Tensorial Derivation of New Oscillator-Strength Sum Rules

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A tensorial method for the derivation of new sum rules for oscillator strengths and their moments and for expressions of similar mathematical structure is presented. For illustration, the method is applied to dipole transitions. Here new rules are found generalizing the Wigner-Kirkwood sum rules from one-electron to many-electron atoms. As a second example a new total sum rule for coherently excited states is reported and its relation to partial sum rules for fixed angular momentum transfer but incoherently excited states is shown.

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The development of Racah algebra has led to a deep understanding of atomic, molecular, and nuclear spectra. Since the theoretical foundations were done so long ago, it is surprising that an almost obvious application of standard Racah algebra to construct sum rules for oscillator strengths, for their moments, and for expressions with similar mathematical structure seems to be unknown. This paper presents and discusses these new sum rules.

Let us consider a rotationally invariant conservative system with energy eigenstates defined by the Schrödinger equation

$$H\,|\,\gamma jm\rangle = E_{\gamma j}\,|\,\gamma jm\rangle. \tag{1}$$

Here j and m label the total angular momentum and its z component; γ stands for all other quantum numbers. The subject of this paper is the evaluation of the quantities

$$S_k^{(n)} = \sum_{\gamma'} 2(E_{\gamma j} - E_{\gamma' j'})^n\,|\langle \gamma j \| T_k \| \gamma' j'\rangle|^2, \tag{2}$$

where n is a nonnegative integer and T_k is an irreducible spherical tensor of rank k. The reduced matrix element[1] $\langle \gamma j \| T_k \| \gamma' j'\rangle$ describes a transition of the system between energy eigenstates $\gamma j \to \gamma' j'$. Electric and magnetic multipole transitions and inelastic form factors are familiar examples for this; the right-hand side of Eq. (2) has then the structure of an oscillator strength or of a moment of it. The summation over γ' runs over all allowed final states with given j' value.

For the evaluation of the sum in Eq. (2), it is convenient to introduce the multiple commutator

$$C_k^{(n)}(T_k) = \underbrace{[H,[H,\ldots[H,T_k]\ldots]]}_{n\text{-fold}} \tag{3}$$

which is again an irreducible spherical tensor operator of rank k. With Eq. (1) the relation

$$\langle \gamma j \| C_k^{(n)}(T_k) \| \gamma' j'\rangle = (E_{\gamma j} - E_{\gamma' j'})^n \langle \gamma j \| T_k \| \gamma' j'\rangle \tag{4}$$

follows which is used to eliminate the energy factor in Eq. (2). Let us write in Eq. (2)

$$|\langle \gamma j \| T_k \| \gamma' j'\rangle|^2 = (-1)^{j'-j}\langle \gamma j \| T_k \| \gamma' j'\rangle\langle \gamma' j' \| T_k^\dagger \| \gamma j\rangle$$

and we find, with the help of Eq. (4),

$$S_k^{(n)} = (-1)^{j'-j}\sum_{\gamma'}\{\langle \gamma j \| C_k^{(n)}(T_k) \| \gamma' j'\rangle\langle \gamma' j' \| T_k^\dagger \| \gamma j\rangle + (-1)^n \langle \gamma j \| T_k \| \gamma' j'\rangle\langle \gamma' j' \| C_k^{(n)}(T_k^\dagger) \| \gamma j\rangle\}. \tag{5}$$

The essential point is now that the right-hand side of Eq. (5) allows for a tensorial recoupling transformation. It is evident that Eq. (5) contains two angular momentum couplings with the coupling scheme $(j,k)j'$, $(j',k)j$. These can be recoupled to $(k,k)K$, $(Kj)j$; this transformation is proportional to the recoupling coefficient $\langle (k,k)Kj\,|\,(j,k)j',k\rangle^{(j)}$. The reader less familiar with Racah algebra may inspect the standard expression for the reduced matrix element of a tensorial product $[T_{k_1} \times T_{k_2}]^{(K)}$ of two tensors T_{k_1} and T_{k_2} acting on the same system[2]; the inverse of this transformation is

