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by

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SUM RULES IN QUANTUM MECHANICS

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ABSTRACT

The sum rules usually derived for the squares of the matrix elements of the co-ordinate operator between eigenstates of a Schrödinger Hamiltonian are here extended to the matrix elements of more general operators taken between the states of any complete set of states. For that purpose extensive use is made of the closure relation for the set of eigenstates of a hermitian operator. Several applications of the sum rules obtained are made.

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1. INTRODUCTION

The purpose if this paper is to review the sum rules of quantum mechanics (of the type of the Thomas-Reiche-Kuhn sum rule), to identify their limitations, and to generalize them in several respects. It will be shown how a wide family of related sum rules can be written by direct application of the closure relation for the eigenstates of hermitian operators. The generalization will include the use of operators more general than a Schrödinger Hamiltonian to form the set of base states, and the freedom to sum matrix elements of arbitrary operators.

The well-known THOMAS-REICHE-KUHN sum rule [1], states that for a one-particle Hamiltonian of the form

$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}) \ , \tag{1}$$

where $V(\vec{r})$ is a static potential (i.e., $V(\vec{r})$ commutes with $\vec{r}$) the following sum rule for the matrix element of the co-ordinate operator x is valid:

$$\sum_k (E_k - E_j) |\langle k|x|j\rangle|^2 = \hbar^2/2m \ . \tag{2}$$

Here $|j\rangle$ and $|k\rangle$ are the eigenstates of the operator H with eigenvalues E_j and E_k respectively. The summation symbol means the sum over the discrete set of states and integration over the continuum spectrum. In the literature this rule is derived by noticing that

$$[x, H] = \frac{i\hbar}{m} p_x \ , \tag{3}$$

so that

$$(E_j - E_k)\langle k|x|j\rangle = \frac{ih}{m}\,\langle k|p_x|j\rangle .$$

Multiplying both members by $\langle k|x|j\rangle^* = \langle j|x|k\rangle$, this becomes

$$(E_j - E_k)|\langle k|x|j\rangle|^2 = \frac{ih}{m}\langle j|x|k\rangle\langle k|p_x|j\rangle .$$

Interchanging the indices j and k and subtracting, we obtain

$$2(E_j - E_k)|\langle k|x|j\rangle|^2 = \frac{ih}{m}\Big\{\langle j|x|k\rangle\langle k|p_x|j\rangle -$$

$$-\langle k|x|j\rangle\langle j|p_x|k\rangle\Big\} .$$

Summing over k, using the fact that the states $|k\rangle$ form a complete set and the fundamental relation

$$x\,p_x - p_x\,x = ih \qquad (4)$$

the sum rule (2) is obtained. In this derivation of eq. (2) the essential points are only the form of the commutator in eq. (3), the fact that the eigenstates of H form a complete set, and the fundamental relation (4). If the commutator $[x, H]$ fails to be of the form (3), the sum rule (2) may be not valid, i.e., the second member of (2) may be different from the constant $\hbar^2/2m$. This will occur, for example, in the case of the particle being subject to a velocity-dependent potential, or in the presence of exchange forces in systems of several particles [2]. We shall see how the necessary modification in the form of the sum rule appears in a straightforward way if an appropriate form of the sum rule is written which does not make use of the explicit form of the commutator (3).

The possible usefulness of a sum rule like this derives from the following. Suppose that the sum in the left-hand side has

some physical meaning (for example, an integrated cross-section, or a total transition probability), or enters as a term in an experimentally measurable quantity (such as an average value of some physical quantity). Then by comparing this value with the second member of the sum rule we can tell whether or not the Hamiltonian governing the system is of the form (1), or whether the matrix element relevant to the process is actually of the assumed form. In the cases where a non-static interaction has to be introduced, the use of the sum rule allows us to obtain information on the strength and form of these new terms. This procedure has actually been used to get information on the amount of exchange and velocity-dependent forces present in the nucleon-nucleon interaction [3]. The application of the sum rule (2) is, however, strongly limited by the condition that the operator in the matrix element relevant for the process being studied be of the form of a single co-ordinate x. This is of course a strong restriction and has implied that the sum rule could be used for the photo-nuclear processes only in the so-called dipole approximation. Some effort was made to extend the sum rule to matrix elements of higher multipole moments [4], but only approximated forms were obtained. We shall show how more general sum rules, referring to matrix elements of more general operators, can easily be written (and perhaps applied successfully to problems of physical interest).

The sum rule (2) is often called the sum rule for the oscillator strengths, because oscillator strength f_{kj} is defined as

the quantity

$$f^{x}_{kj} = \frac{2m}{\hbar}(E_k - E_j)|\langle k|x|j\rangle|^2 ,$$

which appears under the summation symbol.

