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Multiple Ionization Processes in Helium

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Double-ionization processes in helium by photon and electron impact are analyzed, and it is shown that the inclusion of atomic correlation is very important. Detailed calculations are performed for the case of photo-ionization over the whole range of photon energies, and the asymptotic behavior of the cross section in the limit of large photon energies is discussed. Excellent agreement is found with recent experimental data. Conclusions are drawn concerning the related electron-impact problem at high incident electron energies. The leading term of the cross section is evaluated, and comparison is made with the presently available experiments.

I. INTRODUCTION

RECENT experiments on multiple-ionization phenomena in noble gases by photon[1] or electron[2–4] impact have stimulated interest in the theoretical investigation of these problems. In addition, among the various multiparticle scattering processes occurring in atomic physics, multiple-ionization phenomena deserve special attention since they are extremely sensitive probes of the details of atomic structure.[5,6]

In this paper we present a theoretical analysis of double-ionization phenomena in helium, where calculations from first principles can be done. Let us first recall that the problem of *single* ionization of this atom by photon impact has been successfully analyzed by Migneron and Levinger[7] on the basis of calculations by Salpeter and Zaidi[8] and Stewart and Webb.[9] The agreement with experiment[10,11] is excellent. For *double* ionization, however, the situation is more complicated because this last process depends so delicately[5] on correlation effects[12,13] between atomic electrons. Physically, this sensitivity is very reasonable. Indeed, if we neglect the interaction between the atomic electrons completely, then in first Born approximation, where the interaction with the projectile acts just once, only single ionization is possible. Thus, the amount by which the first Born approximation differs from zero depends precisely on those small deviations which arise from the interelectronic interactions in the target.

As will be seen later, even the Hartree-Fock ground-

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[1] Thomas A. Carlson, Phys. Rev. **156**, 142 (1967).

[2] B. L. Schram, A. J. H. Boerboom, and J. Kistemaker, Physica **32**, 185 (1966).

[3] B. L. Schram, F. J. de Heer, A. J. H. Boerboom, M. J. Van der Wiel, H. R. Moustafa, J. Schutten, and J. Kistemaker, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Hastings-on-Hudson, New York, 1965), p. 434.

[4] F. Fiquet-Fayard, F. Muller, and J. P. Ziesel, in Ref. 3, p. 413.

[5] F. W. Byron, Jr., and C. J. Joachain, Phys. Rev. Letters **16**, 1139 (1966).

[6] F. W. Byron, Jr., and C. J. Joachain, Phys. Letters **24A**, 616 (1967). In Eq. (1) of this reference π should be replaced by π^2 and the last formula should read

$$a=(4\pi^2\alpha a_0^2)^{-1}\int_{B_i}^{\infty}\frac{\sigma_\gamma^{++}(E_\gamma)dE_\gamma.}{E_\gamma}$$

[7] R. Migneron and J. S. Levinger, Phys. Rev. **139**, A646 (1965).

[8] E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).

[9] A. L. Stewart and T. G. Webb, Proc. Phys. Soc. (London) **A82**, 532 (1963).

[10] J. F. Lowry, D. L. Ederer, and D. H. Tomboulian, Phys. Rev. **137**, A1054 (1965).

[11] A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, Opt. i Spektroskopiya, **17**, 438 (1964) [English transl.: Opt. Spectry. (USSR) **17**, 234 (1964)].

[12] F. W. Byron, Jr., and C. J. Joachain, Phys. Rev. **146**, 1 (1966).

[13] F. W. Byron, Jr., and C. J. Joachain, Phys. Rev. **157**, 1 (1967); **157**, 7 (1967).

state wave function is inadequate to describe the effect of *initial-state interactions* in double-ionization processes, whereas in the case of single ionization it gives a reasonably good account of experimental results. At this point, it is worth noting that single ionization means the ejection of one electron, the remaining singly charged ion being left in any possible bound state. Thus, single ionization is a combination of *basic* single ionization, where the residual ion is left in its ground state, and double excitation (bound-free) in which the ion is left in an excited state. This last process is very similar to double ionization and therefore an accurate description of it also requires a precise wave function for the initial state.

In Sec. II we review briefly the theory of double-ionization processes. We examine the asymptotic behavior of double photo-ionization cross sections in the limit of large incident photon energies. We also show that the cross section for double ionization by *electron* impact at high incident electron energies is related to the corresponding photo-ionization process, and discuss the use of approximate wave functions to describe the helium atom in the initial and final states.

Section III is devoted to the detailed calculations of the relevant cross sections. Finally, in Sec. IV we discuss our results in connection with recent experimental data.[1–4]

II. GENERAL THEORY

Let us first consider double ionization by photon absorption. To first order in the interaction between the atomic electrons and the electromagnetic field, we get the Born-approximation total cross section

$$\sigma_\gamma^{++}(E_\gamma)=\frac{4\pi^2\alpha a_0^2}{E_\gamma}\sum_l\int d\epsilon\int d\epsilon' \times\left|\left\langle\Psi_f^{(l)}(\mathbf{r}_1,\mathbf{r}_2)\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\Psi_i(\mathbf{r}_1,\mathbf{r}_2)\right\rangle\right|^2 \times\delta(E_\gamma-B_i-\epsilon-\epsilon')\,,\qquad(1)$$

where we have neglected retardation effects. The wave function $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$ describes the initial ground state of the helium atom and $\Psi_f^{(l)}(\mathbf{r}_1,\mathbf{r}_2)$ is the final state of the helium system containing an α-particle and two unbound electrons. The two electrons are labelled in the final state by their single-particle energies, ϵ and ϵ', and by their orbital angular momentum quantum numbers, $(l+1)$ and l which must couple to one since the photon carries a total angular momentum of $\hbar$. The quantity E_γ is the energy of the incident photon and B_i is the binding energy of the helium ground state ($B_i=2.904$ a.u.). All energies are in atomic units (a.u.), α is the fine structure constant, and a_0 is the Bohr radius.

