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Analytical calculation of logarithmic mean excitation energies for hydrogen and helium

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The four logarithmic mean excitation energies $I(\nu)$, for $\nu=-1$, 0, 1, and 2, have been calculated analytically for hydrogen and helium. They appear in the expressions of total cross section, stopping power, and straggling effect for fast charged particles, and in the expression of the Lamb shift of atomic energy levels. The method is based on a generalization of a method by Dalgarno and Lewis [Proc. R. Soc. London, Ser. A **233**, 70 (1956)]. The only input is the wave function of the initial state of the atom (in the present paper only the ground state is considered). For hydrogen the method is rigorous. For helium, Hartree-Fock-type wave functions were used, which is the only approximation of the present method. The accuracy of the method is essentially independent of the value of ν.

I. INTRODUCTION

The object of the present work[1] is to calculate analytically four mean excitation energies $I(\nu)$ which play a fundamental role in atomic physics. The mean excitation energies in question are defined by

$$\ln I(\nu)=L(\nu)/S(\nu),\quad \nu=-1,0,1,2 \tag{1}$$

where the logarithmic sums $L(\nu)$ are defined by

$$L(\nu)=\sum_n f_n(E_n-E_0)^\nu \ln(E_n-E_0)\ , \tag{2}$$

(E_n-E_0) being the excitation energies measured from the energy of the initial state. The sums $S(\nu)$ are

$$S(\nu)=\sum_n f_n(E_n-E_0)^\nu\ . \tag{2'}$$

The sums are over the complete set of energy eigenstates of the atom. The quantities f_n are the oscillator strengths

$$f_n=(E_n-E_0)\,|\,Z_{0n}\,|^2\ ,$$

where Z is the z component of the total dipole moment operator of the electrons of the atom. In the present work the initial state is taken to be the ground state of the atom. The four mean excitation energies are directly connected with the following physical phenomena.

(i) $I(-1)$ appears in the expression of the total cross section for particle-atom collisions.[2]

(ii) $I(0)$ appears in the expression of the atomic stopping power.[2]

(iii) $I(1)$ appears in the expression of the mean fluctuation of the stopping power, called the straggling effect.[3]

(iv) $I(2)$ appears in the expression of the Lamb shift of energy levels.[4]

A number of diverse methods have been developed in recent years to calculate these sums. Excluding the precise calculation of $L(\nu)$ when f_n is known over the entire spectrum (true for hydrogen only), none of the methods are completely rigorous. It is thus desirable to have as many independent approaches as possible. The methods known up until now include complicated Green's-function calculations, variational principles, and a simpler technique, discussed recently, which consists of calculating $L(\nu)$ by taking the derivative of $S(\nu)$ with respect to ν.[5,6] Obviously, the quality of this approach hinges entirely on the knowledge of the function $S(\nu)$, where ν is treated as a continuous variable.

We have developed a method by which these sum rules can be calculated analytically, the only *input being the wave function of the initial state.* It works equally well for all four values of ν. The method is based on a generalization of a method by Dalgarno and Lewis,[7] originally proposed for the calculation of long-range forces between atoms. In this approach an auxiliary operator F is introduced, which enables one to perform the summation over the whole spectrum by closure relation. The operator F is determined by a certain inhomogeneous differential equation, which depends functionally on the initial wave function of the atom. This is explained in detail in Sec. II. In Sec. III, F is derived for hydrogen and the four mean excitation energies $I(\nu)$ are calculated. In Sec. IV we discuss briefly the case of hydrogenlike ions. It is reduced to the hydrogen case by a simple scaling procedure. The treatment of the hydrogen and hydrogenlike cases is completely rigorous. Thus the numerical results can be made as accurate as one pleases. Finally, in Sec. V the mean excitation energies for helium are calculated. In the present paper only Hartree-Fock-type wave functions were taken into consideration. It is the only approximation of the present method. This reduces the helium case to the hydrogen case, essentially. Three different wave functions were considered.

Energies are measured in rydberg units; all other quantities in atomic units.

II. BASIC METHOD

In order to calculate the four sums of Eq. (2) we shall make use of the integral representation of the logarithmic function

$$-\ln(E_n-E_0)=\lim_{\Lambda\to\infty}\left[\int_0^{\Lambda}\frac{1}{\lambda+E_n-E_0}d\lambda-\ln\Lambda\right] . \qquad (3)$$

We then get, taking into consideration the definition of the oscillator strengths,

$$-L(\nu)=\lim_{\Lambda\to\infty}\left[\int_0^{\Lambda}d\lambda\sum_n\frac{|\langle 0\,|\,Z\,|\,n\rangle|^2}{\lambda+E_n-E_0}(E_n-E_0)^{\nu+1}-(\ln\Lambda)\sum_n|\langle 0\,|\,Z\,|\,n\rangle|^2(E_n-E_0)^{\nu+1}\right] , \qquad (4)$$

where we have put, for simplicity,

$$Z=\sum_{i=1}^{N}z_i . \qquad (5)$$

Let F be an operator which satisfies the equation

$$Z\psi_0=[H_0,F]\psi_0+\lambda F\psi_0 . \qquad (6)$$

Here H_0 is the Hamiltonian of the atom, and ψ_0 is the ground-state wave function. From Eq. (6) we get

$$\langle n\,|\,Z\,|\,0\rangle=(\lambda+E_n-E_0)\langle n\,|\,F\,|\,0\rangle . \qquad (7)$$

Thus the denominator in Eq. (4) cancels out, and we remain with the expression

$$-L(\nu)=\lim_{\Lambda\to\infty}\left[\int_0^{\Lambda}S_\nu(Z,F)d\lambda-S(\nu)\ln\Lambda\right] , \qquad (8)$$

where $S_\nu(Z,F)$ and $S(\nu)$ are the sums

$$S_\nu(Z,F)=\sum_n\langle 0\,|\,Z\,|\,n\rangle(E_n-E_0)^{\nu+1}\langle n\,|\,F\,|\,0\rangle , \qquad (9)$$

$$S(\nu)=\sum_n|\langle 0\,|\,Z\,|\,n\rangle|^2(E_n-E_0)^{\nu+1} . \qquad (10)$$

Closed expressions for these sums are derived in the Appendix by making use of closure relation. Thus the analytical evaluation of our sums $L(\nu)$ has been reduced to the calculation of the operator F with the help of Eq. (6) and a simple integration over the parameter λ according to Eq. (8). Note that $S_{-1}(Z,F)$ in Eq. (8) at $\lambda=0$ yields the second-order energy shift of the Stark effect.[8]

Our next task is to calculate F. This will be done under the assumption that F depends only on the coordinates $\mathbf{r}_i$ of the electrons but not on the momenta. Thus we have $F=F(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;\lambda)$. By Eq. (6) it depends functionally on the ground-state wave function of the atom or ion in question and therefore has to be calculated separately for each case. We shall show that the F's of hydrogenlike ions and helium atoms are related by scaling to the F of hydrogen.

