General restrictions for the relaxation constants of the polarization moments of the density matrix

M.P. Auzinsh

The University of Latvia, 226098, 19 Rainis Boulevard, Riga, Latvia

Received 26 March 1992; in final form 14 July 1992

General inequalities for the relaxation constants of polarization moments are examined. Concrete numerical limitations for the values of these constants are obtained.

In recent years it has been generally accepted to characterize the distribution of the angular momentum j of atomic as well as molecular states in the framework of the irreducible tensorial operators $\hat{T}^K_Q$. The state is described by means of polarization moments ρ^K_Q, which are the expansion coefficients of the angular momentum density matrix $\rho_{mm'}$ on the tensorial operators $\hat{T}^K_Q$:

$$\rho_{mm'} = \sum_{K=0}^{2j} \sum_{Q=-K}^{K} \rho^K_Q (T^K_Q)_{mm'} . \tag{1}$$

Polarization moments have a very clear physical meaning. Thus a moment with rank $K=0$ characterizes the population of the level, with $K=1$ the orientation, and with $K=2$ the alignment [1].

One of the general advantages of this approach is that for isotropic relaxation processes the components of polarization moments change independently, and the relaxation rates of these components γ_K depend only on the rank K of the polarization moment [1]. In the case of molecules, when the quantum number j of the angular momentum appears to be high there is a great number of polarization moments characterizing the state. As has been demonstrated in ref. [2] by using polarization moment relaxation rate measurements in simple thermal cells the information on stereochemical forces in molecular collision dynamics may be obtained. Such measurements were performed first for the case of I_2 and later for many other diatomic molecules, see ref. [2] and work cited therein.

If the information about the relaxation of different polarization moments is obtained from the laser-induced fluorescence measurements then only polarization moments up to rank $K=4$ have a direct influence on the dependence of the fluorescence intensity on the polarization of the absorbed and detected photons [3]. Nevertheless the higher rank moments may play an important role for example in experiments with optical pumping of molecules. So at rather moderate laser light intensity the polarization moments up to rank $K=10$ due to nonlinear coupling with smaller-rank polarization moments have a significant influence on the laser-induced fluorescence signals [4].

For all that, as demonstrated in refs. [1,5], the relaxation rates γ_K cannot be absolutely arbitrary. They must satisfy certain inequalities. Thus, in ref. [5] the system of inequalities

$$\sum_K (2K+1)(-1)^{m-m_1} \times \begin{pmatrix} j & j & K \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} j & j & K \\ m_1 & -m_1 & 0 \end{pmatrix} \tilde{\gamma}_K \leqslant 0 , \quad m \neq m_1 , \tag{2}$$

has been obtained, where $\tilde{\gamma}_K$ is $\gamma_K - \gamma_0$ and the quantity in brackets is a $3j$ symbol. Another system of inequalities

Correspondence to: M.P. Auzinsh, The University of Latvia, 226098, 29 Rainis Boulevard, Riga, Latvia.

$$(-1)^{\chi+2j+1}\sum_K (-1)^K(2K+1)\begin{Bmatrix} j & j & K \\ j & j & \chi \end{Bmatrix}\tilde{\gamma}_K \geqslant 0\,,$$

$$1 \leqslant \chi \leqslant 2j\,, \qquad (3)$$

different from the previous one, is given in ref. [1], where the quantity in curly brackets is a $6j$ symbol. It should be stressed that different authors use different normalizations of polarization moments; nevertheless the inequalities (2) and (3) are valid independent of normalization. For example, the authors of the cited papers [1] and [5] use a different, K-dependent, normalization of $\hat{T}^K_Q$, which leads to a different normalization of ρ^K_Q, yet both systems (2) and (3) are valid in both cases.

