High-energy limit of the double-electron photoionization cross section of the helium atom

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(Received 24 February 2000; published 15 November 2000)

Using a particularly accurate and locally correct helium wave function, obtained by direct solution of the three-body Schrödinger equation, calculations were performed for double- and single-electron photoionization cross sections of the helium atom in the limit of high but nonrelativistic photon frequencies. In the dipole approximation, the cross-section ratio is frequency independent and equal to 0.016 45, which should be compared with the values 0.016 44, 0.0167, and 0.0168 calculated recently in the literature using different variational wave functions.

PACS number(s): 32.80.Fb, 31.15.Ja

I. INTRODUCTION

The aim of this paper is to calculate the double $[\sigma^{++}(\omega)]$ and single $[\sigma^{+}(\omega),\sigma^{+*}(\omega)]$ ionization cross sections, with ejection of two and one electrons, of the helium atom in collision with a single photon of high but nonrelativistic frequency ω.[1] In this case one can limit oneself to the dipole approximation in the photon-electron interaction. The values of $\sigma^{++}(\omega),\sigma^{+}(\omega)$, and $\sigma^{+*}(\omega)$ can be expressed directly via the initial-state atomic helium wave function, thus opening an additional possibility of checking its quality by comparison of the theoretical predictions and the experimental results.

The problem of double-electron ionization by a single photon has a relatively long history, which goes back, as far as we know, to Ref. [1]. Interest in this process is motivated by the fact that, without taking into account the interaction between atomic electrons, the ejection of two of them by a single photon is impossible. The simplest mechanism to explain double ionization by one photon is the shake-off [1], in which one of the electrons absorbs the photon and therefore leaves the atom. As a result, the atomic field is altered, causing another electron (or even electrons) to be shaken off due to this field variation. This mechanism works best for high photon energies and nonequivalent electrons, namely, one loosely and the other tightly bound. Obviously, this is not the case for helium, and it was not a surprise that the shake-off model gave results for it considerably different from experimental data [1]. Soon after [1], two purely theoretical papers were published [2,3] discussing double-electron photoionization. Most attention was given to high but nonrelativistic frequencies ω and important conditions on the radial dependence of the two-electron wave function were discovered [2]. The gauge dependence of the cross section was demonstrated as well, at least in the case when the interaction between two outgoing electrons was neglected [3]. Soon a many-body approach to this problem was developed [4,5], based on general perturbation theory, which automatically led to gauge-invariant results. It is clear, however, that the perturbative approach is not enough to describe the interelectron interaction at least in the initial state. Giving special attention to high ω, namely, to $I \ll \omega \ll c^2$, where I is the double-electron ionization potential, one can express the double-ionization cross section directly via the initial-state wave function [6,7]. Recently, due to rapid progress in experimental technology [8,9] and construction of new sources of high-energy and high-intensity electromagnetic radiation, it has become possible to measure $\sigma^{++}(\omega)$ at $\omega \leqslant 8.8$ keV with quite high accuracy [9]. This experimental progress was accompanied by a burst of theoretical investigations of two-electron ionization in a broad region of ω—from the very threshold up to the asymptotic values $I \ll \omega \ll c^2$ [10–15].

Although as ω increases above $\omega > c$ the nondipole corrections to $\sigma^{++}(\omega)$ become more and more important [5,16,17], it is of great interest to learn the value of the asymptotic ratio

$$R = \left. \frac{\sigma^{++}(\omega)}{\sigma^{+}(\omega)+\sigma^{+*}(\omega)} \right|_{\omega \to \infty} \tag{1}$$

calculated in the dipole approximation, but with as good a two-electron initial-state wave function as possible. Usually a multiparameter variational wave function is used, which is able to reproduce the experimentally well-known helium ground-state energy with high accuracy. There exists a widespread belief that the wave function which gives the ground-state energy accurately enough is equally good in reproducing other measurable ground-state atomic characteristics. In principle it is possible, however, that different wave functions which reproduce the ground state energy equally well can be rather different in describing other atomic characteristics (such as, for instance, the photoionization cross section), which are determined by quite specific space parts of the atomic wave function. Despite the fact that several methods can now provide good values of most physical observables in these systems, the precision of their description of wave functions, especially of their local properties, has not been properly addressed.

[1]The atomic system of units is used in this paper: $m_e = e = \hbar = 1$, with m_e being the electron mass, e its charge, and $\hbar$ the Planck constant.