III. HYDROGEN

For hydrogen, Eq. (6) becomes

$$z\psi_0=-(\nabla^2F)\psi_0-2\nabla F\cdot\nabla\psi_0+\lambda F\psi_0 , \qquad (11)$$

where

$$\psi_0=e^{-x}/\sqrt{\pi} \qquad (12)$$

is the ground-state wave function of hydrogen. As $\nabla\psi_0=-\psi_0\hat{r}$, the above equation becomes

$$-\nabla^2F+2\frac{\partial F}{\partial x}+\lambda F=z . \qquad (13)$$

We now introduce the function g by

$$F=g(x,\lambda)z . \qquad (14)$$

Then $\partial F/\partial x=(g'+g/x)z$ and $\nabla^2F=(\nabla^2g)z+2g'z/x$. We thus obtain a separation of variables with a radial equation for g given by

$$xg''+(4-2x)g'-(2+\lambda x)g=-x . \qquad (15)$$

To solve this equation it is advantageous to make the substitution

$$g=e^{-(t-1)x}u(x,\lambda) , \qquad (16)$$

where $t=\sqrt{1+\lambda}$. The function u is then a solution of the equation

$$xu''+(4-2tx)u'-(4t-2)u=-xe^{(t-1)x} . \qquad (17)$$

The solution of this equation is readily achieved by the well-known method of variation of parameters.[9] We get

$$u(x,\lambda)=u_1\int_0^x\frac{u_2(x')}{W(u_1,u_2)}e^{(t-1)x'}dx'-u_2\int_0^x\frac{u_1(x')}{W(u_1,u_2)}e^{(t-1)x'}dx'+Au_1+Bu_2 . \qquad (18)$$

Here the two functions u_1 and u_2 are the fundamental solutions of the homogeneous equation and $W=u_1u_2'-u_1'u_2$ is the Wronskian. The two constants A and B will be determined by conditions of finiteness. Now the two independent solutions of the homogeneous equation, which is called the Kummer equation,[10] are the regular solution

$$u_1(x)={}_1F_1(2-1/t;4;2tx) , \qquad (19)$$

where ${}_1F_1(a;b;x)$ is the confluent hypergeometric function, and the irregular solution

$$u_2(x)=U(2-1/t;4;2tx) . \qquad (19')$$

The explicit expressions of these two functions are given in the literature.[10] The Wronskian is calculated by the Abel identity[11]

$$W=\alpha\exp\left[-\int_0^x\frac{4-2tx'}{x'}dx'\right]=\alpha e^{2tx}/x^4 . \qquad (20)$$

The value of α is determined by u_1 and u_2 at the origin.

We have[12] $u_1(0)=1$, $u_1'(0)=t-\frac{1}{2}$, and

$$u_2(0)\to\frac{1}{4t^3\Gamma(2-1/t)}\frac{1}{x^3}\ . \tag{21}$$

Hence, for $x\to 0$,

$$W(x)\to-\frac{3}{4t^3\Gamma(2-1/t)}\frac{1}{x^4}\ , \tag{22}$$

which gives

$$\alpha=-\frac{3}{4t^3\Gamma(2-1/t)}\ . \tag{23}$$

So at this stage our function $u(x,\lambda)$ is

$$\begin{aligned}\frac{3u(x,\lambda)}{4t^3\Gamma(2-1/t)}=&-{}_1F_1(2-1/t;4;2tx)\int_0^x U(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'\\&+U(2-1/t;4;2tx)\int_0^x {}_1F_1(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'\\&+A\,{}_1F_1(2-1/t;4;2tx)+BU(2-1/t;4;2tx)\ .\end{aligned} \tag{24}$$

To complete the derivation of $u(x,\lambda)$ the two coefficients A and B have to be determined. We do this by imposing the conditions that $g(x,\lambda)$ would be finite in the physical regions of x and that at infinity it would not diverge exponentially. These conditions follow from the fact that the operator F is closely connected with perturbation theory, and if these conditions are not met, nonphysical solutions will be obtained. At $x=0$ we have according to Eqs. (21) and (19′), $U\to x^{-3}$. Now the integral which multiplies U in Eq. (24) behaves like x^5, thus this term vanishes when $x\to 0$. Therefore, if $B\neq 0$, we have $g\to x^{-3}$. It follows that we must have $B=0$. The coefficient A is determined by the behavior of g at $x\to\infty$. The function ${}_1F_1$ behaves like $\exp(2tx)$ at infinity;[12] the integral which multiplies ${}_1F_1$ assumes some finite value. Thus $g\to\exp[(t+1)x]$ which is untenable because of the above-mentioned conditions. In the context of the present paper it would mean that the expressions of the four sums $L(\nu)$ diverge. To solve this problem we must demand that the function which multiples ${}_1F_1$ in Eq. (24),

$$-\int_0^x U(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'+A\ , \tag{25}$$

vanishes at infinity. Hence we get

$$A=\int_0^\infty U(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'\ . \tag{26}$$

It is then easily verified that g does not diverge exponentially at infinity. This follows from Eq. (16) and the fact that U decreases at infinity. Consequently, our function $u(x,\lambda)$ is given by

$$\begin{aligned}\frac{3u(x,\lambda)}{4t^3\Gamma(2-1/t)}=&\,{}_1F_1(2-1/t;4;2tx)F_1(x)\\&+U(2-1/t;4;2tx)F_2(x)\ ,\end{aligned} \tag{27}$$

where

$$F_1(x)=\int_x^\infty U(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'\ , \tag{27$'$}$$

$$F_2(x)=\int_0^x {}_1F_1(2-1/t;4;2tx')e^{-(t+1)x'}(x')^4\,dx'\ . \tag{27$''$}$$

From this expression we obtain immediately the value of u at $x=0$,

$$\begin{aligned}u(0,\lambda)=\tfrac{4}{3}t^3\Gamma(2-1/t)\int_0^\infty &U(2-1/t;4;2tx')\\&\times e^{-(t+1)x'}(x')^4\,dx'\ .\end{aligned} \tag{28}$$

This Laplace transform is given in the literature.[13] We get

$$u(0,\lambda)=\frac{{}_2F_1(5,2;4-1/t;\frac{1}{2}(1-1/t))}{(2t-1)(3t-1)}\ , \tag{29}$$

where ${}_2F_1(a,b;c;x)$ is the hypergeometric function.

From Eq. (27) it is obvious that u can be represented by a power series with an infinite radius of convergence

$$u(x,\lambda)=\sum_{l=0}^{\infty}a_l(\lambda)x^l\ . \tag{30}$$

It is of course possible to calculate the expansion coefficients a_l directly from Eq. (27). However, it is easier to derive a recursion formula by making use of the differential equation of u, Eq. (17). It is a straightforward matter to show that the coefficients a_l are determined by the two-term recursion formula

$$a_{l+1}-\alpha_l a_l=\beta_l\ , \tag{31}$$

where

$$\alpha_l=2\frac{(l+2)t-1}{(l+1)(l+4)}\ , \tag{31$'$}$$

$$\beta_l=-\frac{(t-1)^{l-1}}{(l+1)(l+4)(l-1)!} \tag{31$''$}$$

with $\beta_0=0$. Thus all the a_l's are expressible in terms of a_0 which is given by Eq. (29). That Eq. (17) gives rise to a two-term recursion formula follows from a theorem by Sommerfeld.[14] The equation of g, Eq. (15), on the other hand, yields a three-term recursion formula which, of course, is much more difficult to handle.