In principle, Ψ_i and $\Psi_f^{(l)}$ are, respectively, the *exact* wave functions of the helium system in the initial and final state, thus taking into account completely the effect of initial- and final-state interactions between the two atomic electrons. While for Ψ_i very accurate wave functions are available, the situation is much more complicated for $\Psi_f^{(l)}$, since we are dealing in this case with two electrons in the continuum. We will come back to this problem in Sec. III, but at this point we show that in the limit of *large incident photon energies*, Eq. (1) simplifies considerably. Indeed, as $E_\gamma\to\infty$, at least one of the ejected electrons must have very large energy and can be represented by a plane wave,[14] so that ψ_f can be written as

$$\Psi_f(\mathbf{r}_1,\mathbf{r}_2)=2^{-1/2}[k_f/(2\pi)^3]^{1/2} \times[e^{i\mathbf{k}_f\cdot\mathbf{r}_1}\phi_n(\mathbf{r}_2)+\phi_n(\mathbf{r}_1)e^{i\mathbf{k}_f\cdot\mathbf{r}_2}]\,,\qquad(2)$$

i.e., a symmetrized product of a plane wave normalized to unit energy times a single-particle Coulomb wave function. Under these circumstances, it is easy to show using the method of Kabir and Salpeter[15] that the "asymptotic" cross section $\sigma_\gamma(E_\gamma\to\infty)$ for any ionization process in which at least one electron is ejected is given by

$$\sigma_\gamma(E_\gamma\to\infty)=\frac{256\pi^2\alpha a_0^2}{3\sqrt{2}E_\gamma^{7/2}}\sum_n\left|\int\Psi_i(0,\mathbf{r})\phi_n(\mathbf{r})d\mathbf{r}\right|^2,\qquad(3)$$

where the energy E_γ is expressed in atomic units and the sum (integral) on final states is to be determined by the process of interest. For example, the "asymptotic" cross section for all ionization processes (both single and double) is given by

$$\sigma_\gamma^{+,++}(E_\gamma\to\infty)=\frac{256\pi^2\alpha a_0^2}{3\sqrt{2}E_\gamma^{7/2}}\int|\Psi_i(0,\mathbf{r})|^2d\mathbf{r}\,,\qquad(4)$$

where we have made use of the closure relation since the ϕ_n form a complete orthonormal set. Similarly, the asymptotic cross section for single ionization is just

$$\sigma_\gamma^{+}(E_\gamma\to\infty)=\frac{256\pi^2\alpha a_0^2}{3\sqrt{2}E_\gamma^{7/2}}\sum_n\left|\int\Psi_i(0,\mathbf{r})\phi_n(\mathbf{r})d\mathbf{r}\right|^2,\qquad(5)$$

where the sum runs over all *bound* states of the He$^+$ ion. Clearly,

$$\sigma_\gamma^{++}(E_\gamma\to\infty)=\sigma_\gamma^{+,++}(E_\gamma\to\infty)-\sigma_\gamma^{+}(E_\gamma\to\infty)\,.\qquad(6)$$

The utility of Eq. (6) lies in the fact that it allows an evaluation of $\sigma_\gamma^{++}(E_\gamma\to\infty)$ even for very accurate initial-state wave functions Ψ_i of the Hylleraas type.[16] Indeed, in computing the integrals appearing on the right-hand side of Eqs. (4) and (5), the function Ψ_i enters only through a simple s-wave function of one

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[14] Note that the use of a plane wave for the asymptotic form of the wave function is justified if one calculates the dipole matrix element in the manner of Salpeter and Zaidi (Ref. 8), i.e., if one uses the operator d/dz rather than z.

[15] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957).

[16] E. A. Hylleraas, Z. Physik **54**, 347 (1929); **65**, 209 (1930).

variable. It is clear from Eq. (1) that for nonasymptotic values of E_γ we must use initial-state wave functions Ψ_i which are simpler in form and less accurate. Thus Eq. (6) gives a way of estimating the accuracy of our initial-state wave function by comparison, in the asymptotic region, with an accurate calculation of $\sigma_\gamma{}^{++}(E_\gamma\to\infty)$ using a very precise Hylleraas-type ground-state wave function.

Let us turn now to the process of double ionization by electron impact. We assume that the incident electron, although nonrelativistic, has sufficiently high energy so that exchange effects between the incident and (initially) bound electrons may be neglected. Applying the first Born approximation, we get for the double-ionization cross section by electron impact

$$\sigma_e{}^{++}(E_e)=\frac{4\pi a_0{}^2}{E_e}\sum_f\int_{k_i-k_f}^{k_i+k_f}\frac{1}{\Delta^3}|\langle\Psi_f(\mathbf{r}_1,\mathbf{r}_2)|e^{i\Delta\cdot\mathbf{r}_1}+e^{i\Delta\cdot\mathbf{r}_2}|\Psi_i(\mathbf{r}_1,\mathbf{r}_2)\rangle|^2d\Delta\,,\quad(7)$$

where E_e is the incident electron energy (in a.u.), $\mathbf{k}_i$ and $\mathbf{k}_f$ are the initial and final propagation vectors of the projectile electron, Ψ_i is the ground-state helium wave function, and Ψ_f is any possible final state in which the two atomic electrons are unbound. Because of the factor Δ^{-3}, the most important values of Δ in the integration are small ones. Thus the important contribution to $\sigma_e{}^{++}$ comes from electrons which are ejected with *low* velocities (such that k_i-k_f is small). If one wants the *dominant* term in $\sigma_e{}^{++}$ at high energies, one can further concentrate on a particular term in the expansion of $\exp(i\mathbf{\Delta}\cdot\mathbf{r}_1)$ or $\exp(i\mathbf{\Delta}\cdot\mathbf{r}_2)$ in Legendre polynomials. Indeed, if we write

$$e^{i\Delta\cdot r_1}=\sum_{l=0}^{\infty}(2l+1)i^lj_l(\Delta r_1)P_l(\cos\theta_1)\,,\quad(8)$$

where we have taken $\mathbf{\Delta}$ in the z direction, then the term in $j_1(\Delta r_1)$ makes maximum use of the limit $k_i\simeq k_f$, since $j_1(\Delta r_1)\sim\Delta r_1$ for small values of Δ. Thus the Δ integration will give a term in $\ln(k_i-k_f)$ from the region of small Δ. Since the action of the bound-state wave function guarantees that only values of $r\simeq a_0$ will be important in the inner product of Eq. (7), we can isolate the logarithmic contribution. We find

