Numerical Values for Hydrogen Fine Structure*

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Bethe's "average excitation potentials" for states 1s through 4p of hydrogen are calculated numerically. These lead to values of the $n_0\,{}^2S_{\frac{1}{2}}-n_0\,{}^2P_{\frac{1}{2}}$ level shifts in hydrogen for $n_0=3$ and 4 of $\mathcal{S}_H(3)=314.690\pm0.047$ Mc/sec and $\mathcal{S}_H(4)=132.998\pm0.020$ Mc/sec, which are 1.44 Mc/sec and 0.85 Mc/sec larger than previous estimates. For $n_0=2$, a value of $\mathcal{S}_H(2)=1057.21\pm0.16$ Mc/sec is obtained, which is in close agreement with previous calculation. In conjunction with this work, the oscillator strengths $f(n_0l_0,nl)$ are obtained for $n_0=1$, 2, 3, and 4; $n<50$; and all values of l_0 and l. A generalization of the Wigner-Kirkwood sum rule is derived.

THE "average excitation potentials" of the 2s and 2p levels of hydrogen were calculated several years ago by Bethe, Brown, and Stehn.[1] All spectroscopic investigations of higher states[2] have been based on the assumption that these potentials are nearly independent of the principal quantum number n_0. The present paper extends the calculations from 1s through the 4p level in order to determine the exact values of the average excitation energies in anticipation of microwave measurements now being made by Sanders and Lamb which will yield to a high degree of accuracy the level shift for $n_0=3$.

The formula[1] for the energy shift of a hydrogen level n_0l_0, with fixed Coulomb field and $Z=1$, is for s states

$$\Delta E(n_00)=\frac{8}{n_0^3}\frac{\alpha^3Ry_\infty}{3\pi}\left(\ln\frac{mc^2}{k_0(n_00)}-\ln2+\frac{5}{6}-\frac{1}{5}\right),\quad (1)$$

and for states $l_0\neq0$

$$\Delta E(n_0l_0)=\frac{8}{n_0^3}\frac{\alpha^3Ry_\infty}{3\pi}\left(\ln\frac{Ry_\infty}{k_0(n_0l_0)}+\frac{3}{8}\frac{C_{lj}}{2l_0+1}\right),\quad (2)$$

where

$$\begin{aligned} C_{lj}&=1/(l_0+1) \quad \text{for} \quad j=l_0+1/2,\\ C_{lj}&=-1/l_0 \quad \text{for} \quad j=l_0-1/2, \end{aligned}\quad (2a)$$

α is the fine structure constant; Ry_∞ is the Rydberg energy for infinite nuclear mass; and m is the electronic mass.

Bethe's average excitation energy k_0 may be evaluated from the expression[1]

$$\ln[k_0(n_0l_0)/Ry_\infty]=\sum_{nl}(3n_0^3/16)f(n_0l_0,nl)\nu^2\ln|\nu|,\quad (3)$$

with the energy change in Rydberg units:

$$\nu(n,n_0)=(E_n-E_0)/Ry_\infty.\quad (4)$$

The oscillator strength is given by[3]

$$f(n_0l_0,nl)=\begin{cases}[\max(l,l_0)/(2l_0+1)](R_0^n)^2\nu/3a^2, & \text{for} \quad l=l_0\pm1,\\ 0, \quad \text{otherwise;} \end{cases}\quad (5)$$

where

$$R_0^n=\int_0^\infty R(n_0l_0)R(nl)r^3dr,\quad (6)$$

and a is the first Bohr radius.