The above recursion formula has been solved by mathematical induction and simple algebra. We get

$$a_l=\left[{}_2F_1(5,2;4-1/t;\tfrac{1}{2}(1-1/t))\right.$$
$$\left.-\sum_{k=0}^{l-3}\frac{(5)_k(2)_k}{(4-1/t)_k}\frac{[\tfrac{1}{2}(1-1/t)]^k}{k!}\right]$$
$$\times\frac{(2t)^l(2-1/t)_l}{(2t-1)(3t-1)(4)_l l!}-\frac{(t-1)^{l-2}}{l(l+3)(l-2)!}\,, \tag{32}$$

where Pochhammer's symbols $(b)_l=\Gamma(b+l)/\Gamma(b)$. By making use of the Gauss series

$${}_2F_1(5,2;4-1/t;\tfrac{1}{2}(1-1/t))=\sum_{k=0}^{\infty}\frac{(5)_k(2)_k}{(4-1/t)_k k!}\times[\tfrac{1}{2}(1-1/t)]^k$$

and some simple algebraic manipulations, the above expression reduces to

$$a_l=\frac{(t-1)^{l-1}}{(2t)l!}\sum_{j=0}^{\infty}[\tfrac{1}{2}(1-1/t)]^j(l+j)\times\frac{\Gamma(l+j+4)\Gamma(l+2-1/t)}{\Gamma(l+j+3-1/t)\Gamma(l+4)}\,. \tag{32$'$}$$

Finally, this can be expressed in terms of two hypergeometric functions,

$$a_l=\frac{(t-1)^{l-1}}{[2t(l+2-1/t)]l!}\left[l\,{}_2F_1(1,l+4;l+3-1/t;\tfrac{1}{2}(1-1/t))\right.$$
$$\left.+\frac{(t-1)(l+4)}{2t(l+3-1/t)}\,{}_2F_1(2,l+5;l+4-1/t;\tfrac{1}{2}(1-1/t))\right]\,. \tag{32$''$}$$

It is possible to sum the infinite series of u, Eq. (30). To accomplish this use is made of the integral representation[15] of ${}_2F_1$,

$${}_2F_1(a,b;c;z)=\frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)}\int_0^1 x^{b-1}(1-x)^{c-b-1}(1-xz)^{-a}dx\,, \tag{33}$$

which is valid for $c>b>0$. The hypergeometric functions in Eq. (32″) do not satisfy these conditions. We therefore change these functions into functions which satisfy these conditions by applying the linear transformation[16]

$${}_2F_1(a,b;c;z)=(1-z)^{-b}{}_2F_1(b,c-a;c;z/(z-1))\,. \tag{34}$$

We then get for a_l

$$a_l=\left[\frac{t-1}{t+1}\right]^{l-1}\frac{(2t)^{l+3}}{(t+1)^5}\frac{1}{l!}\left[l\int_0^1 x^{(l+1)/t}\left[1+\frac{t-1}{t+1}x\right]^{-(l+4)}dx\right.$$
$$\left.+(l+4)\frac{t-1}{t+1}\int_0^1 x^{(l+1)/t}(1-x)\left[1+\frac{t-1}{t+1}x\right]^{-(l+5)}dx\right]\,. \tag{32$'''$}$$

It is now evident that the series of Eq. (30) can indeed be summed. We find

$$u(x,t)=\frac{(2t)^3}{(t+1)^5}\int_0^1\frac{y^{1-1/t}}{\left[1+\frac{t-1}{t+1}y\right]^5}\times\left[\frac{2tx}{t-1}f(y)+4(1-y)\right]e^{xf(y)}dy \tag{35}$$

with

$$f(y)=\frac{2t(t-1)y}{t+1+(t-1)y}\,. \tag{35$'$}$$

It is easily verified that this expression yields the correct results for the following special cases.

(i) $x=0$, by Eqs. (33) and (34), we get back for $u(0,t)$ the expression of Eq. (29).

(ii) $t=1$, we get $u(x,1)=(1+x/2)/2$, which is a solution of Eq. (17) as can be shown by substitution. It corresponds to the Stark effect and is given in the literature.[8]

Finally, we derive the behavior of g for $x\to\infty$. This is easily carried out by starting from the above expression for u [one gets the same result by starting from Eq. (27), but the calculation is much more involved] and making a change of variable from y to $z=f(y)$. The required result is then obtained by repeated integration by parts. Keeping only the first two terms, we get

$$u(x,\lambda)=\frac{1}{\lambda}\left[1-\frac{2}{\lambda x}+O((\lambda x)^{-2})\right]e^{(t-1)x} \tag{36}$$

or

$$g(x,\lambda)=\frac{1}{\lambda}\left[1-\frac{2}{\lambda x}+O((\lambda x)^{-2})\right]. \tag{36'}$$

Now that we have completely explored the function g, we are ready to calculate the sums $L(\nu)$.

A. Total cross section ($\nu=-1$)

According to Eqs. (8) and (9), the relevant expectation value is given by

$$S_{-1}(z,F)=\sum_{n}\langle 0|z|n\rangle\langle n|F|0\rangle=\langle 0|zF|0\rangle . \tag{37}$$

Changing from F to g by Eq. (14) and introducing the ground-state wave function of hydrogen, Eq. (12), this becomes

$$S_{-1}(z,F)=\tfrac{4}{3}\int_0^\infty g(x,\lambda)e^{-2x}x^4\,dx . \tag{37'}$$

There are a number of ways to calculate this expectation value. One possibility, which we expected to be the most promising, was to use the method of Padé approximants. In this approach one approximates the function g by successive ratios of two polynomials of order n. In first order one puts

$$g(x,\lambda)=\frac{p_0+p_1x}{1+q_1x} . \tag{38}$$

The λ dependence of p_0,p_1 is uniquely determined by the first two terms in the expansion of g, and we have the additional requirement $p_1/q_1=1/\lambda$, according to Eq. (36'). The analytical evaluation of S_{-1} is immediate, and the integration over λ of Eq. (8) was done numerically. We obtained $[L(-1)]_1=0.0487$. Next, we applied the second order. In this case g is approximated by the ratio of two second-degree polynomials. We found $[L(-1)]_2=-0.091$. Although the numerical results seemed to approach the exact value quite rapidly, we decided to abandon the Padé approach simply because the evaluation of the p_i and q_i as a function of λ for the third- and higher-order approximants became forbiddingly complicated.

The direct approach is much more effective. Starting from the integral representation of $u(x,\lambda)$, Eq. (35), the integral of Eq. (37') is immediate, which leaves us with an integral over the variable y. This turns out to be the integral representation of two hypergeometric functions. We thus obtain

$$S_{-1}(z,F)=\frac{128}{3-1/t}\frac{(2t)^3}{(t+1)^{12}}\left[5t^2\,{}_2F_1(6,3-1/t;4-1/t;[(t-1)/(t+1)]^2)\right.$$
$$\left.+\frac{(t+1)^2}{2-1/t}\,{}_2F_1(5,2-1/t;4-1/t;[(t-1)/(t+1)]^2)\right] . \tag{39}$$

$L(-1)$ is then obtained by Eq. (8) from the expression

$$-L(-1)=2\int_1^{\sqrt{2}}S_{-1}t\,dt+2\int_{\sqrt{2}}^{\infty}\left[S_{-1}-\frac{1}{t^2-1}\right]t\,dt , \tag{40}$$

because $S(-1)=1$ for hydrogen. We have not pursued this approach because for the other three cases, $\nu=0,1,2$, the matrix elements S_ν turn out to be more complicated than Eq. (39), and the approach below is more suitable for computational purposes. For $\nu=-1$ we got the very good result $\ln I(-1)=-0.073\,238$.

A closely related approach to the above, which we adopted in the end, is as follows. Start with the function g,

$$g(x,\lambda)=e^{-(t-1)x}\left[\sum_{l=0}^{\infty}a_lx^l-\frac{1}{\lambda}e^{(t-1)x}\right]+\frac{1}{\lambda} , \tag{41}$$

where we purposely separated the behavior of g at infinity. Expanding the exponential function in the parenthesis and integrating over x according to Eq. (37'), we get

$$S_{-1}(z,F)=\tfrac{4}{3}\sum_{l=0}^{\infty}\mathscr{L}_{l,4}^{(1)}+\frac{1}{\lambda} , \tag{42}$$

where we have introduced the quantity

$$\mathscr{L}_{l,\kappa}^{(1)}=(l+\kappa)!\left[a_l-\frac{(t-1)^l}{l!(t^2-1)}\right]\frac{1}{(t+1)^{l+\kappa+1}} . \tag{43}$$

We also introduce the related quantity

TABLE I. $\ln I(\nu)$ for hydrogen, taking into account only the first term of the asymptotic expansion of g.

