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PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Double Photoionization of Helium

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(Received 17 October 1969)

The helium double-photoionization cross section has been evaluated using a Hylleraas wave function for the ground state in order to include correlation between the atomic electrons more directly than in previous calculations. Good agreement is found between the present results, the experimental data, and the theoretical work of Byron and Joachain. An interpretation of the differential electron spectrum is used to motivate an asymptotic calculation of the double-photoionization cross section which agrees well with the more exact treatment at high energies.

I. INTRODUCTION

Interest in the helium double-photoionization cross section was stimulated by the observation[1,2] that the oscillator strength for this transition made a non-negligible contribution to the average excitation energy term in the expansion of the Lamb shift. Carlson,[3] who measured the helium double-ionization cross section and noticed that the data could not be interpreted by the electron shake-off process[4] which is based on single electron wave functions, concluded that an adequate description of the data could be obtained only if a many-body approach was employed.

In a series of papers, Byron and Joachain[5,6] arrived at a similar result by pointing out that double ionization depends critically on the way in which correlation effects between atomic electrons are included in the initial-state wave function. These authors expanded the wave function of the bound state of helium in relative partial waves and calculated the double-photoionization cross section[7]; good agreement with Carlson's data was obtained. However, from a comparison with an asymptotic double-ionization calculation,[1] Byron and Joachain estimated the uncertainties in their cross section to be of the order of 25% arising principally from the failure of their ground-state wave function to be of sufficiently high precision.

It is the purpose of this paper to reevaluate the helium double-photoionization cross section using a very accurate Hylleraas wave function for the ground state (Sec. II), and to compare these results with Carlson's data and Byron and Joachain's calculation. An interpretation of the differential cross section is used in Sec. III to stimulate an asymptotic calculation which is found to be applicable at energies greater than 600 eV.

II. DOUBLE-PHOTOIONIZATION CROSS SECTION

Since the double-ionization process depends so critically on correlation of the atomic electrons in the initial state,[4-6] it is important to employ a wave function for the bound state which includes a high degree of correlation: For helium, Hylleraas-type wave functions which explicitly include interelectronic r_{12} terms best fulfill this criterion. In the work that follows, the ground state will be represented by the six-parameter Hylleraas wave function,[8]

$$\Psi_b(\vec{r}_1,\vec{r}_2)=N_b\, e^{-\beta s}\,(1+c_1 u+c_2 t^2 +c_3 s+c_4 s^2+c_5 u^2), \qquad (1)$$

where $s=r_1+r_2$, $t=r_2-r_1$, and $u=r_{12}$. This description (1) of the $1s^2$ state of helium (with the parameters recently reevaluated by Stewart and Webb[9]) not only includes electron correlation directly but it also gives a better ground-state energy than does the Byron-Joachain (BJ) wave function, in spite of the fact that the latter representation uses 15 parameters in each of three partial waves. This wave function gives a ground-state energy of − 2.90332 a.u., while BJ obtain − 2.9020 a.u. Complications introduced by use of the Hylleraas description will be considered below.

The final state of the helium atom with two electrons in the continuum is represented by a symmetrized product of uncorrelated Coulomb wave functions,

$$\Psi_f(\vec{r}_1,\vec{r}_2)=\frac{1}{\sqrt{2}}\sum_{m=-l}^{l}(l+1,m,l,-m\,|\,1,0) \times[R_{\epsilon,l+1}(r_1)Y_{l+1,m}(\Omega_1)R_{\epsilon',l} \times(r_2)Y_{l,-m}(\Omega_2)+2\longleftrightarrow 1]. \qquad (2)$$

Both of the free electrons are assumed to be influenced by a central field of charge $Z=2$, i.e., they exhibit a negligible screening effect on each other.[10]

The double-photoionization cross section $\sigma(\mathrm{He}^{++})$ has been evaluated using

$$\sigma(\mathrm{He}^{++})=\frac{4\pi^2\alpha a_0^{\,2}}{\hbar\omega}\sum_l\int d\epsilon \times\int d\epsilon'\;\delta(\epsilon+\epsilon'+I_2-\hbar\omega)\,|M_{bf}|^2 ,$$

where α is the fine structure constant, a_0 is the Bohr radius, $\hbar\omega$ is the energy of the incident photon, ϵ and ϵ' are the energies of the ejected electrons, and I_2 is the two-electron ionization potential. (Atomic units are used throughout, with energies in rydbergs.) If k and k' are the momenta of the ejected electrons, i.e., $k^2=\epsilon$ and $k'^2=\epsilon'$, the δ function can be used to eliminate one integral, and the differential cross section becomes

$$\frac{1}{k}\frac{d\sigma(\mathrm{He}^{++})}{dk}=\frac{4\pi^2\alpha a_0^{\,2}}{\hbar\omega} \times\sum_l|M_{bf}|^2{}_{k'^2=\hbar\omega-I_2-k^2}\,. \qquad (3)$$

