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Logarithmic mean excitation energies. II. Helium, lithium, beryllium, and the 2s state of hydrogen

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The four logarithmic excitation eneriges $I(\nu)$ for $\nu=-1$, 0, 1, and 2 have been calculated for helium, lithium, beryllium, and the 2s state of hydrogen. They appear in the expressions of the total cross section, the stopping power, and the straggling effect for fast charged particles, and in the expressions of the Lamb shift of atomic energy levels. The method was introduced some years ago [Rosendorff and Birman, Phys. Rev. A **31**, 612 (1985)]. For hydrogen the method is rigorous. Exact one-particle wave functions given by Clementi were used. Thus, correlation and symmetrization effects were neglected. For the nonhydrogen states, the relevant differential equations were solved by using a computer. An effective charge was defined which has interesting features. It is helpful in gaining some physical insight into the results obtained for helium and the 1s and 2s states of lithium and beryllium.

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I. INTRODUCTION

A few years ago a method was introduced [1–3] to calculate four logarithmic mean excitation energies. They are related to (i) the total cross section of particle-atom collisions, (ii) the atomic stopping power, (iii) the straggling effect, and (iv) the Lamb shift of atomic energy levels. In Ref. [1] (hereafter referred to as Paper I) the general idea of the method was represented, and the 1s hydrogen case was treated extensively. In Sec. IV of the present paper we shall take advantage of these results. Also, in the same paper the mean excitation energies of helium were calculated by a parametrization procedure which turned out to be not very accurate. In Ref. [3] (hereafter referred to as Paper II) the helium case was treated much more accurately by solving the underlying differential equation by using a computer. Three different wave functions were used which consisted of two basic functions [Eq. (18), Paper II]. They yielded results which were all within a range of about 1%. In the present paper the calculation was further improved by introducing the one-particle was functions of Clementi [4] (see Sec. IV). In the same section we also represent results for the 1s lithium and the 1s beryllium states. They are summarized in Tables I and II. An effective charge is also discussed which has simple but surprisingly interesting features.

The calculation of the 2s state of hydrogen is extensively discussed in Sec. V. This case is more complicated than the 1s state because the 2s wave function has one nodal point. However, it turns out that the 2s state can essentially be reduced to the 1s state. This enabled us to solve the 2s case very accurately. As a matter of fact, all s states are intimately connected to the 1s state. The results of the 2s hydrogen states are summarized in Table III. In Sec. VI the 2s states of lithium and beryllium are treated. In this case the problem of the nodal point of the wave function is more involved than in hydrogen. However, a way has been found to circumvent these difficulties. The results are summarized in Tables IV and V. In the same section the results for the atoms of lithium and beryllium are represented and summarized in Table VI. In Sec. II the basic approach of the method is summarized. In Sec. III the relevant explicit expressions of the sums are given and extensively discussed. Energies are measured in Rydberg units; all other quantities are in atomic units.

II. BASIC RELATIONS OF THE METHOD

In this section the basic ideas of the method are summarized. The four logarithmic mean excitation energies $I(\nu)$ are defined by

$$\ln I(\nu)=L(\nu)/S(\nu)\ , \quad \nu=-1,0,1,2\ . \tag{2.1}$$

The logarithmic sums are given by

$$L(\nu)=\sum_n |\langle 0|Z|n\rangle|^2(E_n-E_0)^{\nu+1}\ln(E_n-E_0)\ , \tag{2.2}$$

and the sums $S(\nu)$ are given by

$$S(\nu)=\sum_n |\langle 0|Z|n\rangle|^2(E_n-E_0)^{\nu+1}\ , \tag{2.3}$$

where Z is the z component of the total dipole moment operator of the electrons of the atom. The sums are over the complete set of energy eigenstates of the atom.

In order to calculate $L(\nu)$, we make us of the identity

$$-\ln(E_n-E_0)=\lim_{\Lambda\to\infty}\left[\int_0^\Lambda \frac{d\lambda}{E_n-E_0+\lambda}-\ln\Lambda\right]\ . \tag{2.4}$$

We now define the operator F by the equation

$$[H_0,F]\psi_0+\lambda F\psi_0=Z\psi_0 \ . \tag{2.5}$$

Here H_0 is the Hamiltonian of the atom, $\psi_0\equiv|0\rangle$ is the wave function of the initial state and E_0 is the corresponding energy. From Eq. (2.5) follows the relation

$$(E_n-E_0+\lambda)\langle n|F|0\rangle=\langle n|Z|0\rangle \ . \tag{2.6}$$

We then get, in combination with Eq. (2.4), the expression of $L(\nu)$ in terms of F:

$$-L(\nu)=\int_0^1 S_\nu(\lambda)d\lambda+\int_1^\infty [S_\nu(\lambda)-S(\nu)/\lambda]d\lambda \ , \tag{2.7}$$

where we have defined the sum

$$S_\nu(\lambda)=\sum_n \langle 0|Z|n\rangle(E_n-E_0)^{\nu+1}\langle n|F|0\rangle \ . \tag{2.8}$$

Our main task is to calculate the operator F. We assume that it depends only on the coordinates of the electrons (but not on the momenta). This by no means restricts the generality of the method. According to Eq. (2.5), it depends also on λ and is functionally dependent on the initial state ψ_0 of the atom. If we introduce the function

$$\mathcal{F}=F\psi_0 \ , \tag{2.9}$$

then Eq. (2.5) becomes

$$(H_0-E_0+\lambda)\mathcal{F}=Z\psi_0 \ . \tag{2.10}$$

In the present paper we deal with s electrons only. Thus the right-hand side (rhs) of the above equation is a p state, and therefore $\mathcal{F}$ is also a p state. We shall make use of the above equation in order to solve the 2s state of hydrogen. This is discussed in detail in Sec. V.

Next, we derive from Eq. (2.5) the differential equation for F for an N-electron system. The z component of the dipole operator is given by

$$Z=\sum_{i=1}^N z_i \ . \tag{2.11}$$

For the ground-state wave function we take the product of the one-particle wave functions of Clementi [4],

$$\psi_0(1,2,\ldots)=\varphi_{1s}(1)\varphi_{1s}(2)\varphi_{2s}(3)\varphi_{2s}(4)\ldots \ . \tag{2.12}$$

Thus, Eq. (2.5) becomes

$$\left\{-\left[\left[\sum_{i=1}^N \nabla_i^2\right],F\right]+\lambda F\right\}\prod_i \varphi_i=\left[\sum_{i=1}^N z_i\right]\prod_i \varphi_i \ . \tag{2.13}$$

Next, we put

$$F(1,2,\ldots)=F_{1s}(1)+F_{1s}(2)+F_{2s}(3)+F_{2s}(4)+\cdots \ , \tag{2.14}$$

then the above equation assumes the form

$$-\left[\sum_i \nabla_i^2 F_i\right]\prod_j \varphi_j-2\sum_i (\nabla_i F_i)\cdot(\nabla_i\varphi_i)\prod_{j(\neq i)}\varphi_j +\lambda\left[\sum_i F_i\right]\prod_j \varphi_j=\left[\sum_i z_i\right]\prod_j \varphi_j \ . \tag{2.15}$$

Obviously, this expression breaks up into N one-particle differential equations of the form

$$\nabla_i^2 F_i+2\nabla_i(F_i)\cdot\frac{\nabla_i\varphi_i}{\varphi_i}-\lambda F_i=-z_i \ . \tag{2.16}$$

As our initial state is an s state, the second term of the above equation becomes simply $2(\varphi_i'/\varphi_i)(\partial F_i/\partial r_i)$. Finally, as the F_i's are p states, it is convenient to put $F_i=z_i g_i(r,\lambda)$. Putting this back into the above equation, we get the radial equation for g_i,

$$xg_i''+(4+2x\varphi_i'/\varphi_i)g_i'+(2\varphi_i'/\varphi_i-\lambda x)g_i=-x \ . \tag{2.17}$$

In Papers I and II the above equation has been solved analytically and numerically for the 1s states of hydrogen and helium, respectively. In Sec. IV of the present paper the 1s states of helium, lithium, and beryllium are solved with the help of this equation. The 2s states are more complicated because the wave functions have one nodal point. Thus, the logarithmic derivatives of these wave functions in the above equation have one pole. This gives rise to some complications, which, however, can be solved satisfactorily. For hydrogen this is worked out in Sec. V, and for lithium and beryllium in Sec. VI.

III. THE SUMS $S_\nu(\lambda)$ AND $S(\nu)$

In this section the sums $S_\nu(\lambda)$, Eq. (2.8), and $S(\nu)$, Eq. (2.3), are discussed. Obviously, $S(\nu)$ is obtained from S_ν by putting $F\equiv Z$. We consider each of the four cases separately. We shall make explicit use of the dipole operator Z, Eq. (2.11); the wave function ψ_0, Eq. (2.12); and the F function, Eq. (2.14).