ν	l	$[\ln I(\nu)]_l$	R	$\ln I(\nu)$	Direct numerical calculation	$10^3\Delta_\nu$
-1	26	$-0.079\,45$	0.0046	$-0.074\,85$	$-0.073\,253$	1.597
0	26	$0.091\,86$	0.0038	0.09566	0.0970	1.34
1	26	0.5681	0.0022	0.5703	0.5709	0.6
2	26	2.9870	-0.0020	2.9850	2.9850	<-0.1

TABLE II. ln$I(\nu)$ for hydrogen, taking also into account the second term of the asymptotic expansion of g.

ν	l	ln$I(\nu)$ (present work)	ln$I(\nu)$ (Ref. 5)	Direct numerical calculation	$10^4\Delta_\nu$
-1	26	$-0.073\,17$	$<-0.073\,05$ $>-0.073\,41$	$-0.073\,253$	-0.83
0	20	$0.097\,10$	<0.0981 >0.0956	0.0970	-1.0
1	20	$0.570\,94$	<0.5910 >0.5490	0.5709	-0.40
2	20	2.9841	$>2.409\,38$	2.9850	9.0

$$\mathscr{L}^{(2)}_{l,\kappa}=\mathscr{L}^{(1)}_{l,\kappa}+2[(l+\kappa-1)!]\frac{(t-1)^{l-1}}{l!(t^2-1)(t+1)^{l+\kappa+1}} \; . \tag{43'}$$

All the expectation values $S_\nu(z,F)$ and sums $L(\nu)$ can be written in terms of these two expressions. In the integration over t of Eq. (42) the divergence at infinity cancels in the $l=0$ term. We find

$$[-L(-1)]_0=64\int_1^\infty \frac{a_0}{(t+1)^5}t\,dt+\tfrac{113}{60}-\ln 4 \; , \tag{44}$$

and for $l\geq 1$,

$$[-L(-1)]_l=\tfrac{8}{3}\int_1^\infty \mathscr{L}^{(1)}_{l,4}t\,dt \; . \tag{44'}$$

The numerical result is given in Table I. We see that for less than 30 terms one gets an error of about 2%. It is possible to improve the convergence of the series by adding the second term of the asymptotic expansion of g, Eq. (36'). We thus write, instead of Eq. (41),

$$g(x,\lambda)=e^{-(t-1)x}\left[\sum_{l=0}^\infty a_l x^l-\left[\frac{1}{\lambda}-\frac{2}{x\lambda^2}\right]e^{(t-1)x}\right]+\frac{1}{\lambda}-\frac{2}{x\lambda^2} \; . \tag{45}$$

We then find that the sum of the first two terms of $L(-1)$ is given by

$$[-L(-1)]_0+[-L(-1)]_1=\tfrac{8}{3}\int_1^\infty\left[\frac{24a_0}{(t+1)^5}+\mathscr{L}^{(1)}_{1,4}\right]t\,dt+\tfrac{21}{20}-\ln 4 \; , \tag{46}$$

and for $l\geq 2$, we get the

$$[-L(-1)]_l=\tfrac{8}{3}\int_1^\infty \mathscr{L}^{(2)}_{l,4}t\,dt \; . \tag{46'}$$

The numerical result which follows from these expressions is given in Table II. We see that for the same number of terms the computational error has been reduced from about 2% to about 0.1%. It is obvious that the precision can be further improved by several orders of magnitude simply by increasing the number of terms to be summed.

B. Stopping power ($\nu=0$)

The relevant expectation value in this case is

$$S_0(z,F)=\sum_n \langle 0\,|\,z\,|\,n\,\rangle(E_n-E_0)\langle n\,|\,F\,|\,0\rangle \; , \tag{47}$$

which according to Eq. (A7) is given by

$$S_0=\langle 0\,|\,(\nabla z\cdot\nabla F)\,|\,0\rangle \; . \tag{47'}$$

In terms of the function g, this becomes

$$S_0=\tfrac{8}{3}\int_0^\infty g(x,\lambda)e^{-2x}x^3\,dx \; . \tag{47''}$$

Also, in this case we tried first the Padé approximants. In first order we obtained $[L(0)]_1=0.2054$ and for the second order we got $[L(0)]_2=0.0850$. In spite of these encouraging results, here, too, for the same reasons as in the total cross-section case, we abandoned the Padé approach because of the complication in calculating the polynomial functions of λ for the higher-order approximants.

In order to calculate the value of $L(0)$ we used the direct approach, in complete analogy to the case of the total cross section. Starting from the expression Eq. (41) for g, the above expectation value S_0 becomes

$$S_0(z,F)=\tfrac{8}{3}\sum_{l=0}^\infty \mathscr{L}^{(1)}_{l,3}+\frac{1}{\lambda} \; . \tag{48}$$

The contribution of the $l=0$ term to $L(0)$ turns out to be

$$[-L(0)]_0=32\int_1^\infty \frac{a_0}{(t+1)^4}t\,dt+\tfrac{19}{12}-\ln 4 \; , \tag{49}$$

and the contributions of the $l\geq 1$ terms are

$$[-L(0)]_l=\tfrac{16}{3}\int_1^\infty \mathscr{L}^{(1)}_{l,3}t\,dt \; . \tag{49'}$$

In the derivation of Eq. (49) use was made of the fact that $S(0)=1$. This follows from its definition, Eq. (10) in conjunction with Eqs. (9) and (47'). Adding the second term of the asymptotic expansion of g, the value of $L(0)$ is determined by

$$[-L(0)]_0+[-L(0)]_1=\tfrac{16}{3}\int_1^\infty\left[\frac{6a_0}{(t+1)^4}+\mathscr{L}^{(1)}_{1,3}\right]t\,dt+\tfrac{47}{60}-\ln 4 \; , \tag{50}$$

for the $l=0,1$ terms, and for the $l \geq 2$ terms we get

$$[-L(0)]_l = \tfrac{16}{3} \int_1^\infty \mathscr{L}_{l,3}^{(2)} t\, dt \ . \tag{50$'$}$$

C. Straggling effect ($\nu=1$)

In this case the expectation value

$$S_1(z,F) = \sum_n \langle 0 | z | n \rangle (E_n - E_0)^2 \langle n | F | 0 \rangle \tag{51}$$

is, according to Eq. (A8), given by

$$S_1 = -2\langle 0 | \nabla \cdot \nabla z)(\nabla^2 F - 2\nabla F \cdot \nabla | 0 \rangle \ , \tag{51$'$}$$

which in terms of g becomes

$$S_1 = \tfrac{16}{3} \int_0^\infty g(x,\lambda) e^{-2x} x\, dx \ . \tag{51$''$}$$

Making use of Eqs. (41) and (43), we obtain

$$S_1 = \tfrac{16}{3} \sum_{l=0}^{\infty} \mathscr{L}_{l,1}^{(1)} + \frac{4}{3\lambda} \ . \tag{51$'''$}$$

