

Sum Rules for Atomic Transition Probabilities

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Some new sum rules for atomic transition probabilities are developed; they are similar to the well-known rule of Kuhn, Reiche, and Thomas. They give, if unpolarized light is incident on any gaseous element in any given discrete energy level, the total absorption, excitation plus ionization, with various types of frequency weighting. The results are similar to those of Dirac and Harding, but are more general in that they apply to any discrete state of any atom, rather than to the ground state of hydrogen only. The method differs from that of Dirac and Harding.

INTRODUCTION

THERE are well-known relations connecting the coefficients of spontaneous and induced transitions in atomic systems (the Einstein A 's and B 's) with the matrix components of electric moment between the initial and final states and the corresponding frequency differences. A_{0n} , the spontaneous transition probability from a state n to a lower state 0 is equal (in the dipole approximation) to a universal constant multiplied by the cube of the frequency difference and the square of the absolute value of the matrix component of electric moment, $e^2(|x_{0n}|^2 + |y_{0n}|^2 + |z_{0n}|^2)$, where ex , ey , ez , are the rectangular components of electric moment, so that e.g., x is equal to the sum of the x coordinates of all the electrons. B_{0n} , the induced transition probability, is proportional directly to $e^2(|x_{0n}|^2 + |y_{0n}|^2 + |z_{0n}|^2)$, where in this case, either 0 or n may be the lower state.

x_{0n} is given by an integral of the form $\int \bar{\psi}_0(\sum_{\mu=1}^N x_{\mu})\psi_n d\tau$, where ψ_0 and ψ_n are the wave functions of the atom for the states 0 and n , N is the number of extranuclear electrons in the atom, and the integration is extended over the coordinates of all the electrons. We see, then, that in general one must know the wave functions of the atom for the states concerned in order to calculate A_{0n} and B_{0n} . One can, however, give some general relations satisfied by the A 's or B 's without knowing any wave functions, or knowing at the most the wave function of one discrete state only.

The sum rule of Kuhn, Reiche, and Thomas¹ is an example of the type of thing one can say about the matrix components, and thus about the A 's and B 's, without knowing any wave functions. Using atomic units, and letting x denote $\sum_1^N x_{\mu}$, the sum of the N cartesian coordinates, W_n the energy of the state n with reversed sign, this rule can be expressed in the form $\sum_n (W_0 - W_n) |x_{0n}|^2 = N$, where the state 0 denotes an arbitrary state of the discrete spectrum, and the summation is understood to include a summation over all the discrete states that have dipole combinations with the state 0, and an integral

¹ W. Kuhn, *Zeits. f. Physik* **33**, 408 (1925). F. Reiche and W. Thomas, *Zeits. f. Physik* **34**, 510 (1925).

over the continuous spectrum. (Similar relations hold for the y and z components of electric moment.) This rule is directly deducible from the commutation rules and the relation connecting the matrix components of momentum and coordinate. In terms of the A 's it enables us to evaluate at once $\sum_n A_{0n}/\nu_{0n}^2$, where ν_{0n} is the frequency of the spectral line associated with the transition from a *running* state n to the *base* state 0. Furthermore, Wigner² has shown that this rule may be *sharpened* by dividing transitions into three classes: $+$, $-$, and 0 , $+$ transitions being those in which the total azimuthal quantum number L increases by 1—those in which it diminishes by 1, and 0 those in which it does not change. Wigner's rule then gives the sum $g_+(L)\Sigma^+ + g_0(L)\Sigma^0$ in terms of the L -value of the state 0, where g_+ and g_0 are simple functions of L , and the summands are the f values A_{0n}/ν_{0n}^2 . We wish to mention at this point that all the sum rules developed in this paper can be sharpened in a similar way.

Matrix multiplication of the simple type $xx = x^2$ furnishes another general relation connecting the matrix components:

$$\sum_n |x_{0n}|^2 = (x^2)_{00}.$$

Here, as above, 0 means a discrete state and the summation is to be extended by means of integration over the continuous spectrum. This relation can also be looked on as a sum rule, although of a less general type, since the evaluation of the sum depends on a knowledge of the wave function of the state 0. It gives directly $\sum_n B_{0n}$, if one knows ψ_0 .