$$\sigma_e{}^{++}(E_e)=\frac{4\pi a_0{}^2}{E_e}\sum_f\left[\tilde{a}\ln(k_i-k_f)^{-1}+\tilde{b}+O\left(\frac{1}{E_e}\right)\right],\quad(9)$$

where

$$\tilde{a}=|\langle\Psi_f|r_1\cos\theta_1+r_2\cos\theta_2|\Psi_i\rangle|^2\quad(10)$$

and $\tilde{b}$ is energy-independent and involves contributions from *all* terms of the multipole Legendre expansion (8), including a contribution from the partial wave $l=1$ in addition to the logarithmic term written above. Thus, the calculation of $\tilde{b}$ is much more difficult than the corresponding one for $\tilde{a}$. Now, since

$$\tfrac{1}{2}(k_i{}^2-k_f{}^2)=B_i+\epsilon+\epsilon'\,,$$

where ϵ and ϵ' are the energies (in a.u.) of the two ejected electrons, we find for large incident energies ($E_e=\frac{1}{2}k_i{}^2$)

$$k_f=k_i-\frac{(B_i+\epsilon+\epsilon')}{(2E_e)^{\frac{1}{2}}}+\cdots,$$

and thus

$$k_i-k_f=\tilde{c}(E_e)^{-1/2},$$

where $\tilde{c}$ is a function of ϵ and ϵ'. Thus

$$\sigma_e{}^{++}(E_e)=\frac{2\pi a_0{}^2}{E_e}\left[a\ln E_e+b+O\left(\frac{1}{E_e}\right)\right],\quad(11)$$

where

$$a=\sum_f|\langle\Psi_f|r_1\cos\theta_1+r_2\cos\theta_2|\Psi_i\rangle|^2$$
$$\equiv\sum_f|\langle\Psi_f|z_1+z_2|\Psi_i\rangle|^2\quad(12)$$

and b is a constant directly related to $\tilde{b}$ and $\tilde{c}$. In the sum over final states appearing in Eq. (12), only states with total orbital angular momentum $L=1$ contribute, so that we can write a in the form

$$a=\sum_l\int d\epsilon\int d\epsilon'|\langle\Psi_f{}^{(l)}|z_1+z_2|\Psi_i\rangle|^2,\quad(13)$$

where $\Psi_f{}^{(l)}$ is precisely the quantity defined in Eq. (1) in connection with the double-ionization process by photon impact.

While we are still working in terms of exact wave functions, we note that since

$$\left\langle\Psi_f{}^{(l)}\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\Psi_i\right\rangle=-(B_i+\epsilon+\epsilon')$$
$$\times\langle\Psi_f{}^{(l)}|z_1+z_2|\Psi_i\rangle,\quad(14)$$

we can also write a as

$$a=\sum_l\int d\epsilon\int d\epsilon'\frac{\left|\left\langle\Psi_f{}^{(l)}\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\Psi_i\right\rangle\right|^2}{(B_i+\epsilon+\epsilon')^2},\quad(15)$$

and thus

$$a=\int_{B_i}^{\infty}dE_\gamma\sum_l\int d\epsilon\int d\epsilon'\frac{1}{E_\gamma{}^2}$$
$$\times\left|\left\langle\Psi_f{}^{(l)}\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\Psi_i\right\rangle\right|^2{}^2\delta(E_\gamma-B_i-\epsilon-\epsilon')\,.\quad(16)$$

But, according to Eq. (1),

$$\sum_l\int d\epsilon\int d\epsilon'\left|\left\langle\Psi_f{}^{(l)}\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|\Psi_i\right\rangle\right|^2$$
$$\times\delta(E_\gamma-B_i-\epsilon-\epsilon')=\frac{E_\gamma\sigma_\gamma{}^{++}(E_\gamma)}{4\pi^2\alpha a_0{}^2},\quad(17)$$

and therefore the quantity a is related to the cross section for double photo-ionization by

$$a=(4\pi^2\alpha a_0^2)^{-1}\int_{B_i}^{\infty}\frac{\sigma_\gamma^{++}(E_\gamma)}{E_\gamma}dE_\gamma. \tag{18}$$

It should bee mphasized that Eqs. (13) and (18) are completely equivalent only if both Ψ_i and Ψ_f are *exact* solutions of the Schrödinger equation, not if approximate solutions are used. This problem is not too serious for the initial state Ψ_i. Indeed, by the use of the Rayleigh-Ritz variational method it is possible to obtain extremely accurate expressions for Ψ_i. The most accurate functions are those which make use of the Hylleraas[16] variables $s=r_1+r_2$, $t=r_1-r_2$, and $u=r_{12}$ in the trial functions. Since one of these variables is the interelectronic distance r_{12}, such functions are practically impossible to handle in evaluating expressions like Eq. (1). For this reason we have expanded Ψ_i in relative partial waves

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{4\pi}\sum_l F_l(r_1,r_2)P_l(\cos\theta_{12}), \tag{19}$$

where

$$F_l(r_1,r_2)=\sum_{m\geq n}A_{mn}^{(l)}r_1^l r_2^l(r_1^m r_2^n+r_1^n r_2^m)\times e^{-\beta(r_1+r_2)/2}. \tag{20}$$

In Eq. (20), the sum on m and n runs from 0 to 5 with $m+n\leqslant 6$, thus giving 15 terms in each partial wave. We find that with just the first three relative partial waves, a binding energy of $B_i=2.9020$ a.u. was obtained, which is very close to the "experimental" value $B_i=2.9037$ a.u. We used the value $\beta=3.7$. The coefficients $A_{mn}^{(l)}$ are displayed in Table I.