(i) $\nu=-1$. By the definition of $S_{-1}(\lambda)$, Eq. (2.8), we get

$$S_{-1}(\lambda)=\langle\psi_0|ZF|\psi_0\rangle =\sum_{i=1}^N \langle\varphi_i|z_iF_i|\varphi_i\rangle \ ; \tag{3.1}$$

the latter follows from the fact that $\langle\varphi_i|z_i|\varphi_i\rangle=0$. Thus, $S_{-1}(\lambda)$ becomes, after integrating over the angles, for *each* electron,

$$S_{-1}(\lambda)=\tfrac{1}{3}\int_0^\infty \varphi^2 g(x,\lambda)x^4dx \ . \tag{3.1$'$}$$

For the remaining three cases, we make use of the results which appear in the Appendix of Paper I.

(ii) $\nu=0$. By Eqs. (A6) and (A2$'$) of Paper I, there are two possible expressions for S_0, namely,

$$S_0^{(10)}(\lambda)=-\langle\psi_0|Z_1F|\psi_0\rangle \tag{3.2}$$

and

$$S_0^{(01)}(\lambda)=\langle\psi_0|ZF_1|\psi_0\rangle \ , \tag{3.2$'$}$$

where, in general, $A_\nu=[H_0,A_{\nu-1}]$ and $A_0=A$. If ψ_0 is an *exact* eigenstate of the Hamiltonian, these two expressions are equal to each other. However, our wave functions are not completely rigorous; for instance, correlation and symmetrization effects have been neglected. Thus, the question arises as to which of the two expressions is more accurate. The interesting point in the present case is that we can prove that both expressions are identical without making the assumption that ψ_0 is an eigenstate of the Hamiltonian. The proof is simple: suppose $S_0^{(10)}$ and $S_0^{(01)}$ are equal; then we should have explicitly

$$-\langle\psi_0|[H_0,Z]F|\psi_0\rangle=\langle\psi_0|Z[H_0,F]|\psi_0\rangle\ , \tag{3.3}$$

and therefore the following equality must be satisfied:

$$\langle\psi_0|H_0ZF|\psi_0\rangle=\langle\psi_0|ZFH_0|\psi_0\rangle\ . \tag{3.4}$$

Now all three operators H_0, Z, and F are Hermitian and real. Thus, the left-hand side (lhs) becomes $\langle H_0\psi_0|ZF\psi_0\rangle$, and the rhs becomes

$$\langle FZ\psi_0|H_0\psi_0\rangle=\langle ZF\psi_0|H_0\psi_0\rangle\ ; \tag{3.5}$$

the latter follows from the fact that Z and F commute. As the ground state ψ_0 is real, the identity of $S_0^{(10)}$ and $S_0^{(01)}$ has been established. Obviously, the same holds for $S(0)$; we get

$$S^{(10)}(0)=S^{(01)}(0)=1\ .$$

That $S(0)=1$ is in accordance with the Thomas-Reiche-Kuhn sum rule.

By Eqs. (2.11), (2.12), and (2.14) and the fact that $Z_1=-2iP_z$, the expression (3.2) becomes

$$\begin{aligned}S_0(\lambda)&=2i\langle\psi_0|P_zF|\psi_0\rangle\\&=2i\sum_{j=1}^{N}\langle\varphi_j|p_{jz}F_j|\psi_j\rangle\ ;\end{aligned} \tag{3.6}$$

the latter follows from the fact that $\langle\varphi_i|p_{iz}|\varphi_i\rangle=0$. Thus, $S_0(\lambda)$ becomes, after integrating over the angles, for *each* electron,

$$S_0(\lambda)=-\tfrac{2}{3}\int_0^\infty\varphi'\varphi g(x,\lambda)x^3dx\ . \tag{3.6'}$$

We skip the $\nu=1$ problem and consider next the $\nu=2$ case which is very similar to the $\nu=0$ case.

(iii) $\nu=2$. We consider the two expressions

$$S_2^{(30)}(\lambda)=-\langle\psi_0|Z_3F|\psi_0\rangle \tag{3.7}$$

and

$$S_2^{(21)}(\lambda)=\langle\psi_0|Z_2F_1|\psi_0\rangle\ . \tag{3.7'}$$

Suppose they are equal, i.e.,

$$-\langle\psi_0|Z_3F|\psi_0\rangle=\langle\psi_0|Z_2F_1|\psi_0\rangle\ ,$$

then making use of the definition $Z_3=[H_0,Z_2]$, we get

$$-\langle\psi_0|[H_0Z_2]F|\psi_0\rangle=\langle\psi_0|Z_2[H_0,F]|\psi_0\rangle\ .$$

Thus we get the equality

$$\langle\psi_0|H_0Z_2F|\psi_0\rangle=\langle\psi_0|Z_2FH_0|\psi_0\rangle\ .$$

Now Z_2 is given by

$$Z_2=[H_0,Z_1]=[V,Z_1]\ ,$$

where V is the potential energy of the atom; thus Z_2 is real and a function of the coordinates only. We have, therefore, a similar situation to that in (*ii*); the rest of the proof thus follows immediately: $S_2^{(30)}$ and $S_2^{(21)}$ are identical.

A word is due concerning the two additional expressions $S_2^{(12)}$ and $S_2^{(03)}$. We cannot prove that they are equal to the ones discussed above without assuming that ψ_0 is an eigenstate of H_0. It should, however, be pointed out that these quantities are unsuitable for numerical calculations in any case because their expressions involve high-order derivatives of the wave functions. Obviously, these derivatives are rather inaccurate.

We should emphasize at this point that the above expression (3.7) [or (3.7′)] yields very good results for the Lamb shift. This will become clear in Sec. IV.

To obtain an explicit expression for $S_2(\lambda)$, we start with Eq. (3.7). We thus are in need of Z_3 which, in turn, is determined by Z_2. The latter is given by

$$Z_2=[H_0,Z_1]\ . \tag{3.8}$$

As

$$Z_1=-2iP_z=-2i\sum_i p_{iz}\ ,$$

we get

$$Z_2=2i\sum_i[p_{iz},V]\ , \tag{3.8'}$$

where the potential energy is

$$V=\sum_i V_i+\sum_{\substack{k,l\\k<l}}V_{kl}\ . \tag{3.9}$$

Hence we get

$$Z_2=2i\sum_i\left[p_{iz},\sum_j V_j\right]+2i\sum_i\left[p_{iz},\sum_{\substack{k,l\\k<l}}V_{kl}\right]\ . \tag{3.8''}$$

Obviously, the commutators $[p_{jz},V_{kl}]$ with $j\neq k,l$ are zero, and the commutators of the form $[p_{iz}+p_{jz},V_{ij}]$ are zero too, because of the action-reaction principle. It follows that Z_2 is given by

$$\begin{aligned}Z_2&=2i\sum_i\left[p_{iz},\sum_j V_j\right]\\&=2\sum_i\frac{\partial V_i}{\partial z_i}\ .\end{aligned} \tag{3.10}$$

From this we get for Z_3,

$$\begin{aligned}Z_3&=2\left[\sum_j p_j^2,\sum_i\frac{\partial V_i}{\partial z_i}\right]\\&=-2\sum_i\left[\nabla_i^2\frac{\partial V_i}{\partial z_i}+2\nabla_i\left[\frac{\partial V_i}{\partial z_i}\right]\cdot\nabla_i\right]\ .\end{aligned} \tag{3.11}$$

As ψ_0 is an s state, this becomes

$$Z_3=-2\sum_i\frac{\partial}{\partial z_i}(\nabla_i^2V_i)-4\sum_i\frac{\partial^2V_i}{\partial r_i\partial z_i}\frac{\partial}{\partial r_i}\ . \tag{3.11'}$$

Now, V_i is the nucleus-electron interaction; therefore,

$\nabla_i^2 V_i = 8\pi Z_N \delta(\mathbf{r}_i)$, where Z_N is the charge of the nucleus; hence we get finally

$$Z_3 = -16\pi Z_N \sum_i \delta(x_i)\delta(y_i)\delta'(z_i) - 4\sum_i \frac{\partial^2 V_i}{\partial r_i \partial z_i} \frac{\partial}{\partial r_i} \; . \tag{3.11''}$$

We are now ready to derive the explicit expression of S_2, Eq. (3.7):

$$S_2 = -16\pi Z_N \sum_i \left\langle \delta(x_i)\delta(y_i)\delta'(z_i)\psi_0 \left| \sum_\alpha F_\alpha \right| \psi_0 \right\rangle - 4\sum_i \left\langle \frac{\partial^2 V_i}{\partial r_i \partial z_i} \frac{\partial}{\partial r_i} \psi_0 \left| \sum_\alpha F_\alpha \right| \psi_0 \right\rangle \; , \tag{3.12}$$

where we have made use of the fact that Z_3 is an anti-Hermitian operator. Again, the cross terms vanish; in the first term because $\delta'(z)$is an odd function and in the second term because $\langle \varphi_i | z_i | \varphi_i \rangle = 0$. Therefore, together with $z\delta'(z) = -\delta(z)$ and $F_i(r_i) = Z_i g_i(r_i)$, we get

$$S_2 = 16\pi Z_N \sum_i \langle \delta(\mathbf{r}_i) \varphi_i^2(r_i) g_i(r_i) \rangle - 4\sum_i \langle V_i'' \varphi_i' \cos^2(\theta_i) r_i g_i \varphi_i \rangle \; . \tag{3.12'}$$

