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# Asymptotic Double-Photoexcitation Cross Sections of the Helium Atom

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A relative cross section for simultaneous excitation and ionization of the helium atom is derived from the sudden approximation. It is shown to agree with that obtained from the velocity form of the cross section in the Coulomb approximation. It is connected to the asymptotic cross section of Kabir and Salpeter through the cusp condition at the nucleus. An analysis of the influence of ground-state correlations on the asymptotic double-excitation cross section is carried out.

## INTRODUCTION

Relative photoabsorption cross sections for simultaneous excitation and ionization and for double ionization in helium have been measured by Carlson[1] and Samson.[2] The results were shown to be much larger than those predicted by the sudden approximation in the Hartree-Fock scheme.[1] Soon after that, several investigations made it apparent that the inclusion of correlation in the ground-state wave function is very important.[3–7] In the calculations of Byron and Joachain[3,4] and of Brown,[6,7] the final-state wave function is a symmetric product of uncorrelated Coulomb wave functions corresponding to the charge $Z=2$, whereas the author[5] has introduced the correlation in the sudden-approximation method. The influence of radial ground-state correlations on double excitation has been discussed by Fano and Cooper.[8]

At low incident energies near the threshold, there is a good agreement between the calculations using the Coulomb approximation and the experimental results. For the simultaneous $1s \to 2s$ excitation and ejection of the photoelectron, the result of Brown[6] agrees well with that of Salpeter and Zaidi,[9] who used the Hartree approximation for the final state. This is somewhat surprising, since the Coulomb approximation neglects the screening and correlation between the excited and ejected electron. At large incident energies, there is a considerable scattering of various data which vary within 30%, depending on the choice of the correlated ground-state wave function. The form of the cross section also strongly influences the results.[4] However, for large energies, since the screening and correlation in the final state are not important, asymptotic cross sections should only reveal the influence of the ground-state correlation.

In this paper we derive an expression for the asymptotic cross section which is shown to be connected with that of Kabir and Salpeter[10] through the cusp condition[11,12] at the nucleus.[13] It allows us to analyze the influence of the ground-state correlation on the double excitation in a simple and systematic way.

## ASYMPTOTIC CROSS SECTIONS

At high incident photon energies, at least one of the electrons of the He atom is excited into the continuum with a momentum $\vec{k}$. The electron of the $He^+$ ion is left in a bound or an unbound state $\varphi_n$. According to the sudden approximation, the cross section $\sigma(n,\vec{k})$ for ejection of the photoelectron in the direction of $\vec{k}$ must fulfill the relation[5]

$$\sigma(n,\vec{k}) \propto |\langle \varphi_n | \tilde{\psi}\rangle|^2, \tag{1}$$

where $\tilde{\psi}$ is the Fourier transform

$$\tilde{\psi} = (2\pi)^{-3/2} \int \psi(r_1, r_2, r_{12}) e^{-i\vec{k}\cdot\vec{r}_2} d^3 r_2 \quad . \tag{2}$$

The ground-state wave function $\psi$ can be expressed as a function of the electronic distances $r_1$ and $r_2$ from the nucleus and of the interelectronic separation $r_{12}$. Relation (1) is simplified further by the limiting property of the Fourier transform (2):

$$\lim_{k\to\infty} k^4 \tilde{\psi} = -2\left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} \quad . \tag{3}$$

From this equation, which is proved in the Appendix,[13] it follows that the differential or total cross section becomes proportional to

$$M = \left|\left\langle \varphi_n \left| \left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} \right.\right\rangle\right|^2 \tag{4}$$

in the high-energy limit. It means that the highest-order term of the cross section must vanish unless $\varphi_n$ corresponds to $l=0$. Thus, among the transitions from the initial ($1s^2$; $^1S$) state to all the possible final states $[nl, k(l\pm 1); {}^1P]$, those corresponding to the $(ns, kp)$ states dominate at high incident energies. This conclusion confirms the result of the recent calculation of transition probabilities to $(ns, kp)$ and $(np, ks)$ states

$(2 \leq n \leq 10)$ by Brown.[6]

By using either the Born or Coulomb approximations, we obtain the proportionality factor between the velocity form of the cross section and $M$ in the high-energy limit (see the Appendix). The result for the total cross section $\sigma(ns, E)$, corresponding to the ejection of the photoelectron in any direction by absorption of polarized or unpolarized light, is

$$\sigma_1(ns, \infty) = \lim_{E\to\infty} \sigma(ns, E) = \frac{2^6\pi^2\alpha a_0^2}{3(\sqrt{2})E^{7/2}} M, \qquad (5)$$

where $\alpha$ is the fine-structure constant and $a_0$ the Bohr radius. The energy of excitation $E$ is given in a.u..