The above rules tell us how to evaluate $\sum_n (W_0 - W_n)^j |x_{0n}|^2$ when j has the value 1 or 0. We develop in this paper other rules of the same general type, letting j take on the values 2, 3 and 4. They constitute rules for the summation of the A 's and B 's (of a given base state) over all the states of the atom, with various kinds of frequency weighting.

SECTION I

We begin with the case $j=2$, and attempt to evaluate $\sum_n (W_0 - W_n)^2 (|x_{0n}|^2 + |y_{0n}|^2 + |z_{0n}|^2)$. (We abbreviate expressions of this type hereafter to $\sum_{n,xyz} (W_0 - W_n)^2 |x_{0n}|^2$). Let x_μ, y_μ, z_μ denote the coordinates of the μ th electron, N the total number of extranuclear electrons in the atom, $p_{x\mu}, p_{y\mu}, p_{z\mu}$ the components of momentum of the μ th electron, and $p_{x\mu}(0n)$ the matrix component of $p_{x\mu}$ between the stationary states 0 and n . Also, we shall use the contractions:

$$\sum_{\mu=1}^N x_\mu = x, \quad \sum_{\mu=1}^N p_{x\mu} = p_x, \quad \text{and} \quad W_0 - W_n = W_{0n}.$$

Now

$$p_{x\mu}(0n) = (h/2\pi i) \int \bar{\psi}_0 \frac{\partial}{\partial x_\mu} \psi_n d\tau,$$

² E. Wigner, Phys. Zeits. **11**, 450 (1931).

and it is well known that when at least one of the states 0 and n is a discrete state (to insure the vanishing of surface integrals at infinity which occur in the derivation), this can be thrown into the form $m(2\pi i/h)W_{0n}x_\mu(0n)$, where $x_\mu(0n)$ is the matrix component of x_μ between the states 0 and n , and m is the rest mass of the electron. On summing over the index μ from 1 to N , we obtain the relation:

$$p_x(0n) = m(2\pi i/h)W_{0n}x_{0n}. \quad (1)$$

Similarly

$$p_x(n0) = \bar{p}_x(0n) = m(2\pi i/h)W_{n0}x_{n0}, \quad (2)$$

(since p_x is hermitian, and $W_{n0} = -W_{0n}$). On multiplying (1) by (2) we obtain:

$$p_x(0n)p_x(n0) = m^2(2\pi/h)^2W_{0n}^2|x_{0n}|^2. \quad (3)$$

Summing (3) over all states n (complete set), and making use of the simple rule for a matrix product, *viz*:

$$\sum_n p_x(0n)p_x(n0) = (p_x^2)_{00},$$

we obtain the relation:

$$m^2(2\pi/h)^2 \sum_n W_{0n}^2|x_{0n}|^2 = (p_x^2)_{00}. \quad (4)$$

Similar relations hold on replacing x by y or z . Adding,

$$m^2(2\pi/h)^2 \sum_{n,xyz} W_{0n}^2|x_{0n}|^2 = (p_x^2 + p_y^2 + p_z^2)_{00}. \quad (5)$$

We next attempt to give the right hand side of (5) a physical meaning. Since

$$p_x^2 = \sum_\mu \sum_\nu p_{x_\mu} p_{x_\nu} = \sum_{\mu=1}^N p_{x_\mu}^2 + \sum_{\mu \neq \nu} p_{x_\mu} p_{x_\nu},$$

$$(p_x^2)_{00} = \sum_{\mu=1}^N (p_{x_\mu}^2)_{00} + \sum_{\mu \neq \nu} (p_{x_\mu} p_{x_\nu})_{00}.$$

The right side of (5) thus decomposes into two parts:

$$\sum_{\mu=1}^N (p_{x_\mu}^2 + p_{y_\mu}^2 + p_{z_\mu}^2)_{00} \text{ and } \sum_{\mu \neq \nu} (p_{x_\mu} p_{x_\nu} + p_{y_\mu} p_{y_\nu} + p_{z_\mu} p_{z_\nu})_{00}.$$

