Double Photoionization and Transfer Ionization of He: Shakeoff Theory Revisited

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The shakeoff theory of Aberg [Phys. Rev. A **2**, 1726 (1970) is revisited. With the sudden approximation, we calculate the shakeoff probability when one of the electrons in He is ejected with a finite velocity. This theory is used to examine ratios of cross sections for double to single photoionization and transfer ionization to single electron capture. It is also shown that the momentum distribution of the shakeoff electron provides a means to measure the correlation of the ground state wave function directly.

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In the past decade, there have been many theoretical and experimental papers devoted to the studies of double to single photoionization cross section ratios of He. The issue was hardly settled when this subject was last reviewed in 1995 [1]. Since then, following the measurements of Dörner *et al.* [2] and of Samson *et al.* [3], the experimental ratios for photon energies from threshold up to about 1 keV are now in good shape, and they are in good agreement with the more recent elaborate calculations [4–8].

One of the early goals of studying double to single photoabsorption cross section ratios of He at high photon energies is to test the prediction of the intuitive shakeoff theory [9]. This theory states that the sudden removal of one fast electron can lead to the emission of the second electron, and its probability can be calculated using only the helium ground state wave function which is known almost exactly. In comparison with experiment, however, Compton scattering becomes important for photon energies above 6 keV. Fortunately, the two processes can be separated experimentally with the use of COLTRIMS apparatus where the photoabsorption process is distinguished from the Compton scattering by its larger recoil momentum. From such measurements, the shakeoff limit appears to have been confirmed experimentally at photon energy around 7 keV, but with relatively large errors [10].

Despite the recent success of theories in predicting double to single photoabsorption cross section ratios, $R_\nu(\omega)$ (Compton scattering part is excluded hereafter), the mechanism of double photoabsorption is not transparent from these sophisticated calculations. In the original shakeoff theory, Aberg obtained a ratio of 1.66% in the limit *when the photon energy approaches infinity.* This is the commonly quoted shakeoff ratio. To our knowledge, the shakeoff theory has never been examined for an electron escaping with a large but finite velocity, even though a similar expression appeared in the impulse approximation of the Compton double ionization of helium [11] previously. In this Letter, we reexamine the shakeoff theory for a fast escaping electron. Such a calculation is timely in view of the recent experiments of Schmidt *et al.* [12] and of Knapp *et al.* [13]. In the former, the ratio $R_{TI}(v)$ of transfer ionization (TI) with respect to single capture of He by high energy protons has been measured from 2.5–4.5 MeV. The ratio $R_{TI}(v)$ was found to be very similar to the ratio of double to single photoabsorption cross sections of He. In the latter, the momentum distributions of both electrons for double ionization of helium at photon energy of 530 eV have been reported. In both experiments the physical processes are characterized by a fast escaping electron, followed by the emission of a second electron. Intuitively, one would like to check if these experiments, together with the double photoabsorption of He, can be understood within a single framework, i.e., within the shakeoff theory. For this purpose, the theory should be extended to an electron escaping with large but finite velocity, and the momentum distribution of the shakeoff electron should also be extracted from the shakeoff theory.

In the shakeoff theory, the first electron in He is ejected into the continuum with a momentum $\vec{k}$, or velocity $\vec{v}$. Let $\Psi(\vec{p}_1, \vec{r}_2)$ be the helium ground state wave function in the mixed coordinate and momentum space. If $\vec{p}_1 = \vec{v}$, the spatial wave function of the second electron is described by

$$\psi_v(\vec{r}_2) = \Psi(\vec{v}, \vec{r}_2)/N_v, \tag{1}$$

where $N_v^2 = \langle\psi(\vec{v}, \vec{r}_2)|\psi(\vec{v}, \vec{r}_2)\rangle$ is the normalization constant. (The angle bracket implies integration over the position of the second electron.) Within the shakeoff theory, one takes $\psi_v(\vec{r}_2)$ to be the wave function of the remaining electron at the moment when the first electron is removed at velocity $\vec{v}$, either by photoabsorption or by electron capture process. According to the sudden approximation, the probability amplitude for the second electron to end up at the ith excited state (a shakeup process) of He^+ is given by

$$\alpha_i(v) = \langle\phi_i(\vec{r}_2)|\psi_v(\vec{r}_2)\rangle, \tag{2}$$

where ϕ_i is the bound state wave function of the He^+ ion with i denoting the quantum numbers n, l, m. The total probability for the second electron to remain bound in He^+ is then given by $P_b(v) = \sum_i |\alpha_i(v)|^2$, where the summation is over all the bound states, and the probability for it being ejected into the continuum is $1 - P_b(v)$. Thus, according to the shakeoff theory, the ratio of double to single photoionization $R_\nu(v)$, or the ratio $R_{TI}(v)$ of TI/SC, are both given by $r(v) = [1 - P_b(v)]/P_b(v)$. The above formulation is identical to the generalized shakeoff theory of Aberg [14] except that the equations are expressed more transparently in terms of wave functions in the mixed coordinate and momentum space.