Finally, substituting for V_i'' and integrating over the angles, we get for *each* electron,

$$S_2(\lambda) = 4Z_N \left[g_\alpha(0,\lambda)[\varphi_\alpha(0)]^2 + \tfrac{2}{3}\int_0^\infty (\varphi_\alpha^2)' g_\alpha(x,\lambda) dx \right] \; . \tag{3.13}$$

(iv) $\nu = 1$. We first consider the two expressions

$$S^{(11)}(1) = -\langle \psi_0 | Z_1 Z_1 | \psi_0 \rangle \tag{3.14}$$

and

$$S^{(20)}(1) = \langle \psi_0 | Z_2 Z | \psi_0 \rangle \; . \tag{3.14'}$$

We shall prove that for wave functions of the type used in the present work [see Eq. (1.12)], the above expressions are not equal to each other, except for hydrogen. We have $Z_1 = -2iP_z$; thus,

$$\begin{aligned} S^{(11)}(1) &= 4\langle \psi_0 | P_z P_z | \psi_0 \rangle \\ &= \tfrac{4}{3}\sum_i \int_0^\infty (\varphi_i')^2 r_i^2 dr_i \; . \end{aligned} \tag{3.15}$$

On the other hand, by Eq. (3.10), $S^{(20)}(1)$ becomes

$$\begin{aligned} S^{(20)}(1) &= 2\left\langle \psi_0 \left| \left[\sum_i \frac{\partial V_i}{\partial z_i} \right] z \right| \psi_0 \right\rangle \\ &= 2\sum_i \left\langle \varphi_i \left| \frac{\partial V_i}{\partial z_i} z_i \right| \varphi_i \right\rangle \\ &= \tfrac{4}{3} Z_N \sum_i \int_0^\infty \varphi_i^2 r_i dr_i \; . \end{aligned} \tag{3.16}$$

Consider the mean kinetic energy of the system. For wave functions given by Eq. (2.12), it is

$$K = \sum_i \int_0^\infty (\varphi_i')^2 r_i^2 dr_i \; . \tag{3.17}$$

Comparison with Eq. (3.15) yields

$$S^{(11)}(1) = \tfrac{4}{3}K \; . \tag{3.18}$$

The mean nucleus-electron energy of the system is

$$V_{ne} = -2Z_N \sum_i \int_0^\infty \varphi_i^2 r_i dr_i \; , \tag{3.19}$$

and comparison with Eq. (3.16) yields

$$S^{(20)}(1) = -\tfrac{2}{3} V_{ne} \; . \tag{3.20}$$

It follows that, due to the virial theorem ($2K = -V$), *only* for one-electron systems do we have the equality $S^{(11)} = S^{(20)}$. For all the many-electron systems we get $S^{(11)} < S^{(20)}$. This follows from the fact that in the above expression only V_{ne} appears and not the total potential energy $V = (V_{ne} + V_{ee})$, where V_{ee} is the electron-electron energy.

It stands to reasons that only functions which are not products of one-particle wave functions will yield equal values for $S^{(11)}$ and $S^{(20)}$. In the present case, where the wave function is a product of one-particle functions, the question arises as to which of the two expressions $S^{(11)}$ and $S^{(20)}$ is more correct. The answer is, $S^{(11)}$ is quite accurate, where $S^{(20)}$ is inaccurate. By the relation

$$S^{(11)} = 4\langle \psi_0 | P_z P_z | \psi_0 \rangle \; ,$$

we get, in general, $S^{(11)} = \frac{4}{3}K + \Delta$, where Δ reflects electron correlations. For wave functions which are products of one-particle functions, $\Delta = 0$. It turns out that for He, Li, and Be, Δ amounts to 1–2 % only (for more details the reader is referred to Ref. [5]). As the binding energy E of the system is equal to $(-K)$, we get a good approximation $E = -\frac{3}{4}S^{(11)}$, and indeed, making use of Eq. (3.15), we obtain the experimental data of the energies (within 1–2 %). There is another strong indication that $S^{(11)}$ is correct and $S^{(20)}$ is incorrect. This is explained in Sec. VI [before Eq. (6.16)].

From the above discussion it follows that the correct expression of $S_1(\lambda)$ should be

$$\begin{aligned} S_1(\lambda) &= S^{(11)}(\lambda) \\ &= \langle \psi_0 | Z_1 F_1 | \psi_0 \rangle \; . \end{aligned} \tag{3.21}$$

We have

$$\begin{aligned} F_1 &= [P^2, F] \\ &= -\sum_i [\nabla_i^2 F_i + 2(\nabla_i F_i)\cdot\nabla_i] \; . \end{aligned} \tag{3.22}$$

with $Z_1 = -2iP_z$, and two integrations by parts we get for *each* electron,

$$S_1(\lambda) = \tfrac{2}{3}\int_0^\infty [-(\varphi^2)' + 2x\Theta + x^2\Theta'] g(x,\lambda) x \, dx \; , \tag{3.23}$$

where $\Theta = \varphi^2(\varphi'/\varphi)'$ [see Paper I, Eq. (74)]. Putting $g \equiv 1$, we easily get $S(1)$, Eq. (3.15).

IV. THE 1s STATES OF HELIUM, LITHIUM, AND BERYLLIUM

In this section we summarize the results for helium, lithium, and beryllium. The differential equation

$$xg_i''+(4+2x\varphi_i'/\varphi_i)g_i'+(2\varphi_i'/\varphi_i-\lambda x)g_i=-x \tag{2.17}$$

was solved by computer for all values of λ with an upper limit of 10^6. The upper limits on x were 20, 10, and 3.5 for helium, lithium, and beryllium, respectively. For (i) $x\lambda > 10^4$, $\lambda > 10^2$ and (ii) $x\lambda > 10^2$, $\lambda > 0.1$, the following asymptotic expansion was used:

$$g_i(x,\lambda)=\frac{1}{\lambda}-\frac{2Z_i}{\lambda^2 x}+\frac{4Z_i}{\lambda^3 x^3}+\frac{16Z_i^2}{\lambda^4 x^4}+\frac{96Z_i^3}{\lambda^5 x^5}+\cdots, \tag{4.1}$$

which is easily derived from the above equation. (For more details, the reader is referred to Paper I, Sec. IV.) In the above expansion, Z_i is given by $Z_i=-\varphi_i'/\varphi_i$; it turns out to be a slowly varying function of x. Thus, Eq. (4.1) is not an exactly rigorous asymptotic expansion, but is believed that the error introduced by this is very small.

The expressions of S_ν for $\nu=-1,0,1,2$ are given in terms of the functions $g_i(x,\lambda)$ by Eqs. (3.1′), (3.6′), (3.23), and (3.13), respectively. The corresponding expressions of the $S(\nu)$'s are obtained by simply putting $g_i\equiv 1$. Finally, the $L(\nu)$'s are calculated by Eq. (2.7). The values of the $L(\nu)$'s and the $S(\nu)$'s for the 1s states of helium, lithium, and beryllium are listed in Table I.

In order to obtain a deeper understanding of the results represented in this section and Sec. VI, we introduced the notion of an effective charge Z_{eff}.

This is done as follows: It is well known that for hydrogenlike ions the wave functions for *any* state are obtained from the hydrogen states by introducing the coordinate $\mathbf{r}'=Z_N\mathbf{r}$, where Z_N is the charge of the nucleus. It is then an easy matter to prove that for hydrogenlike ions $\ln I(\nu)$ is related to $[\ln I(\nu)]_H$ of hydrogen by

$$\ln I(\nu)=[\ln I(\nu)]_H+\ln Z_N^2 \; . \tag{4.2}$$

(For details, the reader is referred to Paper I, Sec. IV.) The Clementi wave functions, of course, have no resemblance to hydrogenlike wave functions. However, for these states, we can use the above equation by introducing an effective charge Z_{eff}, defined by

$$\ln Z_{\text{eff}}^2=\ln I(\nu)-[\ln I(\nu)]_H \; . \tag{4.3}$$

The values of $\ln I$ and Z_{eff}, both as functions of ν for 1s states of helium, lithium, and beryllium, are listed in Table II.

Z_{eff} essentially determines the region which contributes significantly to the values of $\ln I(\nu)$. A number of remarks concerning our results for Z_{eff} are given below.

(i) For any system we should have $Z_{\text{eff}} < Z_N$; our values of Z_{eff} satisfy this condition.

(ii) According to Table II, we see that for the same atom, Z_{eff} increases with increasing ν. This is easily explainable for the two extreme cases: In the calculation of the total cross section ($\nu=-1$), the term which depends on $\ln I(-1)$ is derived from the "outer region" of the atom, which is essentially the average distance of the 1s electrons from the nucleus. In other words, one expects a value of Z_{eff} which, roughly speaking, follows from the mutual screening of the two electrons. Our results certainly bear this out.

