

## A GENERAL THEOREM ON THE TRANSITION PROBABILITIES OF A QUANTUM MECHANICAL SYSTEM WITH SPATIAL DEGENERACY

by H. A. TOLHOEK and S. R. DE GROOT

Institute for theoretical physics, The University, Utrecht, Netherlands

### Summary

In the general case of a quantum mechanical system with a Hamiltonian that is invariant for rotations spatial degeneracy will exist. So the initial state must be characterized except by the energy also by e.g. the magnetic quantum number. Both for emission of light and electrons plus neutrinos ( $\beta$ -radioactivity) of a quantum mechanical system the following theorem is important: the total transition probability from an initial level with some definite magnetic quantum number  $m_i$  to every possible final level belonging to one energy does not depend on  $m_i$ . A simple proof is given for this theorem that embraces the case of forbidden transitions, which case is not covered by the usual proof. In the proof a Gibbs ensemble of quantum mechanical systems is used; the necessary and sufficient conditions for the rotational invariance of such an ensemble are given.

§ 1. *Introduction.* If transitions of a quantum mechanical system are considered, the usual case is that there is spatial degeneracy: we can specify a state of the system by  $n$  (determining its energy  $E_n$ ) and e.g.  $m$  that defines the  $z$ -component of the angular momentum  $j$ . The total transition probability of any initial level with a certain value  $m_i$  for  $m$  to all final levels (belonging to one energy value specified by  $n_f$ ) is given by a sum:

$$A_{if}(m_i) = \sum_{m_f} A(n_i, m_i; n_f, m_f) \quad (1)$$

( $A(n_i, m_i; n_f, m_f)$  is a partial transition probability). This sum might depend on  $m_i$ , as the wave function of the initial level can have different forms. However, one can deduce that  $A_{if}$  does not depend on  $m_i$ , under the condition that the Hamiltonian is invariant for rotations of space (which means that no privileged directions in space

exist) Roughly speaking we can say:  $m_i$  specifies only to a certain extent an orientation of the system and all orientations are equivalent if the Hamiltonian is invariant for rotations. This gives already an intuitive idea of the correctness of the theorem in question but is of course no exact proof of the statement. Similarly the sums of all partial transition probabilities with one final level, are independent of  $m_j$ :

$$A'_{j_i}(m_j) = \sum_{m_i} A(n_i, m_i; n_j, m_j) \quad (2)$$

An immediate consequence of the independence of  $A_{ij}$  of  $m_i$  and  $A'_{ij}$  of  $m_j$  is that:

$$A_{ij}/A'_{ji} = (2j_j + 1)/(2j_i + 1) \quad (3)$$

$$\text{for: } \sum_{m_i} A_{ij}(m_i) = \sum_{m_j} A'_{ji}(m_j) = \sum_{m_i, m_j} A(n_i, m_i; n_j, m_j)$$

$$\text{or: } (2j_i + 1) A_{ij} = (2j_j + 1) A'_{ji}$$

The property (3) has long been known for the case of light and allowed transitions (electric dipole) and is called the sum rule of Ornstein-Burger<sup>1)</sup>. In this paper a very general proof is given for the independence of  $A_{ij}$  of  $m_i$  and of  $A'_{ji}$  of  $m_j$ , which is also valid for the case of multipole radiation ("forbidden" transitions). The usual proof of the sum rule starts from the expressions for the relative magnitude of the matrix elements<sup>4)</sup> for dipole radiation and is only valid for this type of radiation (cf. also<sup>3)</sup>). The experimental check of the sum rule consists of the measurement of the relative intensities of the lines in a Zeeman splitting. In this case the invariance for rotations of the Hamiltonian is not strictly valid. In the first and sufficiently accurate approximation, however, the only effect of the Zeeman splitting is that the degeneracy is removed without alteration of the partial transition probabilities. In this manner partial transition probabilities can be measured separately.

The same questions as for the emission of light occur in the theory of  $\beta$ -radioactivity. However, for this case „forbidden” transitions are very common. The independence of  $A_{ij}$  of  $m_i$  is again important and it is necessary to prove this property as well for forbidden as for allowed transitions. The use of this property is essential for the discussion of the matrix elements that determine the transition probabilities<sup>2) 3) 5)</sup>.