Until recently by far the most accurate estimates of observables were obtained in different variational calculations [18–22]; see also [23] and references therein. These, however, sophisticated and precise as they currently are, do not reproduce the correct analytical structure of the three-body wave functions, since the inclusion or omission of logarithmic terms [22], or negative powers of interparticle distances [24], has negligible effect on the value of the calculated energy. A variational function coincides with the precise one only on the average, and could wildly or even infinitely deviate from it locally [24]. These local discrepancies could lead to wrong estimates of expectation values of different operators that have significant contributions from the regions of the configuration space where the deviations occur. Therefore a thorough analysis of the quality of the wave function is needed. Its necessity was first raised in the literature by Bartlett, Gibbons, and Dunn [25,26] many years ago. It was more recently discussed once again in [27,28].

Recently [27], the local behavior of wave functions calculated by two precise contemporary methods, the stochastic variational method (SVM) [18] and the correlation function hyperspherical harmonic method (CFHHM) [29,30] was compared. Although the energies calculated by both methods coincide to ten significant figures, it was found that the values of the relative local deviation defined as

$$D=\frac{H\Psi}{E\Psi}-1 \tag{2}$$

at and near the coalescence points were larger in the SVM by five orders of magnitude than in the CFHHM. Thus considerably more accurate expectation values of the $\langle \delta(\mathbf{r}_{ep})\rangle$ operators were given by the CFHHM, despite the fact that most other SVM observables converge to significantly more digits than CFHHM observables for the comparable number of basis functions.

The local accuracy of the CFHHM wave function was previously studied in Ref. [28] for the ground and the $2\ ^1S$ state of the helium atom and for the ground state of the positronium ion (Ps^-). It was analyzed in more detail and for higher excitations as well in Ref. [31].

The necessity of proper description of local properties of wave functions in variational calculations was stressed in Ref. [32] where a variational principle for the minimization of the local energy $\epsilon=H\Psi/\Psi-E$ instead of E was developed and realized within the quantum Monte Carlo method. The two best calculations of the helium atom ground state gave E with errors of 0.004 and 2×10^{-6}, respectively. The corresponding standard deviations of the local energy, σ, were 0.14 and 0.001, respectively, showing that the error in energy was still decreasing faster than σ. An example of a CFHHM calculation with the same precision 2×10^{-6} in energy is the CFHHM calculation of the $2\ ^1S$ state with $K_m=32$ [33]. Here K_m is the maximum global angular momentum used in the expansion basis. The measure of local accuracy analogous and comparable to σ, the expectation value $\langle|\epsilon|\rangle=E\langle|D|\rangle$, was 0.0023. This is of the same order of magnitude as 0.001 of Ref. [32], indicating that the proposed variational principle [32], while giving better accuracy of the wave function than the usual Ritz variational approach, is roughly equivalent in precision to the CFHHM approach using relatively small K_m. That is, the CFHHM calculation in Ref. [33] was done for K_m up to 56, where $\langle|\epsilon|\rangle$ fell to 0.0003 (and E improved by two digits).

Given this specific feature of the CFHHM wave function, that it is locally better than several of the above-mentioned variational wave functions, our aim in this paper is to check whether this wave function can lead to results different from those obtained in the previous calculations. In fact, the asymptotic value of R depends only on the ground-state wave function [2,12]. In Ref. [7], an old parametric correlated representation was used, giving $R=0.0168$. In Ref. [12], a seven-term multiconfiguration Hartree-Fock (MCHF) wave function, which gave energy with three-digit precision only, was used, yielding $R=0.0167$. In Ref. [14], which utilizes a finite-element approach, the resulting wave function gave energy accurate to four digits, and the asymptotic extension of $R(\omega)$ was not computed. Reference [15] is the only work known to us utilizing rather accurate variational wave functions.