The former term is recognizable as $2mT_{00}$, where T_{00} is the diagonal component of kinetic energy in the state 0. By the virial theorem, making use of the fact that the interaction potentials in the atom are all Coulombian, we can equate T_{00} to $-W_0$. The cross-product term is expressible as

$$-(h/2\pi)^2 \int \bar{\psi}_0 \nabla_\mu \cdot \nabla_\nu \psi_0 d\tau,$$

or

$$\sum_{\mu \neq \nu} (\vec{p}_\mu \cdot \vec{p}_\nu)_{00}, \text{ where } \vec{p}_\mu = (p_{x_\mu}, p_{y_\mu}, p_{z_\mu}).$$

Then

$$m^2(2\pi/h)^2 \sum_{n,xyz} W_{0n}^2 |x_{0n}|^2 = -2mW_0 + \sum_{\mu \neq \nu} \sum (\vec{p}_\mu \cdot \vec{p}_\nu)_{00} \quad (6)$$

where $|W_0|$ is the energy necessary to strip the atom of all its electrons when in the state 0.

Eq. (6), then, is the general sum rule for the case $j=2$. If the wave function of the state 0 is simple enough so that $\sum_{\mu \neq \nu} (\vec{p}_\mu \cdot \vec{p}_\nu)_{00}$ can be evaluated, it is of use. For states like the ground state of helium, where one can assume separability to a good approximation,

$$(\dot{p}_{x\mu} \dot{p}_{x\nu})_{00} = \tilde{p}_{x\mu} \tilde{p}_{x\nu}$$

where the tilde indicates an average with respect to the wave function of that electron alone. But

$$\tilde{p}_{x\mu} = \tilde{p}_{x\nu} = 0.$$

In such a case, and for one-electron atoms, the rule becomes

$$\sum_{n,xyz} W_{0n}^2 |x_{0n}|^2 = -(h^2/2\pi^2m)W_0. \quad (7)$$

For those cases above mentioned in which the cross term vanishes, it is of interest to express the rule in terms of the A and B coefficients:

$$\sum_n \frac{A_{0n}}{\nu_{0n}} = \frac{32\pi^2e^2}{3mc^3h^2} |W_0| \quad (8)$$

or

$$\sum_n \nu_{0n}^2 B_{0n} = \frac{4\pi e^2}{3mh^2} |W_0| \quad (9)$$

the Kuhn-Reiche rule ($j=1$) being expressible as

$$\sum_n \frac{A_{0n}}{\nu_{0n}^2} = \frac{8\pi^2e^2}{mc^3} N$$

or

$$\sum_n \nu_{0n} B_{0n} = -\frac{\pi e^2}{3m} N.$$

Alternative method

The sum $\sum_n W_{0n}^2 |x_{0n}|^2$ can be expressed alternatively as $\sum_n \sum_{\mu} W_{0n}^2 x_{\mu}(0n) \sum_{\nu} x_{\nu}(n0)$. (In the rest of the paper matrix components of coordinates and momenta are understood to have time factors of the form $\exp[(2\pi i/h)W_{0n}t]$.) As before, $\dot{p}_{x\mu}(0n) = m(2\pi i/h)W_{0n}x_{\mu}(0n)$, and making use of the above convention as to the time factor of a matrix component, we have, letting the dot denote differentiation with respect to time:

$$\dot{p}_{x\mu}(0n) = m(2\pi i/h)^2 W_{0n}^2 x_{\mu}(0n)$$

so that

$$W_{0n}^2 x_{\mu}(0n) = (1/m)(h/2\pi i)^2 \dot{p}_{x\mu}(0n).$$

The sum then becomes $(1/m)(\hbar/2\pi i)^2 \sum_n \sum_\mu \sum_\nu \dot{p}_{x\mu}(0n)x_\nu(n0)$. We now make use of the fact that $\dot{p}_{x\mu}(0n) = -(\partial V/\partial x_\mu)_{0n}$, where V is the potential energy of the atom,³ and of the rule for a matrix product, obtaining for the sum the expression

$$\frac{1}{m} \left(\frac{\hbar}{2\pi} \right)^2 \sum_\mu \sum_\nu \left(\frac{\partial V}{\partial x_\mu} x_\nu \right)_{00}.$$