We define

$$g(n_0l_0,nl)=(3n_0^3/16)f(n_0l_0,nl)\nu^2(n,n_0),\quad (7)$$

so that (3) becomes

$$\ln[k_0(n_0l_0)/Ry_\infty]=\textstyle\sum_n g(n_0l_0,n)\ln|\nu(n,n_0)|.\quad (8)$$

The values of $g(n_0l_0,n)$ are then given by

$$g(1s,n)=(16/n^3\nu_1^2)\gamma(n,1),\quad (9a)$$

$$g(2s,n)=(16/n^5\nu_2^3)(n^2-1)\gamma(n,2),\quad (9b)$$

$$g(2p,n)=(4/9n^5\nu_2^4)[8(n^2-1)+n^2\nu_2]\gamma(n,2),\quad (9c)$$

$$g(3s,n)=(16/729n^9\nu_3^5)(n^2-1)(7n^2-27)^2\gamma(n,3),\quad (9d)$$

$$g(3p,n)=(128/2187n^7\nu_3^5)[18(n^2-1)(n^2-4)+(n^2-3)^2]\gamma(n,3),\quad (9e)$$

$$g(3d,n)=(256/18\,225n^7\nu_3^6)(n^2-1)[6(n^2-4)+n^2\nu_3]\gamma(n,3),\quad (9f)$$

$$g(4s,n)=(1/36\,864n^{13}\nu_4^7)(n^2-1)(23n^4-288n^2+768)^2\gamma(n,4),\quad (9g)$$

$$g(4p,n)=(1/2\,949\,120n^{11}\nu_4^7)\times[512(n^2-1)(n^2-4)(9n^2-80)^2+(57n^4-608n^2+1280)^2]\gamma(n,4),\quad (9h)$$

where

$$\nu_{n0}=\nu(n,n_0),\quad (9i)$$

$$\gamma(n,n_0)=[(n-n_0)/(n+n_0)]^{2n}.\quad (9j)$$

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[1] Bethe, Brown, and Stehn, Phys. Rev. **77**, 370 (1950).

[2] See, for example, H. Kuhn and G. W. Series, Proc. Roy. Soc. (London) **A202**, 127 (1950).

[3] H. A. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 1, pp. 434–443.

For large n (≥ 50), the values are taken as

$$g(1s,n)=0.293050n^{-3}+0.195n^{-5}, \quad (10a)$$

$$g(2s,n)=0.343514n^{-3}+0.114n^{-5}, \quad (10b)$$

$$g(2p,n)=0.314887n^{-3}+1.338n^{-5}, \quad (10c)$$

$$g(3s,n)=0.390182n^{-3}+0.110n^{-5}, \quad (10d)$$

$$g(3p,n)=0.403453n^{-3}+1.594n^{-5}, \quad (10e)$$

$$g(3d,n)=0.280293n^{-3}+3.636n^{-5}, \quad (10f)$$

$$g(4s,n)=0.433493n^{-3}+0.267n^{-5}, \quad (10g)$$

$$g(4p,n)=0.458086n^{-3}+1.829n^{-5}. \quad (10h)$$

For transitions to the continuum, the quasi-principal quantum number n is defined by

$$E_n=+Ry_\infty/n^2, \quad (11)$$

and the summation over n is replaced by an integration over $d\nu$. The oscillator strength for transitions into an interval $d\nu$ of the continuous spectrum $df/d\nu$ is then given by (5) with the discrete-discrete matrix element (6) replaced by the discrete-continuum matrix element which Stobbe[4] calls $C(\nu)$. Then

$$dg(1s)/d\nu=8\nu_1^{-2}K(n,1), \quad (12a)$$

$$dg(2s)/d\nu=2\nu_2^{-2}(4+3\nu_2^{-1})K(n,2), \quad (12b)$$

$$dg(2p)/d\nu=(2/3)\nu_2^{-3}(3+2\nu_2^{-1})K(n,2), \quad (12c)$$

$$dg(3s)/d\nu=(8/81)\nu_3^{-2}(81+96\nu_3^{-1}+208\nu_3^{-2}/9+128\nu_3^{-3}/81)K(n,3), \quad (12d)$$

$$dg(3p)/d\nu=(64/729)\nu_3^{-3}(27+26\nu_3^{-1}+28\nu_3^{-2}/9)K(n,3), \quad (12e)$$