Since, as already mentioned, it is desirable to have a very precise initial-state wave function, we checked the function given in Table I by calculating with it the ratio

$$\rho_\gamma(E_\gamma)=\sigma_\gamma^{++}(E_\gamma)/\sigma_\gamma^{+}(E_\gamma) \tag{21}$$

in the asymptotic region $E_\gamma\to\infty$, i.e., by using Eqs. (4), (5), and (6). The same quantity $\rho_\gamma(E_\gamma\to\infty)$ was also calculated using the extremely accurate ground-state wave function of Kinoshita,[17] which gives $B_i=2.903722$ a.u. The results are shown in Table II, along with the values of $\rho_\gamma(E_\gamma\to\infty)$ obtained from several other approximations to Ψ_i. Our wave function [Eqs. (19) and (20)] gives a value of $\rho_\gamma(E_\gamma\to\infty)$ only 8% greater than the very precise result obtained with the Kinoshita wave function. The 18-parameter, Hylleraas-type wave function of Chandrasekhar and Herzberg[18] gives a result approximately 3% larger than the result calculated with the Kinoshita wave function. The Hartree-Fock ground-state wave function,[19] on the other hand, gives a value of $\rho_\gamma(E_\gamma\to\infty)$ which is smaller than the best value by more than a factor of three. The screened hydrogenic ($Z^*=27/16$) wave function also does very poorly. Thus the calculation of $\rho_\gamma(E_\gamma)$ in the asymptotic region $E_\gamma\to\infty$ is a striking illustration of the fact that noncorrelated initial-state wave functions are not expected to give a correct description of double-ionization phenomena.

TABLE I. The coefficients $A_{mn}^{(l)}$ of the ground-state wave function Ψ_i [see Eqs. (19) and (20)].

(m,n)	$A_{mn}^{(0)}$	$A_{mn}^{(1)}$	$A_{mn}^{(2)}$
(0,0)	8.69519	−14.2888	−14.1186
(0,1)	2.84923	37.5271	36.4897
(0,2)	8.24437	−14.0944	−16.0409
(0,3)	−4.74978	0.264419	2.93842
(0,4)	1.36195	0.593035	−0.211587
(0,5)	−0.111747	−0.0647055	0.00361276
(1,1)	−7.73456	−35.2189	−23.3933
(1,2)	5.82892	35.2792	19.3197
(1,3)	2.35973	−5.25726	−3.17959
(1,4)	−1.27994	−0.0307959	0.197619
(1,5)	0.116503	0.0317287	−0.00270782
(2,2)	−5.00189	−9.50410	−3.45314
(2,3)	1.99741	3.00342	0.880129
(2,4)	0.00885715	−0.110612	−0.0342703
(3,3)	−0.222887	−0.159411	−0.0314348

TABLE II. The asymptotic ratio $\rho_\gamma(E_\gamma\to\infty)$ calculated by using Eqs. (4), (5), and (6) with various helium ground-state wave functions Ψ_i. BJ 45 refers to the 45-parameter wave function used in this paper [see Eqs. (19) and (20) and Table I]. CH 18 corresponds to the 18-parameter, Hylleraas-type wave function of Chandrasekhar and Herzberg (Ref. 18), while K 39 refers to the 39-parameter Kinoshita wave function (Ref. 17).

Ψ_i	$\rho_\gamma(E_\gamma\to\infty)$
Screened hydrogenic ($Z^*=27/16$)	0.0072
Hartree-Fock	0.0051
BJ 45	0.0181
CH 18	0.0171
K 39	0.0166

We now turn to the problem of representing the final state of the helium atom with two unbound electrons. We have taken a symmetrized product of uncorrelated Coulomb wave functions for central charge $Z=2$,

$$\Psi_f^{(l)}(\mathbf{r}_1,\mathbf{r}_2)=(2)^{-1/2}\sum_{m=-l}^{+l}(l+1,m,l,-m|1,0)\times[R_{\epsilon,l+1}(r_1)R_{\epsilon',l}(r_2)Y_{l+1,m}(\Omega_1)Y_{l,-m}(\Omega_2)+1\leftrightarrow 2], \tag{22}$$

where the radial wave function $R_{\epsilon,l}$ is "normalized" so that

$$\int_0^\infty R_{\epsilon,l}(r)R_{\epsilon',l}(r)r^2dr=\delta(\epsilon-\epsilon'). \tag{23}$$

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[17] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[18] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[19] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

The reason that we neglect the interelectronic interaction in the final state is twofold. First, it seems very reasonable that the two outgoing electrons should have a negligible screening effect on each other. Hence we take the charge seen by each electron to be $Z=2$. Second, if one elects to calculate the relevant cross sections using the momentum matrix elements, the *correlation* effects in the final state will be shown in Sec. III to be unimportant. The choice of momentum matrix elements instead of position matrix elements is also discussed in Sec. III. We note that this choice is consistent with other related atomic calculations.[8,15]

III. CALCULATION OF THE DOUBLE-IONIZATION CROSS SECTIONS

With Ψ_i and Ψ_f chosen in the manner described in the previous section, the problem of evaluating the cross section for ionization by photons as given in Eq. (1) comes down to calculating matrix elements of the form

$$f_\nu(\epsilon,Z,Z^*)=\langle R_{\epsilon,0}{}^Z(r)\,|\,r^\nu e^{-Z^*r}\rangle\,,\quad (\nu=0,1,\cdots)\qquad\text{(24a)}$$

$$g_\nu(\epsilon,Z,Z^*)=\langle R_{\epsilon,1}{}^Z(r)\,|\,r^\nu e^{-Z^*r}\rangle\,,\quad (\nu=0,1,\cdots)\qquad\text{(24b)}$$

and

$$h_\nu(\epsilon,Z,Z^*)=\langle R_{\epsilon,2}{}^Z(r)\,|\,r^\nu e^{-Z^*r}\rangle\,,\quad (\nu=1,2,\cdots).\qquad\text{(24c)}$$

Matrix elements involving $R_{\epsilon,3}$, $R_{\epsilon,4}$, etc. are not needed in this work (although they can be computed with little difficulty) because it turns out that the contributions to $\sigma_\gamma{}^{++}$ from the relative d wave (and higher waves) are unimportant. Since that leaves just a relative s wave and relative p wave in the initial state, and since the operator which causes the photon absorption is a *vector* operator, we see that the highest angular momentum which could be attained by one of the ejected atomic electrons is $l=2$. The reason that h_0 is not required is that the lowest power of r_1 or r_2 occurring in the relative p-wave part of Ψ_i is the *first* power, not the zero power, as is the case with the relative s wave. This is fortunate since h_0 would be rather difficult to evaluate.