Other sum rules have been written down, with different powers of the difference $(E_k - E_j)$ multiplying the square of the matrix element. That is, sums of the type

$$S_p(x, x) = \sum_k (E_k - E_j)^p |\langle k|x|j\rangle|^2 , \qquad (5)$$

with $p = 0, 1, 2, 3, 4$ have been explicitly computed for Hamiltonians of the type (1) [5]. For $p = 0$ the sum rule is of course only the closure property

$$\sum_k |\langle k|x|j\rangle|^2 = \langle j|x^2|j\rangle$$

of the set of states $|k\rangle$ and no assumption of the form of H is implied. For $p = 1$ we have the sum rule for the oscillator strengths. The derivation of each of these sum rules was made in a rather special way, using repeatedly expressions like (3) and (4). We shall show how a more straightforward derivation of them which has several advantages can be presented. First, we do not have to be restricted to the coordinate operator x but we can write sum rules for the matrix element of any operator. Second, the form of the hermitian operator H is left unspecified so that we can easily perform the sum for any given H. This will be shown in some examples.

Let H be <u>any</u> hermitian operator (not necessarily an operator representing a Hamiltonian, but any one which represents a constant of motion of our system). We indicate by $|i\rangle$ and E_j its eigenstates and corresponding eigenvalues. Let A and B be any two operators acting on the Hilbert space of the eigenstates of H. We shall be concerned with obtaining closed forms for sums of the type

$$S_p(A, B) = \sum_k (E_k - E_j)^p \langle j|A|k\rangle\langle k|B|j\rangle \qquad (6)$$

where the sum is extended to all eigenstates of H (whether in the discrete or in the continuum spectrum, in this last case the sum means also the appropriate integration over continuum variables).

Nothing physically or mathematically new is introduced or obtained when a sum rule of the kind discussed here is derived. The only fact that is used and is responsible for the closed form written for the infinite sum of matrix elements is the closure property of the eigenstates of a hermitian operator. If the closure property is applied in a straightforward manner to the proper expression, the derivation of such sum rules appears trivial. However, calling attention to this point seems to be necessary since in the literature we often find derivations, using specific models or long calculations, of expressions which are nothing more than a particular example of the completeness property of a set of states.

The closure property of the set of states k implies directly

in the sum rule

$$S_o(A, B) = \sum_k \langle j|A|k\rangle \langle k|B|j\rangle = \langle j|AB|j\rangle . \qquad (7)$$

Here we have a sum of the type given in eq. (6) with p = 0.

2. GENERALIZATION OF THE SUM RULE FOR THE OSCILLATOR STRENGTHS

We now consider the case p = 1. Let us calculate the average value of the quantity $[A, H] B$ in a state $|j\rangle$. We obtain, using the closure property and the fact that $H|k\rangle = E_k|k\rangle$,

$$\langle j|[A, H] B|j\rangle =$$

$$= \sum_k \langle j|A|k\rangle \; E_k \langle k|B|j\rangle - E_j \langle j|A|k\rangle \langle k|B|j\rangle \Big\} .$$

Thus we have a sum rule

$$S_1(A,B) = \sum_k (E_k - E_i) \langle j|A|k\rangle \langle k|B|j\rangle = \langle j|[A, H]B|j\rangle , \qquad (8)$$

relating a sum of a certain combination of matrix elements of arbitrary operators over a complete set of states with the average value of a related operator in a single state. Aplications of this formula can easily be made to reproduce the results for special cases reported in the literature and to obtain new formulas. For A = B = x and for H being the Schrödinger Hamiltonian we obtain in the left-hand side the sum of the oscillator strengths that appear in the Thomas-Reiche-Kuhn formula (2).

A similar sum rule, but not completely equivalent to (8), can be obtained by considering the double commutator $[[A, H] B]$. Taking the expectation value of this quantity in the state $|j\rangle$

and introducing in the appropriate places the complete set of intermediate states we obtain

$$S_1'(A, B) = \sum_k (E_k - E_j)(\langle j|A|k\rangle\langle k|B|j\rangle + \langle j|B|k\rangle\langle k|A|j\rangle) =$$

$$= \langle j|\left[\left[A, H\right] , B\right]|j\rangle , \qquad (9)$$

which is formally more complicated than eq. (9), but may result in being simpler in applications. This is due to the fact that the double commutator $\left[\left[A, H\right] , B\right]$ may have a form which is actually simpler than that of the product $[A, H]B$. If A and B are hermitian operators, and $B \equiv A$, eq. (9) becomes

$$\sum_k (E_k - E_j)|\langle j|A|k\rangle|^2 = \frac{1}{2}\langle j|\left[\left[A, H\right] , A\right]|j\rangle .$$

We consider a few examples.

a) <u>One-particle Schrödinger Hamiltonian</u> - Let H be the Schrödinger Hamiltonian for one-particle subjected to a static potential, as in eq. (1). Let operators A and B be functions of the co-ordinates only, $A = f(\vec{r})$ and $B = g(\vec{r})$. Then

$$[f(\vec{r}), H] = \frac{i\hbar}{2m}(\vec{\nabla}f \cdot \vec{p} + \vec{p} \cdot \vec{\nabla}f) \qquad (10)$$

and

$$\left[\left[f(\vec{r}), H\right] , g(\vec{r})\right] = \frac{\hbar^2}{m}\vec{\nabla}f \cdot \vec{\nabla}g , \qquad (11)$$

so that the sum rule becomes

$$\sum_k (E_k - E_j)(\langle j|f|k\rangle\langle k|g|j\rangle + \langle j|g|k\rangle\langle k|f|j\rangle) = \frac{\hbar^2}{m}\langle j|\vec{\nabla}f \cdot \vec{\nabla}g|j\rangle . \qquad (12)$$