II. APPROXIMATIONS

In order to obtain an expression for the parameter R, the approach of Ref. [34] can be used. In the approximation where the energy of one of the electrons is high, the double-excitation cross section is given by the formula (correcting misprints in [34])

$$\sigma^{++}(\omega)\approx\frac{32\sqrt{2}Z^2\pi^2}{3c\omega^{7/2}}\left\{\int|\Psi(\mathbf{0},\mathbf{s})|^2d\mathbf{s}-\sum_{nlm}\left|\int\Psi(\mathbf{0},\mathbf{s})\psi_{nlm}(\mathbf{s})d\mathbf{s}\right|^2\right\}, \tag{3}$$

where Ψ is the three-body wave function obtained by the CFHHM, and $\psi_{nlm}(s)$ is the unperturbed single-particle wave function of the second electron in the field of the nucleus, after the first electron has left the atom. Here Ψ depends on Jacobi coordinates $\mathbf{r}$ and $\mathbf{s}$, where $\mathbf{r}$ connects the nucleus and one electron, and $\mathbf{s}$ connects the center of mass of these two particles with the other electron. In the framework of the present approximation, we set $\mathbf{r}=\mathbf{0}$; then $\mathbf{s}$ represents the distance of the second electron from the nucleus. Thus $\Psi(\mathbf{0},\mathbf{s})$ represents the three-body wave function at the coalescence, or cusp, region, in which, as one can see from the discussion in the Introduction and from references therein, local high accuracy of the wave function is especially difficult to obtain. Finally, n is the single-particle principal quantum number, l and m are the angular momentum quantum numbers, and c is the speed of light.

The first integral is equal to the expectation value $\langle\delta(\mathbf{r})\rangle$ provided Ψ is normalized in the six-dimensional space corresponding to the volume element $d\mathbf{r}\,d\mathbf{s}$. Since we are using a wave function with total angular momentum $L=0$, Eq. (3) simplifies, at $\omega\to\infty$, to

$$\sigma^{++}(\omega)=\frac{32\sqrt{2}Z^2\pi^2}{3c\omega^{7/2}}\left(\langle\delta(\mathbf{r})\rangle-\sum_n I_{n0}\right), \tag{4}$$

where

$$I_{n0}=4\pi\left|\int_0^\infty \Psi(0,s)R_{n0}(qs)s^2ds\right|^2, \tag{5}$$

$q=2Zm_\alpha/(1+m_\alpha)$, Z is the charge of the nucleus, and R_{nl} are the two-particle bound Coulomb radial functions. Also [34],

$$\sigma^{+}(\omega)+\sigma^{+}{}^*(\omega)=\frac{32\sqrt{2}Z^2\pi^2}{3c\omega^{7/2}}\sum_n I_{n0}, \tag{6}$$

which is the quantity measured in experiments, so that finally

$$R=\frac{\langle\delta(\mathbf{r})\rangle-\Sigma_n I_{n0}}{\Sigma_n I_{n0}}. \tag{7}$$

We have also calculated the values of

$$R_0=\frac{\sigma^{++}(\omega)}{\sigma^{+}(\omega)}=\frac{\langle\delta(\mathbf{r})\rangle-\Sigma_n I_{n0}}{I_{00}} \tag{8}$$

and

$$R_1=\frac{\sigma^{+}(\omega)+\sigma^{+}{}^*(\omega)+\sigma^{++}(\omega)}{\sigma^{+}(\omega)}=\frac{\langle\delta(\mathbf{r})\rangle}{I_{00}}. \tag{9}$$

III. RESULTS

We used the nuclear mass $m_\alpha=7294.2996$ from Ref. [35], giving $q=3.999\,45$. Use of infinite m_α changed $\Sigma_n I_{n0}$ and $\langle\delta(\mathbf{r})\rangle$ in the fourth digit, and does not affect R or R_0 to the quoted precision.

In the CFHHM, the wave function is decomposed as $\Psi=e^f\Phi$, where the correlation function f contains the physical singularities (i.e., cusps) and Φ is a smooth function expanded in the hyperspherical harmonic basis. The calculation was performed with a linear correlation function that satisfies all three cusp conditions exactly:

$$f=\sum_{i<j=2}^{3} Z_iZ_j\frac{m_im_j}{(m_i+m_j)}r_{ij}, \tag{10}$$

where Z_i and m_i, $i=1,2,3$, are the particle charges and masses, respectively, and r_{ij} are the interparticle distances. Such f gives very precise local behavior and precise observables of the helium ground state. We used the CFHHM helium atom ground-state wave function Ψ with $K_m=80$ (441 hyperspherical states) from Ref. [31], where the local energy and different expectation values are also computed. This wave function gives the energy to 10 significant digits and its local accuracy is characterized by $\langle|D|\rangle=7.2\times10^{-5}$ or $\langle|\epsilon|\rangle=E\langle|D|\rangle=2.1\times10^{-4}$. Furthermore, our entire calculation [31] is completely devoid of free parameters.