$$\sum_{\gamma''}\langle \gamma' j' \| T_{k_1} \| \gamma'' j''\rangle\langle \gamma'' j'' \| T_{k_2} \| \gamma j\rangle = \sum_K (2j''+1)(-1)^{K+j+j'}(2K+1)^{1/2}\begin{Bmatrix} k_1 & k_2 & K \\ j & j' & j'' \end{Bmatrix}\langle \gamma' j' \| [T_{k_1} \times T_{k_2}]^{(K)} \| \gamma j\rangle, \tag{6}$$

which follows simply from the orthogonality of the 6-j symbols. We can now employ Eq. (6) to evaluate the sum $S_k^{(n)}$ and find the final result

$$S_k^{(n)} = (2j'+1)\sum_K (-1)^{K+j'+j}(2K+1)^{(1/2)}\begin{Bmatrix} k & k & K \\ j & j & j' \end{Bmatrix}\langle \gamma j \| [C_k^{(n)}(T_k) \times T_k^\dagger]^{(K)} + (-1)^n [T_k \times C_k^{(n)}(T_k^\dagger)]^{(K)} \| \gamma j\rangle. \tag{7}$$

I stress that Eq. (7) represents the sum $S_k^{(n)}$ by a finite number of terms because the summation over K is restricted to integers $0 \le K \le \min(2j,2k)$, whereas the original summation over γ' in Eq. (2) is infinite and includes moreover an integration over the continuum part of the spectrum. As corollary, we can evaluate also the total sum, i.e., sum over all final angular momenta j'. With help of the orthogonality relation for 6-j symbols, we find only from the scalar product ($K=0$) a contribution to the total sum,

$$\sum_{j'} S_k^{(n)} = (2j+1)^{1/2} \langle \gamma j \| C_k^{(n)}(T_k) \cdot T_k^\dagger + (-1)^n T_k \cdot C_k^{(n)}(T_k^\dagger) \| \gamma j \rangle. \tag{7'}$$

Let us come to the physical origin and to the utility of Eqs. (7) and (7'). The origin for the transformation Eq. (6) and therefore for the sum rules is the completeness relation

$$\sum_{\gamma jm} | \gamma jm \rangle \langle \gamma jm | = 1$$

for the total spectrum. Equation (7') follows directly from this completeness. However, for a rotationally invariant system, the spectrum is complete also within each subspace of a fixed value of the total angular momentum. Therefore partial sum rules where the summation runs only over non-angular-momentum quantum numbers do exist. Equation (7) is the most general result in this context. The sum rules given above can be utilized for many physical processes. For example, one can write down partial and total sum rules for arbitrary electric and magnetic multipole transitions, for generalized oscillator strengths (inelastic form factors), for two-photon transitions, and so on. I remark also that such sum rules are important from the practical viewpoint. They allow us, e.g., to extrapolate into spectral regions that are inaccessible experimentally; they serve also as checks for consistency and accuracy in numerical computations.

For the purpose of illustration, I apply the above method to the oscillator strength for electric dipole transitions in atoms[3]:

$$f_{\gamma j \gamma' j'} = [-2\omega_{\gamma j \gamma' j'}/(2j+1)] \sum_{mm'} | \langle \gamma jm | \hat{\epsilon} \cdot \mathbf{r} | \gamma' j' m' \rangle |^2. \tag{8}$$

Here atomic units $\hbar = m = e = 1$ are used; the oscillator strength itself is dimensionless. In Eq. (8), $\hat{\epsilon}$ is the polarization vector, $\mathbf{r} = \sum_n \mathbf{r}_n$ is the dipole operator, and

$$\omega_{\gamma j \gamma' j'} = E_{\gamma j} - E_{\gamma' j'}$$

is the transition frequency. Summation over m and m' yields

$$f_{\gamma j \gamma' j'} = -[2\omega_{\gamma j \gamma' j'}/3(2j+1)] | \langle \gamma j \| \mathbf{r} \| \gamma' j' \rangle |^2. \tag{8'}$$