In the particular case of $f = g = x$ we re-obtain eq. (2). Particular cases of interest are those in which these functions

are such that we obtain the electric and magnetic multipole matrix elements.

b) Many-particle systems - Let H be the Schrödinger Hamiltonian for a system with N particles

$$H = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m + \sum_{i=1}^{N} V(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N} \sum_{j=1}^{N} V_{ij}(r_{ij}) \,, \qquad (13)$$

and let

$$A = f = \sum_{i=1}^{N} f_i(\vec{r}_i)$$

$$B = g = \sum_{i=1}^{N} g_i(\vec{r}_i) \qquad (14)$$

be sums of functions of the co-ordinates of each of the particles. We then have

$$[f, H] = \frac{ih}{2m} \sum_{i=1}^{N} (\vec{\nabla f}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{\nabla f}_i)$$

and

$$\big[[f, H], g\big] = \frac{h^2}{m} \sum_{i=1}^{N} (\vec{\nabla} f_i \cdot \vec{\nabla} g_i) \,,$$

where $\vec{\nabla} f_i$ and $\vec{\nabla} g_i$ mean gradients with respect to the co-ordinates $\vec{r}_i$. The sum rule then becomes

$$S_1'(f, g) = \frac{h^2}{m} \sum_{i=1}^{N} \langle j | \vec{\nabla} f_i \cdot \vec{\nabla} g_i | j \rangle \,. \qquad (15)$$

This sum rule is relevant for the study of the interaction of electromagnetic radiation with the N electrons of an atom. In the dipole approximation it is taken

$$f = \sum_{i=1}^{N} x_i$$

and then

$$\sum_k (E_k - E_j) |\langle j| \sum_{i=1}^{N} x_i |k\rangle|^2 = \frac{\hbar^2}{2m} N ,$$

which is a well-known result.

c) Non-static potentials - A well-appreciated characteristic of the Thomas-Reiche-Kuhn sum rule, which is also a property of the more general form (12), is that the potential itself does not appear in the second member of the sum. This fact is a consequence of the particular form of the Hamiltonian H. If interactions with an electromagnetic field, with a velocity-dependent potential or exchange forces, are introduced, the sum may take a different form from those given in eq. (12) or eq. (2). Let us see what happens if we include in the Schrödinger Hamiltonian a velocity-dependent potential of the form often used in nuclear physics [6]

$$V(\vec{r}, \vec{p}) = -\frac{\lambda}{2m} \vec{p} \cdot J(\vec{r}) \vec{p} , \tag{16}$$

and an electromagnetic field. Then

$$H = \frac{1}{2m} \left(\vec{p} - \frac{e\vec{A}}{c} \right)^2 + V(\vec{r}) - \frac{\lambda}{2m} \left(\vec{p} - \frac{e\vec{A}}{c} \right) \cdot J(\vec{r}) \left(\vec{p} - \frac{e\vec{A}}{c} \right) \tag{17}$$

and

$$[f, H] = \frac{i\hbar}{2m} \left(\left(\vec{p} - \frac{e\vec{A}}{c} \right) \cdot (1 - \lambda J) \vec{\nabla} f + \vec{\nabla} f \cdot (1 - \lambda J) \left(\vec{p} - \frac{e\vec{A}}{c} \right) \right) \tag{18}$$

Then the sum rule becomes

$$S_1'(f, g) = \frac{\hbar^2}{m} \langle j|(1 - \lambda J)\, \vec{\nabla} f \cdot \vec{\nabla} g|j\rangle \qquad (19)$$

We see that in this sum rule the electromagnetic field does not appear explicitly in the second member; it only affects the determination of the eigenstates of H. This is not true of the velocity-dependent potential (16) which appears in the operator whose expectation value represents the summed quantity.

d) Dirac Hamiltonian - Let $f(\vec{r})$ and $g(\vec{r})$ again be two arbitrary functions of the co-ordinates. For the Dirac Hamiltonian $H = c\vec{\alpha}.(\vec{p} - e\vec{A}/c) + \beta mc^2 + V(\vec{r})$ we have $[f, H] = i\hbar\, c\vec{\alpha}.\vec{\nabla} f$ and $[[f, H], g] = 0$. Then the two forms of the sum rule give

$$S_1'(f, g) = \sum_k (E_k - E_j)(\langle j|f|k\rangle\langle k|g|j\rangle + \langle j|g|k\rangle\langle k|f|j\rangle) = 0 \qquad (20)$$

and

$$S_1(f, g) = \sum_k (E_k - E_j)\langle j|f|k\rangle\langle k|g|j\rangle = \langle j|i\hbar\, c\vec{\alpha}.\vec{\nabla} f\, g|j\rangle \qquad (21)$$