Summing on x, y, z , we get

$$\sum_{n,xyz} W_{0n}^2 |x_{0n}|^2 = \frac{1}{m} \left(\frac{\hbar}{2\pi} \right)^2 \sum_\mu \sum_\nu (\nabla_\mu V \cdot R_\nu)_{00}$$

where ∇_μ is the gradient operator in the coordinates of the μ th electron, and R_ν is the radius vector to the ν th electron. This expression can be split into the parts

$$\frac{1}{m} \left(\frac{\hbar}{2\pi} \right)^2 \sum_{\mu=1}^N (\nabla_\mu V \cdot R_\mu)_{00} \text{ and } \frac{1}{m} \left(\frac{\hbar}{2\pi} \right)^2 \sum_{\mu \neq \nu} (\nabla_\mu V \cdot R_\nu)_{00}.$$

The first part can be transformed by Euler's theorem (since V is a homogeneous function of the electron coordinates of degree -1), and becomes $(-1/m)(\hbar/2\pi)^2 V_{00}$. Application of the virial theorem, according to which $V_{00} = 2W_0$, gives finally for the first part $-(\hbar^2/2\pi^2 m)W_0$, agreeing with the non-cross term of the first method. The cross term $(1/m)(\hbar/2\pi)^2 \sum_{\mu \neq \nu} (\nabla_\mu V \cdot R_\nu)_{00}$ must thus be equal to that obtained by the first method, $(1/m^2)(\hbar/2\pi)^2 \sum_{\mu \neq \nu} (\dot{\mathbf{p}}_\mu \cdot \dot{\mathbf{p}}_\nu)_{00}$. It does not appear that this equivalence could be shown in any other way. The new form for the cross term is more useful for calculation, since it does not require us to differentiate a wave function which may be unwieldy. For an atom of atomic number Z with N electrons it becomes:

$$\frac{e^2}{2m} \left(\frac{\hbar}{2\pi} \right)^2 \int \bar{\psi}_0 \left[Z \sum_{\mu \neq \nu}^N \sum_{\mu \neq \nu} \frac{1}{r_\mu^3} (r_\mu^2 + r_\nu^2 - r_{\mu\nu}^2) + \sum_{\mu \neq \nu}^N \sum_{j \neq \mu} \sum_{j \neq \mu} \frac{1}{r_{j\mu}^3} (r_i^2 - r_\mu^2 + r_{\mu\nu}^2 - r_{j\nu}^2) \right] \psi_0 d\tau.$$

For the special case of a two-electron atom the cross term becomes

$$\frac{1}{m} \left(\frac{\hbar}{2\pi} \right)^2 \int \bar{\psi}_0 \left[Z e^2 r_1 r_2 \cos \Theta_{12} \left(\frac{1}{r_1^3} + \frac{1}{r_2^3} \right) + \frac{e^2}{r_{12}} \right] \psi_0 d\tau$$

where Θ_{12} is the angle between the radius vectors. If this is calculated out with a separated wave function, the term e^2/r_{12} leads to a nonvanishing result, in contrast to the first method, which gave zero. This discrepancy is undoubtedly due to the inaccuracy of the assumption of separability.

³ The proof is like that given by Sommerfeld, *Wellenmechanischer Ergänzungsband*, pp. 288, 289 for a diagonal component of momentum. The operators div , grad , and Δ , however, are now operators in 3 N -space, rather than 3-space, and with us the time component of a wave function of a stationary state k is $\exp [-(2\pi i/\hbar)W_{kt}]$ rather than $\exp [+(2\pi i/\hbar)W_{kt}]$, so that $z_{0n} = \int \bar{\psi}_0 z \psi_n d\tau$, rather than $\int \psi_0 z \bar{\psi}_n d\tau$, as with Sommerfeld.