In the shakeoff theory of Aberg, the $v \to \infty$ limit has been considered. In this limit, only the derivative of the wave function at the origin is explored. Using the accurate wave function of Kinoshita [15], the ratio $r(v)$ for $v \to \infty$ was evaluated to be 1.66%. To calculate $r(v)$ at finite v, as outlined above, it is more transparent to use the He ground state wave function in the mixed space. In the literature, practically all the accurate wave functions of He are given in configuration space containing the r_{12} coordinate (the distance between the two electrons). To obtain such wave functions in the mixed space is more tedious and is not pursued here.

We obtained the helium ground state wave function using the standard configuration interaction approach. The wave function is expanded in terms of s^2, p^2, and d^2 orbitals, and the radial wave function of each electron is expanded in terms of B-spline functions. The expansion coefficients are determined variationally in the configuration space. The mixed space wave function is then obtained trivially since the spherical harmonics in coordinate space is directly translated into spherical harmonics in momentum space. The primitive B-spline functions in the momentum space are obtained from the coordinate space by a simple Bessel transform. Using 16 B-splines for each electron, we obtained the nonrelativistic He ground state energy to be -2.90251 a.u., as compared to the nearly exact nonrelativistic energy of -2.90372 a.u. To make sure that the wave function thus obtained is accurate enough for investigating momentum properties of the electrons, we used the momentum space wave function to calculate the mass polarization energy which is defined as $\varepsilon = \frac{m}{M}\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$, with m and M being the mass of the electron and the α particle, respectively, and $\frac{m}{M} = 1.370\,933\,7 \times 10^{-4}$. This term measures the electron-electron correlation and has been calculated using accurate coordinate space wave functions [16]. We obtain ε to be 4.8714 cm^{-1}, to be compared to the accurate result of 4.7855 cm^{-1} [16]. We comment that the mass polarization measures the contributions of p^2 and d^2 components to the He ground state indirectly. Their contributions are quite small. From our calculations, the p^2 carries a weight of 0.4% while the d^2 carries a weight of 0.02% only. As shown below, such small weights are manifested directly by the nonisotropic momentum distribution of the shakeoff electron.

From the ground state wave function, we calculated $r(v)$. In Fig. 1, this ratio is compared to $R_\nu(v)$ and $R_{TI}(v)$ from experiments. For the photoionization process, we assume that the first electron receives all the excessive energy from the photon. For TI, v is taken to be the velocity of the projectile. In Fig. 1, the $r(v)$ from the present shakeoff theory is shown in a solid line. It has been drawn to the $v \to 0$ limit even though the theory is not expected to be valid for small v. On the same figure, we show in dashed lines the new experimental $R_\nu(v)$ from Samson *et al.* [3] which has been measured up to 820 eV, or $v = 7.38$ a.u. We emphasize that the new $R_\nu(\omega)$ in the low-v region has been confirmed by many newer elaborate theoretical calculations [4–8]. Clearly, the present shakeoff results do not agree with these accurate measurements at low v. For v greater than 8 a.u., the dashed lines are from the theoretical results of Kheifets *et al.* [5]. The shakeoff theory results from the present calculation are slightly higher. The difference could be due to the limitation of the shakeoff theory in this velocity regime, but some part could be due to the accuracy of the ground state wave function used here. The $r(v)$ in Fig. 1 approaches the asymptotic shakeoff limit slowly. At $v = 20$ a.u., our value is 2.10%. Extrapolating the curve to $v \to \infty$, we obtained 1.78%, which is larger than the accepted value of 1.66%. We expect that the more accurate He ground state wave function will improve the agreement.

In Fig. 1, we also show the ratio $R_{TI}(v)$ of TI to single electron capture cross sections of He by protons. The filled squares and the open circles at high velocities are from the measurement of Schmidt *et al.* [12]. In their experiment, the recoil momentum of He^{2+} was determined, thus allowing the separation of kinematic transfer ionization (KTI) from the Thomas mechanism. In the KTI process, the first electron is captured at close impact,

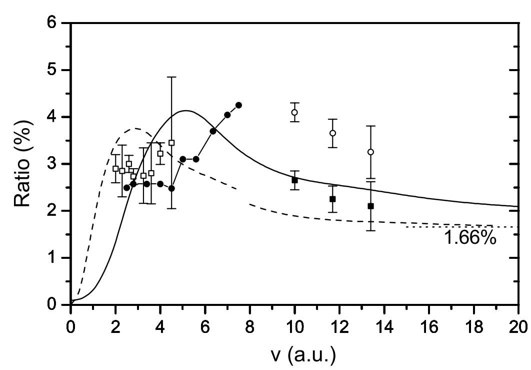

FIG. 1. Ratio of double to single photoionization of He (R_ν) and ratio of transfer ionization to single electron capture in proton impact on He (R_{TI}), as a function of the velocity v of the fast ejected electron. Solid line: present shakeoff results; dashed lines: experimental (low v) [3] and theoretical (for $v \geq$ 8) [5] R_ν. All the symbols are for R_{TI}: filled squares, kinematic transfer ionization only [12]. Total R_{TI}: open circles [12]; open squares [17]; solid circles [18].