Using the cusp condition at the nucleus,[11] which, for the helium atom, takes the form[12]

$$\left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} = -2\psi(r_1, 0, r_1), \qquad (6)$$

we also obtain

$$\sigma_2(ns, \infty) = [2^8\pi^2\alpha\, a_0^2/3(\sqrt{2})E^{7/2}] \times \left| \int \varphi_{ns}(r_1)\psi(r_1, 0, r_1) d^3r_1 \right|^2. \qquad (7)$$

This is the cross-section limit obtained by Kabir and Salpeter[10] from the Born approximation and from their approximation of $\psi$ in the momentum space.

We see that a good approximate ground-state wave function should yield $\sigma_1 = \sigma_2$, which is a property of the exact wave function. We know that the Hartree-Fock ground-state wave function satisfies the cusp condition (6), but also that it describes double excitations very poorly.[1,4] Hence, the wave function must describe both the correlation and satisfy the cusp condition.

In order to obtain the limiting forms (5) and (7), we must assume that $E \simeq \frac{1}{2}k^2 \gg I_{ns}$. This is not necessarily true, if $ns$ is a continuum state. However, if the $s$ electron is regarded as the photoelectron, then the highest-order term of the cross section for the $(k's, kp)$ states must vanish. Consequently, $\sigma$ is proportional to $E'^{-n}$, where $n$ is at least 4 ($E'$ is the kinetic energy of the $s$ electron) and continuum $s$ states of high energy can be neglected. It follows that the high-energy limit of the total cross section $\sigma_t(E)$ satisfies the relation

$$\sigma_t(\infty) \propto \left\langle \left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} \middle| \left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} \right\rangle$$

or

$$\langle \psi(r_1, 0, r_1) | \psi(r_1, 0, r_1) \rangle , \qquad (8)$$

with proportionality coefficients given by Eqs. (5) and (7).

## CALCULATIONS AND DISCUSSION

It is easy to calculate the integrals appearing in Eqs. (5), (7), and (8) even for the most complicated ground-state wave function. Here we have done this for an Eckart-type wave function (Ec2),[7] for the partial-wave-expansion–type wave function of Byron and Joachain (BJ46),[4] for two Hylleraas-type wave functions[14,15] (SW6 and CH18) and for Kinoshita's best wave function[16] (Ki39), where the number of variational parameters in each case is given in the parentheses. The results are listed in Table I, where $\sigma^{++}/\sigma^{+}$ is the double-to-single ionization ratio given by

$$\sigma^{++}/\sigma^{+} = [\sigma_t(\infty) - \sum_{n=1}^{\infty} \sigma(ns, \infty)] / \sum_{n=1}^{\infty} \sigma(ns, \infty). \qquad (9)$$

Thus, only the bound $s$-state wave functions[17] of the $He^{+}$ ion are involved.

Exact calculations were performed up to $n = 10$. The contribution from the rest of the states ($n \geq 11$) was approximated by the fact that $\sigma(ns, \infty) \propto n^{-3}$ for high $n$.

TABLE I. Calculation of various asymptotic double-photoexcitation cross-section ratios of the helium atom. The values are given in percentages.

| Wave function | Ec2 | | BJ46 | | SW6 | | CH18 | | Ki39 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cusp[a] | −1.684 | | −1.686 | | −1.901 | | −1.896 | | −1.991 | |
| Cross-section ratio | $\sigma_1$ | $\sigma_2$ | $\sigma_1$ | $\sigma_2$ | $\sigma_1$ | $\sigma_2$ | $\sigma_1$ | $\sigma_2$ | $\sigma_1$ | $\sigma_2$ |
| $1-\sigma(1s)/\sigma_t$ | 13.1 | 9.47 | 7.32 | 7.16 | 8.16 | 7.37 | 7.24 | 7.08 | 7.04 | 7.06 |
| $\sigma(2s)/\sigma_t$ | 10.0 | 7.35 | 4.12 | 4.45 | 5.06 | 4.67 | 4.42 | 4.43 | 4.43 | 4.45 |
| $\sum_{n=3}^{10}\sigma(ns)/\sigma_t$ | 1.32 | 0.933 | 0.798 | 0.908 | 1.14 | 1.01 | 0.959 | 0.945 | 0.938 | 0.937 |
| $\sum_{n=11}^{\infty}\sigma(ns)/\sigma_t$ | 0.054 | 0.038 | 0.036 | 0.040 | 0.051 | 0.045 | 0.043 | 0.042 | 0.042 | 0.042 |
| $\sigma^{++}/\sigma^{+}$ | 1.75 | 1.17 | 2.43 | 1.79 | 1.95 | 1.66 | 1.86 | 1.69 | 1.66 | 1.65 |