Eqs. (24a), (24b), and (24c) are now readily reduced to

$$f_\nu(\epsilon,Z,Z^*)=(-1)^\nu\frac{d^\nu}{dZ^{*\nu}}f_0(\epsilon,Z,Z^*)\,,\qquad(\nu=0,1,\cdots)\qquad\text{(25a)}$$

$$g_\nu(\epsilon,Z,Z^*)=(-1)^\nu\frac{d^\nu}{dZ^{*\nu}}g_0(\epsilon,Z,Z^*)\,,\qquad(\nu=0,1,\cdots)\qquad\text{(25b)}$$

and

$$h_\nu(\epsilon,Z,Z^*)=(-1)^{\nu-1}\frac{d^{\nu-1}}{dZ^{*\nu-1}}h_1(\epsilon,Z,Z^*)\,,\quad(\nu=1,2,\cdots).\qquad\text{(25c)}$$

Using the integral representation of the Coulomb wave functions,[20] f_0, g_0, and h_1 are easily evaluated. One finds, setting $(2\epsilon)^{1/2}=k$,

$$f_0(\epsilon,Z,Z^*)=-4(Z-Z^*)[Z/(1-e^{-2\pi Z/k})]^{1/2}(e^{(-2Z/k)\,\tan^{-1}(k/Z^*)})/(k^2+Z^{*2})^2\,,\qquad\text{(26a)}$$

$$g_0(\epsilon,Z,Z^*)=-4[Z(k^2+Z^2)/(1-e^{-2\pi Z/k})]^{1/2}(e^{(-2Z/k)\,\tan^{-1}(k/Z^*)})/(k^2+Z^{*2})^2\,,\qquad\text{(26b)}$$

and

$$h_1(\epsilon,Z,Z^*)=-8[Z(k^2+Z^2)(k^2+4Z^2)/(1-e^{-2\pi Z/k})]^{1/2}(e^{(-2Z/k)\,\tan^{-1}(k/Z^*)})/(k^2+Z^{*2})^3.\qquad\text{(26c)}$$

With these three formulas as starting points, all the f_ν, g_ν, and h_ν can be calculated from Eqs. (25a), (25b), and (25c).

The evaluation of the cross section for double ionization by photons can now be carried out. Using f_ν, g_ν, and h_ν upon substituting Eqs. (19), (20), and (22) into Eq. (1), we find

$$\sigma_\gamma{}^{++}(E_\gamma)=\sigma_{\gamma,0}{}^{++}(E_\gamma)+\sigma_{\gamma,1}{}^{++}(E_\gamma)\,,\qquad\text{(27)}$$

where

$$\begin{aligned}\sigma_{\gamma,0}{}^{++}(E_\gamma)=\frac{8\pi^2\alpha a_0{}^2}{3E_\gamma}\int_0^{E_\gamma-B_i}d\epsilon\Bigg[\sum_{m\geq n}A_{mn}{}^{(0)}\bigg\{&\bigg[ng_{n-1}(\epsilon,2,\beta/2)-\frac{\beta}{2}g_n(\epsilon,2,\beta/2)\bigg]f_m(E_\gamma-B_i-\epsilon,2,\beta/2)\\&+\bigg[mg_{m-1}(\epsilon,2,\beta/2)-\frac{\beta}{2}g_m(\epsilon,2,\beta/2)\bigg]f_n(E_\gamma-B_i-\epsilon,2,\beta/2)\bigg\}\\+\tfrac{1}{3}\sum_{n\geq m}A_{mn}{}^{(1)}\bigg\{&\bigg[(n+3)f_n(E_\gamma-B_i-\epsilon,2,\beta/2)-\frac{\beta}{2}f_{n+1}(E_\gamma-B_i-\epsilon,2,\beta/2)\bigg]g_{m+1}(\epsilon,2,\beta/2)\\&+\bigg[(m+3)f_m(E_\gamma-B_i-\epsilon,2,\beta/2)-\frac{\beta}{2}f_{m+1}(E_\gamma-B_i-\epsilon,2,\beta/2)\bigg]g_{n+1}(\epsilon,2,\beta/2)\bigg\}\Bigg]^2\end{aligned}\qquad\text{(28a)}$$

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[20] H. A. Bethe and E. E. Salpeter, *The Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

and

$$\sigma_{\gamma,1}^{++}(E_\gamma)=\frac{16\pi^2\alpha a_0^2}{27E_\gamma}\int_0^{E_\gamma-B_i}d\epsilon\Bigg[\sum_{m\geq n}A_{mn}^{(1)}\Bigg\{\Bigg[nh_n(\epsilon,2,\beta/2)-\frac{\beta}{2}h_{n+1}(\epsilon,2,\beta/2)\Bigg]g_{m+1}(E_\gamma-B_i-\epsilon,2,\beta/2)$$

$$+\Bigg[mh_m(\epsilon,2,\beta/2)-\frac{\beta}{2}h_{m+1}(\epsilon,2,\beta/2)\Bigg]g_{n+1}(E_\gamma-B_i-\epsilon,2,\beta/2)\Bigg\}\Bigg]^2. \quad (28\text{b})$$

In these expressions, the integral on ϵ must be done numerically. We can obtain slightly different expressions for $\sigma_{\gamma,0}^{++}$ and $\sigma_{\gamma,1}^{++}$ by using Eq. (14), i.e., by evaluating a *position* dipole matrix element rather than a *momentum* matrix element. In that case we find

$$\sigma_{\gamma,0}^{++}(E_\gamma)=\frac{8\pi^2\alpha a_0^2}{3}E_\gamma\int_0^{E_\gamma-B_i}d\epsilon[\sum_{m\geq n}A_{mn}^{(0)}\{g_{n+1}(\epsilon,2,\beta/2)f_m(E_\gamma-B_i-\epsilon,2,\beta/2)$$

$$+g_{m+1}(\epsilon,2,\beta/2)f_n(E_\gamma-B_i-\epsilon,2,\beta/2)\}$$

$$+\tfrac{1}{3}\sum_{m\geq n}A_{mn}^{(1)}\{f_{n+2}(E_\gamma-B_i-\epsilon,2,\beta/2)g_{m+1}(\epsilon,2,\beta/2)+f_{m+2}(E_\gamma-B_i-\epsilon,2,\beta/2)g_{n+1}(\epsilon,2,\beta/2)\}]^2 \quad (29\text{a})$$

and

$$\sigma_{\gamma,1}^{++}(E_\gamma)=\frac{16\pi^2\alpha a_0^2}{27}E_\gamma\int_0^{E_\gamma-B_i}d\epsilon[\sum_{m\geq n}A_{mn}^{(1)}\{h_{n+2}(\epsilon,2,\beta/2)g_{m+1}(E_\gamma-B_i-\epsilon,2,\beta/2)$$

$$+h_{m+2}(\epsilon,2,\beta/2)g_{n+1}(E_\gamma-B_i-\epsilon,2,\beta/2)\}]^2. \quad (29\text{b})$$