Interchanging f with g in eq. (21) and adding to eq. (21) we obtain the sum (20), which is zero, so that we have a general relation

$$\langle j|\vec{\alpha}.\vec{\nabla} F(\vec{r})|j\rangle = 0\ , \qquad (22)$$

valid for every eigenstate $|j\rangle$ of the Dirac Hamiltonian H, $F(\vec{r})$ being an arbitrary function of the co-ordinates. As a particular case of (22) we have that the current $\vec{J} = c\ \psi_j^+ \vec{\alpha}\, \psi_j$ in a stationary state vanishes when integrated over all space. Eq. (22) can

also be obtained by calculating the expectation value of the commutator $[F, H]$ in an eigenstate of H. If f and g are real functions, the sum in eq. (21) is a pure imaginary quantity.

The zero obtained in performing the sum in eq. (20) over all states is due to the compensating contributions from positive and negative energy states. By inserting in eq. (21) projection operators for positive or negative energy states $P_{\pm}$ and adding to the same expression with f and g exchanged we get

$$\sum_k (E_k - E_j)(\langle j|f\ P_{\pm}|k\rangle\langle k|g|j\rangle + \langle j|g\ P_{\pm}|k\rangle\langle k|f|j\rangle) =$$

$$= ihc\ \langle j|(\vec{\alpha}.\vec{\nabla}f)P_{\pm}\ g + (\vec{\alpha}.\vec{\nabla}g)P_{\pm}\ f|j\rangle . \qquad (23)$$

In the non-relativistic limit $P_{\pm} = (mc^2 \pm H)/mc^2$ so that the above sum becomes

$$\pm \frac{h^2}{m}\langle j|\vec{\nabla}f\ .\ \vec{\nabla}g|j\rangle$$

which should be compared to the expression given in eq. (12).

e) Integrals involving eigenfunctions - Applications of mathematical or physical interest can be found for the sum rules, consisting in writing directly the values of certain integrals involving eigenfunctions of a hermitian operator. Let us, for example, consider eq. (12) where the states are the eigenstates of a Schrödinger Hamiltonian with static potential and in the presence of the electromagnetic field. For simplicity, let all eigenfunctions be written so as to be real functions. Let us choose $f = \psi_p / \psi_j$ and $g = \psi_q / \psi_j$, where ψ_p and ψ_q are eigen-

functions of H with eigenvalues E_p and E_q respectively. To avoid zeros in the denominator, we restrict ourselves to the case in which $|j\rangle$ is the eigenstate of H corresponding to the lowest energy (so that ψ_j has no zeros and f and g are well behaved); we indicate the eigenfunction corresponding to this ground state by ψ_o. The formulas obtained can be extended to other states if care is taken in the definition or interpretation of the expressions written. The sum rule eq. (12) then gives

$$\sum_k (E_k - E_o)\int \psi_p \psi_k \, d\tau \int \psi_q \psi_k \, d\tau = \frac{\hbar^2}{2m} \int \psi_o^2 \vec{\nabla}\left(\frac{\psi_p}{\psi_o}\right)\cdot\vec{\nabla}\left(\frac{\psi_p}{\psi_o}\right) d\tau$$

Using the orthogonality property of the wave functions, this becomes

$$\int \psi_o^2 \vec{\nabla}\left(\frac{\psi_p}{\psi_o}\right)\cdot\vec{\nabla}\left(\frac{\psi_q}{\psi_o}\right) d\tau = \frac{2m}{\hbar^2}(E_p - E_o)\,\delta_{pq} \qquad (24)$$

If ψ_p and ψ_q are eigenfunctions corresponding to the continuum spectrum with delta function normalization, δ_{pq} in the above expression must be understood as $\delta(\vec{p}-\vec{q})$, where $\vec{p}$ and $\vec{q}$ are the momenta of the particle in the states ψ_p and ψ_q.

This formula is valid whenever ψ_p, ψ_q and ψ_o are eigenfunctions of the same Schrödinger Hamiltonian. It can be useful in evaluating certain integrals once the eigenvalues of H are known. Eq. (24) is a consequence of the completeness and orthogonality of the set of eigenfunctions of H. For spherically symmetric states or for one-dimensional problems, it takes particularly simple forms.

Physical applications for relations such as eq. (24) can be

of the following kind. Suppose the fundamental state and the corresponding eigenvalue are known. Then, given empirically an approximate wave function ψ_p for an excited state, the corresponding eigenvalue can be extracted from the above expression. Conversely, if the eigenvalue is experimentally or empirically given, and the wave function is parametrized in some way, we can use eq. (24) to obtain information on the parameters determining the wave function. Of course, local relations involving two wave functions and the corresponding eigenvalues but not the potential can be easily written; integral forms such as the above are, however, of much advantage when the knowledge or the description of the wave function is only approximate, since then an average over small local fluctuations is already performed by the integration process.