At the other end ($\nu=2$) we have the Lamb shift. It is well know that the dominating contribution to this effect is derived from the immediate vicinity of the nucleus (the effect is proportional to $[\varphi(0)]^2$). This also follows from the expressions of Z_3, Eq. (3.11′), and S_2, Eq. (3.13). Thus, Z_{eff} should be very close to the charge of the nucleus Z_N. This is in complete agreement with our results.

For the remaining two cases ($\nu=0$ and 1), the values of Z_{eff} are between the above two cases. The physical explanation is less transparent. It is connected to the facts that S_0 and S_1 are determined by the finite operators P_z and P_z^2, respectively [see Eqs. (3.2) and (3.21)]. The corresponding average distances are intermediate between the two discussed above, which are essentially determined by $P_z^0(\nu=-1)$ and $P_z^3(\nu=2)$.

(iii) As to the values of Z_{eff} for different atoms, we see that for all the four values of ν, the difference ΔZ_{eff} between two adjacent atoms is almost exactly equal to 1. In other words, if $s(\nu)$ is the screening factor, defined by $s(\nu)=Z_N-Z_{\text{eff}}$, it turns out to be essentially independent of the charge of the nucleus. The fact that $s(2)$ has some fluctuations is most probably spurious. It is due to the fact that the screening factors are very small and thus very sensitive to very small changes of $\ln I(\nu)$. It is worthwhile pointing out that in many textbooks on quantum mechanics, a one-parameter wave function of the form $\exp(-Z_0 r)$ is derived for a two-electrons system. The value of Z_0 is derived by variational methods to be $Z_0=Z_N-\frac{5}{16}$. Thus, the screening factor is 0.3175. This is very different from our results where $s(\nu)$ changes from $s(-1)=0.436$ to about $s(2)=0.0338$.

Finally, it should be pointed out that our relatively simple method yields for the Lamb shift of helium a value which is smaller by 0.8% than the one computed [6,7] by

TABLE I. $L(\nu)$ and $S(\nu)$ for 1s states of helium, lithium, and beryllium.

	Helium		1s lithium		1s beryllium	
ν	$L(\nu)$	$S(\nu)$	$L(\nu)$	$S(\nu)$	$L(\nu)$	$S(\nu)$
−1	0.324 40	0.394 95	0.269 60	0.148 94	0.191 60	0.077 65
0	1.070 74	1.00	2.027 73	1.00	2.671 43	1.00
1	6.586 90	3.815 71	25.156 88	9.631 96	58.350 26	18.094 51
2	260.981 20	60.254 10	1772.395 0	343.503 2	6596.769	1149.014

TABLE II. $\ln I(\nu)$ and $Z_{\text{eff}}(\nu)$ for 1s states of helium, lithium, and beryllium.

	Hydrogen[a]	Helium		1s lithium		1s beryllium	
ν	$\ln I(\nu)$	$\ln I(\nu)$	$Z_{\text{eff}}(\nu)$	$\ln I(\nu)$	$Z_{\text{eff}}(\nu)$	$\ln I(\nu)$	$Z_{\text{eff}}(\nu)$
−1	−0.073 254	0.8215	1.5642	1.8101	2.5643	2.4675	3.5622
0	0.096 981	1.0707	1.6272	2.0277	2.6257	2.6714	3.6227
1	0.570 87	1.7263	1.7820	2.6118	2.7749	3.2248	3.7696
2	2.984 12	4.3313	1.9613	5.1598	2.9679	5.7413	3.9693

[a] Paper II.

complicated variational methods, yielding $\ln I = 4.366$. This difference is most probably due to the neglect of correlation effects in our approach. It is very likely that the errors on the mean excitation energies for $\nu = -1, 0, 1$ due to the neglect of correlation effects are of the same order of magnitude, though they may be ν dependent.

V. THE 2s HYDROGEN STATE

The radial part of the 2s wave function of hydrogen is

$$\varphi_2 = \frac{1}{\sqrt{2}}(1-\tfrac{1}{2}x)e^{-x/2} . \tag{5.1}$$

Thus, Eq. (2.17) is of the form

$$x(1-\tfrac{1}{2}x)g_{2s}'' + (4-4x+\tfrac{1}{2}x^2)g_{2s}' + (-2+\tfrac{1}{2}x-\lambda x+\tfrac{1}{2}\lambda x^2)g_{2s} = -x(1-\tfrac{1}{2}x) . \tag{5.2}$$

As a first step to solve this equation, we make the substitution

$$g_{2s} = e^{-(t_2-1/2)x}u_2(x,t_2) , \tag{5.3}$$

where $t_2 = \sqrt{\lambda + \frac{1}{4}}$. The equation of u is of the form

$$x(1-\tfrac{1}{2}x)u_2'' + [4-(2t_2+3)x+t_2x^2]u_2' + [-4t_2+(3t_2-1)x]u_2 = -x(1-\tfrac{1}{2}x)e^{(t_2-1/2)x} . \tag{5.4}$$

In order to find the solution of this equation, we go back to the equation mentioned in Sec. II:

$$(H-E_2+\lambda)\mathcal{F}_2(\mathbf{r}) = z\varphi_2 . \tag{2.10}$$

As the energies are measured in rydberg units, the above equation assumes the form

$$(H+t_2^2)\mathcal{F}_2(\mathbf{r}) = z\varphi_2 . \tag{2.10$'$}$$

Now let $\bar{\mathcal{F}}_2(\mathbf{r};t_2)$ be the solution of the homogeneous (reduced) equation

$$(H+t_2^2)\bar{\mathcal{F}}_2(\mathbf{r};t_2) = 0 . \tag{5.5}$$

We recognize immediately that for the ground state of hydrogen we get *exactly* the same equation with t_2^2 replaced by $t_1^2 = \lambda + 1$. Our problem for the ground state of hydrogen has been solved explicitly in Paper I. As the ground-state wave function $\varphi_1 \propto \exp(-x)$, the corresponding $\bar{\mathcal{F}}_1$ function is given by

$$\bar{\mathcal{F}}_1 = e^{-x}\bar{F}_1(x,t_1) = xe^{-x}\bar{g}_{1s}(x,\lambda) . \tag{5.6}$$

In Paper I, the function $\bar{u}_1$ was introduced by the relation

$$\bar{g}_{1s} = e^{-(t_1-1)x}\bar{u}_1 \tag{5.7}$$

(the same relation holds between u_1 and g_1). Therefore, we get

$$\bar{\mathcal{F}}_1 = xe^{-t_1x}\bar{u}_1(x;t_1) . \tag{5.8}$$

Here $\bar{u}_1$ is one of the two independent solutions of the Kummer equation. On the other hand, the function $\bar{\mathcal{F}}_2$ is given by

$$\bar{\mathcal{F}}_2 = \varphi_2\bar{F}_2(x;t_2) , \tag{5.9}$$

which becomes, by Eqs. (5.1) and (5.3), for the reduced equation,

$$\bar{\mathcal{F}}_2 = \left(1-\frac{x}{2}\right)e^{-x/2}x\bar{g}_{2s} = \left(1-\frac{x}{2}\right)xe^{-t_2x}\bar{u}_2(x;t_2) . \tag{5.9$'$}$$

Referring to Eq. (5.5), this function must be equal to $\bar{\mathcal{F}}_1$, Eq. (5.8), at t_2, which yields the relationship

$$\bar{u}_2(x;t_2) = \frac{\bar{u}_1(x;t_2)}{1-x/2} \tag{5.10}$$

(the same relation holds between u_1 and u_2). Substituting the above expression into the reduced equation of Eq. (5.4) indeed yields the Kummer equation. In other words, Eq. (5.4) becomes, with the help of Eq. (5.10),

$$xu_1'' + (4-2t_2x)u_1' + (2-4t_2)u_1 = -x(1-\tfrac{1}{2}x)e^{(t_2-1/2)x} , \tag{5.11}$$

the lhs being identical to the lhs of the 1s equation [Paper I, Eq. (17)], except for the replacement of t_1 by t_2. The two fundamental solutions of the homogeneous equation are

$$v_1 = {}_1F_1\left(2-\frac{1}{t_2};4;2t_2x\right) ,$$

$$v_2 = U\left(2-\frac{1}{t_2};4;2t_2x\right) ,$$

and the Wronskian is given by

$$W=-\frac{3}{4t_2^3\Gamma(2-1/t_2)}\frac{1}{x^4}e^{2t_2x} . \tag{5.12}$$

Therefore, the solution of Eq. (5.12) is of the general form

$$\begin{aligned}\frac{3}{4t_2^3\Gamma(2-1/t_2)}u_1 &= -{}_1F_1\int_0^x Ue^{-(t_2+1/2)x'}(1-\tfrac{1}{2}x')x'^4dx'\\ &\quad +U\int_0^x {}_1F_1e^{-(t_2+1/2)x'}(1-\tfrac{1}{2}x')x'^4dx'\\ &\quad +A\,{}_1F_1+BU . \end{aligned}\tag{5.13}$$