It should be emphasized that the equivalence between the momentum and position dipole matrix elements is only precise if one uses exact initial- and final-state wave functions for the helium system. This is not the case in our calculation where in the final state we make an important simplification (neglect of correlation). Therefore we would expect to find a difference between σ_γ^{++} when calculated with these two different matrix elements. That this is indeed the case is seen in Fig. 1, where we plot $\sigma_\gamma^{++}(E_\gamma)$ as a function of E_γ for both cases. We see a particularly striking difference between the two cases for large values of E_γ.

The main reason for this fact can be seen as follows. If we ask for the dependence of the momentum cross section on E_γ for large values of E_γ, it is easy to see from Eq. (28a) that the dominant term is proportional

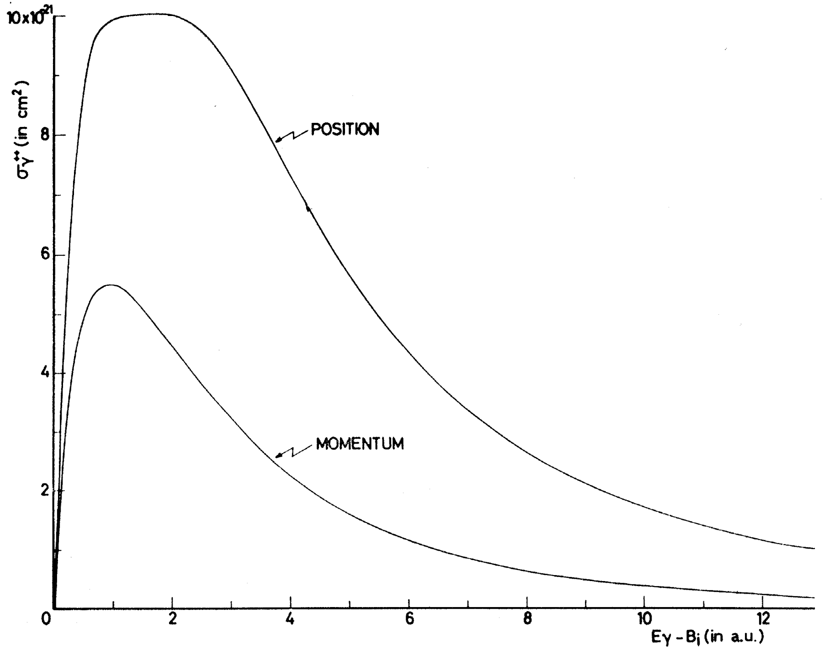

FIG. 1. The cross section σ_γ^{++} for double ionization by photon impact as a function of $E_\gamma-B_i$. The top curve corresponds to the cross section calculated by using position dipole matrix elements. The bottom curve shows the cross section obtained from momentum matrix elements.

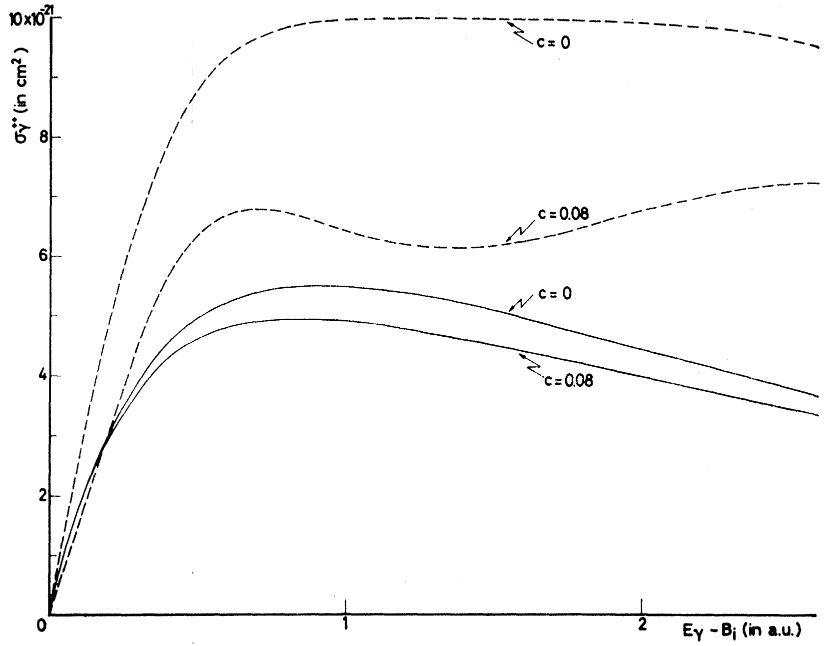

FIG. 2. The cross section σ_γ^{++} for double ionization by photon impact as a function of $E_\gamma - B_i$. Dashed curves: cross sections calculated by using position dipole matrix elements without ($c=0$) and with ($c=0.08$) inclusion of angular correlation in the final state. Solid curves: cross sections obtained from momentum matrix elements with $c=0$ and $c=0.08$.

to $E_\gamma^{-7/2}$. This contribution comes from the terms in g_0; if one collects all such terms one finds

$$\sigma_\gamma^{++}(E_\gamma) \xrightarrow[E_\gamma\to\infty]{} 25.8\left(\frac{\alpha a_0^2}{E_\gamma^{7/2}}\right), \tag{30}$$

where E_γ is in a.u. This result agrees to within 25% with what one obtains by using Eqs. (4), (5), and (6); namely,

$$\sigma_\gamma^{++}(E_\gamma) \xrightarrow[E_\gamma\to\infty]{} 19.2\left(\frac{\alpha a_0^2}{E_\gamma^{7/2}}\right). \tag{31}$$