Another formula which can be useful when the wave functions are not real can be obtained in the following way. Putting $g \equiv \equiv f$ in eq. (12), and choosing $f = \psi_p / \psi_j$ we get

$$\sum_k (E_k - E_j) \int \psi_j^* \frac{\psi_p}{\psi_j} \psi_k \, d\tau \int \psi_k^* \psi_p \, d\tau = \frac{\hbar^2}{2m} \int \psi_j^* \psi_j \vec{\nabla}\left(\frac{\psi_p}{\psi_j}\right) \cdot \vec{\nabla}\left(\frac{\psi_p}{\psi_j}\right) d\tau .$$

Using the property of orthogonality of the wave functions in the second integral of the first member, and performing the sum over k, we get

$$\int \psi_j^* \vec{\nabla}\left(\frac{\psi_p}{\psi_j}\right) \cdot \vec{\nabla}\left(\frac{\psi_p}{\psi_j}\right) \psi_j \, d\tau = \frac{2m}{\hbar^2} (E_p - E_j) \int \psi_j^* \frac{\psi_p}{\psi_j} \psi_p \, d\tau \quad . \qquad (25)$$

Again in this formula the meaning of the integrals should be

studied in each particular case in which the wave function ψ_j has zeros.

3. SUM RULES WITH HIGHER POWERS OF $(E_k - E_j)$

Again let H be a hermitian operator with eigenstates $|j\rangle$ and eigenvalues E_j, and let A and B be any operators. Then it is easy to see that

$$\langle j|\Big[[A, H]\ ,\ H\Big]\ B|j\rangle = \sum_k \langle j|A|k\rangle\langle k|B|j\rangle\ \ (E_k^2 - 2E_j\ E_k + E_j^2)\ ,$$

so that we obtain a sum rule

$$S_2(A, B) = \sum_k (E_k - E_j)^2\ \langle j|A|k\rangle\langle k|B|j\rangle = \langle j|\Big[[A, H]\ ,\ H\Big]B|j\rangle\ . \tag{26}$$

It is interesting to remark that the second member can also be written

$$-\langle j\Big[[A, H]\ .\ [B, H]|j\rangle \tag{27}$$

since this form may be more convenient when doing actual computations.

Let us look at some particular examples.

For the Schrödinger Hamiltonian with a static potential and in the presence of the electromagnetic field we obtain, f and g being functions of the co-ordinates only, that

$$S_2(f, g) = \sum_k (E_k - E_j)^2\ \langle j|f|k\rangle\langle k|g|j\rangle =$$

$$= \frac{h^2}{4m}\langle j|(\vec{\nabla}f\,.\,\vec{P} + \vec{P}\,.\,\vec{\nabla}f)(\vec{\nabla}g\,.\,\vec{P} + \vec{P}\,.\,\vec{\nabla}g)|j\rangle \tag{28}$$

where $\vec{P} = \vec{p} - e\vec{A}/c$. We should note that the electromagnetic field

appears explicitly in the second member of the above expression.

For f = x we obtain a well-known result. By adding the corresponding expressions for f = y and f = z we obtain

$$\sum_k (E_k - E_j)^2 \left\{ |\langle j|x|k\rangle|^2 + |\langle j|y|k\rangle|^2 + |\langle j|z|k\rangle|^2 \right\} =$$

$$= \frac{\hbar^2}{m^2} \langle j|\vec{P}^2|j\rangle = \frac{2\hbar^2}{m} \langle j|E_j - V(\vec{r})|j\rangle \, . \qquad (29)$$

It is interesting to remark that in this last form the electromagnetic field does not appear explicitly in the second member of the sum.

If a velocity-dependent potential is included so that the Hamiltonian is of the form (16) we obtain

$$S_2(f, g) = \frac{\hbar^2}{4m} \langle j|(\vec{\nabla}f \cdot (1 - \lambda J)\, \vec{P} + \qquad (30)$$

$$+ \vec{P}(1 - \lambda J)\, \vec{\nabla}f)(\vec{\nabla}g\, (1 - \lambda J)\, \vec{P} + \vec{P}(1 - \lambda J)\, \vec{\nabla}g)|j\rangle$$

where $\vec{P} = \vec{p} - e\vec{A}/c$. The differences between this expression and eq. (28) must be noted.

For the Dirac Hamiltonian in the presence of an electromagnetic field and with a static potential we obtain

$$S_2(f, g) = \hbar^2 c^2 \langle j|\vec{\nabla}f \cdot \vec{\nabla}g + i\vec{\sigma} \cdot \vec{\nabla}f \times \vec{\nabla}g|j\rangle \, . \qquad (31)$$

For f = g = x we get

$$\sum_k (E_k - E_j)^2 \, |\langle j|x|k\rangle|^2 = \hbar^2 \qquad (32)$$

which is different from the result obtained with the Schrödinger Hamiltonian. Here again, projection operators can be introduced to separate the contributions coming from positive and negative

energy states.

Now we consider sum rules where higher powers of $(E_k - E_j)$ appear, that is, sums of the form (6), with $p > 2$.