Integration over t yields for the $l=0$ term

$$[-L(1)]_0 = \tfrac{32}{3} \int_1^\infty \frac{a_0}{(t+1)^2} t\, dt + \tfrac{2}{3} - \tfrac{4}{3} \ln 4 \ , \tag{52}$$

and for $l \geq 1$ terms

$$[-L(1)]_l = \tfrac{32}{3} \int_1^\infty \mathscr{L}_{l,1}^{(1)} t\, dt \ . \tag{52$'$}$$

In the derivation of Eq. (52) use was made of the fact that $S(1) = \frac{4}{3}$. This is most easily obtained from Eq. (51$''$) by putting $g \equiv 1$ [see Eqs. (10) and (9)]. Adding the second term of the asymptotic expansion of g, we get for the sum of the first two terms

$$[-L(1)]_0 + [-L(1)]_1$$
$$= \tfrac{32}{3} \int_1^\infty \left[\frac{a_0}{(t+1)^2} + \mathscr{L}_{1,1}^{(1)} \right] t\, dt - \tfrac{2}{9} - \tfrac{4}{3} \ln 4 \ , \tag{53}$$

and for the $l \geq 2$ terms we get

$$[-L(1)]_l = \tfrac{32}{3} \int_1^\infty \mathscr{L}_{l,1}^{(2)} t\, dt \ . \tag{53$'$}$$

D. Lamb shift ($\nu=2$)

For the Lamb shift of the ground state the expectation value

$$S_2(z,F) = \sum_n \langle 0 | z | n \rangle (E_n - E_0)^3 \langle n | F | 0 \rangle \tag{54}$$

is, according to Eq. (A9),

$$S_2 = -4\langle 0 | \partial V / \partial z (\nabla^2 F + 2\nabla F \cdot \nabla) | 0 \rangle \ , \tag{54$'$}$$

$V = -1/r$ being the electron-nucleus interaction. S_2 becomes in terms of g

$$S_2 = 16 g(0,\lambda) - \tfrac{64}{3} \int_0^\infty g(x,\lambda) e^{-2x} dx \ . \tag{54$''$}$$

By Eqs. (41) and (43) we obtain

$$S_2 = 16 a_0 - \tfrac{64}{3} \sum_{l=0}^{\infty} \mathscr{L}_{l,0}^{(1)} - \frac{32}{3\lambda} \ . \tag{54$'''$}$$

In the derivation of the contribution of S_2 to the $l=0$ term of $L(2)$, one has to take into consideration two results. (i) $g(0,\lambda) = a_0$ behaves like $1/\lambda$ when $\lambda \to \infty$. This can be derived either from Eq. (32) together with the relation ${}_2F_1(2,5;4;\frac{1}{2}) = 6$, or, from the integral representation of $u(x,\lambda)$, Eq. (35) with $x=0$. (ii) $S(2) = \frac{16}{3}$ obtained from Eq. (54$''$) by putting $g=1$, which is a direct consequence of the definitions, Eq. (10) and (9) of S_2 and $S(2)$.

We then obtain

$$[-L(2)]_0 = 32 \int_1^{\sqrt{2}} a_0 t\, dt + 32 \int_{\sqrt{2}}^\infty \left[a_0 - \frac{1}{t^2-1} \right] t\, dt$$
$$- \tfrac{128}{3} \int_1^\infty \frac{a_0}{t+1} t\, dt + \tfrac{32}{3}(1 + \ln 4) \ , \tag{55}$$

and for the $l \geq 1$ terms we get

$$[-L(2)]_l = -\tfrac{128}{3} \int_1^\infty \mathscr{L}_{l,0}^{(1)} t\, dt \ . \tag{55$'$}$$

Adding the second term of the asymptotic expansion of g, we get, for the sum of the first two terms,

$$[-L(2)]_0 + [-L(2)]_1$$
$$= 32 \int_1^{\sqrt{2}} a_0 t\, dt + 32 \int_{\sqrt{2}}^\infty \left[a_0 - \frac{1}{t^2-1} \right] t\, dt$$
$$- \tfrac{128}{3} \int_1^\infty \left[\frac{a_0}{t+1} + \mathscr{L}_{1,0}^{(1)} \right] t\, dt + \tfrac{32}{3}(\tfrac{3}{2} + \ln 4) \ , \tag{56}$$

and for the $l \geq 2$ terms we get

$$[-L(2)]_l = -\tfrac{128}{3} \int_1^\infty \mathscr{L}_{l,0}^{(2)} t\, dt \ . \tag{56$'$}$$

All the results of this section are summarized in Tables I and II. In Table I are listed our results for $\ln I(\nu)$, taking into account only the first term $1/\lambda$ of the asymptotic expansion of g. They are based on the four expressions, Eqs. (44) and (44$'$), (49) and (49$'$), (52) and (52$'$), (55) and (55$'$) for $\nu = -1$, 0, 1, and 2, respectively. l is the number of terms taken. In the fourth column are listed our values of the remainder R, which are easy to estimate because for larger values of l the series become more and more geometrical in nature. In the next to the last column are given the exact values of $\ln I(\nu)$, which were obtained by direct numerical calculation; this, of course, is possible only for hydrogen. In the last column are given the differences Δ_ν between the exact and the calculated values. Taking into account also the second term, $(-2/x\lambda^2)$, of the asymptotic expansion of g, one gets the results listed in Table II. They are based on the expressions, Eqs. (46) and (46$'$), (50) and (50$'$), (53) and (53$'$), (56) and (56$'$), for $\nu = -1$, 0, 1, and 2, respectively. There is an improvement of between 1 and 2 orders of magnitude. In the same table are also listed the results of Shimamura and Inokuti[5] who have calculated upper and lower bounds. We should point out that the results of the present paper also are actually upper and lower bounds. In Table I our values for $\nu = -1$, 0, and 1 are lower bounds, and for $\nu=2$, it is an upper bound; in Table II the reverse is true. This is not fortuitous. It follows directly from the structure of the above-mentioned mathematical expressions. Our results could be further improved by taking into consideration the next term of the asymptotic expansion of g, or simply by increasing the number of terms, or both. Our present results in Table II are much better than the results of Ref. 5. In particular, for the Lamb shift, the difference between the exact value and our value is $\Delta_2=0.0009$, whereas the corresponding value of Ref. 5 is $\Delta_2=0.5756$. Furthermore, our upper bound for the Lamb shift is off by less than 10^{-4} (see Table I), whereas there is no way to evaluate it by the method of Ref. 5. An alternative way to weigh the two methods against each other is to compare the upper-lower bounds differences. By this measure, the results for total cross section of Ref. 5 is superior to the present one, whereas for the $\nu=0$ and 1 cases the results of the present work are more accurate. For the Lamb shift this comparison becomes meaningless because, as previously mentioned, there exists no upper bound in the method of Ref. 5.

IV. HYDROGENLIKE IONS

It is a straightforward matter to derive the sum rules of one-electron ions in terms of hydrogen sum rules. The simplest approach is dictated by the recognition that the excitation energies are equal to Z^2 times the excitation energies of hydrogen and the matrix elements $\langle 0\,|\,Z\,|\,n\,\rangle$ are equal to those of hydrogen divided by Z. Here Z is the charge of the nucleus. An alternative, more complicated approach is to derive the function g, for $Z\neq 1$. We shall pursue the second approach because it will be useful later for the evaluation of the sum rules for helium.