Let us now ask for partial sums performed at fixed values of $\Delta j = j' - j = 0, \pm 1$;

$$\sigma_{\Delta j} = \sum_{\gamma'} f_{\gamma j \gamma' j'}. \tag{9}$$

With $T_1 = T_1^\dagger = \mathbf{r}$ and $C_1^{(1)}(\mathbf{r}) = -i\mathbf{p}$, where $\mathbf{p}$ is the dipole operator in velocity representation, one finds from Eq. (7)

$$\sigma_{\Delta j} = i \frac{2j'+1}{3(2j+1)} \sum_K (-)^{1+K+j'+j} (2K+1)^{1/2} \begin{Bmatrix} 1 & 1 & K \\ j & j & j' \end{Bmatrix} \langle \gamma j \| [\mathbf{r} \times \mathbf{p}]^{(K)} - [\mathbf{p} \times \mathbf{r}]^{(K)} \| \gamma j \rangle. \tag{10}$$

Note that in Eq. (10) only the terms $K=0$ and 1 contribute because of the symmetry of the second-rank tensor, $[\mathbf{r} \times \mathbf{p}]^{(2)} = [\mathbf{p} \times \mathbf{r}]^{(2)}$. The scalar contribution ($K=0$) leads to the canonical commutation relation,

$$[\mathbf{r} \times \mathbf{p}]^{(0)} - [\mathbf{p} \times \mathbf{r}]^{(0)} = -3^{-1/3} \times 3Ni,$$

where N is the number of electrons. This scalar contribution describes the total sum

$$\sum_{j'} \sigma_{\Delta j} = N. \tag{11}$$

This well-known Thomas-Reiche-Kuhn sum rule[4] is in fact easily obtained by summing of Eq. (10) over j'. The orthogonality for 6-j symbols then restricts the sum over K to the sole value $K=0$; see also Eq. (7'). The vector contribution ($K=1$) can be expressed in terms of the usual vector product,

$$[\mathbf{r} \times \mathbf{p}]^{(1)} = -[\mathbf{p} \times \mathbf{r}]^{(1)} = i2^{-1/2} (\mathbf{r} \times \mathbf{p}).$$

Evaluation of the 6-j symbols in Eq. (10) yields finally the result

$$\sigma_{\Delta j} = \frac{2j'+1}{3(2j+1)} [(N-M) + \tfrac{1}{2}(j'-j)(j'+j+1)M], \tag{12}$$

with M given by

$$M = [j(j+1)(2j+1)]^{-1/2} \langle \gamma j \| \mathbf{r} \times \mathbf{p} \| \gamma j \rangle. \tag{13}$$

In the trivial case of a nonrelativistic one-electron atom,

the above result is known as the Wigner-Kirkwood sum rules[5]; see also Fano and Cooper.[6] Putting $\mathbf{r}\times\mathbf{p}=\mathbf{l}$, $j=l$, and $N=1$, we find $M=1$ and

$$\sigma_{\Delta l}=(l'-l)(2l'+1)(l'+l+1)/6(2l+1), \qquad (12')$$

in agreement with Ref. 6. The sum rules given in Eq. (12) may therefore be regarded as generalization of the Wigner-Kirkwood sum rules for one-electron atoms to arbitrary many-electron atoms. The quantity M defined in (13) can be determined experimentally by the observation of the absorption and emission of circularly polarized light by an oriented state.

To see this, consider instead of the m-averaged oscillator-strength, Eq. (10), the oscillator strength for a coherently populated initial state,

$$f^c_{\gamma j\gamma' j'}=-2\omega_{\gamma j\gamma' j'}\sum_{m'}\left|\sum_m c_m\langle\gamma jm\,|\,\boldsymbol{\epsilon}\cdot\mathbf{r}\,|\,\gamma' j'm'\rangle\right|^2, \qquad (14)$$

where the c_m's are excitation amplitudes normalized to $\sum_m |c_m|^2=1$. It is straightforward to eliminate again the frequency and to sum over all final states. Following formally an analysis developed by Fano and Macek,[7] we can separate $\hat{\boldsymbol{\epsilon}}$ and $\hat{\boldsymbol{\epsilon}}^*$ from $\mathbf{r}$ and $\mathbf{p}$ with use of the recoupling formula