SECTION II

We continue with the case $j=3$. The problem is to evaluate $\sum_n W_{0n^3} |x_{0n}|^2$. First, $W_{0n^3} |x_{0n}|^2$, because of the hermitian character of our matrices, can be expressed as $-(W_{0n^2 x_{0n}})(W_{n0 x_{n0}})$. The factor $W_{n0 x_{n0}}$ can be then placed equal, as before, to $(h/2\pi im)p_x(n0)$. Also, as before,

$$\dot{p}_x(0n) = m \left(\frac{2\pi i}{h} \right)^2 W_{0n^2 x_{0n}}$$

Thus

$$W_{0n^2 x_{0n}} = \left(\frac{h}{2\pi i} \right)^2 \frac{1}{m} \dot{p}_x(0n)$$

and

$$W_{0n^3} |x_{0n}|^2 = \frac{h}{2\pi i} \frac{h^2}{4\pi^2 m^2} \dot{p}_x(0n) p_x(n0).$$

Now

$$\dot{p}_x(0n) = \sum_{\mu=1}^N \dot{p}_{x\mu}(0n)$$

and

$$\dot{p}_{x\mu}(0n) = - \left(\frac{\partial V}{\partial x_\mu} \right)_{0n}$$

Thus $\dot{p}_x(0n) = - \sum_{\mu} (\partial V / \partial x_\mu)_{0n}$, so that

$$W_{0n^3} |x_{0n}|^2 = - \frac{h}{2\pi i} \frac{h^2}{4\pi^2 m^2} \sum_{\mu} \sum_{\nu} \left(\frac{\partial V}{\partial x_\mu} \right)_{0n} p_{x\nu}(n0).$$

Upon summing on n , making use of the rule for a matrix product, we obtain

$$\sum_n W_{0n^3} |x_{0n}|^2 = - \frac{h}{2\pi i} \frac{h^2}{4\pi^2 m^2} \sum_{\mu} \sum_{\nu} \left(\frac{\partial V}{\partial x_\mu} p_{x\nu} \right)_{00}. \tag{10}$$

Eq. (10), then, is the rule for $j=3$ in the general case of an N -electron atom. (The i , of course, is cancelled on performing the indicated operations.) We next consider the special cases $N=1$ and $N=2$.

Case 1: $N=1$

Letting 0 denote any discrete state of an H-like atom

$$\sum_k W_{0k^3} |x_{0k}|^2 = \frac{1}{m^2} \left(\frac{h}{2\pi} \right)^4 \left(\frac{\partial V}{\partial x} \frac{\partial}{\partial x} \right)_{00}$$

and

$$\sum_{k,xyz} W_{0k^3} |x_{0k}|^2 = \frac{1}{m^2} \left(\frac{h}{2\pi} \right)^4 J, \text{ where } J = \int \bar{\psi}_0 \nabla V \cdot \nabla \psi_0 d\tau.$$

But $V = V(r \text{ only})$. So that

$$\nabla V \cdot \nabla \psi_0 = \frac{dV}{dr} \frac{\partial \psi_0}{\partial r} = \frac{Ze^2}{r} \frac{\partial \psi_0}{\partial r},$$

(since $V = -Ze^2/r$). Thus

$$J = Ze^2 \int \bar{\psi}_0 \frac{1}{r^2} \frac{\partial \psi_0}{\partial r} d\tau$$

and since $\psi_0 = R(r)\Theta(\theta)\Phi(\phi)$,

$$J = Ze^2 \int_0^\infty R \frac{dR}{dr} dr \int_0^\pi \Theta^2 \sin \theta d\theta \int_0^{2\pi} \bar{\Phi} \Phi d\phi.$$

Letting R , Θ , and Φ be separately normalized,

$$J = Ze^2 \int_0^\infty R \frac{dR}{dr} dr = \frac{Ze^2}{2} [R^2(\infty) - R^2(0)] = -\frac{Ze^2}{2} R^2(0),$$

since the radial wave function always vanishes at infinity. Then, making use of the properties of the Laguerre polynomials involved in the radial wave function, we find:

$$\begin{aligned} J &= 0, \quad l \neq 0 \\ &= - (2e^2/a_0^3) Z^4/n^3, \quad l = 0 \end{aligned}$$

where a_0 is the Bohr radius, n the principal quantum number, and l the azimuthal quantum number of the state 0. Thus the cube sum vanishes for $l \neq 0$, and equals

$$- \frac{1}{m^2} \left(\frac{\hbar}{2\pi} \right)^4 \frac{2e^2}{a_0^3} \frac{Z^4}{n^3} \text{ for } l = 0.$$

It is interesting to express these relations in terms of the A 's.

