into account all nine vibrational degrees of freedom with resonance 2:1:1:2:2:2:1:1:1 between them.

4. The rational form of the global generating function

From the point of view of practical applications only the several first terms of the power series decomposition of the generating function are of some interest. These terms can be obtained in a quite simple and straightforward way (see the appendix, expressions (A.3, A.4), which solves the problem and does not require us to find the rational function form for the Hadamard square. Nevertheless from the general abstract point of view it is tempting to give the rational form of the generating function which after its power series decomposition can give the correct number of operators in an arbitrary degree. We present below this rational function depending on one parameter. It turns out to be rather complicated. In the most reduced form this rational function has a numerator of degree 74, whereas its denominator includes 17 factors with the sum of their degrees equal to 92. We present this function below with just one purpose: to show that the same standard method leads to the rational form even in such a cumbersome case.

$$G(\text{Total for } \nu_1{:}\nu_2{:}\nu_3{:}\nu_4 = 2{:}1{:}2{:}1;\, \lambda) = \frac{\text{Numer}_{\text{Tot}}}{\text{Denom}_{\text{Tot}}}, \tag{12}$$

where

$$\text{Denom}_{\text{Tot}} = (1-\lambda)^4(1-\lambda^2)^3(1-\lambda^3)(1-\lambda^6)^2(1-\lambda^8)^2(1-\lambda^9)^3(1-\lambda^{12})^2,$$

$$\begin{aligned}
\text{Numer}_{\text{Tot}} = {} & \lambda^{74} - 4\lambda^{73} + 7\lambda^{72} - 5\lambda^{71} + 16\lambda^{70} - 22\lambda^{69} + 85\lambda^{68} \\
& - 9\lambda^{67} + 253\lambda^{66} + 77\lambda^{65} + 872\lambda^{64} + 512\lambda^{63} + 2183\lambda^{62} + 2161\lambda^{61} \\
& + 5175\lambda^{60} + 5608\lambda^{59} + 11\,933\lambda^{58} + 12\,618\lambda^{57} + 23\,269\lambda^{56} \\
& + 27\,037\lambda^{55} + 41\,742\lambda^{54} + 48\,273\lambda^{53} + 72\,619\lambda^{52} + 79\,476\lambda^{51} \\
& + 111\,449\lambda^{50} + 125\,265\lambda^{49} + 160\,991\lambda^{48} + 175\,577\lambda^{47} + 222\,701\lambda^{46} \\
& + 232\,021\lambda^{45} + 280\,315\lambda^{44} + 292\,864\lambda^{43} + 334\,256\lambda^{42} + 337\,189\lambda^{41} \\
& + 381\,867\lambda^{40} + 368\,588\lambda^{39} + 400\,082\lambda^{38} + 385\,396\lambda^{37} + 400\,082\lambda^{36} \\
& + 368\,588\lambda^{35} + 381\,867\lambda^{34} + 337\,189\lambda^{33} + 334\,256\lambda^{32} + 292\,864\lambda^{31} \\
& + 280\,315\lambda^{30} + 232\,021\lambda^{29} + 222\,701\lambda^{28} + 175\,577\lambda^{27} + 160\,991\lambda^{26} \\
& + 125\,265\lambda^{25} + 111\,449\lambda^{24} + 79\,476\lambda^{23} + 72\,619\lambda^{22} + 48\,273\lambda^{21} \\
& + 41\,742\lambda^{20} + 27\,037\lambda^{19} + 23\,269\lambda^{18} + 12\,618\lambda^{17} + 11\,933\lambda^{16} \\
& + 5608\lambda^{15} + 5175\lambda^{14} + 2161\lambda^{13} + 2183\lambda^{12} + 512\lambda^{11} + 872\lambda^{10} \\
& + 77\lambda^{9} + 253\lambda^{8} - 9\lambda^{7} + 85\lambda^{6} - 22\lambda^{5} + 16\lambda^{4} - 5\lambda^{3} + 7\lambda^{2} - 4\lambda + 1.
\end{aligned}$$

Note that although the number of $(1-\lambda^k)$ factors in the denominator of the total generating function is equal to 17, these factors cannot be interpreted as corresponding to algebraically independent invariants in spite of the fact that there should be exactly 17 such algebraically independent invariants. Naturally, there are no linear diagonal operators, whereas the generating function has in the denominator the $(1-\lambda)^4$ factor. We can multiply the numerator and the denominator by the same factor in order to get the numerator with only positive coefficients. To get this, it is sufficient to multiply both the numerator and the denominator by a factor, which is a polynomial of degree 10: $(1+\lambda)^4(1+\lambda^2)^3$. The so-obtained rational function will have only positive terms in the numerator (which becomes a polynomial of degree 84). But in principle this is not a guarantee that this form of generating function corresponds symbolically to the integrity basis construction. In any case, all are not of practical use because the number of terms in the numerator becomes equal to $2^7 \cdot 789\,9480$, where $789\,9480 = 2^3 \cdot 3^2 \cdot 5 \cdot 21\,943$ is the algebraic sum of coefficients in the numerator of the most reduced form of the generating function.