resulting in a large recoil momentum. In the Thomas mechanism, transfer ionization proceeds via double collision and is characterized by a smaller recoil momentum. Only the KTI process can be described by the shakeoff theory. In Fig. 1, the experimental KTI data (in filled squares) are seen to be in quite good agreement with the prediction of the present shakeoff theory. We mention that the open circles give the ratio of the total transfer ionization, i.e., including contributions from the Thomas mechanism.

In Fig. 1, we also show the R_{TI} measured by different groups at lower collision velocities [17–19]. In this energy region, the validity of the shakeoff theory is more questionable and the experiments include both the KTI and other processes. On the other hand, in this lower energy region, the momentum distribution of the ejected electrons has been determined by Mergel *et al.* [20]. In view of the lack of any theoretical predictions for such distributions, we calculated the distributions according to the shakeoff theory. For this purpose, we project $\psi_v(\vec{r}_2)$ into continuum states of He^+ to extract the momentum distribution of the shakeoff electron. In Fig. 2, we show the expectation value of the longitudinal momentum of the shakeoff electron $\langle p_{2z} \rangle$ vs the velocity v of the fast captured electron (the same as the projectile velocity). The average $\langle p_{2z} \rangle$ is negative, meaning that the shakeoff electron is ejected more favorably in a direction opposite to the velocity of the fast captured electron (which is taken to be the $+z$ direction). Its absolute value increases gradually with v. Both features are consistent with the measured electron momentum distributions of Mergel *et al.* [20] (see their Fig. 3) even though at their collision energies (from 200 keV to 1 MeV) the validity of the shakeoff theory is limited. The present calculated $\langle p_{2z} \rangle$ shows some structure near $v = 8$. It is not clear if this is due to the limited accuracy of the present ground state wave function. However, the calculated expectation value $\langle p_{2z} \rangle$ approaches zero at large v is understood (see below).

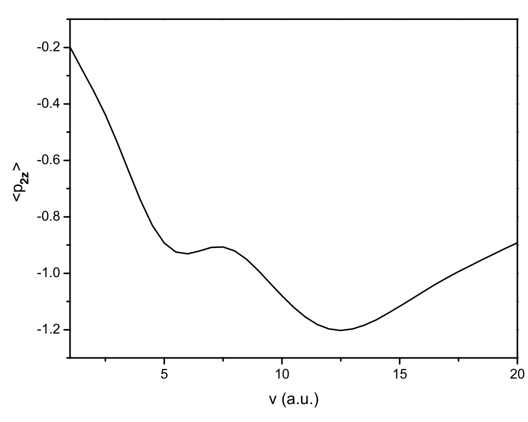

FIG. 2. Expectation values of the longitudinal momentum component, $\langle p_{2z} \rangle$ of the shakeoff electron as a function of the velocity v of the fast ejected electron.

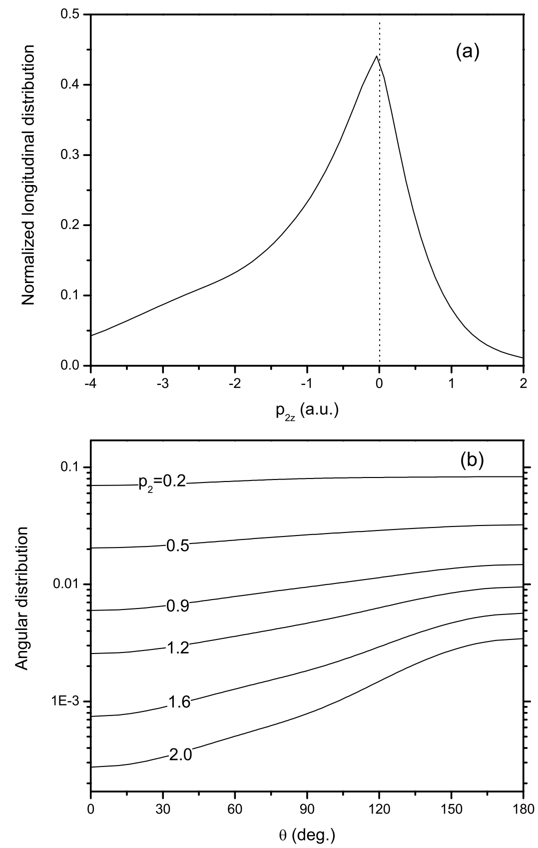

FIG. 3. (a) The longitudinal momentum distributions of the shakeoff electron after the first electron is ejected with $v = 6$ a.u. (b) The angular distributions of the shakeoff electron at different values of the momentum of the shakeoff electron. The first electron is ejected along the z axis at $v = 6$ a.u.