$$dg(3d)/d\nu=(128/32\,805)\nu_3^{-4}(45+46\nu_3^{-1}+48\nu_3^{-2}/9)K(n,3), \quad (12f)$$

$$dg(4s)/d\nu=(1/36)\nu_4^{-2}(288+414\nu_4^{-1}+159\nu_4^{-2}+24\nu_4^{-3}+23\nu_4^{-4}/16+15\nu_4^{-5}/512)K(n,4), \quad (12g)$$

$$dg(4p)/d\nu=(1/960)\nu_4^{-3}(2400+2800\nu_4^{-1}+663\nu_4^{-2}+47\nu_4^{-3}+33\nu_4^{-4}/32)K(n,4), \quad (12h)$$

where

$$K(n,n_0)=\exp[-4n\,\mathrm{arc\,cot}(n/n_0)]/(1-e^{-2\pi n}). \quad (12i)$$

The well-known f-sum rule[3] states that

$$\sum_{nl} f(n_0l_0,nl)=1. \quad (13)$$

Also, one has a generalization derived by Vinti[5]

$$\sum_{nl} g(n_0l_0,nl)=\delta(l_0,0). \quad (14)$$

These sums, together with the corresponding partial sum rules given in the Appendix, were calculated along with those of (8) to provide a check on the accuracy of the calculations.

For the integration, we used the variable $x=n/n_0$,

$$\nu=(1+1/x^2)/n_0^2. \quad (15)$$

In order to make efficient use of the calculator, the numerical integration was performed only for $0.02\leq x\leq 5.0$; power series expansion of the integrands for x outside of this region permitted analytical integration to a prescribed accuracy of 5 parts in 10^9. The expressions we actually integrated numerically were of the form $\int K(x,n_0)x^{-3}\nu_1^{-t}\ln\nu_1 dx$ for the appropriate values of t, with and without the logarithmic term. The Newton-Cotes quadrature formula[6]

$$\int_{x_0}^{x_8} y dx=(8h/28\,350)\sum_{i=0}^{8} a_i y_i-(2368/467\,775)h^{11}y^{(10)} \quad (16)$$

was used, in which the error over a given range of x is proportional to the tenth power of the interval h and to the tenth derivative of y evaluated somewhere within the range. The numerical integration was done with the intervals

$h=0.01125$	for	$0.02\leq x\leq 0.2$,
$h=0.05$	for	$0.2\leq x\leq 1$,
$h=0.25$	for	$1\leq x\leq 5$.

In order to obtain an estimate of the error, the integration was then repeated with twice the interval $h'=2h$. The error, taken as one part in $(2^{10}-1)$ of the algebraic difference of the second integration minus the first, was subtracted from the original result to give the final value of the numerical integration.

The card-programmed calculator (CPC) was set up[7] to use a floating decimal arithmetic based on an eight-digit, seven-decimal number times an appropriate power of 10, the permissible powers being between ± 49. For the numerical integration only, the last digit was automatically rounded. In extended calculations, there are unavoidable losses of significance resulting from the addition of two similar numbers with opposite sign. This is particularly bad if there is no rounding. In this case when the CPC calculates $(1-8/9)$, for example, it adds $+1.0000000$ and -0.8888888 (having scaled the smaller number to the larger exponent) to obtain 0.1111112, which is correct to but six figures; and virtually all of the significance may be lost in such a calculation as $(12\,345\,678-0.87654322)-12\,345\,677$ which yields an answer of 1.0000000 (with rounding, the answer of zero is one place better); whereas, if

[4] M. Stobbe, Ann. Physik **7**, 661 (1930).

[5] J. P. Vinti, Phys. Rev. **41**, 432 (1932).

[6] $a_0=a_8=989$; $a_1=a_7=5888$; $a_2=a_6=-928$; $a_3=a_5=10496$; $a_4=-4540$. See, for example, W. E. Milne, *Numerical Calculus* (Princeton University Press, Princeton, 1949), p. 124.