$$(\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r})(\hat{\boldsymbol{\epsilon}}^*\cdot\mathbf{p})=\tfrac{1}{3}(\mathbf{r}\cdot\mathbf{p})+\tfrac{1}{2}(\hat{\boldsymbol{\epsilon}}\times\hat{\boldsymbol{\epsilon}}^*)\cdot(\mathbf{r}\times\mathbf{p})+[\hat{\boldsymbol{\epsilon}}\times\hat{\boldsymbol{\epsilon}}]^{(2)}\cdot[\mathbf{r}\times\mathbf{p}]^{(2)},$$

where the three terms describe unpolarized, circularly polarized, and linearly polarized radiation, respectively. With help of the canonical commutator, we find

$$\sum_{\gamma' j'}f^c_{\gamma j\gamma' j'}=N-i\sum_{m,n}c_m c_n^*(\hat{\boldsymbol{\epsilon}}\times\hat{\boldsymbol{\epsilon}}^*)\cdot\langle\gamma jm\,|\,\mathbf{r}\times\mathbf{p}\,|\,\gamma jn\rangle. \qquad (15)$$

If we assume a convenient Cartesian detector frame[7] with the z axis parallel to the direction of light propagation, the polarization vector then reads $\hat{\boldsymbol{\epsilon}}=(\cos\beta,\ i\sin\beta,\ 0)$. The Wigner-Eckart theorem, finally, applied to the matrix element on the right-hand side of Eq. (15), yields the desired result

$$\sum_{\gamma' j'}f^c_{\gamma j\gamma' j'}=N-\sin 2\beta\left(\sum_m m\,|c_m|^2\right)M, \qquad (16)$$

where M is given by Eq. (13) and $\beta=+45°$ and $-45°$ for left and right circularly polarized light, respectively. According to Eq. (16), the quantity M can be determined from oscillator-strength measurements provided that the initial state is oriented, i.e., $|c_{-m}|\neq|c_m|$, and that the polarization is circular. So it is seen that an initial orientation in Eq. (14) in general destroys a simple Thomas-Reiche-Kuhn sum rule. On the other hand, an aligned initial state does not contribute to the sum rule Eq. (15) because of the symmetry $[\mathbf{r}\times\mathbf{p}]^{(2)}=[\mathbf{p}\times\mathbf{r}]^{(2)}$.

The quantity M can of course be calculated. We expect M to depend sensitively on electron-electron correlations because the operator

$$\mathbf{r}\times\mathbf{p}=\mathbf{L}+\mathbf{K} \qquad (17)$$

contains beyond the total orbital angular momentum,

$$\mathbf{L}=\sum_n\mathbf{r}_n\times\mathbf{p}_n, \qquad (18)$$

the correlation operator

$$\mathbf{K}=\sum_{n\neq m}\mathbf{r}_n\times\mathbf{p}_m, \qquad (19)$$

which in contrast to $\mathbf{L}$ consists of two-particle operators.

So far I have not introduced any approximation. Often, however, angular momenta couple weakly to each other. In this case, the matrix element appearing in Eq. (13) can then be analyzed further. Consider, e.g., a hyperfine multiplet as initial state. Because $\mathbf{r}\times\mathbf{p}$ does not act in the nuclear-spin space, we get in obvious notation the reduction[1]

$$\langle\gamma(JI)F\|\mathbf{r}\times\mathbf{p}\|\gamma(JI)F\rangle=(-1)^{J+I+F+1}(2F+1)\begin{Bmatrix}J & F & I\\ F & J & 1\end{Bmatrix}\langle\gamma J\|\mathbf{r}\times\mathbf{p}\|\gamma J\rangle.$$

In the case of $(LS)J$ coupling, the last matrix element can be reduced further along the same lines. In this situation only one matrix element, $\langle\gamma L\|\mathbf{r}\times\mathbf{p}\|\gamma L\rangle$, describes all partial sum rules within the whole multiplet.

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[2]Reference 1, Eq. (7.1.1).

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