§ 2. *Remarks on the use of ensembles in quantum mechanics.* To prove the before-mentioned theorem about transition probabilities we make use of ensembles of quantum mechanical systems. We consider especially the rotational invariance of ensembles. Several general properties of transition probabilities follow directly from the ordinary transformation of operators in quantum mechanics<sup>5</sup>). If viz. the matrix  $f$  transforms according to:

$$f = S^+ f^0 S = S^{-1} f^0 S \quad (S \text{ unitary}) \quad (4)$$

(which gives the ordinary transformation to a new representation for operators) the trace of  $f$  is invariant; the same is true for the trace of  $ff$ , as  $ff$  transforms also according to (4). We consider the matrix elements  $f(n, m; n', m')$  in which  $n$  gives the energy level and  $m$  distinguishes the different states for the same energy in case of degeneracy, while  $S$  transforms to a new representation for the  $m$ 's. We can write the invariance of the trace of  $ff$  for this case as:

$$\sum_{m,m'} |f(n, m; n', m')|^2 = \sum_{m,m'} |f^0(n, m; n', m')|^2 \quad (5)$$

which is the mathematical expression of the principle of spectroscopic stability<sup>5</sup>). If we have e.g. transition probabilities given by a vector  $\mathbf{A}$  according to:

$$P(n, m; n', m') = |\mathbf{A}(n', m; n', m')|^2 = |A_x(n, m; n', m')|^2 + |A_y(n, m; n', m')|^2 + |A_z(n, m; n', m')|^2 \quad (6)$$

(5) states for this case the invariance of a double sum of partial transition probabilities if new coordinates are chosen (when the  $m$  refer to spatial degeneracy). The before-mentioned theorem (§ 1) is, however, of a different type; only a single sum occurs in it, whereas a double sum occurs in (5). Now some properties concerning transition probabilities become only clear after introduction of ensembles in quantum mechanics. If e.g. the initial state is a mixed state, one gets, compared with the cases with as initial state a pure state, cross terms in the expression for the transitions to the final state. These cross terms are  $\neq 0$  and can only be omitted after averaging all possible relative phases of the components of the mixed state. Written in formulae: if

$$\varphi_n = \sum_m c_{n,m} \varphi_{n,m} \quad (7)$$

then the probability that the system is in the state  $\varphi_{n,m}$  is:

$$|c_{n,m}|^2 \equiv P_{n,m} \quad (8)$$

If the probability for a transition per unit of time from a state  $\varphi_{n,m}$  to a state  $\varphi_{n',m'}$  is given by  $A_{nm,n'm'}$  then after a short time  $\tau$ , we have for the probability to find the system in the state  $\varphi_{n',m'}$ :

$$A_{nm,n'm'} \tau \quad (9)$$

if the initial state was  $\varphi_{n,m}$ . If the initial state is  $\varphi_n$ , this probability is, however, not given by:

$$\sum_m P_{nm} A_{nm,n'm'} \tau \quad (10)$$

This expression is only correct after averaging the phases. The use of a Gibbs ensemble is only a more technical device for averaging phases that are distributed at random: the precise study of the involved relations was made in this connection <sup>6) 7)</sup>. The introduction of ensembles in quantum mechanics seems rather natural because a measurement that determines the  $\varphi_{n,m}$  will give only the absolute value of the coefficients of the components of mixed states not the relative phases. However, these relative phases have physical significance and they could be determined by other measurements. The result of the first measurements can, however, be expressed only by giving an ensemble.

The first theorem, that is proved in this paper, is that a necessary and sufficient condition for the invariance for rotations of an ensemble is that the density matrix  $\rho$  (cf. <sup>6) 7)</sup> and below) is of the form:

$$\rho_{mm'} = P \delta_{mm'} \quad (11)$$

After this, it is simple to derive as second theorem: the transition probability  $A_{ij}$  is independent of  $m_i$  and  $A'_{ji}$  is independent of  $m_j$ , if the Hamiltonian is invariant for rotations. We saw already that a direct consequence of the second theorem is:

$$A_{ij}/A'_{ji} = (2j_j + 1)/(2j_i + 1) \quad (3)$$

§ 3. *Quantum statistical ensembles with rotational invariance.* We will consider in this section ensembles of quantum mechanical systems that are invariant for rotations of space, and take as members of the ensemble, eigenfunctions belonging to a definite eigenvalue of the angular momentum of the system. The simultaneous eigenfunctions of the total angular momentum and its  $z$ -component will be written as  $\varphi_m(m = j, j - 1, \dots, -j; j$  quantum number

for the total angular momentum,  $m$  for its  $z$ -component). An arbitrary eigenfunction for  $j$  can be developed as:

$$\varphi = \sum_m a_m \varphi_m \tag{12}$$

We normalize all wave functions; hence  $\sum_m |a_m|^2 = 1$ . The density matrix  $\rho$  is the operator, defined for an ensemble of quantum mechanical systems, by its elements.

$$\rho_{mm'} = \overline{a_{m'}^* a_m} \tag{13}$$

The double bar means the average for the ensemble.