The dipole momentum matrix element, which has been shown to be more reliable than the dipole position or acceleration formulation over a wide range of photon energies,[9] is used to express the matrix element

$$M_{bf}=\int d\vec{r}_1\int d\vec{r}_2\,\Psi_b^*(\vec{r}_1,\vec{r}_2) \times\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\Psi_f(\vec{r}_1,\vec{r}_2)\,. \qquad (4)$$

When the wave functions (1) and (2) are used in (4), the integrals are straightforward except those involving products of the Coulomb functions and the interelectronic separation. It is precisely these difficulties that lead Byron and Joachain to introduce a wave function free of the troublesome r_{12} terms. However, all the integrals may be expressed in closed form if the following expansion is made for r_{12}[11,12]:

$$r_{12}=r_>\sum_{n=0}^{\infty}\left(\frac{(r_</r_>)^2}{2n+3}-\frac{1}{2n-1}\right)\left(\frac{r_<}{r_>}\right)^n P_n(\cos\theta), \qquad (5)$$

$$\cos\theta=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2),$$

$$P_n(\cos\theta)=\sum_{n=-m}^{m}\frac{(n-|m|)!}{(n+|m|)!}P_n^{\,m}(\cos\theta_1) \times P_n^{\,m}(\cos\theta_2)\,e^{im(\phi_1-\phi_2)}, \qquad (6)$$

where $r_>(r_<)$ is the larger (smaller) of the two coordinates r_1 and r_2. Such a representation is useful because the angular integrals over the associated Legendre functions in (6) and the spherical harmonics in (2) vanish except for one particular value of n and of m. Consequently, the sums in (6) and (5) also vanish, and the calculation is simplified considerably. A similar expansion of $r_{12}^{\,2}$ in terms of spherical harmonics also facilitates integration.

It is convenient to express the radial Coulomb functions in (2) by means of an integral representation for the confluent hypergeometric function of complex argument,[13]

$$R_{\epsilon,l}(r)=(-1)^{l+1}\left(Z\prod_{s=1}^{l}(s^2+n_0^{\,2})(1-e^{-2\pi n_0})^{-1}\right)^{1/2}\frac{2}{(2kr)^{l+1}}\frac{1}{2\pi}\oint e^{-2ikr\xi}(\xi+\tfrac{1}{2})^{-in_0-l-1}(\xi-\tfrac{1}{2})^{in_0-l-1}d\xi\,, \qquad (7)$$

where $n_0 = Z/k$.

Using these representations the integrals in (4) can now be evaluated directly. The procedure, described in detail elsewhere,[14] consists in interchanging the order of integration so that the integrals over the radial coordinates are performed before those over the contour followed by ξ; the results appear as a finite sum of residues of the Coulomb function [integrand in Eq. (7)].

Evaluating the matrix element (4) in the manner described above at energies from 0.1 to 1.0 keV and then integrating over the differential cross section (3), the helium double-photoionization cross section is obtained. The result, $\sigma_c(6)$ (the subscript c indicates that Coulomb waves were used for both of the ejected electrons and the 6 denotes that the six-parameter Hylleraas ground state was used), normalized to the single ionization cross section at the same energy[15] is plotted in Fig. 1 together with Carlson's data. Both the present calculation and that of Byron and Joachain[7] produce good agreement with the experimental data, although the shape of the theoretical cross sections is somewhat different at energies greater than ~350 eV.

III. ASYMPTOTIC DOUBLE PHOTOIONIZATION CROSS SECTION

An asymptotic approximation to the double-photoionization cross section can be inferred from an interpretation of the differential cross section (3). Figure 2 is a plot of the electron spectrum $(1/k)\,d\sigma(\mathrm{He}^{++})/dk$ as a function of k^2 at $\hbar\omega = 1.0$ keV, and it can be seen that the curve is approximately symmetrical about the midpoint between $k^2 = 0$ and $k^2 = \hbar\omega - I_2$, with the extremes being much greater than the values near the center: This reveals that the double-ionization process proceeds principally by the ejection of one electron of high energy $k_1^2 \sim \hbar\omega - I_2$ while the other barely escapes into the continuum, $k_2^2 \sim 0$. In fact, the probability for the ionization to occur in this manner is nearly two orders of magnitude greater than that for the ejection of both electrons with the same energy $k_1^2 \sim k_2^2 \sim \frac{1}{2}(\hbar\omega - I_2)$. A similar result has been confirmed experimentally by Carlson.[16]