To determine the two coefficients A and B, we impose the condition that $g(x;\lambda)$ would be finite in the physical region $0\leq x\leq\infty$ and that at infinity it does not diverge exponentially. The reason for this restriction is as follows: consider the original equation of F:

$$[H,F]\varphi_2+\lambda F\varphi_2=z\varphi_2 \tag{2.5}$$

from which we get

$$\langle\varphi_n|HF-FH|\varphi_2\rangle+\lambda\langle\varphi_n|F|\varphi_2\rangle=\langle\varphi_n|z|\varphi_2\rangle .$$

Now this expression is identical with our fundamental condition

$$(E_n-E_0+\lambda)\langle\varphi_n|F|\varphi_2\rangle=\langle\varphi_n|z|\varphi_2\rangle \tag{2.6}$$

if

$$\langle H\varphi_n|\mathcal{F}_2\rangle=\langle\varphi_n|H\mathcal{F}_2\rangle , \tag{5.14}$$

which is satisfied if, and only if, $\mathcal{F}_2$ vanishes at infinity and does not diverge at the origin. Thus, if F (or g) satisfies the above-mentioned conditions, Eq. (5.14) is automatically secured. Note that our conditions on F are stricter than is necessary. Now with these conditions in mind, we find immediately that $B=0$ and

$$A=\int_0^\infty Ue^{-(t_2+1/2)x}(1-\tfrac{1}{2}x)x^4dx . \tag{5.15}$$

Consequently, our function $u_1(x;t_2)$ is given by

$$\begin{aligned}\frac{3u_1(x;t_2)}{4t_2^3\Gamma(2-1/t_2)} &= {}_1F_1\left[2-\frac{1}{t_2};4;2t_2x\right]F_1(x)\\ &\quad +U\left[2-\frac{1}{t_2};4;2t_2x\right]F_2(x) ,\end{aligned}\tag{5.16}$$

where

$$\begin{aligned}F_1(x)&=\int_x^\infty U\left[2-\frac{1}{t_2};4;2t_2x'\right]e^{-(t_2+1/2)x'}\\ &\quad\times(1-\tfrac{1}{2}x')x'^4dx\end{aligned}\tag{5.17}$$

and

$$\begin{aligned}F_2(x)&=\int_0^x {}_1F_1\left[2-\frac{1}{t_2};4;2t_2x'\right]e^{-(t_2+1/2)x'}\\ &\quad\times(1-\tfrac{1}{2}x')x'^4dx .\end{aligned}\tag{5.17'}$$

As may be easily verified, u_1 is finite everywhere and behaves like $\exp[(t-\frac{1}{2})x]$ at infinity. Thus, our requirements on g and $\mathcal{F}$ are indeed satisfied.

From this expression we get $u_1(0;t_2)$,

$$u_1(0;t_2)=\tfrac{4}{3}t_2^3\Gamma\left[2-\frac{1}{t_2}\right]F_1(0) .$$

The Laplace transform is given in the literature [8]. We obtain

$$\begin{aligned}u_1(0;t_2)&=\frac{1}{(2t_2-1)(3t_2-1)}\\ &\quad\times\left[{}_2F_1\left[5,2;4-\frac{1}{t_2};x_0\right]\right.\\ &\qquad\left.-\frac{5}{2(4t_2-1)}{}_2F_1\left[6,3;5-\frac{1}{t_2};x_0\right]\right] ,\end{aligned}\tag{5.18}$$

where ${}_2F_1(a,b;c;x_0)$ is the hypergeometric function and $x_0=(1-1/2t_2)/2$.

We now expand u_1 in a power series

$$u_1(x;t_2)=\sum_{n=0}^{\infty}a_nx^n \tag{5.19}$$

and put

$$a_n=a_n^{(1)}-a_n^{(2)} . \tag{5.20}$$

$a_n^{(1)}$ and $a_n^{(2)}$ correspond to the two terms on the rhs of Eq. (5.11). It is a straightforward matter to show that the coefficients $a_n^{(1)}$ are determined by the recursion formula

$$a_{n+1}^{(1)}-\alpha_na_n^{(1)}=\beta_n^{(1)} , \tag{5.21}$$

where

$$\alpha_n=2\frac{(n+2)t_2-1}{(n+1)(n+4)} , \tag{5.21'}$$

$$\beta_n^{(1)}=-\frac{(t_2-\frac{1}{2})^{n-1}}{(n+1)(n+4)(n-1)!} , \tag{5.21''}$$

with $\beta_0^{(1)}=0$. For the coefficients $a_n^{(2)}$ we get the recursion formula

$$a_{n+1}^{(2)}-\alpha_na_n^{(2)}=\beta_n^{(2)} , \tag{5.22}$$

where

$$\beta_n^{(2)}=-\frac{(t_2-\frac{1}{2})^{n-2}}{2(n+1)(n+4)(n-2)!} , \tag{5.22'}$$

with $\beta_0^{(2)}=\beta_1^{(2)}=0$.

Equation (5.21) has been solved by mathematical induction. We get

$$a_n^{(1)}=(\alpha_{n-1}\cdots\alpha_0)a_0^{(1)}+\sum_{k=1}^{n-2}\beta_k^{(1)}\alpha_{k+1}\cdots\alpha_{n-1}+\beta_{n-1}^{(1)}\,, \tag{5.23}$$

where $a_0^{(1)}$, according to Eqs. (5.18) and (5.20), is given by

$$a_0^{(1)}=\frac{{}_2F_1(5,2;4-1/t_2;x_0)}{(2t_2-1)(3t_2-1)}\,. \tag{5.24}$$

Finally, simple but lengthy algebra and use of the Gauss series for the hypergeometric function yield the expression for $a_n^{(1)}$:

$$a_n^{(1)}=\frac{(2t_2x_0)^{n-1}}{2t_2(n+2-1/t_2)n!}\left[n\,{}_2F_1(1,n+4;n+3-1/t_2;x_0)+\frac{x_0(n+4)}{n+3-1/t_2}\,{}_2F_1(2,n+5;n+4-1/t_2;x_0)\right]. \tag{5.25}$$

Next, we evaluate $a_n^{(2)}$. Obviously it is given by the same kind of formula as Eq. (5.23) with $a_0^{(1)}$ and $\beta_k^{(1)}$ replaced by $a_0^{(2)}$ and $\beta_k^{(2)}$, respectively. The expression of $a_0^{(2)}$ follows from Eqs. (5.18) and (5.20):

$$a_0^{(2)}=\frac{5}{2}\,\frac{{}_2F_1(6,3;5-1/t_2;x_0)}{(2t_2-1)(3t_2-1)(4t_2-1)}\,. \tag{5.26}$$

Also, the evaluation of $a_n^{(2)}$ is lengthy and tedious. We find

$$\begin{aligned}a_n^{(2)}=\frac{(2t_2x_0)^{n-2}}{4t_2(n+2-1/t_2)n!}\Bigg[&n(n-1)\,{}_2F_1(2,n+4;n+3-1/t_2;x_0)+2x_0\frac{n(n+4)}{n+3-1/t_2}\,{}_2F_1(2,n+5;n+4-1/t_2;x_0)\\&+2x_0^2\frac{(n+4)(n+5)}{(n+3-1/t_2)(n+4-1/t_2)}\,{}_2F_1(3,n+6;n+5-1/t_2;x_0)\Bigg]\,.\end{aligned} \tag{5.27}$$

Our next task is to derive the integral representation of our function $u_1(x,t_2)$, Eq. (5.19). To accomplish this, use is made of the integral representation [9] of the hypergeometric functions,

$${}_2F_1(a,b;c;x)=\frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)}\int_0^1 y^{b-1}(1-y)^{c-b-1}(1-xy)^{-a}dy\,, \tag{5.28}$$

which is valid for $c>b>0$. As the functions in question do not satisfy these conditions, we apply the transformation [10]

$${}_2F_1(a,b;c;x)=(1-x)^{-b}\,{}_2F_1[b,c-a;c;x/(x-1)]\,. \tag{5.29}$$

By Eqs. (5.25) and (5.27) the expansion coefficients of the function u_1 are composed of five single terms. Let us call them $a_{n1}^{(1)}$, $a_{n2}^{(1)}$, $a_{n1}^{(2)}$, $a_{n2}^{(2)}$, and $a_{n3}^{(2)}$; the first two correspond to the two terms of Eq. (5.25), and the last three correspond to the three terms of Eq. (5.27). We thus get five terms which comprise the function $u_1(x;t_2)$. Each one of them is evaluated with the help of Eqs. (5.28) and (5.29). We reproduce here the five integral representations without going into algebraic details:

(i) $$u_{11}^{(1)}(x,t_2)=\sum_{n=0}^{\infty}a_{n1}^{(1)}x^n=\frac{x}{(t_2+\frac{1}{2})^{2+1/t_2}}\int_0^1 y^{2-1/t_2}\left[2t_2-(t_2-\tfrac{1}{2})y\right]^{1+1/t_2}e^{(t_2-1/2)xy}dy\,. \tag{5.30}$$