Beside their general significance, the given inequalities should be taken into account when relaxation processes are described phenomenologically, as well as in computer approximations of experimental data with theoretical curves, see for example refs. [6–8]. Systems (2) and (3) contain a different number of independent inequalities. Taking into consideration the symmetry properties of $3j$ symbols [9], it is quite simple to show that system (2) contains $j(j+1)$ independent inequalities, when j is an integer, and $j(j+1)+1/4$ inequalities, when j is a half-integer. This means that for $j \geqslant 3/2$ the number of inequalities exceeds (and for large j values by a considerable amount) the number of relaxation constants $\tilde{\gamma}_K$. In the case of (3) the number of inequalities coincides with the number of constants $\tilde{\gamma}_K$. Let us assume that all relaxation constants $\tilde{\gamma}_K$ are measured in units of one of them, say $\tilde{\gamma}_1$. In this case inequalities (2) or (3) in $(2j-1)$-dimensional space define the region of allowed values of $\tilde{\gamma}_K/\tilde{\gamma}_1$. As an illustration, this region is shown in fig. 1 for $j=3/2$. Each straight line in the figure presents one inequality. The region of $\tilde{\gamma}_K/\tilde{\gamma}_1$ allowed by inequalities (2) is denoted by horizontal strokes, and the region allowed by inequalities (3) by vertical ones. As may be seen, in this case system (3) imposes more strict limitations on the constants $\tilde{\gamma}_K$. From the results of a computer analysis presented below we show that a similar situation occurs for arbitrary j values (at least for $j \leqslant 70$).

In the general case of arbitrary j values it is not easy to present in $(2j-1)$-dimensional space the area of allowed $\tilde{\gamma}_K/\tilde{\gamma}_1$ values. In order to characterize this area it is possible to propose the following approach. Of all permitted $\tilde{\gamma}_K/\tilde{\gamma}_1$ values it is necessary to determine the minimal and the maximal one for each rank K. Here it is necessary to take into consideration that all maximum or all minimum values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ cannot always be reached simultaneously. This assertion may be illustrated by fig. 1 in the case of the system of inequalities (2). The minimum value $\tilde{\gamma}_2/\tilde{\gamma}_1 = 0$ is attained when $\tilde{\gamma}_3/\tilde{\gamma}_1 = 1$, but the minimum value $\tilde{\gamma}_3/\tilde{\gamma}_1 = 1/6$ is attained when $\tilde{\gamma}_2/\tilde{\gamma}_1 = 1/2$.

An analysis of (2), in the case when the number of inequalities considerably exceeds the number of constants $\tilde{\gamma}_K/\tilde{\gamma}_1$, shows that it is possible to make use of the Monte Carlo method, i.e. one must generate by means of a computer random points in the $(2j-1)$-dimensional space of $\tilde{\gamma}_K/\tilde{\gamma}_1$ and from all points hit into the allowed region (simultaneously satisfying all inequalities (2)) one must choose the minimal and the maximal values of constants $\tilde{\gamma}_K/\tilde{\gamma}_1$ for each rank K.

In the analysis of (3), when the number of inequalities is equal to $2j$ it is possible to use another method of examination of the permitted region for $\tilde{\gamma}_K/\tilde{\gamma}_1$. One can pass from the system of inequalities to a system of equalities and solve them by alternately "switching off" one equality. In this way we will find in the $(2j-1)$-space "corner point" (see

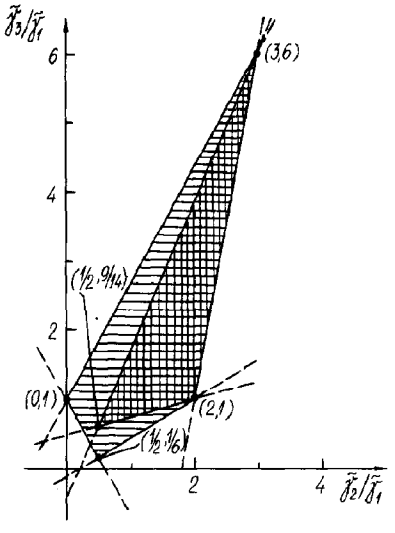

Fig. 1. Allowed region of the parameters $\tilde{\gamma}_K/\tilde{\gamma}_1$ in the case $j=3/2$, determined by the system of inequalities (2) and (3).

fig. 1 in the case of inequalities (3)) coordinates for the region of allowed values of $\tilde{\gamma}_K/\tilde{\gamma}_1$. From all coordinates of these corner points we must select those which correspond to the minimal and the maximal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ for each rank K.