Since

$$\begin{aligned} A_{0k} &= \frac{64\pi^4 e^2}{3c^3 h^4} W_{0k}^3 (|x_{0k}|^2 + |y_{0k}|^2 + |z_{0k}|^2), \\ \sum_k A_{0k} &= 0, \quad l \neq 0 \\ &= -\frac{8e^4}{3m^2 c^3 a_0^3} \frac{Z^4}{n^3}, \quad l = 0. \end{aligned}$$

Expressed in words, in any hydrogen-like atom, the sum of the spontaneous transition probabilities from any state not an S -state to all lower states is equal to the sum of the spontaneous transition probabilities from all higher states down to the given state. For an S -state they are unequal, the difference varying inversely with the cube of the principal quantum number and directly with the fourth power of atomic number; for S -states near the ionization limit they approach equality. (By a *state* is here meant a level with given l and m ; if one wishes to treat state as meaning a given l only, that is, to average over different *orbital orientations*, one must take into account such orbital degeneracy in writing down the formulas for the A 's or the B 's in terms of matrix components. The necessary quantum weight factors can be found most explicitly in a paper by Y. Sugiura.⁴)

⁴ Y. Sugiura, *Phil. Mag.* [7] 4, 495 (1927).

For example, the sum of the spontaneous transition probabilities from all higher states, continuous included, to the state $2P$ (with given m) in hydrogen-like atoms is equal to the spontaneous transition probability from that state to the groundstate $1S$. (m here means magnetic quantum number.)

Applied to the case in which 0 denotes the ground state of an H-like atom, this cube rule furnishes an independent proof of a theorem familiar from direct examination of the hydrogenic functions. We have shown that this sum is of the order Z^4/n^3 for S -states of H-like atoms, and zero for other states. Since for the ground state all the A_{0k} 's have the same sign, it follows that their sum cannot vanish, so that we have: the ground state of an H-like atom must be an S -state.

Case 2: $N=2$, helium-like atoms

On writing out the double sum, we obtain:

$$\sum_n W_{0n}^3 |x_{0n}|^2 = -\frac{\hbar}{2\pi i} \frac{\hbar^2}{4\pi^2 m^2} \left(\frac{\partial V}{\partial x_1} p_{x_1} + \frac{\partial V}{\partial x_2} p_{x_2} + \frac{\partial V}{\partial x_1} p_{x_2} + \frac{\partial V}{\partial x_2} p_{x_1} \right)_{00}.$$

Using $V = -Ze^2/r_1 - Ze^2/r_2 + e^2/r_{12}$, and carrying through the indicated operations in a straightforward way, we obtain:

$$\begin{aligned} \sum_{n,xyz} W_{0n}^3 |x_{0n}|^2 = & \left(\frac{\hbar}{2\pi} \right)^4 \frac{Ze^2}{m^2} \left[\frac{1}{r_1^3} \sum_{xyz} x_1 \frac{\partial}{\partial x_1} + \frac{1}{r_2^3} \sum_{xyz} x_2 \frac{\partial}{\partial x_2} \right. \\ & \left. + \frac{1}{r_1^3} \sum_{xyz} x_1 \frac{\partial}{\partial x_2} + \frac{1}{r_2^3} \sum_{xyz} x_2 \frac{\partial}{\partial x_1} \right]_{00}. \end{aligned}$$

Letting 1_{r_μ} , 1_{θ_μ} , 1_{ϕ_μ} be unit vectors along the radius, meridian, and parallel of latitude through the μ th electron,

$$\sum_{xyz} x_\mu \frac{\partial}{\partial x_\mu} = r_\mu \frac{\partial}{\partial r_\mu}$$

