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Logarithmic mean excitation energies: Hydrogen and helium

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The four logarithmic mean excitation energies $I(\nu)$ for $\nu=-1,\dots,2$ have been calculated for hydrogen and helium by the method introduced a few years ago [S. Rosendorff and A. Birman, Phys. Rev. A **31**, 612 (1985)]. At that time a parametrization procedure was used for helium that yielded up to ±10% accuracy. It is estimated that for a given wave function the present method of calculation yields an accuracy for $I(\nu)$ of 1 part in 10^4. For helium three different Hartree-Fock-type wave functions were used. Correlation effects were thus not included.

I. INTRODUCTION

A few years ago a method was introduced[1,2] to calculate the four logarithmic mean excitation energies $I(\nu)$, defined by

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

The logarithmic sums $L(\nu)$ are given by

$$L(\nu)=\sum_n |\langle 0|z|n\rangle|^2(E_n-E_0)^{\nu+1}\ln|E_n-E_0|\ , \tag{2}$$

and the sum $S(\nu)$ is given by

$$S(\nu)=\sum_n|\langle 0|z|n\rangle|^2(E_n-E_0)^{\nu+1}\ . \tag{3}$$

Here E_n-E_0 are the excitation and deexcitation energies measured from the energy E_0 of the initial state. The sums are over the complete set of energy eigenstates of the atom, and z is the z component of the total dipole moment operator of the electrons of the atom. The four mean energies $I(\nu)$appear in the expressions for (i) total cross section of particle-atom collisions, (ii) atomic stopping power, (iii) straggling effect, and (iv) Lamb shift of atomic energy levels, respectively.

The numerical values of these sums are often obtained by fitting the theory to experimental data. Our method, on the other hand, is based entirely on first principles, *the sole input being the wave function of the initial state.* Knowledge of other entities, such as matrix elements or energy levels, is unnecessary. In this approach an operator F is introduced which enables one to perform the summation over the whole energy spectrum by closure relation. For the present, our program is to calculate the excitation energies $I(\nu)$ for the ground states of all atoms from hydrogen to neon. The operator F is determined by a certain inhomogeneous differential equation which depends functionally on the initial wave function of the atom. We therefore get F's for 1s, 2s, and 2p states (and higher excited states for atoms with $Z>10$). The mathematical treatment of the corresponding equations, as well as the evaluation of the above sums, differs significantly from case to case.

In this paper we report results for hydrogen and helium only. These atoms have already been dealt with in Ref 1 (hereafter referred to as paper I). However, in that paper the helium sums were evaluated by a certain parametrization procedure which, as it turned out, was quite inaccurate. In this paper we show that solving the equation for F by computer yields, for a given wave function, an accuracy for $I(\nu)$ of 1 part in 10^4. The computer calculation is therefore very satisfactory. The discrepancy between the results of this paper and that of paper I is up to ±10%. Three different Hartree-Fock wave functions have been used which give rise to a maximum deviation of 1% for $I(\nu)$. Correlation effects have not been included.

The cases of 2s states (Li, Be), and 2p states (B, . . . , Ne) are planned to be reported in the near future.

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

II. THE METHOD

Take the identity

$$-\ln(E_n-E_0)=\lim_{\Lambda\to\infty}\left[\int_0^\Lambda\frac{d\lambda}{\lambda+E_n-E_0}-\ln\Lambda\right]\ , \tag{4}$$

then $L(\nu)$, Eq. (2) becomes

$$-L(\nu)=\lim_{\Lambda\to\infty}\left[\int_0^\Lambda d\lambda\sum_n\frac{|\langle 0|z|n\rangle|^2}{\lambda+E_n-E_0}(E_n-E_0)^{\nu+1}-(\ln\Lambda)\sum_n|\langle 0|z|n\rangle|^2(E_n-E_0)^{\nu+1}\right]\ . \tag{5}$$

Define an operator F by the equation

$$[H_0,F]\psi_0+\lambda F\psi_0=z\psi_0 \ . \tag{6}$$

Here H_0 is the Hamiltonian of the atom, and ψ_0 is the wave function of the ground state. Equation (5) thus becomes

$$-L(\nu)=\lim_{\Lambda\to\infty}\left[\int_0^{\Lambda}S_\nu d\lambda-S(\nu)\ln\Lambda\right] , \tag{7}$$

where $S(\nu)$ is given by Eq. (3), and

$$S_\nu=\sum_n \langle 0|z|n\rangle(E_n-E_0)^{\nu+1}\langle n|F|0\rangle \ . \tag{8}$$

These sums can be evaluated by the expressions given in the Appendix of paper I.