By these methods we carried out an analysis of the systems of inequalities (2) and (3) for $j \leqslant 70$. It became clear, that for these j values, system (3) introduces more strict limitations on the minimal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ than system (2), and both systems introduce the same limitations on the maximal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$. In table 1 for $j \leqslant 10$ the results of absolute minimal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ given by (3) are presented. In table 2, for the same j values, the simultaneously existing minimal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ from (3) are presented. It may be easily seen that in both cases all these values are positive and do not exceed 0.6. A similar situation holds also for larger j values, at least for $j \leqslant 70$.

Absolute maximal values of $\tilde{\gamma}_K/\gamma_1$ can all be approached simultaneously and are given by $K(K+1)/2$. These values are thus independent of j.

These restrictions lead to one very general consequence to which we want to draw attention. If it is known that the relaxation rate γ_0 of the population equals one particular rate γ_K with $K \neq 0$, then all relaxation rates γ_K must be equal. This statement may be important in the analysis of some relaxation processes in molecules, see for example refs. [10–13].

In some special cases for minimal and maximal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ analytical expressions can be derived. In ref. [1] the following expansion of $\tilde{\gamma}_K$ is presented:

$$\tilde{\gamma}_K = \sum_{\chi \geqslant 1} a_{K\chi} A_\chi , \tag{4}$$

with

$$a_{K\chi} = (2j+1)^{-1} - (-1)^{K+\chi+2j} \begin{Bmatrix} j & j & K \\ j & j & \chi \end{Bmatrix} , \tag{5}$$

but $A_\chi > 0$. It is easy to understand that

$$(a_{K\chi}/a_{1\chi})_{\min} \leqslant \tilde{\gamma}_K/\tilde{\gamma}_1 \leqslant (a_{K\chi}/a_{1\chi})_{\max} . \tag{6}$$

In the last expression the minimum and the maximum is assumed on the parameter χ. As demonstrated in ref. [1]

$$(a_{2\chi}/a_{1\chi})_{\min} = a_{2(2j)}/a_{1(2j)} \tag{7a}$$

and

$$(a_{2\chi}/a_{1\chi})_{\max} = a_{21}/a_{11} . \tag{7b}$$

Unfortunately it is not possible to verify the generalization of (7a) and (7b) for arbitrary values of K. Yet a numerical analysis of (2) and (3) demonstrates that the generalization of (7b),

$$(a_{K\chi}/a_{1\chi})_{\max} = a_{K1}/a_{11} = K(K+1)/2 , \tag{8}$$

is valid for arbitrary values of K. In order to derive an analytical formula for a_{K1}/a_{11} we have made use of the analytical expressions for $6j$ symbols from ref. [9].

With the aid of the analytical formulas for $6j$ symbols it is also possible to obtain

$$\frac{a_{K(2j)}}{a_{1(2j)}} = \frac{1}{1+j/(j+1)} \times \left(1-(-1)^K \frac{(2j-K+1)(2j-K+2)\ldots(2j)}{(2j+2)(2j+3)\ldots(2j+K+1)}\right) , \tag{9}$$

but expression (9) does not lead to the results of table 1. This means that for arbitrary K values this expression does not give the values of the absolute minimum of $\tilde{\gamma}_K/\tilde{\gamma}_1$. Nevertheless, it does give the simultaneously existing minimal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$, presented in table 2, and also for larger j values which are not presented in the table.

In this connection it is useful to derive expressions for $a_{K(2j)}/a_{1(2j)}$ in some special cases. Thus

$$\left(\frac{\tilde{\gamma}_{2j}}{\tilde{\gamma}_1}\right)_{\min(\text{simult})} = \frac{a_{2j(2j)}}{a_{1(2j)}} = \frac{j+1}{2j+1} - (-1)^{2j} \frac{\pi^{1/2}}{2^{4j-1}} \frac{\Gamma(2j)}{\Gamma(2j+1/2)} , \tag{10}$$

with $\Gamma(x)$ being the gamma function. These formulae in the high j limit give

$$\left(\frac{\tilde{\gamma}_{2j}}{\tilde{\gamma}_1}\right)_{\min(\text{simult})} \approx \frac{j+1}{2j+1} . \tag{11}$$

One must understand that the obtained limitations are less strict than inequalities (2) and (3). They do not characterize the shape of the allowed region of relaxation constants. The restrictions de-