The ground-state wave function is

$$\psi_0=\frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zx} . \tag{57}$$

With this function Eq. (11) reduces to the radial equation

$$xg''+(4-2Zx)g'-(2Z+\lambda x)g=-x , \tag{58}$$

which, of course, is identical with Eq. (15) when $Z=1$. Introducing the variables $x'=Zx$ and $\lambda'=\lambda/Z^2$, the above equation assumes the form

$$x'(Z^2g'')+(4-2x')(Z^2g')-(2+\lambda'x')(Z^2g)=-x' , \tag{58$'$}$$

where the derivatives are with respect to x'. It follows that

$$g(x,\lambda;Z)=\frac{1}{Z^2}g(x',\lambda';1) . \tag{59}$$

This relationship, together with the remarks at the beginning of this section, lead to the conclusion that the expectation values S_ν and $S(\nu)$ of Eqs. (9) and (10) are

$$S_\nu=Z^{2(\nu-1)}[S_\nu(\lambda')]_{\rm H} , \tag{60}$$

$$S(\nu)=Z^{2\nu}[S(\nu)]_{\rm H} . \tag{60$'$}$$

The subscript H stands for hydrogen. With these relationships in mind, we can immediately derive the expressions of $L(\nu)$. Starting from Eq. (8) we get

$$-L(\nu)=Z^{2\nu}\lim_{\Lambda'=\infty}\left\{\int_0^{\Lambda'}[S_\nu(\lambda')]_{\rm H}\,d\lambda' - [S(\nu)]_{\rm H}\ln(\Lambda'Z^2)\right\} , \tag{61}$$

which becomes

$$L(\nu)=Z^{2\nu}\{[L(\nu)]_{\rm H}+[S(\nu)]_{\rm H}\ln Z^2\} . \tag{61$'$}$$

Thus the mean excitation energies $I(\nu)$ are given by

$$\ln I(\nu)=\ln\{[I(\nu)]_{\rm H}Z^2\} . \tag{62}$$

V. HELIUM

For helium the function F is, according to Eq. (6), the solution of the equation

$$(z_1+z_2)\psi_0=[H_0,F]\psi_0+\lambda F\psi_0 , \tag{63}$$

which explicitly is of the form

$$(z_1+z_2)\psi_0=-[(\nabla_1^2+\nabla_2^2)F]\psi_0-2\nabla_1F\cdot\nabla_1\psi_0 -2\nabla_2F\cdot\nabla_2\psi_0+\lambda F\psi_0 . \tag{63$'$}$$

In the present work we will consider ground-state wave functions of the Hartree-Fock type only. Thus we put

$$\Psi_0(1,2)=\psi(1)\psi(2) . \tag{64}$$

The above equation then becomes, after dividing by the wave function,

$$z_1+z_2=-\nabla_1^2F-\nabla_2^2F-2\nabla_1F\cdot[\nabla_1\psi(1)]/\psi(1) -2\nabla_2F\cdot[\nabla_2\psi(2)]/\psi(2)+\lambda F . \tag{65}$$

It follows that if we put

$$F(1,2)=F(1)+F(2) , \tag{66}$$

then $F(1)$ and $F(2)$ satisfy the one-particle equation

$$\nabla^2F+2\nabla F\cdot\frac{\nabla\psi}{\psi}-\lambda F=-z , \tag{67}$$

which is identical with the hydrogen equation, Eq. (11). As ψ is spherically symmetric, this becomes

$$\nabla^2F+2\left[\frac{\psi'}{\psi}\right]\frac{\partial F}{\partial r}-\lambda F=-z . \tag{67$'$}$$

Introducing, as before, the function g by $F=gz$, we get a radial equation for g of the form

$$xg''+\left[4+2x\frac{\psi'}{\psi}\right]g'-\left[-2\frac{\psi'}{\psi}+\lambda x\right]g=-x . \tag{68}$$

The function g, and therefore the sum rules, depend functionally on the logarithmic derivative of the one-particle wave function ψ. We have considered three different wave functions.

(i) The simplest possible function is given by[17]

$$\psi_{\rm I}=\frac{\bar{Z}^{3/2}}{\sqrt{\pi}}e^{-\bar{Z}x} , \tag{69}$$

where $\bar{Z}$ is the nuclear effective charge $\bar{Z}=Z-\frac{5}{16}$ for any two-electron atom. Thus for helium, $\overline{Z}=\frac{27}{16}$.

(ii) Wave functions which consist of two basic functions:

$$\psi=\frac{N}{\sqrt{\pi}}(e^{-Z_1x}+\alpha e^{-Z_2x}) . \tag{70}$$

There are two sets of parameters quoted in the literature:[18]

$$\text{(II)}\ Z_1=1.4558,\ Z_2=2.9116,\ \alpha=0.6 , \tag{70$'$}$$

$$\text{(III)}\ Z_1=1.41,\ Z_2=2.61,\ \alpha=0.799 . \tag{70$''$}$$

ψ_{II} is the variational wave function calculated by Löwdin[19] and is a fairly good analytical fit to the Hartree-Fock function. ψ_{III} is a very accurate fit to the Hartree-Fock wave function of Roothaan *et al.*[20] One possible test to estimate the quality of the above three functions is to compare their ionization potentials I. We have found the following values (in Ry): $I_{\text{I}}=1.695\,312$, $I_{\text{II}}=1.719\,050$, $I_{\text{III}}=1.767\,636$. There is also a more elaborate wave function, consisting of five basic functions, known in the literature.[21] The corresponding ionization potential is $I_c=1.723\,360$. It thus seems that, from the energy point of view, ψ_{III} is the "best" wave function in the framework of the Hartree-Fock-type approximation.

Now, the function $(-\psi'/\psi)=\overline{Z}(x)$ is a smooth, slowly varying function of x, and for the wave function ψ_{I} it is exactly equal to the nuclear effective charge. Thus $\overline{Z}(x)$ may be considered to be the nuclear effective charge due to screening of one electron as a function of the distance of the other electron from the nucleus. For ψ_{I} the effective charge $\overline{Z}$ is constant, therefore the equation for g, Eq. (68), reduces to Eq. (58), the solution of which is given by Eq. (59). The equation for g, Eq. (68), cannot be solved analytically for the other two functions ψ_{II} and ψ_{III}. However, as $\overline{Z}(x)$ is slowly varying, we have adopted the following parametrization procedure: First we solve Eq. (68) assuming a definite value for $\overline{Z}$, and then we take the average of the sum rules $L(\nu)$, weighted according to the probability of finding the electron at a distance x from the nucleus. In short, the mean excitation energies $I(\nu)$ were calculated with the help of the expression

$$\ln I(\nu)=\int_0^\infty P(x)\ln I(\nu,\overline{Z}(x))dx , \tag{71}$$

where

$$P(x)=4\pi x^2\psi^2(x) . \tag{71$'$}$$

In connection with this procedure it is worthwhile pointing out that one obtains essentially the same results if one calculates $\ln I(\nu)$ at the expectation value of $\overline{Z}(x)$, given by $\langle\psi\,|\,\overline{Z}(x)\,|\,\psi\rangle$.

Finally, we discuss the expectation values S_ν and $S(\nu)$ for helium. We will show that for wave functions which are products of one-electron functions, the expectation values factorize into sums of one-particle expectation values. Therefore the calculation of the sum rules follows along the same lines as for the hydrogen case. The expectation values $S(\nu)$ are obtained from S_ν by putting $g=1$. All the expectation values S_ν and $S(\nu)$ obtained below reduce to twice the corresponding expectation values of Sec. III for hydrogen if one substitutes the function of Eq. (12) for ψ. The function g which appears in the expressions of S_ν below is $g(x,\lambda;\overline{Z})$, the solution of Eq. (58′).