[7] H. M. Wagner, Stanford Computation Center, Stanford University Technical Report No. 1, 1954 (unpublished); and J. O. Carter and J. G. Herriot, Stanford Computation Center, Stanford University Technical Report No. 2, 1954 (unpublished).

TABLE I. Summation results and average excitation energies. The sum rules $\Sigma f=1$, for the oscillator strength f, $\Sigma\, g=\delta(l_0,0)$, for $g=(3n_0^3/16)\nu^2 f$, are used as indicators of the accuracy of the calculations for $\Sigma\, g \ln\nu$.

		$\sum_{nl} f$	$\sum_{nl} g$	$\sum_{nl} g \ln\nu = \ln(k_0/Ry_\infty)$	
	Discrete	0.56500414	0.06765781	−0.0144949	
	Continuum	0.43500066	0.93234304	2.9986436	
1s	Total	1.00000480	1.00000085	2.984149	±0.000003
	k_0/Ry_∞			19.76967	±0.00006
	Discrete	0.64890758	0.02643361	−0.0464679	
	Continuum	0.35109318	0.97356933	2.8582659	
2s	Total	1.00000076	1.00000294	2.811798	±0.000009
	k_0/R_∞			16.6398	±0.0002
	Discrete	0.70947420	0.01132089	−0.0329799	
	Continuum	0.29052585	0.98868168	2.8006791	
3s	Total	1.00000005	1.00000257	2.767699	±0.000008
	k_0/Ry_∞			15.9214	±0.0002
	Discrete	0.75029035	0.00382507	−0.0198043	
	Continuum	0.24970952	0.99617705	2.7696633	
4s	Total	0.99999987	1.00000212	2.749859	±0.000006
	k_0/Ry_∞			15.6404	±0.0001
	Discrete	0.80925452	−0.081384055	−0.030646255	
	Continuum	0.19074843	0.081383626	0.000629887	
2p	Total	1.00000295	−0.000000429	−0.03001637	±0.00000001
	k_0/Ry_∞			0.97042964	±0.00000001
	Discrete	0.78603312	−0.10103671	−0.009753547	
	Continuum	0.21396913	0.10103671	−0.028434969	
3p	Total	1.00000225	0.00000000	−0.03818852	±0.00000001
	k_0/Ry_∞			0.96253147	±0.00000001
	Discrete	0.79168395	−0.10949294	0.006267802	
	Continuum	0.20831693	0.10949345	−0.048221808	
4p	Total	1.00000088	0.00000051	−0.0419540	±0.0000003
	k_0/Ry_∞			0.9589139	±0.0000003
	Discrete	0.90415898	−0.018593206	0.018752995	
	Continuum	0.09584262	0.018593067	−0.023985130	
3d	Total	1.00000160	−0.000000139	−0.0052321	±0.0000002
	k_0/Ry_∞			0.9947815	±0.0000002

the order of subtractions is reversed, the resulting 0.12345680 is correct to six figures.

Since the terms in the discrete contribution fall off rapidly with increasing n, we recalculated by desk machine all of the terms for $n<10$ in order to reduce the error by at least a factor of 10. This revealed that, in some cases, the CPC results were correct only through five digits and were in error by as much as three parts in 10^6. On this basis we considered the recalculated discrete contribution to have a probable error of three parts in 10^7. The individual values of f obtained in the course of our calculations, as well as those for levels $4d$ and $4f$, were tabulated for each value of l.[8] The sums of f, which we calculated for each value of l and compared with (36), and the sums of g for each l value, which we calculated for $n_0=2$ and compared with (47), were useful in promoting the assumption that the remaining discrepancy in the f-sum or g-sum for any level n_0l_0 was a fairly systematic error in the continuum contribution, for the ratios of error to continuum contribution were about equal in the sums for the two corresponding values of l.