We assume that F depends only on the coordinates $\mathbf{r}_i$ of the electrons but not on the momenta. Thus we have $F=F(\mathbf{r}_1,\cdots,\mathbf{r}_N;\lambda)$. If we introduce the function

$$\mathcal{F}=F\psi_0 \ , \tag{9}$$

then Eq. (6) becomes

$$(H_0-E_0+\lambda)\mathcal{F}=z\psi_0 \ . \tag{10}$$

Thus the quantum-mechanical behavior of the system is determined by $\mathcal{F}$. It is a p state for s electrons, and a superposition of s and d states for p electrons. The homogeneous (reduced) equation of Eq. (10) describes eigenstates with energy eigenvalues $E_0-\lambda$. If λ is such that $E_0-\lambda$ is a physical eigenvalue of H_0, the solution of Eq. (10) might have a divergency because in this case the operator $H_0-E_0+\lambda$ has no inverse.

It has been shown[3] that in the framework of perturbation theory the function $\mathcal{F}$ is equal to the first-order correction to the wave function ψ_0, for $\lambda=0$, and $\nu=-1$. It follows that the operator F should be finite everywhere in the physical region of $\mathbf{r}$, and that at infinity it should not diverge exponentially.

III. HYDROGEN AND HELIUM

We have only s electrons. Therefore $\mathcal{F}$ is a p state. We first consider F for a hydrogenlike ion; thus the wave function $\psi_0\propto\exp(-Zx)$ where Z is the charge of the nucleus. Setting

$$F=zg(x,\lambda;Z) \ , \tag{11}$$

we obtain from Eq. (6) the radial equation for g:

$$xg''+(4-2Zx)g'-(2Z+\lambda x)g=-x \ . \tag{12}$$

We get, by a simple scaling procedure,

$$g(x,\lambda;Z)=\frac{1}{Z^2}g(x',\lambda';1) \ , \tag{13}$$

where

$$x'=Zx, \quad \lambda'=\lambda/Z^2 \ . \tag{13'}$$

The mean excitation energies $I(\nu)$ for hydrogenlike ions are related to those for hydrogen by

$$\ln I(\nu)=\ln\{[I(\nu)]_H Z^2\} \ . \tag{14}$$

For hydrogen the function g has been calculated analytically in paper I. Its integral representation, after a simple transformation, is

$$g(x,\lambda,1) =\frac{(2t)^{2+1/t}}{(t+1)^{3+1/t}}\int_0^1 y^{1-1/t}\left[1-\frac{t-1}{2t}y\right]^{2+1/t} \times\left[xy+\frac{2}{t}\frac{1-y}{1-\frac{t-1}{2t}y}\right]e^{-(t-1)(1-y)x}dy \ , \tag{15}$$

with $t=\sqrt{\lambda+1}$.

Next, for helium we put $z=z_1+z_2$, and for the ground-state wave function

$$\psi_0(1,2)=\phi(1)\phi(2) \ . \tag{16}$$

If we put $F(1,2)=F(1)+F(2)$, then Eq. (6) separates into two identical one-particle equations given by

$$xg''+\left[4+2x\frac{\phi'}{\phi}\right]g'+\left[2\frac{\phi'}{\phi}-\lambda x\right]g=-x \ . \tag{17}$$

We have considered three different wave functions which consist of two basic functions:

$$\phi=\frac{N}{\sqrt{\pi}}(e^{-Z_1x}+\alpha e^{-Z_2x}) \ . \tag{18}$$

The coefficients Z_1, Z_2, and α, together with their corresponding ionization potentials I in units of Ry, and the diamagnetic susceptibilities χ, in units of 10^{-6} cm^3/mol are listed in Table I. ϕ_2 is our fit to the function of Clementi.[6] The value of χ, as quoted in the literature,[7] is -1.88 in above units. Thus the calculated values based on the three functions ψ_i, are excellent. We should point out that the screened hydrogenic wave function $\phi_0\propto\exp(-Z_0x)$ with $Z_0=1.6875$ yields a rather poor result for χ (13% too low). The three functions ϕ_i give rise to a charge distribution which is less contracted than the one due to ϕ_0. As the diamagnetic susceptibility is proportional to the mean square radius of the charge distribution it is plausible that the ϕ_i's, yield the correct distribution away from the nucleus (where most of the contribution to χ comes from). The same functions ϕ_i give rise to ionization potentials which are reasonable but not excellent (the measured value[8] of I is 1.807 Ry). The ener-

TABLE I. The coefficients of the one-particle, ground-state wave functions ϕ_1,ϕ_2,ϕ_3 and the corresponding ionization potentials I, and diamagnetic susceptibilities χ.