It is easy to verify that

$$S_3(A, B) = \sum_k (E_k - E_j)^3 \langle j|A|k\rangle\langle k|B|j\rangle = \langle j|\Big[\Big[[A, H], H\Big], H\Big]B|j\rangle, \tag{33}$$

$$S_4(A, B) = \langle j|\Big[\Big[\Big[[A, H], H\Big], H\Big], H\Big]B|j\rangle,$$

and thus successively. For a power p we have p commutators:

$$S_p(A, B) = \sum_k (E_k - E_j)^p \langle j|A|k\rangle\langle k|B|j\rangle = \tag{34}$$

$$= \langle j|\Big[\ \ldots\Big[[A, H], H\Big]\ \ldots, H\Big]\ldots\ldots, H\Big]B|j\rangle\ .$$

We thus have a straightforward way to compute a set of sum rules which may find several applications. We have only to evaluate the multiple commutator which appear in the second member and calculate its average value in the state $|j\rangle$.

The sum rules imply limitations in the magnitude of the matrix elements of an operator and may be used to obtain information in their rate of convergence to zero as $E_k \longrightarrow \infty$. As p increases the sum tends to increase and may diverge. Suppose we want to obtain indication on the asymptotic behaviour of $\langle k|A|j\rangle$ for very large E_k. We have to evaluate the expectation value

$$\langle j|\Big[\ldots\ldots\Big[[A, H], H\Big]\ldots\ldots, H\Big]A|j\rangle$$

using $p = 1, 2, 3, \ldots$ commutators. Suppose that for $p = s$ the expectation value is infinite, while for $p = s - 1$ it is finite.

Since for high energies the number of states in an interval of momenta is proportional to $k^2 dk$, we have that $\int^{\infty} k^2 E^{S-1} |\langle k|A|j\rangle|^2 dk$ is finite, while we expect that $\int^{\infty} k^2 E_k^S |\langle k|A|j\rangle|^2 dk$ diverges. Then we may say that $\langle k|A|j\rangle|^2 \approx (k^2 E_k^S k)^{-1} k^{\delta_1}$, with $\delta_1 \geqslant 0$, and that $|\langle k|A|j\rangle|^2 \approx (k^2 E_k^S k)^{-1} E_k k^{-\delta_2}$, with $\delta_2 > 0$. The quantities δ_1 and δ_2 have upper bounds determined by the functional dependence between E_k and k, with $k^{\delta_1+\delta_2} \sim E_k$. For a relativistic kinematics, $\delta_1 + \delta_2 = 1$, and the asymptotic behaviour of the matrix elements is determined up to a unit power of the energy. If negative energy states are included in the sum, our argument should be restricted to even values of p, and the indetermination in the dependence with the energy is of two units in the exponent.

If the expectation value appearing in the second member of eq. (34) is finite for all numbers of commutators (all values of p), then the product $\langle j|A|k\rangle\langle k|B|j\rangle$ tends exponentially (or faster) to zero as $E_k \longrightarrow \infty$.

By multiplying sum rule for power p by $\alpha^p/p!$ and summing over p from zero to infinity we get

$$\sum_{p=0}^{\infty} \frac{\alpha^p}{p!} \sum_k (E_k - E_j)^p \langle j|A|k\rangle\langle k|B|j\rangle =$$

$$= \langle j| \Big\{ A + \frac{\alpha}{1!}[A, H] + \frac{\alpha^2}{2!}\Big[[A, H], H\Big] + \frac{\alpha^3}{3!}\Big[\Big[[A, H], H\Big] H\Big] +$$

$$+ \ldots\ldots + \frac{\alpha^p}{p!}\Big[\ldots\ldots\Big[[A, H], H\Big] \ldots\ldots, H\Big] + \ldots\ldots \Big\} B|j\rangle \qquad (35)$$

The term within the brackets is the formal development of $e^{-\alpha H} A e^{+\alpha H}$. Performing in the left-hand side the sum over p

first we get

$$\sum_k e^{\alpha(E_j - E_k)} \langle j|A|k\rangle \langle k|B|j\rangle = \langle j|e^{-\alpha H} A e^{\alpha H} B|j\rangle . \qquad (36)$$

This formula is in fact trivially the closure relation

$$\sum_k \langle j|F|k\rangle \langle k|G|j\rangle = \langle j|FG|j\rangle$$

with $F = e^{-\alpha H} A$ and $G = e^{\alpha H} B$.

The several sum rules for different powers p are then the terms of the expansion of eq. (36) in powers of α. This makes it clear how the closure property, and only that, generates all this family of rules. However they can be useful if the sum concerned has a physical meaning and can be directly measured. Then one can obtain from the sum rule information such as on the structure of the Hamiltonian governing the system, or on the form of the matrix elements responsible for the process being studied, or on the asymptotic behaviour of these matrix elements, and so on.