Often ensembles are considered that represent the result that a measurement has given the probability  $P_m$  for the system being in state  $\varphi_m$ ; we cannot represent the result of such a measurement by a wave function  $\sum_m a_m \varphi_m$ , because the relative phases of the different  $\varphi_m$  do not follow from the measurement, but only by an ensemble in which these phases are taken at random. From this it results that  $\rho_{mm'}$  becomes a diagonal matrix

$$\rho_{mm'} = P_m \delta_{mm'} \tag{14}$$

We can write this also in the form:

$$\rho\varphi = \sum_m \varphi_m P_m \int \varphi_m^* \varphi d\tau \tag{15}$$

and we verify easily that:

$$\int \varphi_m^* \rho \varphi_m d\tau = P_m \tag{16}$$

The diagonal form (14) of  $\rho$  is only valid for a definite system of  $\varphi_m$ 's; by a transformation

$$\varphi'_i = \sum_m S_{im} \varphi_m \quad (S \text{ unitary}) \tag{17}$$

$\rho$  is transformed according to:

$$\rho'_{sr} = \sum_{kl} \rho_{ik} S_{is}^* S_{kr} \tag{18}$$

It is clear that the new matrix will not generally have the diagonal form; the diagonal form is only valid for a definite representation. Analogously the density matrix  $\rho$  for an ensemble will not hold the diagonal form generally, if the members of the ensemble change with time according to the Schrödinger equation.

*Theorem I:* The necessary and sufficient condition that a quantum statistical ensemble, composed of systems  $\varphi_m$  (belonging to a de-

finite angular momentum) is invariant for rotations, is that  $\varrho_{mm'}$  has the form:

$$\varrho_{mm'} = P \delta_{mm'} \quad (19)$$

or if  $\varrho_{mm'}$  has the form (14), this is equivalent with:

$$P_j = P_{j-1} = \dots = P_{-j} \quad (20)$$

*Proof:* We use infinitesimal rotations in the proof of this theorem. We can characterize a rotation of space  $D_\alpha$  by the vector  $(\alpha_x, \alpha_y, \alpha_z)$  that has as direction the axis of rotation and as value the angle of rotation. We now consider the infinitesimal rotation  $D_\beta$  with the infinitesimal vector of rotation  $(\beta_x, \beta_y, \beta_z)$ . A wave function  $\varphi$  is transformed in a certain way by  $D_\beta$ ; we write:

$$D_\beta \varphi = \varphi + \beta_x I_x \varphi + \beta_y I_y \varphi + \beta_z I_z \varphi \quad (21)$$

$I_x$ ,  $I_y$  and  $I_z$  give the infinitesimal transformations of the representation of the rotations of space that is defined by the  $\varphi$  (cf. e.g. <sup>4</sup>) p. 62 ff.).

The invariance of an ensemble for the infinitesimal rotations of space is of course a consequence of the invariance for all rotations of space, but the inverse is also true: the invariance for the infinitesimal rotations  $I_x$ ,  $I_y$  and  $I_z$  is also sufficient for the invariance for all rotations. The invariance for rotations of the ensemble that we considered above, is equivalent with the property that the expectation values of  $\varrho$  do not change if one passes from the  $\varphi_m$  to the  $D\varphi_m$  ( $D$  is an infinitesimal rotation) or in formula (we use a representation, for which  $\varrho$  has the diagonal form (14)):

$$P_{Dm} = P_m, \quad \text{for every } m \quad (22)$$

with:

$$\begin{aligned} P_{Dm} &= \int (D\varphi_m)^* \varrho D\varphi_m d\tau = \\ &= \sum_{m'} [\int (D\varphi_m)^* \varphi_{m'} d\tau] P_{m'} [\int \varphi_{m'}^* D\varphi_m d\tau] = \\ &= \sum_{m'} P_{m'} |\int \varphi_{m'}^* D\varphi_m d\tau|^2 \end{aligned} \quad (23)$$

or:

$$P_{Dm} = \sum_{m'} P_{m'} P_{m'm} \quad (24)$$

if we put:

$$P_{m'm} = |\int \varphi_{m'}^* D\varphi_m d\tau|^2 \quad (25)$$

From (25) follows directly:

$$P_{m'm} = P_{mm'} \quad (26)$$

We can prove this in the following way:

α) if  $m' = m$ , (26) is trivial

β) if  $m' \neq m$ , we can write:

$$\int \varphi_{m'}^* D\varphi_m d\tau = \int \varphi_{m'}^* (\beta_x I_x + \beta_y I_y + \beta_z I_z) \varphi_m d\tau$$

The operators for infinitesimal rotations  $I_x, I_y, I_z$  are Hermitian except for a pure imaginary factor. They give viz. with this factor the operators for the components of the total angular momentum of the system. Now (26) is a direct consequence.