The three sums over both n and l, the f-sum, g-sum, and $g\ln\nu$-sum, are given in Table I. The g-sum is used as the measure of accuracy of the calculations. The error in the g-sum is presumed to be entirely contained in the continuum contribution and is attributed to the intrinsic loss of significance discussed above. The correction to the numerical integration formula (16) for the g-sum ranges in value from $+0.00000016$ for the $1s$ level to -0.00000008 for $3d$ and does not appreciably affect the error. The positive probable error in $\ln(k_0/Ry_\infty)$ is derived from the error in the g-sum in accordance with the proportion of continuum contributions.

One can now evaluate the level shift formulas (1) and (2). For the fine structure constant, we use the value[9]

$$1/\alpha=137.0377+\epsilon_\alpha,\quad |\epsilon_\alpha|\leq 0.0016, \tag{17}$$

to obtain

$$\ln(mc^2/Ry_\infty)\equiv\ln(2/\alpha^2)=10.53366+2\alpha\epsilon_\alpha. \tag{18}$$

Taking a similar expression for the velocity of light

$$c=299\,792.9+\epsilon_c \text{ km/sec},\quad |\epsilon_c|\leq 0.8 \text{ km/sec}, \tag{19}$$

we obtain in frequency units

$$(\alpha^3/3\pi)Ry_\infty c=135.638924-3\epsilon_\alpha+0.00045\epsilon_c \pm 0.000015 \text{ Mc/sec}, \tag{20}$$

the last uncertainty coming from that of the Rydberg constant.

The electromagnetic level shifts for a fixed Coulomb potential are given in Table II. The probable errors shown for the S-level shifts are taken from the uncertainty in our calculations for the average excitation potentials. Any change in the velocity of light in km/sec is given by ϵ_c, and any change in $1/\alpha$ is given directly by ϵ_α.

In order to obtain a final theoretical value for the level shift $S_H(n_0)=\Delta E(n_0\,{}^2S_{\frac{1}{2}}-n_0\,{}^2P_{\frac{1}{2}})$, which is measured experimentally, we must correct for our use of a fixed Coulomb field and other approximations. Some of these corrections have been calculated and are summarized in a paper by Salpeter[10] for the case $n_0=2$. The corrections to the $n_0=2$ level shift in hydrogen whose values have been calculated include (6.20±0.10) Mc/sec for all fourth-order corrections, (−1.175±0.08) Mc/sec for the effect of the nuclear mass, (0.025 ±0.005) Mc/sec for the effect of the electron-nucleon interaction, and an uncertainty (±0.08) Mc/sec from the error in the reduced mass correction factor for the contribution from the electron's anomalous magnetic moment. Although the n_0 dependence of some of these corrections is $1/n_0^3$, for others it has not been calcu-

[8] Copies of a supplementary table of f-values for $n_0\leq 4$ and all values of l_0 and l which we obtained to nine decimals for $n<10$ and to five significant figures for $n\geq 10$ has been deposited as Document number 4705 with the American Documentation Institute Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **25**, 691 (1953).

[10] E. E. Salpeter, Phys. Rev. **89**, 92 (1953).

TABLE II. Level shifts for fixed Coulomb field.