[a]Cusp at the nucleus has been evaluated from $(\partial\psi/\partial r_2)_{r_2=0}/\psi(r_1, 0, r_1)$ at $r_1 = 0$. The exact value of the ratio is −2.

We observe from Table I that the ratio $\sigma^{++}/\sigma^{+}$ is most sensitive to the two different cross-section forms used. However, the better the ground-state wave function satisfies the cusp condition near the nucleus, the better is the agreement between the results based on the two forms. The integral cusp condition[18] has little meaning in this context, since the BJ46 wave function gives a good value for the integral ratio involved, namely, − 2.013.

Kinoshita's wave function gives an excellent agreement between the various $\sigma_1$ and $\sigma_2$ ratios listed in Table I. It gives a value of $\sigma_1^{++}/\sigma_1^{+}$ which is lower than the value given by the BJ46 and SW6 wave functions used hitherto in calculations of the double-ionization cross section as a function of energy.[4,7] Both calculations end at approximately 1 keV, but the same difference (about 15%), as is revealed by the ratio $\sigma_1^{++}/\sigma_1^{+}$ in Table I, is noticeable above 0.5 keV. Thus, we expect that Kinoshita's wave function should yield a double-to-single ionization ratio above 0.5 keV which is about 30% lower than that corresponding to the BJ46 wave function. This completes the Byron-Joachain analysis of the uncertainties in their calculation arising from the ground-state wave function.[4] The simple Eckart wave function gives a reasonable result for $\sigma_1^{++}/\sigma_1^{+}$. Thus, our calculation also confirms Brown's result[6] that it gives a good double-ionization cross section for high energies if the velocity form is used in connection with the Born approximation.

It is also interesting to see whether there is any resemblance between experimental ratios at low energies and the calculated ratios in the high-energy limit. Such a comparison is made in Table II, where the values of the Hartree-Fock (HF) high-energy limit have also been included. The agreement is not as good as it is in the case of simultaneous $K$-shell ionization–$L$-shell excitation, where the correlation effects are unimportant.[5] There, the $\sigma(KL)/\sigma(K)$ ratio becomes amenable to the high-energy limit (sudden approximation) at energies which are only about 1.5 times the threshold energy.[5,19,20] Thus, as correlation becomes more important, the convergence turns out to be slower.

It follows from the application of the sudden approximation to the photoionization process that every acceptable cross section should be strictly proportional to $M$[ given by Eq. (4)] in the high-energy limit. According to the Appendix, the length form of the asymptotic cross section does not meet this requirement within the Born or Coulomb approximations if correlation is introduced in the ground state. Hence, the comparison between $\sigma_1$ and $\sigma_2$ gives a more realistic estimate of the accuracy of double excitation probability calculations than does the comparison between the velocity and length forms.

TABLE II. Comparison between various high- and low-energy data of double-excitation cross-section ratios of the helium atom. The values are given in percentages.

| Cross-section ratio | HF[a] $\sigma_1=\sigma_2$ $E=\infty$ | Ki 39 $\sigma_1\cong\sigma_2$ $E=\infty$ | Refs. 6 and 7 $E=278$ eV | Expt.[b] $E=278$ eV |
|---|---|---|---|---|
| $\sigma(2s)/\sigma(1s)$ | 2.4 | 4.8 | 6.7[c] | $6\pm1$ |
| $\sum_{n=3}^{\infty}\sigma(ns)/\sigma(1s)$ | 0.5 | 1.1 | 1.7[c] | $3\pm1$ |
| $\sigma^{++}/\sigma^{+}$ | 0.5 | 1.7 | 3.6[d] | $3.6\pm0.2$ |

[a]Reference 5.
[b]Reference 1. A measurement of $\sigma^{++}/\sigma^{+}$ is available at a still higher energy (0.6 keV). The result is (3.5 ±1.2)%, so that the decrease of the $\sigma^{++}/\sigma^{+}$ ratio as the energy increases has not been verified.
[c]Based on the BJ 46 wave function.
[d]Based on the SW6 wave function.