	ϕ_1 (Ref. 4)	ϕ_2	ϕ_3 (Ref. 5)
Z_1	1.4558	1.4257	1.41
Z_2	2.9116	2.7132	2.61
α	0.6	0.7478	0.799
I	1.7191	1.7232	1.7676
$-\chi$	1.870	1.866	1.880

gies are quite sensitive to the charge distribution near the nucleus, where correlation effects show most of their influence. Obviously, these effects have not been taken into account in this paper. This may be the main reason for the above-mentioned discrepancy (about 2% for ϕ_3). Our logarithmic mean excitation energies $I(\nu)$ are probably less affected by correlation effects.

For each electron the expressions of $S_\nu(\lambda)$, Eq. (8), in terms of the function $g(x,\lambda)$ of Eq. (17) are given by

$$S_{-1}(\lambda)=\frac{4\pi}{3}\int_0^\infty \phi^2 g(x,\lambda)x^4 dx\ , \tag{19}$$

$$S_0(\lambda)=-\frac{8\pi}{3}\int_0^\infty \phi\phi' g(x,\lambda)x^3 dx\ , \tag{20}$$

$$S_1(\lambda)=\frac{8\pi}{3}\int_0^\infty [-(\phi^2)'+2x\theta+x^2\theta']g(x,\lambda)x\,dx\ , \tag{21}$$

where $\theta=\phi^2(\phi'/\phi)'$. Obviously, for hydrogenic wave functions, $\theta=0$ because $(\phi'/\phi)=\text{const}$:

$$S_2(\lambda)=\frac{16\pi}{3}Z\left[2\int_0^\infty (\phi^2)'g(x,\lambda)dx + 3g(0,\lambda)[\phi(0)]^2\right]\ , \tag{22}$$

where Z is the nucleus charge. To obtain $S(\nu)$, Eq. (3), one simply puts $g=1$ in the above expressions (for details the reader is referred to paper I). For hydrogen, ϕ is the ground-state wave function $\exp(-x)/\sqrt{\pi}$, and $Z=1$.

Finally, the numerical values of the sums $L(\nu)$ are determined, according to Eq. (7), by

$$-L(\nu)=\int_0^1 S_\nu(\lambda)d\lambda+\int_1^\infty\left[S_\nu(\lambda)-\frac{S(\nu)}{\lambda}\right]d\lambda\ . \tag{23}$$

In order to test the convergence of the second integral, we have evaluated, for hydrogen, the behavior of $T_\nu(\lambda)=(S_\nu-S(\nu)/\lambda)$ for $\lambda\to\infty$. We found for the three cases $\nu=-1,0,1$ that $T_\nu(\lambda)$ behaves as $1/\lambda^2$; however for the Lamb shift it behaves as $1/\lambda^{3/2}$; thus for the latter case the convergence is very slow.

IV. NUMERICAL CALCULATION AND RESULTS

The differential equation for $g(x,\lambda)$, Eq. (17) was solved by computer for a large range of $x,\lambda\geq 0$. Our first task was to solve the hydrogen problem. The appropriate equation is Eq. (17) with $\phi'/\phi=-1$, or Eq. (12) with $Z=1$. This provided a very strict test of our numerical procedure because for hydrogen the function $g(x,\lambda)$ is given analytically by the integral representation, Eq. (15).

The function g and its derivative g' were calculated at $(x+\Delta x)$ by

$$g(x+\Delta x)=\sum_{n=0}^{3}\frac{1}{n!}(\Delta x)^n g^{(n)}(x) \tag{24}$$

and

$$g'(x+\Delta x)=\sum_{n=0}^{2}\frac{1}{n!}(\Delta x)^n g^{(n+1)}(x)\ . \tag{25}$$

The second derivative of g is given by Eq. (17); the third derivative of g follows from this equation by simple algebra, and also can be expressed in terms of g and g'. To complete the picture we are in need of g and g' at $x=0$. Call $g(0,\lambda)=a_0$, then

$$g'(0)=\frac{-1}{2}\frac{A_1}{A_0}a_0\ , \tag{26}$$

which follows from expanding g in powers of x. The A_i's are the expansion coefficients of the wave function

$$\phi(x)=\sum_i A_i x^i\ . \tag{27}$$

To facilitate the computation we have also made use of g'' and g''' at the origin. They too are simple functions of the A_i's, and are linear in a_0.