Table 1
Absolute minimum values for $\tilde{\nu}_K/\tilde{\nu}_1$

J	K																		
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	0.6000																		
3/2	0.5000	0.6429																	
2	0.4286	0.6429	0.5952																
5/2	0.3750	0.4792	0.5694	0.5846															
3	0.3333	0.4000	0.5455	0.5758	0.5711														
7/2	0.3000	0.3636	0.5227	0.5717	0.5612	0.5626													
4	0.2727	0.3506	0.5012	0.5711	0.5524	0.5559	0.5555												
9/2	0.2500	0.3510	0.4808	0.5240	0.5442	0.5510	0.5499	0.5500											
5	0.2308	0.3590	0.4615	0.4744	0.5362	0.5475	0.5451	0.5455	0.5455										
11/2	0.2143	0.3714	0.4435	0.4338	0.4864	0.5452	0.5410	0.5418	0.5417	0.5417									
6	0.2000	0.3864	0.4265	0.4011	0.4522	0.5440	0.5372	0.5387	0.5384	0.5385	0.5385								
13/2	0.1875	0.4026	0.4105	0.3749	0.4350	0.5436	0.5336	0.5362	0.5356	0.5357	0.5357	0.5357							
7	0.1765	0.3866	0.3956	0.3543	0.4307	0.5287	0.5301	0.5341	0.5332	0.5334	0.5333	0.5333	0.5333						
15/2	0.1667	0.3754	0.3816	0.3383	0.4355	0.5041	0.5238	0.5326	0.5309	0.5313	0.5312	0.5313	0.5312	0.5313					
8	0.1579	0.3699	0.3684	0.3263	0.4469	0.4810	0.4878	0.5292	0.5289	0.5295	0.5294	0.5294	0.5294	0.5294	0.5294				
17/2	0.1500	0.3688	0.3561	0.3176	0.4627	0.4595	0.4580	0.4985	0.5270	0.5280	0.5277	0.5278	0.5278	0.5278	0.5278	0.5278			
9	0.1429	0.3707	0.3444	0.3116	0.4711	0.4396	0.4339	0.4804	0.5252	0.5266	0.5262	0.5263	0.5263	0.5263	0.5263	0.5263	0.5263		
19/2	0.1364	0.3750	0.3335	0.3078	0.4631	0.4213	0.4151	0.4732	0.5234	0.5255	0.5249	0.5250	0.5250	0.5250	0.5250	0.5250	0.5250	0.5250	
10	0.1304	0.3809	0.3232	0.3060	0.4552	0.4046	0.4012	0.4747	0.5216	0.5245	0.5236	0.5239	0.5238	0.5238	0.5238	0.5238	0.5338	0.5238	0.5238

Table 2
Simultaneously existing minimum values for $\tilde{\gamma}_K/\tilde{\gamma}_1$

J	K																		
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	0.6000																		
3/2	0.5000	0.6429																	
2	0.4286	0.6429	0.5952																
5/2	0.3750	*0.6528*	0.5694	0.5846															
3	0.3333	*0.6667*	0.5455	0.5758	0.5711														
7/2	0.3000	*0.6818*	0.5227	0.5717	0.5612	0.5626													
4	0.2727	*0.6970*	0.5012	0.5711	0.5524	0.5559	0.5555												
9/2	0.2500	*0.7115*	0.4808	*0.5731*	0.5442	0.5510	0.5499	0.5500											
5	0.2308	*0.7253*	0.4615	*0.5769*	0.5362	0.5475	0.5451	0.5455	0.5455										
11/2	0.2143	*0.7381*	0.4435	*0.5821*	*0.5282*	0.5452	0.5410	0.5418	0.5417	0.5417									
6	0.2000	*0.7500*	0.4265	*0.5882*	*0.5201*	0.5440	0.5372	0.5387	0.5384	0.5385	0.5385								
13/2	0.1875	*0.7610*	0.4105	*0.5950*	*0.5120*	0.5436	0.5336	0.5362	0.5356	0.5357	0.5357	0.5357							
7	0.1765	*0.7712*	0.3956	*0.6022*	*0.5038*	*0.5441*	0.5301	0.5341	0.5332	0.5334	0.5333	0.5333	0.5333						
15/2	0.1667	*0.7807*	0.3816	*0.6096*	*0.4956*	*0.5452*	*0.5266*	0.5326	0.5309	0.5313	0.5312	0.5313	0.5312	0.5313					
8	0.1579	*0.7895*	0.3684	*0.6172*	*0.4874*	*0.5469*	*0.5231*	*0.5314*	0.5289	0.5295	0.5294	0.5294	0.5294	0.5294	0.5294				
17/2	0.1500	*0.7976*	0.3561	*0.6248*	*0.4792*	*0.5491*	*0.5196*	*0.5305*	0.5270	0.5280	0.5277	0.5278	0.5278	0.5278	0.5278	0.5278			
9	0.1429	*0.8052*	0.3444	*0.6324*	0.4711	*0.5518*	*0.5159*	*0.5300*	0.5252	0.5266	0.5262	0.5263	0.5263	0.5263	0.5263	0.5263	0.5263		
19/2	0.1364	*0.8123*	0.3335	*0.6399*	0.4631	*0.5548*	*0.5122*	*0.5298*	0.5234	0.5255	0.5249	0.5250	0.5250	0.5250	0.5250	0.5250	0.5250	0.5250	
10	0.1304	*0.8188*	0.3232	*0.6473*	0.4552	*0.5581*	*0.5084*	*0.5300*	0.5216	0.5245	0.5236	0.5239	0.5238	0.5238	0.5238	0.5238	0.5238	0.5238	0.5238