However, when we look at Eq. (29a) for the position cross section we find that as E_γ becomes large this cross section contains terms proportional to $E_\gamma^{-5/2}$ coming from terms in f_0. One finds

$$\sigma_\gamma^{++}(E_\gamma) \xrightarrow[E_\gamma\to\infty]{} 1.08\left(\frac{\alpha a_0^2}{E_\gamma^{5/2}}\right). \tag{32}$$

We see that the numerical coefficient in (32) is very small compared to the one appearing in (31). It is in fact the result of delicate cancelations between terms which are larger in magnitude, and if the initial-state wave function were exact this coefficient would be zero, since the effect of correlation in the final state must vanish when one of the electrons has sufficiently high energy. In this calculation, however, the use of an approximate initial-state wave function means that $\sigma_\gamma^{++}(E_\gamma)$, when calculated using the position dipole matrix element, will fall off much too slowly for large values of E_γ. For example, when $E_\gamma = 10$ a.u., the spurious $E_\gamma^{-5/2}$ term is nearly equal to the term proportional to $E_\gamma^{-7/2}$, as may be seen from Eqs. (30) and (32). It is because of this sensitivity to the initial-state wave function, as well as for other reasons to be discussed below, that we feel that the position cross section is much less reliable than the momentum cross section.

With σ_γ^{++} calculated in the manner indicated above, it is a simple matter, using Eq. (18), to evaluate by numerical integration the leading term in Eq. (11) for $\sigma_e^{++}(E_e)$. We find

$$a = 0.00053,$$

so that

$$\sigma_e^{++}(E_e) = \frac{2\pi a_0^2}{E_e}\left[0.00053 \ln E_e + b + O\left(\frac{}{E_e}\right)\right], \tag{33}$$

where b is an undetermined constant. In obtaining the quantity a we have used the momentum cross section for double ionization by photon impact. If we use the position cross section, we find for a the much larger value

$$a = 0.00130.$$

This is in good agreement with the value $a = 0.00140$ found in Ref. 5 for the case where both of the ejected particles were unscreened. In Ref. 5 the calculation was done by a different method, so it serves as a good check on the present work.

We now turn to the question of final-state correlation. Suppose we write a more general final-state wave function $\tilde{\Psi}_f^{(l)}$ in a form similar to the one used for Ψ_i:

$$\tilde{\Psi}_f^{(l)} = \Psi_f^{(l)}[G_0(r_1,r_2) + G_1(r_1,r_2)P_1(\cos\theta_{12}) + \cdots], \tag{34}$$

where $\Psi_f^{(l)}(\mathbf{r}_1,\mathbf{r}_2)$ is given by Eq. (22). For G_l, we write by analogy with the F_l defined in Eq. (20)

$$G_l(r_1,r_2) = r_1^l r_2^l \sum_{m\geq p} B_{mn}^{(l)}(\epsilon,\epsilon')(r_1^m r_2^n + r_1^n r_2^m), \tag{35}$$

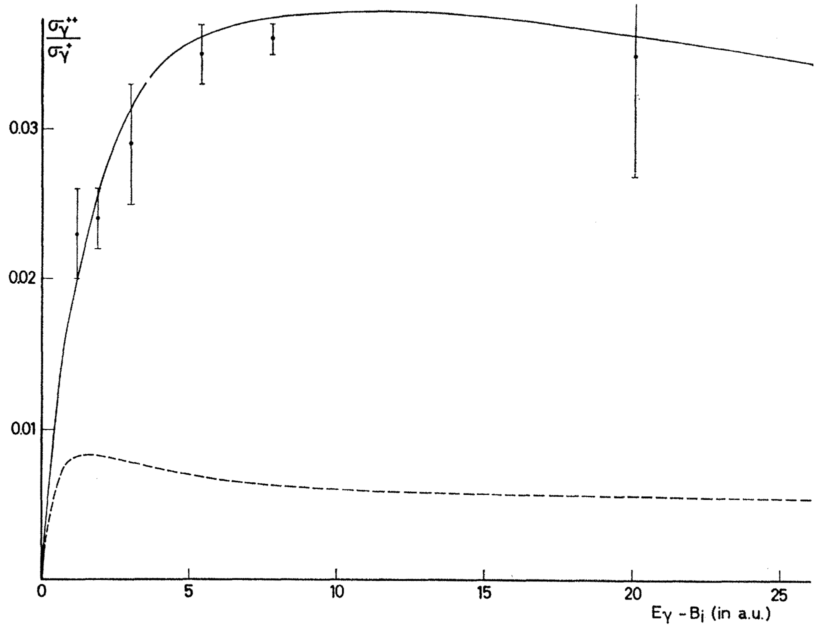

FIG. 3. The ratio $\rho_\gamma = \sigma_\gamma^{++}/\sigma_\gamma^{+}$ as a function of $E_\gamma - B_i$. The solid curve represents the theoretical calculation of this paper, using a fully correlated initial-state wave function. The dashed curve corresponds to a Hartree-Fock ground-state wave function. The points are the experimental results of Ref. 1.

ϵ and ϵ' being the single-particle energies contained in the definition of $\Psi_f^{(l)}$. To obtain the coefficients $B_{mn}^{(l)}$ would of course be a very difficult task, although presumably when either ϵ or ϵ' becomes very large, $B_{mn}^{(l)}$ tends to zero. For the purpose of obtaining an idea of the effect of final-state correlation, let us consider a simple special case of Eq. (34), namely,

$$\tilde{\Psi}_f^{(l)} = \Psi_f^{(l)}(1 + c r_1 r_2 \cos\theta_{12}). \tag{36}$$

Notice that through first order in c, $\tilde{\Psi}_f^{(l)}$ is properly normalized. Since $\Psi_f^{(l)}$ is believed to be a good approximation to the true final-state wave function, the actual value of c in Eq. (34) should be small. (In actual fact the "constant" c should depend on the energies of the outgoing electrons. For purposes of illustration, however, we fix the value of c.) To obtain an idea of the effect of this term proportional to c, we have recalculated σ_γ^{++} in both the position and momentum cases. We find that for small values of c the momentum cross section is very insensitive, while the position cross section is very sensitive, particularly for small values of E_γ. Figure 2 shows the low-energy region in detail for the case $c = 0.08$. We see that the effect of the correlation term on the position cross section is large, while the momentum cross section is scarcely changed at all.