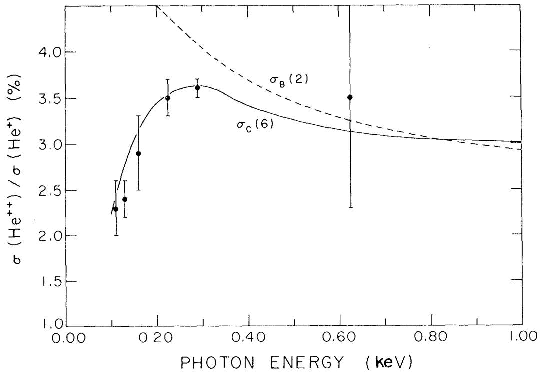

FIG. 1. Ratio of the double-ionization to single-ionization cross sections calculated using uncorrelated Coulomb waves for the free electrons (solid line) and a Born wave for one electron (broken line). The experimental points (Ref. 3) are noted.

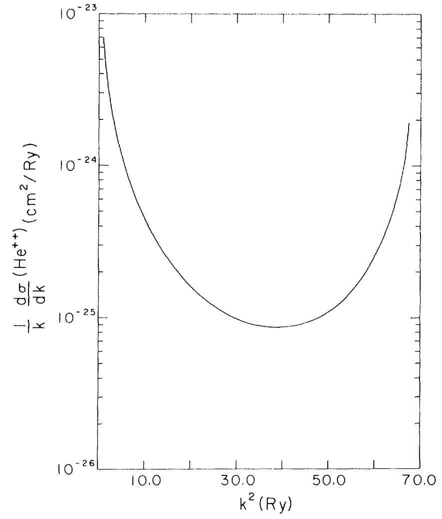

FIG. 2. Differential electron spectrum for double photoionization at 1 keV.

This interpretation of the electron spectrum indicates that an adequate free state for energies substantially above threshold would be obtained if the electron of high excitation was described by a plane wave while the electron of low excitation was represented by the Coulomb function (7) in a central field of charge $Z = 2$.[17] Let the free state (2) be replaced at high energies by the following symmetrized product:

$$\Psi_f(\vec{r}_1, \vec{r}_2) = 2^{-1/2}(u_B(r_1)u_c(r_2) + u_B(r_2)u_c(r_1)) , \tag{8}$$

where $u_B(\vec{r})$ is the plane wave (zeroth Born-approximation solution)

$$u_B(\vec{r}) = (2\pi)^{-3/2} e^{i\vec{k}_1\vec{r}} , \tag{9}$$

and $u_c(\vec{r})$ describes the electron influenced by the Coulomb field,

$$u_c(\vec{r}) = R_{\epsilon,l}(r)Y_{lm}(\Omega) . \tag{10}$$

Since the present calculation is expected to be valid only at energies substantially greater than threshold, it is not necessary to use the very accurate Hylleraas wave function (1) for the bound state of helium, but rather it is sufficient to employ a simple two-parameter Eckart wave function[18] which is a symmetrized product of hydrogenic wave functions characterized by effective nuclear charges Z_0 and Z^*,

$$\Psi_b(\vec{r}_1, \vec{r}_2) = C(e^{-Z_0 r_1 - Z^* r_2} + e^{-Z_0 r_2 - Z^* r_1}), \tag{11}$$

where $C = 8(Z_0 Z^*)^{3/2}/(Z_0 + Z^*)^3$.

It has been shown[14] that this wave function, with the parameters reevaluated using modern computing techniques,[19] may be used to provide a single-photoionization cross section which, at energies substantially greater than threshold, agrees to within a few percent with the results got by Salpeter and Zaidi[2] who used a much more accurate ground-state representation.

Using (8) for the free state, the dipole momentum matrix element (4) can be written as a sum of two contributions,

$$M_{bf}(\vec{r}_1, \vec{r}_2) = M_B(\vec{r}_1, \vec{r}_2) + M_c(\vec{r}_1, \vec{r}_2) \ ,$$

where
$$M_B(\vec{r}_1, \vec{r}_2) = \int d\vec{r}_1 \int d\vec{r}_2 \times \Psi_b(\vec{r}_1, \vec{r}_2) u_c(\vec{r}_1) \frac{\partial}{\partial z_2} u_B^*(\vec{r}_2), \tag{12}$$

and
$$M_c(\vec{r}_1, \vec{r}_2) = -\int d\vec{r}_1 \int d\vec{r}_2 \times \frac{\partial \Psi_b}{\partial z_2}(r_1, r_2) u_B^*(r_1) u_c^*(r_2). \tag{13}$$

If the representations (7), (9), and (10) along with the Eckart bound state (11) are used above, the terms in the matrix element (12) and (13) can be written in closed form.