We have further:

$$\sum_{m'} P_{m'm} = 1 \tag{27}$$

We shall use this equation in the form:

$$P_{mm} = 1 - \sum_{m' \neq m} P_{mm'} \tag{28}$$

We prove (27) by starting from the development:

$$\varphi = \sum_m \varphi_m \int \varphi_m^* \varphi d\tau \tag{29}$$

If we take  $\varphi = D\varphi_m$ , we get from (29):

$$1 = \int (D\varphi_m)^* (D\varphi_m) d\tau = \sum_{m'} [\int (D\varphi_m)^* \varphi_{m'} d\tau] [\int \varphi_{m'}^* (D\varphi_m) d\tau] = \sum_{m'} P_{m'm}$$

and (27) is proved.

If we consider the infinitesimal rotations  $I_x, I_y, I_z$  for which the ensemble must be invariant, we see that  $I_z$  needs no further consideration, for  $I_z$  does not alter the  $\varphi_m$ . The transformations of the eigenfunctions  $\varphi_m$  for the infinitesimal rotations  $I_x$  and  $I_y$  are well known from the treatment of the irreducible representations of the group of the space rotations (cf. e.g. <sup>3)</sup> p. 66). We need only the following properties:

The Hermitian operators  $L_x, L_y, L_z$ , defined by

$$L_x = iI_x \quad L_y = iI_y \quad L_z = iI_z \tag{30}$$

give the following result, if they act on the  $\varphi_m$  ( $|m| \leq j$ )

$$\begin{cases} L_x \varphi_m = a_1 \varphi_{m-1} + b_1 \varphi_{m+1} \\ L_y \varphi_m = a_2 \varphi_{m-1} + b_2 \varphi_{m+1} \\ L_z \varphi_m = m \varphi_m \end{cases} \tag{31}$$

$a_1, a_2, b_1, b_2 \neq 0$  unless  $m = j$ , in which case:  $b_1 = b_2 = 0$ ; or  $m = -j$ , in which case  $a_1 = a_2 = 0$ .

We now consider the invariance of the ensemble for rotations  $I_x$ ; we have, if  $m \neq m'$  and if  $\beta_y = \beta_x = 0$ :

$$P_{mm'} = \left| \int \varphi_m^* D_{\beta} \varphi_{m'} d\tau \right|^2 = |\beta_x|^2 \left| \int \varphi_m^* I_x \varphi_{m'} d\tau \right|^2 \tag{32}$$

so we have for rotations  $I_x$ :

$$\left. \begin{aligned} P_{mm'} &\neq 0 \text{ if } m - m' = \pm 1 \\ P_{mm'} &= 0 \text{ if } |m - m'| > 1 \end{aligned} \right\} \tag{33}$$

According to (22) and (24), we can write the condition for invariance in the form:

$$\sum_{m'} P_{m'} P_{mm'} = P_m \quad \text{for every } m \tag{34}$$

or using (28) and (33):

$$\left. \begin{aligned} P_j (1 - P_{j,j-1}) + P_{j-1} P_{j-1,j} &= P_j \quad (m = j) \\ P_{j-1} (1 - P_{j-1,j} - P_{j-1,j-2}) + P_j P_{j,j-1} + P_{j-2} P_{j-2,j-1} &= \\ &= P_{j-1} \quad (m = j - 1) \\ \dots\dots\dots \end{aligned} \right\} \tag{35}$$

We now find respectively using (26):

$$P_j = P_{j-1}, \quad P_{j-2} = P_{j-1} \text{ etc.}$$

or:

$$P_j = P_{j-1} = \dots = P_{-j} \tag{36}$$

Consideration of the rotation  $I_y$  gives exactly the same result (36) as  $I_x$  gives, as could be expected.

If (36) is satisfied, we can write  $\rho$  as:

$$\rho_{mm'} = P \delta_{mm'} \tag{37}$$

and it is clear from (18) that (36) is also sufficient for the rotational invariance of the ensemble, as the representation  $D$  of the rotation group determines again unitary transformations  $S$ .