fine the multidimensional parallelepiped in $(2j-1)$-dimensional space, which is encircled around the allowed region of $\tilde{\gamma}_K/\tilde{\gamma}_1$ which satisfies the obtained restrictions. Nevertheless the obtained restrictions are much more obvious and they give a good idea about limitations imposed by inequalities (2) and (3).

The presented tables and formulae for the minimal values and the formulae for the maximal values of $\tilde{\gamma}_K/\tilde{\gamma}_1$ seem to be very useful in the case when not all the relaxation constants with $0 \leqslant K \leqslant 2j$ are taken into consideration. In this situation it is impossible to use inequalities (2) or (3) directly, but the limitations for $\tilde{\gamma}_K/\tilde{\gamma}_1$ obtained in this paper are still valid. It is especially important in the case of molecules when the angular momentum values are, as a rule, large and not all the possible polarization moments of the state are taken into account in the description of the physical process, see for example ref. [14].

I am indebted to Professors S.D. Rosner and R.A. Holt for providing me with their computer programs for angular momentum sum coefficients. I would like to acknowledge the assistance of A. Gumilevskij in the computer calculations. This project was supported by the Latvian Science Council grant 90.467.

References

[1] A. Omont, Progr. Quantum Electron. 5 (1977) 69.
[2] A.J. McCaffery, J. Phys. Chem. 91 (1987) 5451.
[3] C.H. Greene and R.N. Zare, J. Chem. Phys. 78 (1983) 6741.
[4] M.P. Auzinsh, in: Collision and radiation processes involving excited particles (Latvian University Press, Riga, 1987) p. 85 (in Russian).
[5] M.I. Dyakonov and V.I. Perel, Phys. Letters A 41 (1972) 451.
[6] M. Ducloy, M.P. Gorza and B. Decomp, Opt. Commun. 8 (1973) 21.
[7] M.P. Auzinsh and R.S. Ferber, Opt. Spectry. (USSR) 55 (1983) 674.
[8] M.P. Auzinsh and R.S. Ferber, Sov. Phys. Usp. 33 (1990) 833.
[9] D.A. Varshalovich, A.N. Moskalev and V.K. Khersonskii, Quantum theory of angular momentum (World Scientific, Singapore, 1988).
[10] J. McCormac, A.J. McCaffery and M.D. Rowe, Chem. Phys. 48 (1980) 121.
[11] M.P. Auzinsh, R.S. Ferber, Ya.A. Harya and I.Ya. Pirags, Chem. Phys. Letters 124 (1986) 116.
[12] M. Kolwas and J. Szonert, Chem. Phys. Letters 130 (1986) 498.
[13] C.P. Fell, A.J. McCaffery and A. Ticktin, J. Chem. Phys. 90 (1989) 852.
[14] M.P. Auzinsh and R.S. Ferber, Phys. Rev. A 43 (1991) 2374.