(ii) $$u_{12}^{(1)}(x,t_2)=\sum_{n=0}^{\infty}a_{n2}^{(1)}x^n=\frac{1}{(t_2+\frac{1}{2})^{3+1/t_2}}\int_0^1 y^{1-1/t_2}\left[2t_2-(t_2-\tfrac{1}{2})y\right]^{1+1/t_2}(1-y)\left[4+(t_2-\tfrac{1}{2})yx\right]e^{(t_2-1/2)xy}dy\,. \tag{5.31}$$

(iii) $$u_{11}^{(2)}(x,t_1)=\sum_{n=0}^{\infty}a_{n1}^{(2)}x^n=\frac{x^2}{2(t_2+\frac{1}{2})^{2+1/t_2}}\int_0^1 y^{3-1/t_2}\left[2t_2-(t_2-\tfrac{1}{2})y\right]^{1+1/t_2}e^{(t_2-1/2)xy}dy\,. \tag{5.32}$$

$$\text{(iv) } u_{12}^{(2)}(x,t_2)=\sum_{n=0}^{\infty} a_{n2}^{(2)} x^n$$

$$=\frac{x}{(t_2+\frac{1}{2})^{3+1/t_2}}\int_0^1 y^{2-1/t_2}[2t_2-(t_2-\tfrac{1}{2})y]^{1+1/t_2}(1-y)[5+(t_2-\tfrac{1}{2})xy]e^{(t_2-1/2)xy}dy \ . \tag{5.33}$$

$$\text{(v) } u_{13}^{(2)}(x,t_2)=\sum_{n=0}^{\infty} a_{n3}^{(2)} x^n$$

$$=\frac{1}{2(t_2+\frac{1}{2})^{4+1/t_2}}\int_0^1 y^{1-1/t_2}[2t_2-(t_2-\tfrac{1}{2})y]^{1+1/t_2}$$

$$\times(1-y)^2[(t_2-\tfrac{1}{2})^2x^2y^2+10(t_2-\tfrac{1}{2})xy+20]e^{(t_2-1/2)xy}dy \ . \tag{5.34}$$

The above expressions yield the function u_1,

$$u_1(x;t_2)=u_{11}^{(1)}+u_{12}^{(1)}-u_{11}^{(2)}-u_{12}^{(2)}-u_{13}^{(2)} \ . \tag{5.35}$$

This follows from Eqs. (5.19) and (5.20). We now define the function $g_1(x;t_2)$ by

$$g_1=(1-x/2)g_{2s} \ , \tag{5.36}$$

which becomes, according to Eqs. (5.3) and (5.10),

$$g_1=e^{-(t_2-1/2)x}u_1 \ . \tag{5.37}$$

The integral representation of g_1 then follows immediately. We get, after some simple rearrangements,

$$(t_2+\tfrac{1}{2})^{4+1/t_2}g_1(x;t)=g_1^{(1)}+g_1^{(2)}+g_1^{(3)} \ , \tag{5.38}$$

where

$$g_1^{(1)}(x;t_2)=2\int_0^1 y^{1-1/t_2}[2t_2-(t_2-\tfrac{1}{2})y]^{1+1/t_2}(1-y)(2t_2-4+5y)e^{-(t_2-1/2)(1-y)x}dy \ , \tag{5.39}$$

$$g_1^{(2)}(x;t_2)=x\int_0^1 y^{2-1/t_2}[2t_2-(t_2-\tfrac{1}{2})y]^{2+1/t_2}(t_2-\tfrac{9}{2}+5y)e^{-(t_2-1/2)(1-y)x}dy \ , \tag{5.40}$$

$$g_1^{(3)}(x;t_2)=-\tfrac{1}{2}x^2\int_0^1 y^{3-1/t_2}[2t_2-(t_2-\tfrac{1}{2})y]^{3+1/t_2}e^{-(t_2-1/2)(1-y)x}dy \ . \tag{5.41}$$

One interesting feature of the above expression is that it diverges when λ→0. More specifically, the function $g_1^{(1)}$ for $\lambda=\epsilon \ll 1$ is given by

$$g_1^{(1)}(x;\lambda=\epsilon)=\left[-\frac{\frac{3}{2}}{\epsilon}+\frac{15}{2}\right]-\tfrac{1}{4}x^2 \ . \tag{5.42}$$

This result is easily derived from the above integral representations, or, alternatively, from the expressions of a_0, Eqs. (5.20), (5.24), and (5.26), plus the corresponding recursion formulas of g_1. This divergence has a simple physical background: consider the equation

$$(E_{np}-E_{2s}+\lambda)\langle np|F|2s\rangle=\langle np|z|2s\rangle \tag{2.6}$$

or, as

$$F=xP_1g_{2s}$$

$$=xP_1g_1/(1-x/2) \ , \tag{5.43}$$

we have

$$(E_{np}-E_{2s}+\lambda)\left\langle np\left|\frac{x}{1-x/2}g_1\right|2s\right\rangle=\langle np|x|2s\rangle \ , \tag{5.44}$$

where the above expressions are the radial parts of the matrix elements. Obviously, the rhs has some finite value. Due to the degeneracy of the $2s$-$2p$ states, we must have

$$\lim_{\lambda=0}\lambda\left\langle 2p\left|\frac{x}{1-x/2}g_1\right|2s\right\rangle=\langle 2p|x|2s\rangle \ . \tag{5.45}$$

This is possible only if g_1 diverges like $1/\lambda$ for λ→0. In conjunction with Eq. (5.42), it is immediately verified that this is indeed numerically correct. Furthermore, by a similar argument, we get, for $n>2$,

$$\left\langle np\left|\frac{x}{1-x/2}\right|2s\right\rangle=0 \ .$$

However, this is nothing but the orthogonality condition of the $2p$ and np states, because $[x/(1-x/2)]|2s\rangle \propto |2p\rangle$.

Next we consider the expressions of $S_\nu(\lambda)$ of Eq. (2.8). They are easily evaluated with the help of the formulas derived in the Appendix of Paper I.

(i) $\nu=-1$. We have

$$S_{-1}(\lambda)=\langle 0|zF|0\rangle$$
$$=\tfrac{1}{6}\int_0^\infty (1-x/2)g_1 e^{-x}x^4 dx \ .$$

This integral diverges for $\lambda\rightarrow 0$ because of the divergence of $g_1^{(1)}$, Eq. (5.42). The reason is simply the fact that $L(-1)$, Eq. (2.2) diverges for hydrogen because of the $2s$-$2p$ degeneracy.

(ii) $\nu=0$. We have

$$S_0(\lambda)=2i\langle 0|p_z F|0\rangle$$
$$=-\tfrac{2}{3}\int_0^\infty \varphi' \frac{g_1}{1-x/2}\varphi x^3 dx$$
$$=-\tfrac{1}{3}\int_0^\infty (1-x/4)g_1(x,\lambda)e^{-x}x^3 dx \ . \tag{5.46}$$

(iii) $\nu=1$. We have

$$S_1(\lambda)=2\left\langle 0\left|\frac{\partial V}{\partial z}F\right|0\right\rangle$$
$$=\tfrac{2}{3}\int_0^\infty (1-x/2)g_1(x,\lambda)e^{-x}x\, dx \ , \tag{5.47}$$

where $V=-2/r$. Note that in the above two expressions the divergent terms for $\lambda\rightarrow 0$ disappear because the corresponding integrals are equal to zero.

(iv) $\nu=2$. We have

$$S_2(\lambda)=-2\left\langle 0\left|\frac{\partial V}{\partial z}(\nabla^2 F+2\nabla F\cdot\nabla)\right|0\right\rangle ,$$

which becomes, after a lengthy calculation,

$$S_2(\lambda)=2g_1(0,\lambda)-\tfrac{8}{3}\int_0^\infty (1-x/4)g_1(x,\lambda)e^{-x}dx \ . \tag{5.48}$$

Again, it is easily verified that the $1/\lambda$ term of g_1, Eq. (5.42), does not contribute to the above expression.

To obtain the values of $S(\nu)$, we have to put $g=1$, i.e., $g_1=1-x/2$. We get $S(0)=1$, $S(1)=\frac{1}{3}$, and $S(2)=\frac{2}{3}$. Finally, the numerical values of the sum $L(\nu)$ are determined according to Eq. (2.7).

We have $\ln I(\nu)$ calculated by three different methods.

(i) Direct numerical calculation [11].

(ii) Analytical calculation: $g_1(x;t_2)$ was calculated according to the integral representation (5.38)–(5.41). The integrations over y and λ were performed numerically.

(iii) Computer calculation: The differential equation for g_1 was solved by computer. The calculation is given below. The rest of the calculation was as in (ii).

For more details concerning these calculations the reader is referred to Paper II. The results are listed in Table III. We see that three methods yield almost identical results.

Finally, as mentioned in (iii), we are in need of the differential equation for $g_1(x,\lambda)$. It is easily derived either from Eqs. (5.2) and (5.36), or from Eqs. (5.11) and (5.37). We obtain

TABLE III. $\ln I(\nu)$ for the $2s$ hydrogen state.