Table I shows the values of I_{n0} and the convergence of their sum. The series turns out to converge as $0.159n^{-3}$, the error of the sum of the first M terms being $\epsilon_M=0.159/(2M^2)$: $\epsilon_{63}=2\times10^{-5}$. The increase of error due to the calculation of R_{n0} at high n is compensated by the short range of the integrands. Further, we checked that for the less converged wave function with $K_m=40$ (121 hyperspherical states), $\Sigma_n I_{n0}$ and $\langle\delta(\mathbf{r})\rangle$ agree to five digits, so that the results stay the same to the quoted precision. The precision of quadrature in the variable s was much higher than the number of quoted digits.

TABLE I. Convergence of I_{n0} with state index n. Numbers in square brackets denote powers of 10.

n	I_{n0}	$\Sigma_n I_{n0}$	n	I_{n0}	$\Sigma_n I_{n0}$
1	0.1682[+1]	1.682 18	16	0.3940[−4]	1.780 10
2	0.8071[−1]	1.762 88	17	0.3278[−4]	1.780 14
3	0.9923[−2]	1.772 81	18	0.2757[−4]	1.780 17
4	0.3283[−2]	1.776 09	19	0.2341[−4]	1.780 19
5	0.1514[−2]	1.777 60	20	0.2005[−4]	1.780 21
6	0.8291[−3]	1.778 43	21	0.1730[−4]	1.780 23
7	0.5054[−3]	1.778 94	22	0.1504[−4]	1.780 24
8	0.3315[−3]	1.779 27	23	0.1315[−4]	1.780 25
9	0.2296[−3]	1.779 50	24	0.1157[−4]	1.780 27
10	0.1657[−3]	1.779 67	25	0.1023[−4]	1.780 28
11	0.1235[−3]	1.779 79	30	0.5906[−5]	1.780 31
12	0.9461[−4]	1.779 88	40	0.2486[−5]	1.780 35
13	0.7409[−4]	1.779 96	50	0.1272[−5]	1.780 37
14	0.5911[−4]	1.780 02	60	0.7356[−6]	1.780 38
15	0.4793[−4]	1.780 07	63	0.6354[−6]	1.780 38

We get $\Sigma_n I_{n0}=1.7804$ and $\langle\delta(\mathbf{r})\rangle=1.809\,67$. From this we obtain $R=0.016\,45$, $R_0=0.017\,41$, and $R_1=1.0758$. The values of R (or R_0) are slightly different from the values calculated earlier in the literature, namely, 0.0168 [7], or 0.0167 [12] calculated by using the so-called close-coupling configuration method. The results are given in Table II. The experimental result is 0.0172 ± 0.0012 at $\omega=8$ keV. In our units, where $c=137.02$, one obtains the following values for the photoionization cross sections:

$$\sigma^{++}(\omega)=0.1273\omega^{-7/2},$$

$$\sigma^{+}{}^*(\omega)=0.4268\omega^{-7/2},$$

$$\sigma^{+}(\omega)=7.311\omega^{-7/2}.$$

Note that, by using as $\Psi(0,s)$ the pure hydrogenlike wave function of the He^+ ion, one would have $\sigma^+(\omega)$

TABLE II. Binding energy (in a.u.) and R values.

Reference	Basis size	E	R
This work	121	2.903 724 364 3	0.016 45
This work	441	2.903 724 376 5	0.016 45
[15]		2.903 724 377 034	0.016 44
[12]	seven-term MCHF	2.901 81	0.016 7
[7]	20	2.903 717 9	0.016 8

$=11.07\omega^{-7/2}$ which is larger than our value by a factor of 1.51. If the Slater effective charge $Z_{\mathrm{eff}}=\frac{27}{16}$ instead of $Z=2$ were used for the hydrogenlike $\Psi(0,s)$, we would have $\sigma^{+}(\omega)=6.65\omega^{-7/2}$ which is smaller than our value by a factor of 0.91. Note also that if $Z_{\mathrm{eff}}=\frac{27}{16}$ substitutes for all Z in the hydrogenic approximation, one obtains a value of $\sigma^{+}(\omega)$ that is only 65% of our value.