To further examine the momentum distribution of the shakeoff electron, we show in Fig. 3(a) its longitudinal momentum distribution when the first electron is ejected with $v = 6$ a.u. Clearly, there is an asymmetry at larger momentum, meaning that the fast shakeoff electron is ejected mostly in the opposite direction to the first escaping electron. If the velocity of the shakeoff electron is small, there is no significant asymmetry. This is further illustrated in Fig. 3(b) where the angular distributions of the shakeoff electron at fixed magnitude of momentum are shown. For small p_2, the distribution is only slightly different from isotropic. This result is consistent with the recent data of Knapp *et al.* [13]. Their data showed that the angular distribution of the low energy electron is nearly isotropic with respect to the velocity of the fast electron in the double photoionization measurements. At larger p_2 of the shakeoff electron, the momentum distribution peaks at 180°. This is not unexpected since, when both p_2 and v are large, the two electrons are close to the nucleus and the Coulomb repulsion tends to favor them away from each other.

Both $r(v)$ in Fig. 1 and the momentum distributions of the shakeoff electron in Figs. 2 and 3 clearly illustrate the

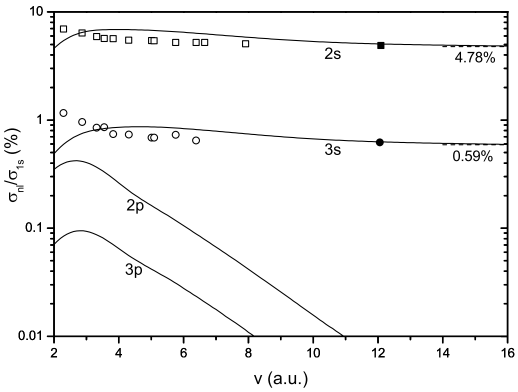

FIG. 4. Ratios of shakeup probabilities to $2s$, $3s$, $2p$, and $3p$ states of He^+ vs the probability of He^+ remaining at $1s$, as a function of the escape velocity v of the photoelectron. The experimental data give the ratios for shakeup to the $n = 2$ and $n = 3$ states of He^+ [21].

role of electron correlation of the He ground state. If the ground state is described by the shell-model designation $1s^2$, the calculated ratio $r(v)$ would be 0.71% and the ratio would be independent of v. Furthermore, the momentum distributions of the shakeoff electron would be isotropic with respect to the velocity vector of the first electron. One also notes that angular correlation information is lost in the $v \rightarrow \infty$ limit. In this limit, only the wave function near $r = 0$ enters the shakeoff theory, thus only the s^2 part of the wave function contributes to the shakeoff process. This explains why $\langle p_{2z} \rangle$ in Fig. 2 approaches zero as v becomes large.

We can also use the present theory to calculate the shakeup probability at different photon energies. In the asymptotic shakeoff model of Aberg, the electron can only be left in the ns state. In the present model, the np and nd states can also be populated (since we included angular momentum of each electron up to $l = 2$ only). We present the ratios of the shakeup probabilities to $2s$, $2p$, $3s$, and $3p$ with respect to $1s$, as a function of v in Fig. 4. The probabilities for $2p(3p)$ are much smaller than for $2s(3s)$; thus, we can compare the calculated $2s$ and $3s$ probabilities with the measured $n = 2$ and $n = 3$ probabilities [21]. The shakeup theory results deviate from the experimental data at lower energies, but are in reasonable good agreement with experiments at higher photon energies. In the figure, we assume that the photon energy is related to v by $\hbar\omega = I_n + \frac{1}{2}mv^2$, where I_n is the excitation threshold. In passing, we mention the centrifugal barriers near the nucleus for the non-s orbitals are responsible for the small shakeup probabilities to np and nd states at high energies.

In summary, we revisited the shakeoff theory where the first electron is ejected with a relative high but finite velocity v. The theory was used to study the cross section ratios of double to single photoionization of He at high energies and cross section ratios of kinematic transfer ionization to single electron capture of He in collisions with fast protons. By focusing on the subsequent ejection of the shakeoff electron, the two different processes were examined on the same footing. Using a correlated wave function, we showed that double photoionization at high photon energies and transfer ionization at high impact velocities can be approximately described by the shakeoff model. We further showed that measurements of the electron momentum distributions of the shakeoff electron offer the possibility of determining experimentally the correlation of the two electrons in the ground state of He directly.

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