ν	Direct numerical calculation	Analytical calculation	Computer calculation
0	−1.4457	−1.4455	−1.4443
1	−0.57852	−0.57768	−0.5778
2	2.81175	2.8128	2.8127

$$xg_1''+(4-x)g_1'-\lambda x g_1=-x(1-x/2) \ . \tag{5.49}$$

Note that the lhs of the above equation is not identical with the corresponding expression of the $1s$ case [Paper I, Eq. (15)], in spite of the fact that the corresponding homogeneous equations for the functions u, Eqs. (5.11) and (17) of Paper I are identical. To obtain identical equations for the functions g, one has to take the relation

$$g_{2s}(x,\lambda)=\frac{g_1(x,\lambda)}{1-x/2}e^{-x/2}$$

instead of Eq. (5.36). This follows from comparison of Eqs. (5.6) and (5.9′).

VI. LITHIUM AND BERYLLIUM

We calculate first the mean excitation energies for the $2s$ states of lithium and beryllium. We start again with our fundamental equation discussed in Sec. II,

$$xg''+\left[4+2x\frac{\varphi_i'}{\varphi_i}\right]g'+\left[2\frac{\varphi_i'}{\varphi_i}-\lambda x\right]g=-x \ , \tag{2.17}$$

where the φ_i's are $2s$ Clementi wave functions. These functions have one nodal point. Obviously, the functions g have a divergence at this point. Even for the relatively simple $2s$ hydrogen case, the corresponding g_{2s} function has a pole at the nodal point [see Eq. (5.36)]. In order to learn how to handle the nonhydrogen $2s$ states, we have made use of a two-parameter wave function of the form

$$\varphi_a=N(1-\tfrac{1}{2}Z_1 x)e^{-Z_2 x/2} \ . \tag{6.1}$$

The parameters Z_1 and Z_2 were determined so as to yield the best possible fit to the corresponding Clementi wave function. (There is more than one method to determine the Z's. Different methods can give rise to quite different values of these parameters. This was one of the reasons that, in the end, we used the proper Clementi functions.) If we now make the substitution, as we did for the $2s$ hydrogen case,

$$g(x,\lambda)=\frac{g_1(x,\lambda)}{1-\frac{1}{2}Z_1 x} ,$$

then together with Eq. (6.1), we obtain the equation

$$x g_1'' + (4 - Z_2 x) g_1' + \left[-\lambda x + \frac{\Delta}{1 - \frac{1}{2} Z_1 x} \right] g_1 = -x\left(1 - \tfrac{1}{2} Z_1 x\right) , \quad (6.2)$$

where $\Delta = Z_1 - Z_2$. Obviously, if $\Delta = 0$, we should get the equation for the 2*s* hydrogenlike ion; indeed, the above equation is identical with Eq. (5.49), if we put $Z_1 = Z_2 = 1$.

Let us now investigate the above equation more thoroughly. To do this, it is advantageous to make the transformation

$$g_1(x,\lambda) = u(x,\lambda) e^{-(t_2 - Z_2/2)x} .$$

The above equation then becomes

$$x u'' + (4 - 2 t_2 x) u' - \left[4 t_2 - 2 - \frac{\Delta}{1 - \frac{1}{2} Z_1 x} \right] u = x f(x) , \quad (6.3)$$

where

$$f(x) = -\left(1 - \tfrac{1}{2} Z_1 x\right) e^{(t_2 - Z_2/2)x} , \quad (6.3')$$

and $t_2 = \sqrt{\lambda + Z_2^2/4}$. Of course, putting $Z_1 = Z_2 = 1$, we regain Eq. (5.11) of the 2*s* hydrogen case. The above equation has one additional pole at $x_0 = 2/Z_1$. Let us consider the homogeneous equation of Eq. (6.3), and let $v_1(x)$ and $v_2(x)$ be the regular and irregular solutions, respectively, in the whole range $0 \le x \le \infty$. For $x \gg x_0$, v_1 behaves like the regular solution and v_2 behaves like the irregular solution of the Kummer equation (see Paper I, Sec. III).

We shall now focus on the neighborhood of x_0. We define the variable $y = \frac{1}{2} Z_1 x - 1$; in terms of y, the homogeneous equation of Eq. (6.3) becomes

$$y(1+y) v'' + y \left[4 - \frac{4}{Z_1} t_2 (1+y) \right] v' - \frac{2}{Z_1} [(4 t_2 - 2) y + \Delta] v = 0 , \quad (6.4)$$

where the derivatives are with respect to y. Expanding v in a power series, we find the regular solution

$$v_1(y, t_2) = y \sum_{n=0} b_n y^n , \quad (6.5)$$

where the b_n's are determined by recursion formulas. The important conclusion of this result is that the regular solution of the above equation vanishes at x_0. Now the irregular solution is intimately connected to the regular solution by the well-known formula [12]

$$v_2(y) = v_1(y) \int^y \frac{W(y')}{[v_1(y')]^2} dy' , \quad (6.6)$$

where $W(y)$ is the Wronskian of the equation. Now for $|y| \ll 1$, we get $W \simeq (1+y)^{-4}$; it is easily verified that the general form of v_2 is

$$v_2(y, t_2) = \sum_{n=0} a_n y^n + (y \ln y^2) \sum_{n=0} b_n y^n , \quad (6.7)$$

the b_n's being the above coefficients of the regular solution. Putting this expression back into Eq. (6.4) yields three-term recursion formulas for the a_n's, as the b_n's (for $n > 0$) are known from the regular solution. One gets simple connections between the a_n's and the b_n's, the most important of which is

$$b_0 = \frac{\Delta}{Z_1} a_0 . \quad (6.8)$$

We now return to our inhomogeneous equation (6.3). The solution in terms of the two functions v_1 and v_2 is readily given by the well-known method of variation of parameters. We get

$$u(x; t_2) = v_1 \int_x^\infty v_2(x') \frac{f(x')}{W(x')} dx' + v_2 \int_0^x v_1(x') \frac{f(x')}{W(x')} dx' , \quad (6.9)$$

where the conditions of finiteness at $x = 0$ and $x \to \infty$ have already been incorporated (for details, see again Paper I, Sec. III). We have shown above that at x_0, we have $v_1(x_0) = 0$ and $v_2(x_0) = a_0 \neq 0$; thus

$$u(x_0) = a_0 \int_0^{x_0} v_1(x') \frac{f(x')}{W(x')} dx' = a_0 I_2(x_0) . \quad (6.10)$$

Hence the solution of Eq. (2.17) at x_0 is different from zero. Consider the derivative of u at x_0. We have

$$u'(x_0) = v_1'(x_0) I_1(x_0) + v_2'(x_0) I_2(x_0) , \quad (6.11)$$

where $v_2'(x_0)$, according to Eqs. (6.7) and (6.8) in the limit $y \to 0$, is given by

$$v_2' = \tfrac{1}{2} a_0 \Delta \ln y^2 + O(y^0) , \quad (6.12)$$

and by Eq. (6.10), we get, for $y \to 0$,

$$\left. \frac{du}{dx} \right|_{x_0} = \tfrac{1}{2} \Delta u(x_0) \ln y^2 . \quad (6.13)$$

Obviously, the behavior of g_1 in the neighborhood of x_0 is the same as that of u. Thus the conclusion is that the solution of Eq. (6.2) has a finite value at x_0, but its first derivative diverges logarithmically.

As mentioned at the beginning of this section, the exact 2*s* Clementi wave functions were used to calculate the 2*s* mean excitation energies. To solve Eq. (2.17) is impossible because g diverges at x_0. We should solve an equation analogous to Eq. (6.2), but to do this by computer is not feasible because of the irregular behavior of the first and second derivatives of g_1 at x_0. (It is obvious that any nonhydrogenic 2*s* wave function gives rise to behavior at the nodal point similar to that of the one discussed above.) To circumvent this problem, we defined the function g_3 by

$$g(x,\lambda)=\frac{g_3(x,\lambda)}{\varphi^3(x)} . \tag{6.14}$$

This function has a zero of second order at the nodal point x_0. The differential equation of g_3 is easily derived from Eq. (2.17):

$$x\varphi g_3''+(4\varphi-4x\varphi')g_3' +[-10\varphi'-3x\varphi''+6x(\varphi'^2/\varphi)-\lambda x\varphi]g_3=-x\varphi^4 . \tag{6.15}$$

This equation was solved by computer for $x<12$, i.e., the upper limit was much beyond the nodal point. For $x>12$ and $x\lambda>20$, the asymptotic expansion of g_1, Eq. (4.1), was used. It is interesting to point out that in the limit $\lambda=0$, the function g is finite, unlike the corresponding hydrogen case [see Eq. (5.42)]. The reason, of course, is simply the nondegeneracy of the 2*s*-2*p* states.

The functions $S_\nu(\lambda)$, $S(\nu)$, and $L(\nu)$ were calculated by the relevant expressions given explicitly in Sec. III. This is explained in Sec. IV. The values of $Z_{\text{eff}}(\nu)$ were evaluated by Eq. (4.3), making use of the 2*s* hydrogen data of Table III.