1. ν = −1

By Eq. (9) we have

$$S_{-1}=\langle 0\,|\,(z_1+z_2)(F_1+F_2)\,|\,0\rangle , \tag{72}$$

where we have put F_1 for $F(1)$ and F_2 for $F(2)$. The cross terms are equal to zero because $\langle 0\,|\,z\,|\,0\rangle=0$. Hence

$$S_{-1}=2\langle 0\,|\,zF\,|\,0\rangle , \tag{72$'$}$$

which becomes, after integrating over the angles,

$$S_{-1}=\frac{8\pi}{3}\int_0^\infty \psi^2 gx^4dx . \tag{72$''$}$$

2. ν = 0

By the results of the Appendix we have

$$\begin{aligned}S_0&=\langle 0\,|\,[(z_1+z_2),(p_1^2+p_2^2)](F_1+F_2)\,|\,0\rangle\\&=2i\langle 0\,|\,(p_{1z}+p_{2z})(F_1+F_2)\,|\,0\rangle .\end{aligned} \tag{73}$$

The cross terms are zero because $\langle 0\,|\,p_z\,|\,0\rangle=0$. Hence

$$S_0=4i\langle 0\,|\,p_zF\,|\,0\rangle ,$$

which becomes

$$S_0=2\langle 0\,|\,\nabla z\cdot\nabla F\,|\,0\rangle .$$

Now the scalar product is

$$\nabla z\cdot\nabla F=(xg)'\cos^2\theta+g\sin^2\theta .$$

Therefore

$$S_0\equiv\frac{8\pi}{3}\int_0^\infty[(xg)'+2g]\psi^2x^2dx , \tag{73$'$}$$

which becomes, after one integration by parts,

$$S_0=-\frac{16\pi}{3}\int_0^\infty \psi\psi' gx^3dx . \tag{73$''$}$$

Putting $g\equiv 1$, we get $S(0)=2$, true for any normalized wave function ψ. This is in accordance with the famous Thomas-Reiche-Kuhn sum rule.

3. ν = 1

By the result of the Appendix we have

$$\begin{aligned}S_1&=\langle 0\,|\,[(z_1+z_2),(p_1^2+p_2^2)][(p_1^2+p_2^2),(F_1+F_2)]\,|\,0\rangle\\&=-2i\langle 0\,|\,(p_{1z}+p_{2z})(\nabla_1^2F_1+2\nabla_1F_1\cdot\nabla_1+\nabla_2^2F_2\\&\qquad+2\nabla_2F_2\cdot\nabla_2)\,|\,0\rangle .\end{aligned} \tag{74}$$

For the same reason as above, the cross terms vanish and we remain with the expression

$$S_1=-4i\langle 0\,|\,p_z(\nabla^2F+2\nabla F\cdot\nabla)\,|\,0\rangle .$$

As

$$\nabla F\cdot\nabla\psi=(xg)'\psi'\cos\theta$$

and

$$\nabla^2 F=(4g'+xg'')\cos\theta ,$$

we get

$$S_1=\frac{16\pi}{3}\int_0^\infty \psi'[4g'\psi+xg''\psi+2(xg)'\psi']x^2dx . \qquad (74')$$

This expression, after two integrations by parts and some algebraic manipulations, assumes the form

$$S_1=\frac{16\pi}{3}\int_0^\infty [-(\psi^2)'+2x\phi+x^2\phi']gx\,dx , \qquad (74'')$$

where $\phi=\psi^2(\psi'/\psi)'$. Putting $g\equiv 1$, we obtain

$$S(1)=\frac{32\pi}{3}\int_0^\infty (\psi')^2x^2dx , \qquad (75)$$

as follows immediately from Eq. (74'), or from Eq. (74'') after some algebraic rearrangements. For wave functions given by Eq. (70), the function ϕ is of the form

$$\phi=\frac{N^2}{\pi}\alpha(Z_1-Z_2)^2e^{-(Z_1+Z_2)x} .$$

Of course, for hydrogenic wave functions, $\phi=0$.

4. $\nu=2$

By the results of the Appendix we have

$$\begin{aligned}S_2&=\langle 0\,|\,[[(p_1^2+p_2^2),(z_1+z_2)]^+,H]\\&\quad\times[(p_1^2+p_2^2),(F_1+F_2)]\,|\,0\rangle\\&=2i\langle 0\,|\,([p_{1z},V]+[p_{2z},V])\\&\quad\times([p_1^2,F_1]+[p_2^2,F_2])\,|\,0\rangle ,\end{aligned} \qquad (76)$$

where

$$V=V_1+V_2+V_{12} ,$$

V_1 and V_2 being the electron-nucleus interactions of the two electrons and V_{12} the electron-electron interaction. Now for any function V_{12} of r_{12}, we have

$$[p_{1z}+p_{2z},V_{12}]=0 ,$$

because $(p_{1z}+p_{2z})r_{12}=0$, which reflects the action-reaction principle. It follows that the electron-electron interaction does not contribute directly to S_2 (only indirectly through the wave function). Equation (76) thus becomes

$$\begin{aligned}S_2=-2(Ze^2)\left\langle 0\left|\left[\frac{z_1}{r_1^3}+\frac{z_2}{r_2^3}\right](\nabla_1^2F_1+2\nabla_1F_1\cdot\nabla_1+\nabla_2^2F_2\right.\right.\\ \left.\left.+2\nabla_2F_2\cdot\nabla_2)\right|0\right\rangle ,\end{aligned}$$

Ze being the charge of the nucleus. For the same reason as before the cross terms vanish. We thus end up with the expression

$$S_2=-8Z\langle 0\,|\,(z/r^3)(\nabla^2F+2\nabla F\cdot\nabla)\,|\,0\rangle . \qquad (76')$$

Substituting for ∇^2F and $\nabla F\cdot\nabla\psi$ the expressions given above, this becomes

$$S_2=-\frac{32\pi}{3}Z\int_0^\infty \psi[4g'\psi+xg''\psi+2(xg)'\psi']dx . \qquad (76'')$$

It is a simple matter to show by repeated integration by parts that this expression reduces to

$$S_2=\frac{32\pi}{3}Z\left[2\int_0^\infty (\psi^2)'g\,dx+3g(0,\lambda;\bar{Z})[\psi(0)]^2\right] . \qquad (76''')$$

Putting $g=1$, we obtain

$$S(2)=\frac{32\pi}{3}Z[\psi(0)]^2 . \qquad (77)$$

It is interesting to derive the general expression of $S(2)$ for any kind of wave function. Starting with Eq. (76) and putting $F_1=z_1$ and $F_2=z_2$, we get

$$S(2)=4\langle 0\,|\,[(p_{1z}+p_{2z}),V](p_{1z}+p_{2z})\,|\,0\rangle . \qquad (78)$$

The commutator is equal to $-i(\partial/\partial z_1+\partial/\partial z_2)V$, thus

$$S(2)=-4\left\langle 0\left|\left[\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]V\right]\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]\right|0\right\rangle ,$$

which becomes

$$S(2)=2\left\langle 0\left|\left[\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]^2V\right]\right|0\right\rangle .$$

As the electron-electron interaction does not contribute, we get

$$S(2)=2\left\langle 0\left|\left[\frac{\partial^2}{\partial z_1^2}V_1+\frac{\partial^2}{\partial z_2^2}V_2\right]\right|0\right\rangle ,$$

or, due to spherical symmetry of $|\,\Psi\rangle$,

$$S(2)=\frac{16\pi}{3}Z\langle 0\,|\,[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)]\,|\,0\rangle . \qquad (78')$$

For Hartree-Fock-type wave functions, this reduces to Eq. (77). This result is easily generalized for n-electron systems, giving

$$S(2)=\frac{16\pi}{3}Z\left\langle 0\left|\sum_{i=1}^{n}\delta(\mathbf{r}_i)\right|0\right\rangle . \qquad (79)$$

The sums $L(\nu)$ for helium were evaluated in the same fashion as the corresponding expressions for hydrogen after making use of the relation $g(x,\lambda;\bar{Z})=g(x',\lambda';1)/\bar{Z}^2$ of Eq. (59). Equation (45) was then applied for the expression of $g(x',\lambda';1)$. The expressions of $L(\nu)$ are rather long and cumbersome and therefore have not been reproduced here. For $\alpha=0$ [see Eq. (70)], or what amounts to the same, for the simple wave function Eq. (69), $L(\nu)$ becomes equal to the expression of Eq. (61') with Z replaced by $\bar{Z}$.