In general, asymptotic cross sections may be useful as first approximations and as tools to check the importance of the ground-state correlation for photoionization processes in more complicated systems than helium.

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## APPENDIX

For large $k$ values, the Fourier transform (2) maps the wave function at points near the nucleus $r_2 \cong 0$, $r_1 \cong r_{12}$ into reciprocal space. It is therefore convenient to consider the Taylor expansion:

$$\psi(r_1, r_2, r_{12}) = \psi(r_1, 0, r_1) + r_2\left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0} - r_2\cos\vartheta_{12}\left(\frac{\partial\psi}{\partial r_{12}}\right)_{r_2=0} + O(r_2^2). \tag{A1}$$

Right multiplication by a factor $e^{-\epsilon r}$ gives a convergent expansion of the Fourier transform:

$$\tilde{\psi} = \left(\frac{2}{\pi}\right)^{1/2}\left[\frac{2\psi(r_1, 0, r_1)\epsilon}{(\epsilon^2+k^2)^2} - 2\left(\frac{\partial\psi}{\partial r_2}\right)_{r_2=0}\frac{k^2}{(\epsilon^2+k^2)^3} + O(k^{-5})\right]. \tag{A2}$$

Letting $\epsilon\to0$, we obtain the final result (3).

Although it can be proved[5] that in the Born approximation the velocity form of the cross section approaches the limiting cross section (5), it is not immediately clear that it does so in the case of the Coulomb approximation. However, this can be proved directly by substituting for $\psi_f$ the symmetrized product of the Coulomb wave function into the cross section

$$\sigma(ns, E) = (4\pi^2 \alpha a_0^2/E) \times \int dE \left| \left\langle \psi_f \left| \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right| \psi \right\rangle \right|^2 \delta(E - I_{ns} - \tfrac{1}{2}k^2) \tag{A3}$$

and taking the high-energy limit. Using the Taylor expansion technique as above, we see that the highest-order term of the cross section will be given by the term associated with $k^{-7}$ in

$$\lim_{\epsilon \to 0} \frac{2^6 \pi^3 \alpha a_0^2 M}{3k^2} \left| \int R_{kp}(r) e^{-\epsilon r} r^2 dr \right|^2 \tag{A4}$$

for $(1s^2) \to (ns, kp)$ transitions. Here $M$ is given by Eq. (4) and $R_{kp}$ is the radial part of the Coulomb wave function for central charge $Z = 2$, normalized in the energy scale. The integral appearing in (A4) can be found, e.g., in Ref. 4. For $(1s^2) \to (np, ks)$ excitations, the same technique yields, in the Coulomb approximation, an asymptotic cross section which goes to zero as $k^{-9}$.

If we apply the commutation rule

$$[z_1 + z_2, H] = \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}, \tag{A5}$$

and assume that $\psi$ and $\psi_f$ are the exact wave functions of the Hamiltonian $H$, then we obtain from the velocity form the length form $\sigma_L$ of the cross section. In this case, it follows from the application of the Taylor expansion technique to the Coulomb approximation that

$$\sigma_L^C(ns, \infty) = (16\pi/M) \left| \int R_{ns}(r_1) \left[ \psi(r_1, 0, r_1) - \frac{r_1}{3} \left( \frac{\partial \psi}{\partial r_{12}} \right)_{r_2 = 0} \right] r_1^2 \, dr_1 \right|^2 \sigma_1(ns, \infty), \tag{A6}$$

where $R_{ns}$ is the radial part of the $ns$ wave function for the $He^+$ ion. Thus, $\sigma_L^C(ns, \infty) = \sigma_1(ns, \infty)$ only if the cusp condition (6) is satisfied and the correlation in the form of the $r_{12}$ dependence is neglected at $r_2 = 0$.

In the case of $(1s^2) \to (np, ks)$ transitions, we obtain an asymptotic cross section which is proportional to the matrix element

$$\left| \left\langle \varphi_{np}(\vec{r}_1) \left| z_1 \right| \left[ 2\psi(r_1, 0, r_1) + \left( \frac{\partial \psi}{\partial r_2} \right)_{r_2 = 0} \right] \right\rangle \right|^2 \tag{A7}$$

and goes to zero as $k^{-5}$. This fact explains the origin of the spurious $k^{-5}$ term found by Byron and Joachain[4] in their calculation of the length form of the double-ionization cross section. The term vanishes if the ground-state wave function satisfies the cusp condition exactly. We also note that the Born approximation gives a wrong limit, if the length form is used.[5]

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