For given λ, the coefficient a_0 determines the value of g at every x because all the derivatives of g at the origin depend uniquely on a_0. As it turns out, g at large x increases or decreases if a_0 increases or decreases, respectively. The coefficient $a_0$is not known *a priori.* On the other hand, $g(x,\lambda)$ is known very accurately for $x>x_{\max}$; for the case of helium $x_{\max}$ is about 10, this will be explained below. Therefore the computational procedure adopted was as follows. We assumed an initial value of a_0 and calculated g by the above procedure. If the calculated value of g at $x_{\max}$ was too high a lower value of a_0 was chosen, and if g was too low at $x_{\max}$ a higher value of a_0 was chosen. We found that this iteration procedure was a very effective one. We demanded a matching accuracy of the values of g at $x_{\max}$ of about one part in 10^4 which was easily attained.

We should, however, point out that g at large x has an extremely sensitive dependence on a_0. This is due to the solutions of the homogeneous equations of Eqs. (17) and (12). For hydrogen the two independent solutions of the homogeneous equations are ${}_1F_1(2-1/t;4;2tx)$ and $U(2-1/t;\ 4;\ 2tx)$, both multiplied by $\exp[-(t-1)x]$. The theoretical exact solution of Eq. (12) was obtained by imposing the conditions that g would be finite in the physical region of x, and that at infinity it would not diverge exponentially [for details see paper I, Eq. (24)]. Now it is easily shown that if a_0 deviates from its exact value by η, then $g(x,\lambda)$ becomes

$$g(x,\lambda)=[g(x,\lambda)]_{\text{exact}}+\eta e^{-(t-1)x}{}_1F_1(2-1/t;4;2tx)\ . \tag{28}$$

Hence in the region where $2tx\gg 1$, we find the deviation of g from its exact value to be

$$\Delta g=6\eta\frac{e^{(t+1)x}}{\Gamma(2-1/t)(2tx)^{2+1/t}}\ , \tag{29}$$

where we have made use of the asymptotic expression of ${}_1F_1$. Thus if this expression is of order 10^{-4}, as pointed out above, assuming η not to be smaller than about 10^{-10}, and $x_{\max}\sim 10$, then even for small values of λ this equation cannot be satisfied. We therefore used a step-by-step method. The first iteration was from $x=0$ to some x_1, the second iteration from x_1 to some x_2, etc., the lengths of the successive steps were such that Eq. (29) was easily satisfied. In this way we got $g(x,\lambda)$ for

TABLE II. $\ln I(\nu)$ for hydrogen and helium. For helium the three wave functions ϕ_1, ϕ_2, ϕ_3 of Table I have been used.

	Hydrogen			Helium		
ν	Direct numerical calculat.	Analytical calculat.	Computer calculat.	ϕ_1	ϕ_2	ϕ_3
-1	$-0.073\,253$	$-0.073\,254$	$-0.073\,254$	0.825 24	0.823 84	0.81662
0	0.096 98	0.096 981	0.096 982	1.0718	1.0773	1.0691
1	0.570 87	0.570 87	0.570 97	1.7250	1.7286	1.7117
2	2.984 12	2.983 97	2.984 08	4.3294	4.3112	4.2804

$0 \le x \le 10$, and $0 \le \lambda \le 10^3$ very accurately. The deviations from the analytical calculated g of Eq. (15), valid for hydrogen, never exceeded one part in 10^4. It is very reasonable to assume that g derived from Eq. (17) for helium has comparable accuracy as the one above for hydrogen.