The sums $L(\nu)$ and $S(\nu)$ diverge for all $\nu=3,4,\ldots$. This follows from the fact that the oscillator strengths behave asymptotically[2] like $E^{-7/2}$. In the context of the technique outlined in the present paper this is reflected in

TABLE III. $\ln I(\nu)$ for helium. $\psi_{\rm I}$, $\psi_{\rm II}$, and $\psi_{\rm III}$ are the ground-state, one-particle wave functions given by Eqs. (69), (70), (70′), and (70″).

ν	l	$\ln I(\nu)$ ($\psi_{\rm I}$)	$\ln I(\nu)$ ($\psi_{\rm II}$)	$\ln I(\nu)$ ($\psi_{\rm III}$)	$\ln I(\nu)$ (Ref. 5)
-1	20	0.9732	0.9058	0.8988	<0.857 >0.855
0	20	1.1435	1.1179	1.1146	<1.135 >1.127
1	20	1.6174	1.6839	1.6747	<1.841 >1.755
2	20	4.0321	3.9288	3.9375	>3.568

the divergence of the corresponding expectation values S_ν. The source of this divergence are the derivatives of the potential function V at the origin. To be explicit, for $\nu=3$ it is easy to show that the dominant term at small distances is given by V'/r^2, thus for a point-charge nucleus the expectation value S_3 diverges [as, of course, does $S(3)$]. Therefore, if one takes into account the structure of the nucleus, the value of S_3 is finite, but it depends on the details of the nuclear charge distribution. Similar results hold for $\nu>3$. On the other hand, the Lamb shift is an exception. Here the derivative V' [see Eq. (76)] appears, and therefore one gets a finite value even for a point-charge nucleus. For $\nu=-1,0,1$, the potential function V does not appear explicitly in the expressions of S_ν.

Our results for helium are listed in Table III. We have calculated the mean excitation energies for the three wave functions of Eqs. (69), (70), (70′), and (70″). The results of Ref. 5 are given for comparison. We see that there is only a small difference between the two functions $\psi_{\rm II}$ and $\psi_{\rm III}$ of Eq. (70). On the other hand, the results based on the simple wave function $\psi_{\rm I}$ of Eq. (69) differ substantially (up to 7.7%) from the other two functions. The results due to $\psi_{\rm III}$ (and $\psi_{\rm II}$, as it turns out) are the more reliable ones as it is the "best" wave function available in the framework of the Hartree-Fock approximation. Note that for $\nu=1$, $\psi_{\rm I}$ yields a lower value than $\psi_{\rm II}$ and $\psi_{\rm III}$, whereas for the other three cases it yields a higher value. There seems to be no obvious explanation for this effect. In connection with this, it is interesting to observe that the matrix element S_1 is the only one which depends on $(\psi')^2$, whereas the other three matrix elements depend on ψ^2 and $(\psi^2)'$. As to the discrepancies between our results and those of Ref. 5 for $\nu=-1,0,1$, the main reason is that neither result is completely accurate; the causes, however, are different: The wave function employed in the present paper are Hartree-Fock-type functions which do not take into consideration the correlation effect between the two electrons. The upper and lower bounds of Ref. 5 were calculated from the sum rules $S(\nu-1)$, $S(\nu)$, and $S(\nu+1)$, which have been studied in the literature,[22] and oscillator strengths of some measured discrete spectral lines. It is impossible to calculate by this method an upper bound for $\ln I(2)$, because $S(3)$ diverges.

To conclude, both methods have their advantages and disadvantages. The method of Ref. 5 is partly based on experimental data, whereas the present method is based entirely on first principles, neglecting correlation effects.

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APPENDIX

A closed expression of the sum rule

$$S_\nu=\sum_n \langle 0\,|\,B\,|\,n\rangle(E_n-E_0)^{\nu+1}\langle n\,|\,A\,|\,0\rangle\;, \qquad \text{(A1)}$$

where A and B are any two operators, is derived. It is not necessary to go into details as the derivation closely follows the one by Bethe and Jackiw[23] who derived it for $B=A^+$. Start with

$$e^{itH}Ae^{-itH}=\sum_{\nu=0}^{\infty}\frac{(it)^\nu}{\nu!}A_\nu\;, \qquad \text{(A2)}$$

where

$$A_0=A,\quad A_\nu=[H,A_{\nu-1}]\;. \qquad \text{(A2′)}$$

Next consider the matrix element

$$\langle 0\,|\,Be^{itH}Ae^{-itH}\,|\,0\rangle=\sum_n\langle 0\,|\,Be^{itH}\,|\,n\rangle\langle n\,|\,Ae^{-itH}\,|\,0\rangle$$

$$=\sum_{\nu=0}^{\infty}\frac{(it)^\nu}{\nu!}S_{\nu-1}\;. \qquad \text{(A3)}$$

On the other hand, because of Eq. (A2), we have

$$\langle 0\,|\,B(e^{itH}Ae^{-itH})\,|\,0\rangle=\sum_{\nu=0}^{\infty}\frac{(it)^\nu}{\nu!}\langle 0\,|\,BA_\nu\,|\,0\rangle\;. \qquad \text{(A4)}$$

Comparing this expression with Eq. (A3) yields

$$S_\nu=\langle 0\,|\,BA_{\nu+1}\,|\,0\rangle\;. \qquad \text{(A5)}$$

This can be simplified to give

$$S_\nu=(-1)^m\langle 0\,|\,B_m A_{\nu+1-m}\,|\,0\rangle \tag{A6}$$

with $m\leq\nu+1$ and $B_m=[H,B_{m-1}]$, $B_0=B$. Let us apply this result to hydrogen. We thus put $B=z$ and $A=F(\mathbf{r})$. Therefore,

$$\begin{aligned}\text{(i)}\ \ S_0&=-\langle 0\,|\,z_1F\,|\,0\rangle\\ &=2i\langle 0\,|\,p_zF\,|\,0\rangle\\ &=\langle 0\,|\,\partial F/\partial z\,|\,0\rangle\ ,\end{aligned} \tag{A7}$$

$$\begin{aligned}\text{(ii)}\ \ S_1&=-\langle 0\,|\,z_1F_1\,|\,0\rangle\\ &=2i\langle 0\,|\,p_z[p^2,F]\,|\,0\rangle\\ &=-2i\langle 0\,|\,p_z(\nabla^2F+2\nabla F\cdot\nabla)\,|\,0\rangle\ ,\end{aligned} \tag{A8}$$

$$\begin{aligned}\text{(iii)}\ \ S_2&=\langle 0\,|\,z_2F_1\,|\,0\rangle\\ &=-2\left\langle 0\left|\frac{\partial V}{\partial z}(\nabla^2F+2\nabla F\cdot\nabla)\right|0\right\rangle\ ,\end{aligned} \tag{A9}$$

because $z_2=2\partial V/\partial z$.

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