We can also write sum rules of the type $S_p(A, B)$ for non-integer values of p. Let us start from eq. (36), and just for convenience call $\alpha = i\lambda$. Multipkying both sides of eq. (36) by $e^{-k\lambda} \cdot \lambda^{p-1}$ and integrating over λ from zero to infinity, we obtain

$$\int_{\lambda=0}^{\infty} d\lambda \sum_k e^{-\lambda\left[K+i(E_k-E_j)\right]} \lambda^{p-1} \langle j|A|k\rangle \langle k|B|j\rangle =$$

$$= \langle j | \int_0^\infty e^{-k\lambda}\ \lambda^{p-1}\ e^{-i\lambda H}\ H'\ e^{-i\lambda H}\ d\lambda\ B | j \rangle \ .$$

Interchanging the order of the summation and the integration processes in the left-hand side, and performing the integration over λ, we get (if the real part of p is not positive the integral is defined as a distribution)

$$\sum_k (K + i\,(E_k - E_j))^{-p} \langle j|A|k\rangle\langle k|B|j\rangle \ = \tag{37}$$

$$= \frac{1}{\Gamma(p)}\ \langle j | \left(\int_0^\infty e^{-k\lambda}\ \lambda^{p-1}\ e^{i\lambda H}\ A\ e^{-i\lambda H}\ d\lambda \right) B | j \rangle \ .$$

The limit $K \longrightarrow 0$ can be taken when so wished. We thus obtain a sum $S_p(A, B)$ for any complex p, expressed in closed form as a single expectation value. The expression is only formal unless we are able to evaluate explicitly the quantity $A(\lambda) = e^{i\lambda H}\ A\ e^{-i\lambda H}$. This means knowing the Heisenberg equation of motion for the operator A in a system governed by the Hamiltonian H.

Sums with functions of E_k and E_j which are not just powers of $(E_k - E_j)$ can also be performed. Thus we have

$$\sum_k \langle j|A|k\rangle\ \langle k|B|j\rangle\ \ (\varphi(E_k) - \varphi(E_i)) = \langle j | [A,\ \varphi(H)] B | j \rangle \ , \tag{38}$$

where $\varphi(H)$ is any function of the operator H. Relations of this kind can also be used to obtain information on the asymptotic behaviour of matrix elements.

Other classes of sum rules, obtained by differentiation of an eigenvalue equation with respect to parameters have been

obtained recently [7].

4. APPLICATION OF THE SUM RULES: THE INTEGRATED CROSS-SECTION FOR THE PHOTO-NUCLEAR EFFECT

The Thomas-Reiche-Kuhn sum rule (2) for the matrix elements of a co-ordinate x has found application in the calculation of the cross-section for the photo-nuclear effect integrated over all energies of the incident photon [3] and in other problems [8]. In the nuclear photo-effect, a photon incident on a nucleus is absorbed, and a proton is ejected. It is the nuclear analogue of the atomic photo-electric effect.

In the usual treatment of the photo-nuclear effect the matrix element responsible for the process in first-order perturbation theory is subjected to the so-called dipole approximation, which consists in considering the extension of the nuclear wave-functions small compared with the wavelength of the incident photon. The purpose of this approximation is to obtain that only matrix elements of a single co-ordinate, such as those appearing in the Thomas-Reiche-Kuhn sum rule, appear in the expressions to be calculated. This approximation can be questioned, however, since in the integrated cross-section we use matrix elements corresponding to photons of high energy.

Since we now know how to write sum rules for more general matrix elements, we are able to avoid the dipole approximation in this calculation. In what follows we show how this can be done. For simplicity and to stress the essential points we

consider the case of a single charged particle bound to a centre of static (non-velocity dependent) forces. The particle is considered as heavy, so that non-relativistic kinematics is used. We assume that the centre of forces admits only one bound state so that we do not have to consider transitions without emission of the charged particle.

A photon of frequency ω, propagation vector $\vec{k}$ along the z-axis, and polarization vector along the x-axis, collides with the heavy particle bound by the centre of forces in a state described by the wave function ψ_j. In the final state the particle in a positive energy state ψ_f, which asymptotically has a plane wave part normalized in a volume V.

In a first-order perturbation theory the differential cross-section for the process is [4]

$$\sigma(\omega;\ \theta,\varphi) = \frac{e^2}{2\pi\hbar c}\ \frac{v}{\omega}\ V \left| \int \psi_f^*\ e^{i\vec{k}\cdot\vec{r}}\ \nabla_x \psi_j\ d\tau \right|^2, \qquad (39)$$

where v is the velocity of the emitted particle. For unpolarized photons we have to average this expression over the x and y directions of polarization. This differential cross-section is in general difficult to evaluate due to the lack of knowledge about the wave functions in the final state.

For our normalization of the final wave functions the number of states is

$$dN = \frac{V\ d_3\ \vec{p}}{(2\pi)^3\ \hbar^3} = \frac{V\ m^2}{(2\pi)^3\ \hbar^3}\ v\ d\Omega\ d(\hbar\omega)$$

where $p = mv$ is the momentum of the emitted particle.