In summary, we see that in order to utilize the position cross section it would be necessary to improve the initial-state wave function even beyond its present rather high degree of accuracy and also to take into account further details of the final-state wave function which would be very difficult to obtain. The momentum cross section does not appear to suffer seriously from either of these difficulties, and we therefore feel that it should give the most reliable results in the scattering problems under discussion.

IV. RESULTS AND DISCUSSION

Having calculated the double-ionization cross section by photon impact as described in Sec. III, we use the calculations of Salpeter and Zaidi[8] and Stewart and Webb[9] for the corresponding single-ionization cross section. In this manner we obtain the ratio

$$\rho_\gamma(E_\gamma) = \sigma_\gamma^{++}(E_\gamma)/\sigma_\gamma^{+}(E_\gamma).$$

The results are shown in Fig. 3 where they are compared with the experimental values of Carlson.[1] The agreement between our calculated values and the experimental points is very good. For comparison we also include in Fig. 3 the result for $\rho_\gamma(E_\gamma)$ calculated using a Hartree-Fock wave function[19] for the initial state and Eq. (22) for the final state. The discrepancy between the two curves is a striking illustration of the importance of correlation effects in multiple ionization problems. It seems clear from the case of helium that attempts to understand multiple-ionization phenomena in heavier atoms in terms of simple Hartree-Fock-type functions are doomed to failure.

Given our simplified assumptions concerning final-state interactions in the double-ionization process and the fact that our initial-state wave function is still not perfectly accurate, we feel that the extremely good agreement between theory and experiment shown in Fig. 3 should not be taken at face value. On the basis of the comparison made in Sec. III between the calculation of $\sigma_\gamma^{++}(E_\gamma \to \infty)$ using the actual momentum matrix elements and the asymptotic method of Kabir and Salpeter,[15] we estimate that uncertainties in our calculations coming from the initial-state wave function are about 25%. In order to reduce such uncertainties and, at the same time, ascertain further the importance of

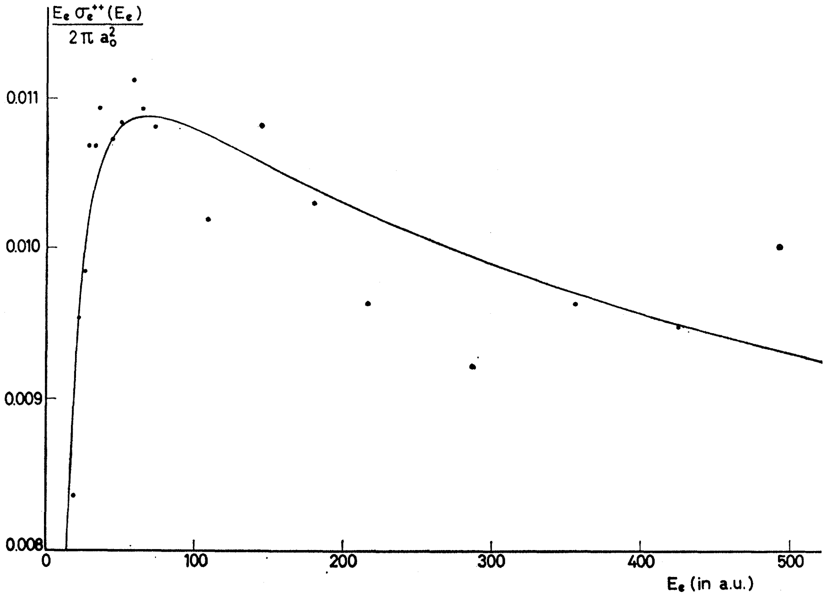

FIG. 4. A least-squares fit to the data of Ref. 2, according to the formula (37) of the text.

final-state interactions in double-ionization processes, an extremely accurate ground-state wave function should be used. This problem is presently under investigation.

We now discuss our calculations of the double-ionization cross section $\sigma_e^{++}(E_e)$ at high incident electron energies for which the result $a=0.00053$ was obtained in Sec. III. Since the values of $\sigma_e^{++}(E_e)$ are very small, a precise experimental determination of a is difficult. The work of Schram *et al.*[2,3] and of Fiquet-Fayard *et al.*[4] indicates that the term b in Eq. (11) is considerably larger than $a \ln E_e$ even at rather high energies ($E_e \simeq 600$ a.u.), so that experimental estimates of a are *very* unreliable. For example, a least-squares fit to the data of Ref. 21, using a representation of σ_e^{++} of the form

$$\sigma_e^{++}(\mathrm{E}_e)=\frac{2\pi a_0^2}{\mathrm{E}_e}\left(\mathrm{a}\ \ln E_e+b+\frac{\mathrm{c}}{\mathrm{E}_e}\right), \qquad (37)$$

is shown in Fig. 4, and yields the values

$$a=-0.0014, \quad b=0.018, \quad c=-0.096;$$

i.e., a negative value is obtained for a, which is clearly inadmissable. However, the *magnitude* of a determined in this way may be taken as an estimate of the experimental *uncertainties* in the determination of the true a. Since this magnitude is $|a| \simeq 0.001$, we conclude that our calculations—and hence Carlson's experimental data on photo-ionization[1]—are at least compatible with the electron-impact experiments.[2–4]

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One of us (F.W.B.) would like to thank Professor M. Demeur for his hospitality during the academic year 1966–1967 at the Université Libre de Bruxelles.

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[21] The ratio $\sigma_e^{++}(E_e\rightarrow\infty)/\sigma_e^{+}(E_e\rightarrow\infty)=1/200$ quoted in Ref. 5 was suggested by experiments which were not asymptotic. In the light of experiments performed at higher energies, this ratio is considerably reduced, in accordance with the improved calculations reported in this paper. The use of an effective charge in the work of Ref. 5 was a crude attempt to take into account the effect of final-state correlations which, as shown above, are much more important when calculating "position" cross sections than "momentum" cross sections.