IV. CONCLUSION

In summary, the double- to single-electron photoionization cross sections and their ratios were calculated in the high-photon-energy limit in the framework of the dipole approximation. The accurate and locally correct three-body helium wave function employed, obtained by direct solution of the three-body Schrödinger equation, gives for this ratio the value 0.016 45, which should be compared with the results of previous calculations, 0.016 44 of Ref. [15], 0.0167 of Ref. [12], and 0.0168 of Ref. [7], which used variational wave functions. These differences with respect to results in the literature reflect the small differences in wave functions at the electron-nucleus cusp region in view of the fact [2] that the value of R depends only on the wave-function contribution there [see Eqs. (5) and (7)].

[1] T. A. Carlson, Phys. Rev. **156**, 142 (1967).
[2] T. Åberg, Phys. Rev. A **2**, 1726 (1970).
[3] F. W. Byron and C. J. Joachain, Phys. Rev. **164**, 1 (1967).
[4] M. Ya. Amusia and M. P. Kazachkov, Phys. Lett. **28A**, 27 (1968).
[5] M. Ya. Amusia, E. G. Drukarev, V. G. Gorshkov, and M. P. Kazachkov, J. Phys. B **8**, 1248 (1975).
[6] A. Dalgarno and A. L. Stewart, Proc. R. Soc. London, Ser. A **76**, 49 (1960).
[7] A. Dalgarno and H. R. Sadeghpour, Phys. Rev. A **46**, R3591 (1992).
[8] J. A. R. Samson, Z. X. He, R. J. Bartlett, and M. Sagurton, Phys. Rev. Lett. **72**, 3329 (1994).
[9] J. Ullrich *et al.*, J. Phys. B **30**, 2917 (1997).
[10] T. Ishihara, K. Hino, and J. H. McGuire, Phys. Rev. A **44**, R6980 (1991).
[11] M. Pont, R. Shakeshaft, F. Maulbetsch, and J. S. Briggs, Phys. Rev. A **53**, 3671 (1996).
[12] A. S. Kheifets and I. Bray, Phys. Rev. A **54**, R995 (1996).
[13] J. H. McGuire *et al.*, J. Phys. B **28**, 913 (1995).
[14] K. W. Meyer, C. H. Green, and B. D. Esry, Phys. Rev. Lett. **78**, 4902 (1997).
[15] R. C. Forrey, H. R. Sadeghpour, J. D. Baker, J. D. Morgan, III, and A. Dalgarno, Phys. Rev. A **51**, 2112 (1995).
[16] E. G. Drukarev, Phys. Rev. A **52**, 3910 (1995).
[17] M. A. Kornberg and J. E. Miraglia, Phys. Rev. A **60**, R1743 (1999).
[18] Y. Suzuki and K. Varga, *Stochastic Variational Approach to Quantum Mechanical Few-Body Problems*, Vol. 54 of Lecture Notes in Physics (Springer-Verlag, Berlin, 1999).
[19] Y. K. Ho, Phys. Rev. A **48**, 4780 (1993).
[20] A. M. Frolov, Phys. Rev. A **57**, 2436 (1998).
[21] K. Varga, J. Usukura, and Y. Suzuki, Few-Body Syst., Suppl. **10**, 11 (1999).
[22] K. Frankowsky and C. L. Pekeris, Phys. Rev. A **146**, 46 (1966); **150**, 366(E) (1966).
[23] G. W. F. Drake, in Atomic, Molecular and Optical Physics Handbook, edited by Gordon W. F. Drake (AIP, Woodbury, NY, 1996).
[24] D. E. Freund, B. D. Huxtable, and J. D. Morgan, III, Phys. Rev. A **29**, 980 (1984).
[25] J. H. Bartlett, J. J. Gibbons, and C. G. Dunn, Phys. Rev. **47**, 679 (1935).
[26] J. H. Bartlett, Phys. Rev. **98**, 1067 (1955).
[27] R. Krivec, V. B. Mandelzweig, and K. Varga, Phys. Rev. A **61**, 062503 (2000).
[28] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **42**, 6324 (1990).
[29] M. I. Haftel and V. B. Mandelzweig, Ann. Phys. (N.Y.) **189**, 29 (1989).
[30] M. Haftel, R. Krivec, and V. B. Mandelzweig, J. Comput. Phys. **123**, 149 (1996).
[31] R. Krivec and V. B. Mandelzweig (unpublished).
[32] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988).
[33] R. Krivec, M. I. Haftel, and V. B. Mandelzweig, Phys. Rev. A **44**, 7158 (1991).
[34] M. Ya. Amusia, Atomic Photoeffect (Plenum, New York, 1990).
[35] V. H. Smith and A. M. Frolov, J. Phys. B **28**, 1357 (1995).