The total cross-section integrated over the photon energy is then

$$\sigma_{int.} = \int_0^\infty \sigma(\omega) d(\hbar\omega) = \int_0^\infty d(\hbar\omega) \int d\Omega \sigma(\omega; \theta, \varphi) = \tag{40}$$

$$= \left(\frac{2\pi e \hbar}{m} \right)^2 \frac{1}{c} \sum_f \frac{1}{\omega} \left| \int \psi_f^* \, e^{i\vec{k}\cdot\vec{r}} \nabla_x \psi_j \, d\tau \right|^2 ,$$

where $\sum_f$ means sum over all possible final states.

$\omega = E_f - E_i$ is the difference between the energies of the final and initial states. Since $1/(E_f - E_i)$ cannot be expanded in powers of $(E_f - E_j)$, we do not have a sum rule to be applied directly to the above expression. However we can rely on properties of the matrix element to perform the sum in an approximate way.

The ground state wave function ψ_j occupies a limited region of space, so that the integral over $d\tau$ can be restricted to a finite region of radius R. On the other hand, the matrix elements are likely to tend rapidly to zero as k increases.

It may then be that we can neglect, both in the sum over states and in the integration in the space volume, the contributions coming from the regions which do not satisfy the condition $k\,r \ll 1$. In these conditions we can expand exp(i kz) in power series and keep only a few terms.

The dipole approximation consists in putting simply

$\exp(i\,kz) \approx 1$. Then the matrix element can be approximated by

$$\int \psi_f^* \nabla_x \psi_j \, d\tau = \frac{m}{\hbar^2} \int \psi_f^* \, [x, H] \, \psi_i \, d\tau = -\frac{m}{\hbar^2} (E_f - E_j) \int \psi_f^* \times \psi_j \, d\tau \tag{41}$$

In this approximation the integrated cross-section becomes

$$\sigma_{int.}(\text{dipole}) = \left(\frac{2\pi e\hbar}{m}\right)^2 \frac{1}{c} \left(\frac{m^2}{\hbar^3}\right) \sum_f (E_f - E_j) \left| \int \psi_f^* \times \psi_j \, d\tau \right|^2. \tag{42}$$

The sum here indicated can be performed. For pure static potentials in the Hamiltonian it gives the classical Thomas-Reiche-Kuhn result. If exchange or velocity-dependent forces are present, the sum will be modified accordingly, and this has in fact been used for a test of the presence of these terms in the Hamiltonian [2, 3]. The dipole approximation was the only contribution to σ_{int} considered in previous calculations, because of the limitations in the sum rules available. We now show how other terms of the expansion of $\exp(i\,k\,z)$ can be included. The next term is usually referred to as the quadrupole contribution. The contribution of the interference terms between dipole and quadrupole matrix elements to the integrated cross-section is

$$\sigma_{int.}\ (\text{interf.}) = \left(\frac{2\pi e\hbar}{m}\right)^2 \frac{1}{c} \sum_f \frac{\hbar}{(E_f - E_j)} \left\{ \right.$$

$$\left. \int \psi_f^* \, \nabla_x \psi_j \, d\tau \int \psi_f^* \, ikz \, \nabla_x \psi_j \, d\tau + \text{c.c.} \right\} =$$

$$= \left(\frac{2\pi e\hbar}{m}\right)^2 \frac{1}{c} \left(-\frac{m}{c\hbar^2}\right) \sum_f (E_f - E_j) \left\{ \right.$$

$$\left| \psi_f^* \times \psi_j \, d\tau \int \psi_f^* \, iz \nabla_x \psi_j \, d\tau + c.c. \right\} \tag{43}$$

We should notice that a factor $\omega = E_f - E_j$ coming from the dipole term and another from the $k = \omega/c$ appearing in the quadrupole matrix element were able to eliminate $(E_f - E_j)$ from the denominator. We thus obtained an expression which fits into our sum rule (8) and can be put in closed form. For every other term in the expansion we have that the matrix elements will bring a factor ω raised to a power larger than two, and all sums to be effected will fall into the general form (34).

For the contribution arising purely from the quadrupole matrix element we have

$$\sigma_{int.}(\text{quadrupole}) = \left(\frac{2\pi e\hbar}{m}\right)^2 \frac{1}{c} \frac{1}{\hbar c^2} \sum_f (E_f - E_j) \left| \int \psi_f^* iz \nabla_x \psi_j \, d\tau \right|^2 \tag{44}$$

The sum can again be performed by using eq. (8).

Up to quadrupole terms we then have for the integrated cross-section, using the sum rules

$$\sigma_{int.} = \left(\frac{2\pi e\hbar}{m}\right)^2 \frac{1}{c} \langle j \Big| \left\{ \frac{m^2}{\hbar^3} \left[[x,H], x \right] - \frac{m}{c\hbar^2} \left[[x,H], iz \nabla_x \right] + \right. \tag{45}$$

$$\left. + \frac{1}{\hbar c^2} \left[[iz \nabla_x, H], iz \nabla_x \right] \right\} \Big| j \rangle$$

Knowledge of the Hamiltonian and the ground state wave function is necessary to evaluate this expression.

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