We want to emphasize that (36) or (37) are essential for rotational degeneracy and are not at all valid for every case of degeneracy. If we have e.g. a quantum mechanical system which has two different systems of levels at an energy  $E_n$  (fortuitous degeneracy), one with  $j = 0 : \varphi^{(1)}$ , the other with  $j > 0 : \varphi_m^{(2)}$ , we have  $(2j + 1) + 1$  levels with the same energy. The  $2j + 1$  eigenfunctions  $\varphi_m^{(2)}$  are transformed in each other;  $\varphi^{(1)}$  is, however, not transformed at all, if a rotation is performed. If we use  $m$  merely as an index to distinguish the different degenerate states with the same energy



(put  $m = 0$  for  $\varphi^{(1)}$  and  $m = 1, \dots, 2j + 1$  for  $\varphi_m^{(2)}$ ), the form of  $\rho$  becomes:

$$\rho_{mm'} = \begin{cases} P^{(1)} \delta_{mm'} & \text{if } m = 0 \\ P^{(2)} \delta_{mm'} & \text{if } m \geq 1 \end{cases} \quad (38)$$

This form is again invariant for rotations, though it is not a multiple of the unit-matrix if  $P^{(1)} \neq P^{(2)}$ , and though it does not remain a diagonal matrix for the most general unitary transformations.

§ 4. *Application of theorem I: A general proof of the sum rule.*  
*Theorem II:* The sum  $A_{ij}$  of partial transition probabilities (cf. (1)) is independent of  $m_i$  and the sum  $A'_{ji}$  (2) is independent of  $m_j$ , if the Hamiltonian of the quantum mechanical system is invariant for rotations.

The proof of theorem II is easy with the use of theorem I; we consider again a quantum statistical ensemble that is invariant for the rotations of space. We take, however, the case that the ensemble contains states that differ not only in the magnetic quantum number  $m$ , but also in other quantum numbers, which we denote together by  $n$ . Hence we write the eigenfunctions  $\varphi_{n,m}$  and the expectation values of the density matrix:  $P_{n,m}$ . The energy eigenvalue  $E_n$  for  $\varphi_{n,m}$  will, generally, be different for different  $n$ 's, though it is independent of  $m$  (spatial degeneracy).

We now consider the case that the  $P_{n,m}$  depend on the time  $t$ , which is the case that transitions between different states are possible; we write  $P_{n,m}(t)$  for the value at time  $t$ . The necessary and sufficient condition for invariance for rotations of such an ensemble is (according to theorem I):

$$P_{n,j} = P_{n,j-1} = \dots = P_{n,-j} \quad \text{for every } n \quad (39)$$

(It is supposed that the  $n$ 's are not affected by rotations)

We had for the ensemble that was considered in theorem I:

$$\sum_m P_m = 1 \quad (40)$$

However, we have for the ensemble considered in theorem II

$$\sum_{n,m} P_{n,m} = 1 \quad (41)$$

We now consider the case of 2 values of  $n$ : between 2 spatially degenerate energy-levels transitions are possible. Let  $P_{m_i}^i$  be the

probabilities for the initial level,  $P'_{m_f}$  for the final level. If  $P^i_{m_i}(0)$  and  $P^f_{m_f}(0)$  are the values at time  $t = 0$ , the values at a short time  $\tau$  afterwards can be given in terms of the initial probabilities and the transition probabilities.

If we take:

$$P^i_{m_i}(0) = P \quad \text{the same for all } m_i^{\dagger} \quad (42)$$

and:

$$P^f_{m_f}(0) = 0 \quad \text{for all } m_f \quad (43)$$

then we have after a short time  $\tau$  (cf. (1)):

$$P^i_{m_i}(\tau) = P^i_{m_i}(0) [1 - \Sigma_{m_f} A(n_i, m_i; n_f, m_f)\tau] = P[1 - A_{ii}(m_i)\tau] \quad (44)$$

and (cf. (2)):

$$P^f_{m_f}(\tau) = \Sigma_{m_i} P^i_{m_i}(0) A(n_i, m_i; n_f, m_f)\tau = P A'_{fi}(m_f)\tau \quad (45)$$

Now if the Hamiltonian is invariant for rotations and if (42) is valid ((42) expresses the invariance for rotations of the initial ensemble) the ensemble must remain invariant for rotations; thus  $P^i_{m_i}(\tau)$  and  $P^f_{m_f}(\tau)$  must be independent respectively of  $m_i$  and  $m_f$ , or:  $A_{ii}(m_i)$  and  $A'_{fi}(m_f)$  must be independent of  $m_i$  respectively  $m_f$ . Hence theorem II is proved.

The sum rule (3) is an immediate consequence of this theorem, as we saw already in § 1.

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