State	Parentheses in Eq. (1)	Level shift in Mc/sec
$1S$	$7.489696+2\alpha\epsilon_\alpha\pm0.000003$	$8127.154-164\epsilon_\alpha+0.027\epsilon_c\pm0.004$
$2S$	$7.662047+2\alpha\epsilon_\alpha\pm0.000009$	$1039.2718-21\epsilon_\alpha+0.0035\epsilon_c\pm0.0014$
$3S$	$7.706146+2\alpha\epsilon_\alpha\pm0.000008$	$309.7047-7.6\epsilon_\alpha+0.0011\epsilon_c\pm0.0004$
$4S$	$7.723986+2\alpha\epsilon_\alpha\pm0.000006$	$130.9591-2.6\epsilon_\alpha+0.00045\epsilon_c\pm0.0002$
State	Parentheses in Eq. (2)	Level shift in Mc/sec
$2P_{1/2}$	-0.09498363 ± 0.00000001	$-12.883477+0.3\epsilon_\alpha-0.000043\epsilon_c\pm0.000002$
$2P_{3/2}$	0.09251637 ± 0.00000001	$12.548821-0.3\epsilon_\alpha+0.000042\epsilon_c\pm0.000002$
$3P_{1/2}$	-0.0868115 ± 0.0000001	$-3.488894+0.08\epsilon_\alpha-0.000013\epsilon_c\pm0.000005$
$3P_{3/2}$	0.1006885 ± 0.0000001	$4.046601-0.09\epsilon_\alpha+0.000014\epsilon_c\pm0.000005$
$4P_{1/2}$	-0.0830460 ± 0.0000003	$-1.408034+0.03\epsilon_\alpha-0.000005\epsilon_c\pm0.000006$
$4P_{3/2}$	0.1044540 ± 0.0000003	$1.771004-0.04\epsilon_\alpha+0.000005\epsilon_c\pm0.000006$
$3D_{3/2}$	-0.0322679 ± 0.0000002	$-1.29682+0.03\epsilon_\alpha-0.0000045\epsilon_c\pm0.00001$
$3D_{5/2}$	0.0302321 ± 0.0000002	$1.21501-0.03\epsilon_\alpha+0.0000043\epsilon_c\pm0.00001$

lated.[11] As the latter corrections are small, we assume a $1/n_0^3$ law for these as well.

The calculated values for the level shifts $\mathcal{S}_H(n_0)$ are given in Table III. For the $2s$ level, our value for $\ln(k_0/Ry_\infty)$ of 2.8118 is in good agreement with the Bethe, Brown, and Stehn value of 2.8121 and represents an increase in the level shift of 0.04 Mc/sec. The theoretical value for $\mathcal{S}_H(2)$ is still about one-half Mc/sec below the experimental value of (1057.77±0.10) Mc/sec.[12] It may be seen from Table II that if the average excitation energies were independent of n_0, as assumed heretofore, the $3s$ and $4s$ level shifts based on the $2s$ shift would be 307.932 Mc/sec and 129.909 Mc/sec for a fixed Coulomb field. These are 1.77 Mc/sec and 1.05 Mc/sec below our results, and making allowance for negative shifts of $3P_{1/2}$ and $4P_{1/2}$, the estimates for $\mathcal{S}_H(3)$ and $\mathcal{S}_H(4)$ would be too small by 1.44 Mc/sec and 0.85 Mc/sec.

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TABLE III. Final results for the $(n_0\,{}^2S_{1/2}-n_0\,{}^2P_{1/2})$ level shifts.

Eqs. (1) and (2)	$1052.155-22\epsilon_\alpha+0.0035\epsilon_c\pm0.002$
Corrections	5.05 ± 0.15
$\mathcal{S}_H(2)$ in Mc/sec	1057.21 ± 0.16
Eqs. (1) and (2)	$313.1936-7.7\epsilon_\alpha+0.0011\epsilon_c\pm0.0004$
Corrections	1.496 ± 0.045
$\mathcal{S}_H(3)$ in Mc/sec	314.690 ± 0.047
Eqs. (1) and (2)	$132.3672-2.7\epsilon_\alpha+0.00045\epsilon_c\pm0.0002$
Corrections	0.631 ± 0.019
$\mathcal{S}_H(4)$ in Mc/sec	132.998 ± 0.020

[11] E. E. Salpeter (private communication).

[12] Triebwasser, Dayhoff, and Lamb, Phys. Rev. **89**, 98 (1953).