Also

$$\sum_{xyz} x_\mu \frac{\partial}{\partial x_\nu} = r_\mu 1_{r_\mu} \cdot \nabla_\nu,$$

where ∇_ν is the gradient in the coordinates of the ν th electron. Using these abbreviations, we can write the cube sum for $N=2$ in the form:

$$\left(\frac{\hbar}{2\pi} \right)^4 \frac{Ze^2}{m^2} \int \bar{\psi}_0 \left[\frac{1}{r_1^2} \frac{\partial}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} + \frac{1}{r_1^2} 1_{r_1} \cdot \nabla_2 + \frac{1}{r_2^2} 1_{r_2} \cdot \nabla_1 \right] \psi_0 d\tau.$$

Knowing the wave function of any discrete state of a helium-like atom, we have here a rule for the evaluation of $\sum_n A_{0n}$ for the atom. We might mention that for S -states (e.g., $(1s)^2$ or $(1s)(2s)$), an approximate function of the form $\psi_0 = \psi_0(r_1, r_2)$ (no angular dependence) is often used. In such a case

$$1_{r_1} \cdot \nabla_2 \psi_0 = \cos \Theta_{12} \frac{\partial}{\partial r_2} \psi_0$$

$$1_{r_2} \cdot \nabla_1 \psi_0 = \cos \Theta_{12} \frac{\partial}{\partial r_1} \psi_0,$$

where Θ_{12} is the angle between the radius vectors \vec{r}_1 and \vec{r}_2 . But $\int \cos \Theta_{12} \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 = 0$. Thus if $\psi_0 = \psi_0(r_1, r_2)$, the terms involving both electrons drop out of the integrand and the cube sum reduces to the integral

$$\left(\frac{h}{2\pi}\right)^4 \frac{Ze^2}{m^2} \int \bar{\psi}_0 \left(\frac{1}{r_1^2} \frac{\partial}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \right) \psi_0 d\tau.$$

In applying this to the ground state of helium, it is convenient to express the cube sum in atomic units, in which case the factor in front of the integral becomes $8Z$. Using a simple screening constant wave function $\psi_0 = -(\alpha^3/\pi)^{1/2} e^{-\alpha(r_1+r_2)}$ where $\alpha = Z - 5/16$, the cube sum becomes $-32Z(Z - 5/16)^3$.

SECTION III $j=4$

To evaluate $\sum_{n,xyz} W_{0n}^4 |x_{0n}|^2$. Taking the general case of an N -electron atom, we begin as before:

$$\begin{aligned} \left(\frac{\partial V}{\partial x_\mu}\right)_{0n} &= -\dot{p}_{x_\mu}(0n) \\ &= m(2\pi/h)^2 W_{0n}^2 x_\mu(0n). \end{aligned}$$

Thus

$$\sum_\mu \left(\frac{\partial V}{\partial x_\mu}\right)_{0n} = m(2\pi/h)^2 W_{0n}^2 x_{0n}$$

and

$$m^2(2\pi/h)^4 W_{0n}^4 |x_{0n}|^2 = \sum_\mu \sum_\nu \left(\frac{\partial V}{\partial x_\mu}\right)_{0n} \left(\frac{\partial V}{\partial x_\nu}\right)_{n0}.$$

Summing over all the states n ,

$$\begin{aligned} \sum_n (2\pi/h)^4 m^2 W_{0n}^4 |x_{0n}|^2 &= \sum_\mu \sum_\nu \left(\frac{\partial V}{\partial x_\mu} \frac{\partial V}{\partial x_\nu}\right)_{00} \\ &= \left\{ \left(\sum_{\mu=1}^N \frac{\partial V}{\partial x_\mu} \right)^2 \right\}_{00} \\ &= \int \bar{\psi}_0 \left(\sum_{\mu=1}^N \frac{\partial V}{\partial x_\mu} \right)^2 \psi_0 d\tau. \end{aligned}$$