Our results of the $L(\nu)$'s and $S(\nu)$'s as functions of ν for the 2*s* states of lithium and beryllium are listed in Table IV; the corresponding results of $\ln I(\nu)$ and the effective charge Z_{eff} are listed in Table V.

Of course, no values of Z_{eff} exist for $\nu=-1$, simply because for hydrogen, $\ln I(-1)$ diverges. For $\nu=0$, the dominant region which contributes to the mean excitation energies is the "outer region" (as in the case of the total cross section) of the atom. In the present case, this region lies just outside the average distance of the 2*s* electrons from the nucleus. As these electrons are relatively far from the nucleus, it is understandable that, for a system with one 2*s* electron only, Z_{eff} should be about equal to (Z_N-2); thus, for lithium it should be about 1. Finally, for beryllium, due to the mutual screening of the two 2*s* electrons, Z_{eff} should be between 1 and 2. Our results are therefore very reasonable. As a matter of fact, from the point of view of the 2*s* electrons, the beryllium atom has a certain similarity to the helium atom. Therefore, the values of the respective Z_{eff}'s should not be very far from each other. This is indeed the case. As for the $\nu=2$ cases, the results are very similar to the corresponding 1*s* cases, as indeed they should be because the underlying physics is the same (see Sec. IV).

Finally, a remark concerning the $\nu=1$ case. In Sec. III, paragraph (iv), we pointed out that there are two different values for $S^{(11)}$ and $S^{(20)}$. Furthermore, we showed there that $S^{(11)}$ is the correct one for $\nu=1$. All the values listed in Tables I, II, IV, and V have been calculated by the expression $S^{(11)}$, Eq. (3.23). But we have also calculated Z_{eff} by $S^{(20)}$. (The explicit expression is not given in this paper.) As we see from Tables II and V, the values of both $\ln I(\nu)$ and $Z_{\text{eff}}(\nu)$ increase steadily with increasing ν. That for Z_{eff} this makes sense from the physical point of view has been explained in Sec. IV and in this section. However, the values of Z_{eff} calculated by $S^{(20)}$ for the 2*s* states violate this rule. We get $Z_{\text{eff}}^{(20)}=0.6$ for lithium, and $Z_{\text{eff}}^{(20)}\simeq 1$ for beryllium, both are off by about a factor of 3.

TABLE IV. $L(\nu)$ and $S(\nu)$ for 2*s* states of lithium and beryllium.

	2*s* lithium		2*s* beryllium	
ν	$L(\nu)$	$S(\nu)$	$L(\nu)$	$S(\nu)$
−1	−10.878	5.9133	−3.2534	2.8091
0	−1.4701	1.00	−0.71996	1.00
1	0.4294	0.5568	2.2474	1.3364
2	41.755	8.4164	211.25	38.265

TABLE V. $\ln I(\nu)$ and $Z_{\text{eff}}(\nu)$ for 2*s* states of lithium and beryllium.

	2*s* lithium		2*s* beryllium	
ν	$\ln I(\nu)$	$Z_{\text{eff}}(\nu)$	$\ln I(\nu)$	$Z_{\text{eff}}(\nu)$
−1	−1.8396		−1.1582	
0	−1.4701	0.988	−0.71996	1.437
1	0.7712	1.963	1.6817	3.095
2	4.9611	2.928	5.5207	3.873

Finally, we evaluate the results of $\ln I(\nu)$ for the atoms lithium and beryllium. They are defined by

$$\ln I(\nu)=\frac{2L^{(1s)}(\nu)+nL^{(2s)}(\nu)}{2S^{(1s)}(\nu)+nS^{(2s)}(\nu)} , \tag{6.16}$$

where for lithium we have $n=1$ and for beryllium we have $n=2$. The results are listed in Table VI. The values of $L(\nu)$ and $S(\nu)$ for the 1*s* and 2*s* states were taken from Tables I and IV, respectively.

We notice that for the total cross section ($\nu=-1$), the outer electrons dominate, whereas for the Lamb shift ($\nu=2$), the inner electrons dominate. This is due to the fact that for $\nu=-1$, the dominant contribution is derived from the large values of r [there is an effective cutoff for $r\ll 1$; see Eq. (3.1′)]; in this region we have $\varphi_{2s}^2\gg\varphi_{1s}^2$. This essentially explains the dominance of the 2*s* state for $\nu=-1$. On the other hand, for $\nu=2$, $S(2)$ is proportional to $[\varphi(0)]^2$; as

$$[\varphi_{1s}(0)]^2\gg[\varphi_{2s}(0)]^2 ,$$

it is obvious that the 1*s* states should dominate. For the straggling effect ($\nu=1$), this is also true, but to a lesser extent. Finally, for the stopping power ($\nu=0$), the 1*s* and 2*s* states yield contributions which are both of the same

TABLE VI. $\ln I(\nu)$ for the atoms lithium and beryllium.

	Lithium	Beryllium
ν	$\ln I(\nu)$	$\ln I(\nu)$
−1	−1.6645	−1.0606
0	0.8618	0.9757
1	2.560	3.1186
2	5.157	5.734

order of magnitude. In a subsequent paper we will report on the calculation of the excitation energies $I(\nu)$ for the ground states of all atoms from boron to neon.

VII. SUMMARY

The four logarithmic mean excitation energies ($\nu=-1,0,1,2$) have been calculated for the $2s$ states of hydrogen, and the ground states of helium, lithium, and beryllium.

(1) The $2s$ state of hydrogen has been calculated in Sec. V. It can essentially be reduced to the $1s$ state, which has been dealt with in Paper I. The results are summarized in Table III. Our accuracy is relatively low (4–6 digits). This could be greatly improved by expanding $S_\nu(\lambda)$, Eq. (2.8), in powers of $1/\lambda$, but this calculation has not yet been completed. Shimamura [13] has calculated the same quantities by the Coulomb Green's-function method. His accuracies are much higher (14 digits) than ours. Our results coincide completely (within the limits of our digits) with Shimamura's results.

(2) The logarithmic mean excitation energies for the $1s$ states of He, Li, and Be have been calculated with the help of Eq. (2.17). The results are summarized in Tables I and II. For the Lamb shift ($\nu=2$) of helium, we get a result which is smaller by 0.8% than the one computed [6,7] by complicated variational methods. This discrepancy is most probably due to our neglect of correlation effects. As the logarithmic mean excitation energies for $\nu=-1,0,1$ have been evaluated by exactly the same method, it is very likely that the corresponding errors are of the same order of magnitude as for the $\nu=2$ case, though they may have some ν dependence. Other methods have been employed to calculate these quantities. We have in mind, in particular, the method [5,14] in which $L(\nu)$ is calculated by taking the derivative of $S(\nu)$ with respect to ν, which is treated as a continuous variable. Upper and lower bounds were calculated from $S(\nu-1)$, $S(\nu)$, and $S(\nu+1)$. As $S(3)$ diverges, it is impossible to calculate by this method an upper bound for the Lamb shift, and the lower bound turns out to be rather poor. Our $\nu=-1,0,1$ results for helium are in agreement with the results of Ref. [5]. However, our results are lower by a few percent than the corresponding lower limits given in Ref. [14] (4%, 5%, and 1.7% for $\nu=-1,0,1$, respectively). In Ref. [14] the upper-limit–lower-limit differences are smaller than the corresponding upper-lower limits given in Ref. [5]. The discrepancies between our results and those of Ref. [14] are somewhat larger than we should expect from the remarks made at the beginning of this paragraph. Of course, we really do not know how accurate the results of Ref. [14] are. Our results for the atoms lithium and beryllium are summarized in Table VI. The discrepancies between our values and the lowest values of Ref. [5] are 1.6% for lithium ($\nu=-1$), 3.6% for lithium ($\nu=0$), and 6.7% for beryllium ($\nu=0$). We should point out that in the last case the upper-limit–lower-limit difference in Ref. [5] is more than 50%, which should be an indication that these data are unreliable.

(3) In Sec. IV we introduced the effective charges Z_{eff} defined by Eq. (4.3). For the $1s$ states the values of Z_{eff} for He, Li, and Be are listed in Table II. They have remarkably simple features. We found that $Z_{\text{eff}}=Z_N-s(\nu)$, where Z_N is the charge of the nucleus and $s(\nu)$ is the screening factor. The latter is essentially independent of Z_N. The $s(\nu)$'s decrease monotonously from 0.43 for $\nu=-1$ to 0.03 for $\nu=2$. We have also evaluated the Z_{eff}'s for the $1s$ states of boron and carbon. These data are in agreement with our present results for the lighter atoms, but their explicit values are not listed in the present paper. All known data of ours for the $1s$ states can be summarized by the simple formula

$$I(\nu)=I(\nu)_{\text{H}}[Z_N-s(\nu)]^2 ,$$

where $I(\nu)_{\text{H}}$ are the logarithmic mean excitation energies of hydrogen.

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