APPENDIX. GENERALIZED SUM RULES

In order to use as many sum rules as possible to check our calculations, we derive the rule for $\sum_n g(n_0l_0, nl_0\pm1)$ by means of projection operators. As an illustration of the method, we calculate the rule for $\sum_n f(n_0l_0, nl_0\pm1)$ which has been found by other means.[13]

With the notation

$$\beta_{n0}\equiv\int\psi^*(nlm)\beta\psi(n_0l_0m_0)d\tau, \tag{21}$$

$$\nu(n,n_0)\equiv(E_n-E_0)/Ry_\infty, \tag{22}$$

and making use of the angular momentum operator,

$$L_{nn}^2=l(l+1)\hbar^2, \tag{23}$$

we introduce projection operators,

$$\Omega^+\equiv[\hbar^{-2}L^2-l_0(l_0-1)]/(4l_0+2), \tag{24a}$$

$$\Omega^-\equiv[(l_0+1)(l_0+2)-\hbar^{-2}L^2]/(4l_0+2), \tag{24b}$$

with the properties

$$\Omega_{nn}^+=\begin{cases}1 \text{ if } l=l_0+1\\ 0 \text{ if } l=l_0-1,\end{cases}\qquad \Omega_{nn}^-=\begin{cases}0 \text{ if } l=l_0+1\\ 1 \text{ if } l=l_0-1,\end{cases} \tag{25a}$$

$$\Omega_{00}^+=l_0/(2l_0+1),\qquad \Omega_{00}^-=(l_0+1)/(2l_0+1). \tag{25b}$$

From the commutation relation

$$[r_i,p_j]=i\hbar\delta_{ij}, \tag{26}$$

it can be shown that

$$L^2=(\mathbf{r}\times\mathbf{p})^2=\mathbf{r}^2\mathbf{p}^2-(\mathbf{r}\cdot\mathbf{p})(\mathbf{r}\cdot\mathbf{p})+i\hbar(\mathbf{r}\cdot\mathbf{p}), \tag{27}$$

and

$$\mathbf{r}\cdot[L^2,\mathbf{p}]=2i\hbar L^2+2\hbar^2(\mathbf{r}\cdot\mathbf{p}). \tag{28}$$

It follows that

$$(\mathbf{r}\cdot\Omega^\pm\mathbf{p})_{00}=(\mathbf{r}\cdot\mathbf{p})_{00}[\Omega_{00}^\pm\pm1/(2l_0+1)] \pm i\hbar^{-1}L_{00}^2/(2l_0+1). \tag{29}$$

[13] E. Wigner, Physik. Z. **32**, 450 (1931); and J. G. Kirkwood, Physik. Z. **33**, 521 (1932).

Since, for an operator F not explicitly time dependent,

$$\dot{F}_{n0}=(-i/\hbar)[F,H]_{n0}=i(Ry_\infty/\hbar)\nu(n,n_0)F_{n0}, \quad (30)$$

we can write

$$\mathbf{p}_{n0}=i\mu(Ry_\infty/\hbar)\nu(n,n_0)\mathbf{r}_{n0}, \quad (31a)$$

$$\dot{\mathbf{p}}_{0n}=-\mu(Ry_\infty/\hbar)^2\nu^2(n,n_0)\mathbf{r}_{0n}. \quad (31b)$$

Combining Eqs. (22), (26), and (31a) gives

$$(\mathbf{r}\cdot\mathbf{p})_{00}=\sum_{nlm}\mathbf{r}_{0n}\cdot\mathbf{p}_{n0}=-(\mathbf{p}\cdot\mathbf{r})_{00}=3i\hbar/2. \quad (32)$$

The oscillator strength

$$f(n_0l_0,nl)=(2\mu/3\hbar)(Ry_\infty/\hbar)\textstyle\sum_m \nu(n,n_0)|\mathbf{r}_{0n}|^2 \quad (33)$$

can be written

$$f(n_0l_0,nl)=\textstyle\sum_m(-2i/3\hbar)\mathbf{r}_{0n}\cdot\mathbf{p}_{n0}, \quad (34)$$

and by making use of (25a), we can form the sum

$$\sum_n f(n_0l_0,\ nl_0\pm1)=\sum_{nlm}\left(-\frac{2i}{3\hbar}\right)\mathbf{r}_{0n}\cdot\Omega_{nn}{}^{\pm}\mathbf{p}_{n0}$$

$$=-\frac{2i}{3\hbar}(\mathbf{r}\cdot\Omega^{\pm}\mathbf{p})_{00}, \quad (35)$$

which may be evaluated from Eqs. (23), (25b), (29), and (32), to give

$$\textstyle\sum_n f(n_0l_0,\ nl_0\pm1)$$
$$=\pm(2l_0+1\pm1)(2l_0+1\pm2)/[6(2l_0+1)]. \quad (36)$$