5. Conclusions

We have demonstrated the relevance of the 'Hadamard product' operation to the construction of the generating functions for effective operators in terms of bosonic creation and annihilation operators under additional restriction on the relative numbers of these operators. Such additional requirement naturally appears, for example, for vibrational polyads formed by vibrational modes in resonance. Adding a second parameter into generating functions allows us to take into account arbitrary resonance relations between vibrational modes. Application of the Hadamard product operation leads to the representation of the final result in a rational function form, and this is the main message to the readers of this paper. Application of the same technique to transition operators or to any covariants is straightforward for finite groups with known character tables. Extension to continuous groups is more delicate due to the fact that even for rather simple examples the module of covariants turns out not to be free [16]. Further qualitative analysis of effective operators constructed in terms of the integrity basis will certainly use new mathematical tools like nonlinear algebra [4] which are currently used mainly in high-energy physics, string theory and quantum gravitation. To mention the relevance of 'non-conventional' mathematical tools to 'trivial' molecular problems is another goal of the present communication.

Appendix. Calculation of the initial terms of the generating function

As soon as we have the power series representation for the generating functions giving the number of tensor operators of Γ_{fin} symmetry type constructed from elementary operators, it is quite easy to calculate the associated series for the operators diagonal in Δn and in addition satisfying the time-reversal property. This can be done in the following way. Let us write the generating function for the number of creation operators of Γ_{fin} symmetry formed from initial operators spanning the Γ_{in} representation in its formal power series form:

$$g(\Gamma_{\text{fin}}, \Gamma_{\text{in}}; \lambda, k) = \sum_{n=0}^{\infty} P_n^{\Gamma_{\text{fin}}}(\lambda) k^n, \tag{A.1}$$

where the polynomials $P_n^{\Gamma_{\text{fin}}}$ are the initial terms of the power series representation of the generating function. The final expression for the diagonal and time-reversal invariant operators constructed from (A.1) has the form

$$g(\text{TR}, \Delta n = 0; \lambda, k) = \sum_{\Gamma_{\text{fin}}} \sum_{n=0}^{\infty} \frac{1}{2}\left(\left[P_n^{\Gamma_{\text{fin}}}(\lambda)\right]^2 + P_n^{\Gamma_{\text{fin}}}(\lambda^2)\right) k^n. \tag{A.2}$$

We can name this operation the symmetrized Hadamard square because the standard Hadamard square for each power series in k gives the contribution

$$\sum_{n=0}^{\infty} \left[P_n^{\Gamma_{\rm fin}}(\lambda)\right]^2 k^n.$$

The passage to (A.2) corresponds to the replacement of the operation of standard square by symmetrized square in the representation theory.

From the point of view of practical construction of operators of different degree it may be more interesting to represent some initial terms of the formal series instead of total generating function (12). We illustrate here this partial representation by collecting terms with the same value of λ and with different k values in one group,

$$\begin{aligned} 1 &+ (2k + 2k^2)\lambda^2 + 4k^2\lambda^3 + (7k^4 + 13k^3 + 10k^2)\lambda^4 + (30k^3 + 31k^4)\lambda^5 \\ &+ (36k^3 + 128k^4 + 65k^5 + 18k^6)\lambda^6 + (143k^6 + 184k^4 + 297k^5)\lambda^7 \\ &+ (45k^8 + 234k^7 + 771k^6 + 713k^5 + 125k^4)\lambda^8 + \cdots. \end{aligned} \tag{A.3}$$

Expression (A.3) follows directly from the calculation of several first terms in the power series (A.2). One should note, that expression (A.3) includes all k-dependent contributions up to λ^8 terms. In order to get the complete calculation of the number of operators up to degree n, (i.e. up to λ^n in λ series), it is necessary to calculate the contributions to symmetrized Hadamard square up to k^n as well.

It is also interesting to see the simplified version of the same series decomposition where the role of k is neglected, i.e., by imposing $k = 1$. In such a case we have the series whose coefficient gives the number of tensor operators of the given degree

$$1 + 4\lambda^2 + 4\lambda^3 + 30\lambda^4 + 61\lambda^5 + 247\lambda^6 + 624\lambda^7 + 1888\lambda^8 + \cdots.$$

This decomposition coincides with the first terms of the power series expansion of the total generating function (12).

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