The asymptotic double-photoionization cross section is

$$\sigma_B(2) = \frac{4\pi^2 \alpha a_0^2}{\hbar\omega} \int d\epsilon \int d\epsilon' \sum_{l,m} |M_{bf}|^2 \times \delta(\epsilon + \epsilon' + I_2 - \hbar\omega) \ ,$$

where $\sum_{l,m} |M_{bf}|^2 = 2|M_B|^2 + 4|M_c|^2$.

The extra factor of 2 in front of M_C occurs because M_B is nonzero only for $(l, m) = (0, 0)$, whereas M_c vanishes unless $(l, m) = (1, \pm 1)$.

The asymptotic double-photoionization cross section $\sigma_B(2)$(the B indicates that the Born approximation was used to describe one of the ejected electrons, and the 2 denotes the two-parameter Eckart wave function was used for the ground state), normalized to the single-ionization cross section results of Salpeter and Zaidi[2] and Stewart and Webb,[9] is included in Fig. 1.

IV. DISCUSSION

An inspection of Fig. 1 shows that although the two double-photoionization cross sections, $\sigma_C(6)$ and $\sigma_B(2)$, calculated here, employed quite different wave functions for both the initial and final states, nevertheless the agreement between them is relatively good at high energies ($\hbar\omega \gtrsim 600$ eV) where the approximations inherent in $\sigma_B(2)$ can be expected to be reliable. At lower energies, the asymptotic cross section exhibits a maximum at about twice the double-ionization threshold energy as is expected in applications of the Born approximation.[13]

The small discrepancies between the present calculation $\sigma_C(6)$, Carlson's data, and the results obtained by Byron and Joachain at low energies imply that much greater confidence can be placed in this cross section than the uncertainty of ~25% originally suggested by the latter authors. The differences between the calculated cross sections at energies greater than ~300 eV must be ascribed to variations manifest in the two different representations used to describe the ground state of helium. But even if the discrepancies between these two results are indicative of the uncertainties in the calculations, then the error implied is less than ~10%.

These results could be improved further by use of a still more accurate bound-state wave function, but such a calculation should be deferred until correlation can be explicitly included in the final state.

ACKNOWLEDGMENTS

Many useful discussions with Dr. R. J. Gould and Dr. T. Delmer are gratefully acknowledged. This work was carried out at the University of California at San Diego under grants from the National Science Foundation and the National Aeronautics and Space Administration.

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[*] Operated by Associated Universities, Inc., under contract with the National Science Foundation.

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PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Rotational Line Intensities in $^3\Sigma^+$-$^1\Sigma^+$ Electronic Transitions*

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(Received 22 September 1969)

The rotational intensity distribution was measured for $^3\Sigma^+$-$^1\Sigma^+$ electric dipole transition which occurs only by violating the spin-selection rule. The photographic intensities, obtained using a 5-m two-mirror vacuum spectrograph, were reduced by means of the Seidel function and the intensity alternation which exists for homonuclear molecules with $\Lambda = 0$. The results are in disagreement with theoretical intensity distributions.

1. INTRODUCTION

Despite the tremendous amount of information that has been obtained on diatomic molecules, there have been very few experimental tests on line intensities in forbidden transitions, and none on $^3\Sigma^+$ - $^1\Sigma^+$ electric-dipole transitions which occur only by violating the spin-selection rule, $\Delta S = 0$. The reason for this is not only that reliable measurements of intensities are difficult to make but also, in this case, the very weak intensities involved are not compatible with the high dispersion and resolution required for precision measurements of the individual lines in the molecular bands.

The proof of the selection rule, $\Delta S = 0$, depends on the possibility of separating the wave function of any state of the stationary molecule into the product of two factors; one depending on the orbital motions, and the other on the electron spins. This separation cannot be made, however, when the spin-orbit interaction is taken into account; the resulting modified wave function now permits intersystem transitions of small intensity. In the analogous case of intercombinations between singlet and triplet states in an atom with two electrons, it is necessary to solve the perturbation problem completely before the intensities can be calculated. The molecular problem is simpler, however, since all that is required here is the dependence of the intensities on the rotational quantum number J for a given electronic transition, and not, as in the atomic case, with the intensities of different electronic transitions. Thus, the perturbation problem need not be completely solved, nor indeed would this be possible without definite knowledge of the complete molecular wave functions.

This problem was investigated theoretically by Schlapp[1] who, by including the spin-orbit interaction, obtained formulas for the intensities of rotational lines of intersystem transitions for the case when the spin vector is not coupled to the internuclear axis (Hund's case b). More recently, Watson[2] included the effects of spin-spin interaction and derived different intensity formulas which