For a hydrogen-like atom, $N=1$, we obtain for the fourth-power sum:

$$\left(\frac{h}{2\pi}\right)^4 \frac{Z^2 e^4}{m^2} \left(\frac{1}{r^4}\right)_{00}$$

where

$$\left(\frac{1}{r^4}\right)_{00} = \frac{\frac{3}{2} Z^4 \left[1 - \frac{l(l+1)}{3n^2}\right]}{a_0^4 n^3 (l + 3/2)(l+1)(l + \frac{1}{2})l(l - \frac{1}{2})}.$$

This fourth-power rule gives a rule for summing $\sum_k \nu_{0k} A_{0k}$. The presence of l in the denominator of the above expression leads to the result that a sum of transition probabilities with this sort of frequency weighting diverges for S -states of hydrogen-like atoms.

For a helium-like atom, this rule takes a simple form. Using

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}},$$

we find

$$\left(\sum_{\mu} \frac{\partial V}{\partial x_{\mu}}\right)^2 = Z^2 e^4 \left(\frac{x_1^2}{r_1^6} + \frac{x_2^2}{r_2^6} + 2\frac{x_1 x_2}{r_1^3 r_2^3}\right).$$

Summing over x, y, z ,

$$\sum_{xyz} \left(\sum_{\mu} \frac{\partial V}{\partial x_{\mu}}\right)^2 = Z^2 e^4 \left(\frac{1}{r_1^4} + \frac{1}{r_2^4} + \frac{2}{r_1^2 r_2^2} \cos \Theta_{12}\right)$$

where Θ_{12} is the angle between the radius vectors \vec{r}_1, \vec{r}_2 , from which is obtained the fourth-power sum:

$$\left(\frac{h}{2\pi}\right)^4 \frac{Z^2 e^4}{m^2} \int \bar{\psi}_0 \left(\frac{1}{r_1^4} + \frac{1}{r_2^4} + \frac{2}{r_1^2 r_2^2} \cos \Theta_{12}\right) \psi_0 d\tau.$$

Going back to H-like atoms, we can use the cube and fourth-power rules to deduce the asymptotic behavior of the A 's between the ground state and the continuous spectrum. $\sum_k \nu_{0k} A_{0k}$ diverges for S -states, and therefore for the ground state. For this state the $\nu_{0k} A_{0k}$ all have the same sign. For the discrete spectrum (Lyman series), $\nu_{0k} A_{0k}$ is asymptotically of the order $1/n_k^3$, and since $\sum_{1}^{\infty} 1/n_k^3$ is known to converge, it follows that the sum $\sum_k \nu_{0k} A_{0k}$ over the discrete spectrum only must converge. Thus $\int \nu (dA_{0\nu}/d\nu) d\nu$ over the continuous spectrum must diverge. In a similar manner, using the cube rule, it follows that $\int (dA_{0\nu}/d\nu) d\nu$ over the continuous spectrum must converge. Writing $dA_{0\nu}/d\nu$ asymptotically (large ν) as $\text{const.}/\nu^{1+\epsilon}$ we see that $\int_{\nu_0}^{\infty} d\nu/\nu^{1+\epsilon}$ must converge and $\int_{\nu_0}^{\infty} d\nu/\nu^{\epsilon}$ must diverge, (where ν_0 = frequency of Lyman series limit). The first requirement gives $\epsilon > 0$, the second $\epsilon \leq 1$, so that $0 < \epsilon \leq 1$. Thus the f -value $df_{0\nu}/d\nu (= \nu^{-2} dA_{0\nu}/d\nu)$ is of the order $1/\nu^j$, where

$3 < j \leq 4$. This example serves to illustrate how the sum rules can be used to obtain information about the intensity distribution in the continuous spectrum without knowing anything about the continuous wave functions.

It should be mentioned that Dirac and Harding⁵ have already obtained the sum rules of this paper for the special case when the state 0 is the ground state of hydrogen. Besides this restriction, their method encounters an ambiguity of a peculiar sort, in that part of an operator may operate backwards and part forwards; this ambiguity has to be removed by a special investigation.

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⁵ Dirac and Harding, Proc. Camb. Phil. Soc. **28**, 209 (1932).