The reason the differential equation, Eq. (17), for helium was solved by computer only for $x \le 10$ is as follows. The logarithmic derivatives ϕ_i'/ϕ_i, $i = 1,2,3$ of the wave function for $x \gg 1$ assume the form

$$\frac{\phi'}{\phi} = -Z_1 - \alpha \frac{Z_2 - Z_1}{\alpha + \exp[(Z_2 - Z_1)x]} \ . \tag{30}$$

For $x \ge x_{\max}$, where $\exp\ [(Z_2 - Z_1)x_{\max}] \gg \alpha$, the second term is of the order of 10^{-6}. Therefore, in this region of x the outer electron "sees" the nuclear effective charge Z_1 due to the screening of the inner electron. Now if ϕ'/ϕ is constant the function $g(x,\lambda)$ is simply given by the integral representation, Eq. (15), together with Eqs. (13) and (13'), and $Z = Z_1$.

Our results for hydrogen and helium are listed in Table II.

For hydrogen, $\ln I(\nu)$ has been calculated by three different methods.

(i) Direct numerical calculation: This is based on the fact that for hydrogen all the matrix elements for the transition $1s \rightarrow np$ to the discrete and the continuum states are known[9] exactly.

(ii) Analytical calculation: $g(x,\lambda)$ was calculated analytically; it is given by the integral representation, Eq. (15). $L(\nu)$ was obtained from Eq. (23), via Eqs. (19)–(22) by two integrations over y from 0 to 1, and over λ from 0 to 10^{12}. These double integrals were evaluated by computer. The reason for the extremely high value of λ needed was the very slow convergence of the second integral of Eq. (23) for $\nu = 2$.

(iii) Computer calculation: The differential equation, Eq. (12) with $Z = 1$, was solved by computer for $0 \le x \le 10$ and $0 \le \lambda \le 10^3$. The deviation of g from the analytically calculated g never exceeded one part in 10^4. For $x > 10$, $g(x,\lambda)$ was evaluated by Eq. (15). For $\lambda > 10^3$, and $x > 0.1$ the asymptotic expansion of $g(x,\lambda)$ was used (see paper I). The rest of the calculation was as in (ii).

We see that the results in these three columns are essentially identical, as they should. This is a convincing proof that our computer calculation was indeed sound. (That the analytical calculated g was correct had already been shown in paper I.)

In the last three columns are listed the results of $\ln I(\nu)$ for helium, calculated for the three wave functions given by Eq. (18) and Table I. The function $g(x,\lambda)$ was calculated by computer for $0 \le x < 10$ from Eq. (17), and by Eqs. (15), (13), and (13') with $Z = Z_1$ for $x > 10$. For $\lambda > 10^3$, the asymptotic expansion of g was used again. We have also evaluated $\ln I(\nu)$ for the screened hydrogen wave function ϕ_0, which constituted a very good test of the method because of its connection with hydrogen, given by Eq. (14). The results obtained for $\ln I(\nu)$ were rather poor, as expected.

We see that the $[\ln I(\nu)]$'s derived from ϕ_i, $i = 1,2,3$, are very similar to each other. The maximum difference between them is about 1%. The mean excitation energies are thus slightly less sensitive to the quality of the wave function than the corresponding ionization potentials. It is, however, not possible to decide which of the three functions yields the best result. If to judge by the ionization potentials, obviously ϕ_3 is the best of the three functions under consideration. But from this it does not necessarily follow that ϕ_3 yields the best value for $\ln I(\nu)$. To obtain the best wave function from the $\ln I(\nu)$ point of view it would be necessary to solve a different variational principle. We are, however, fairly confident that our values of $\ln I(\nu)$ for helium are quite accurate. This makes sense in view of the fact that our ϕ_i's yield excellent values for the diamagnetic susceptibilities χ and reasonable good values for the ionization potentials I. In our approach, the correlation effects between the two electrons have been neglected. Most probably this effect will increase our values only by about 1%. For the lamb shift $(\nu = 2)\ln I$ has been approximately calculated[10,11] by variational methods, yielding $\ln I = 4.366$. This is higher by about 1% than our result in which correlation effects have not been accounted for. The influence of the correlation effects on $\ln I(\nu)$ for $\nu = -1,0,1$, is most probably of the same order of magnitude.

Another method[12,13] which has been employed to calculate $I(\nu)$ for helium and other atoms is based on the relation $L(\nu) = \partial S(\nu)/\partial \nu$ assuming ν to be a continuous variable, and $S(\nu)$ to be well known in the neighborhood of $\nu=-1,0,\ldots$. The function $S(\nu)$ is determined by interpolating techniques, which is a somewhat dubious procedure as $S(\nu)$ is a rapidly varying functions; this is true, in particular, in the neighborhood of $\nu=2$. Thus for the Lamb shift this procedure yields very poor results.

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