Similarly, from Eqs. (31) and (33), we can write

$$\nu^2(n,n_0)f(n_0l_0,nl)=(2i/3\mu\hbar)(\hbar/R_\infty)^2\textstyle\sum_m\dot{\mathbf{p}}_{0n}\cdot\mathbf{p}_{n0}, \quad (37)$$

and form the g-sum using Eq. (7),

$$\textstyle\sum_n g(n_0l_0,\ nl_0\pm1)=(in_0^3/8\mu\hbar)(\hbar/Ry_\infty)^2(\dot{\mathbf{p}}\cdot\Omega^{\pm}\mathbf{p})_{00}. \quad (38)$$

Using $(R_\infty/\hbar)^2=e^2/16\pi^2ma^3$, we obtain

$$\textstyle\sum_n g(n_0l_0,\ nl_0\pm1)=(ia^3n_0^3/2\hbar e^2)(\dot{\mathbf{p}}\cdot\Omega^{\pm}\mathbf{p})_{00}. \quad (39)$$

Since for a spherically symmetric potential energy $V(r)$

$$\dot{\mathbf{p}}=-\nabla V=-(1/r)(dV/dr)\mathbf{r}, \quad (40)$$

and

$$(\dot{\mathbf{p}}\cdot\mathbf{p})_{00}=i\hbar\left(\frac{dV}{dr}\frac{\partial}{\partial r}\right)_{00}=-\tfrac{1}{2}i\hbar(\nabla^2V)_{00}, \quad (41)$$

we find from Eq. (29) the expression

$$(\dot{p}\cdot\Omega^{\pm}p)_{00}=-\tfrac{1}{2}i\hbar(\nabla^2V)_{00}\left[\Omega_{00}{}^{\pm}\pm\frac{1}{(2l_0+1)}\right]$$
$$\mp i\hbar\left(\frac{1}{r}\frac{dV}{dr}\right)_{00}\frac{\hbar^{-2}L_{00}{}^2}{2l_0+1}, \quad (42)$$

which, when substituted into Eq. (39), gives

$$\sum_n g(n_0l_0,\ nl_0\pm1)=\frac{a^3n_0^3}{2e^2}\left[\frac{l_0+\frac{1}{2}\pm\frac{1}{2}}{2(2l_0+1)}(\nabla^2V)_{00}\right.$$
$$\left.\pm\frac{l_0(l_0+1)}{2l_0+1}\left(\frac{1}{r}\frac{dV}{dr}\right)_{00}\right]. \quad (43)$$

For a Coulomb field, $V=-Ze^2/r$, it has been shown that[5]

$$(\nabla^2V)_{00}=-2\int\psi_0{}^*\frac{dV}{dr}\frac{\partial\psi_0}{\partial r}d\tau$$
$$=\begin{cases}4e^2Z^4/a^3n_0^3, & \text{for } l_0=0\\ 0, & \text{for } l_0\neq0,\end{cases} \quad (44)$$

and that[14]

$$(Ze^2/r^3)_{00}=2e^2Z^4/[a^3n_0^3l_0(l_0+1)(2l_0+1)]. \quad (45)$$

Hence, from (43) the desired sum rule becomes for $l_0=0$:

$$\textstyle\sum_n g(n_00,n1)=Z^4, \quad (46)$$

and for $l_0\neq0$:

$$\textstyle\sum_n g(n_0l_0,\ nl_0\pm1)=\pm Z^4/(2l_0+1)^2. \quad (47)$$

[14] See reference 3, p. 286.