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Theory of the photoelectron spectrum in double ionization through two-photon absorption from He($2s^2$)

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We analyze in this paper the role of the correlations during double-electron ejection through two-photon absorption from the lowest autoionizing state ${}^1S^e$ of helium. Emphasis will be put on the pertinence of the notion of simultaneity for double-electron ejection when this process does not require electron interaction.

INTRODUCTION

In the course of our ongoing work on the assessment of double ionization through multiphoton transitions [1,2], we have been led to examine the probability for two-electron ejection in two-photon absorption from the $2s^2\,{}^1S^e(1)$ doubly excited (autoionizing) state of He. This represents the second "step" of four-photon resonant six-photon ionization and double ionization from the ground state of the atom. The requirement of four-photon resonance with the $2s^2$ fixes the photon energy at $\hbar\omega \cong 14.45$ eV, which makes energetically possible the process $2s^2+2\hbar\omega \rightarrow \mathrm{He}+2e^-$. We shall present the detailed calculation and results for the complete six-photon process in a longer paper. The purpose of this paper is to report a somewhat surprising result on the photoelectron energy spectrum in two-photon double-electron ejection.

It is well known that double-electron ejection by single-photon absorption [3] can take place only if correlation exists in the initial (and/or final) state. As a consequence, the photoelectron energy spectrum [4] is represented by a continuum which typically exhibits a broad minimum around the middle; i.e., corresponding to equipartition of the total kinetic energy between the two electrons. The main point we wish to make here is that in two-photon double-electron ejection, the process is dominated by transition channels that require no interaction between the electrons. In fact, it can occur even in an independent-particle model. As we show in the following section, this leads to a photoelectron energy spectrum qualitatively different from that of single-photon absorption. A further consequence of this feature is that the distinction between sequential and simultaneous double ionization becomes rather subtle.

FORMALISM

In order to derive an expression for the photoelectron energy spectrum, we consider $|2s^2\rangle$ as an initial state in the presence of a field represented by the photon number state $|N\rangle$ where $|2s^2\rangle$ will for the moment be understood as the product of two hydrogenic $2s$ (with $Z=2$) orbitals. We shall employ the resolvent operator in the notation of our earlier papers [1] and shall denote the initial state of the interacting system "atom + field" by $|A\rangle=|2s^2\rangle|N\rangle$. Considering for now only transitions through channels that do not include electron interaction, the absorption of two photons can only lead to final states of the form $|F\rangle=|Kl,K'l'\rangle|N-2\rangle$ where $|Kl,K'l'\rangle$ denotes the properly antisymmetrized product of two independent-particle continuum wave functions (calculated with $Z=2$) specified by the wave vector K and the angular momentum l of the appropriate partial wave, dictated by the electric dipole selection rules. Having fixed the final state, the only possible intermediate states allowing the two-photon transition (without electron interaction) are of the type $|C\rangle=|2s,Kl\rangle|N-1\rangle$. Within the above notation, the energies of the respective states are $E_A=E_{2s^2}+N\hbar\omega, E_C=E_{2s}+E_K+(N-1)\hbar\omega$, and $E_F=E_K+E_{K'}+(N-2)\times\hbar\omega$, where ω is the frequency of the photon and E_{2s} denotes the energy of He$^+(2s)$. Denoting V as the dipole interaction between atom and field, we have the following set of equations for the relevant matrix elements of the resolvent operator $G(z)$:

$$(z-\omega_A)G_{AA}=1+\sum_C V_{AC}G_{CA}-\frac{i}{2}\Gamma G_{AA}\,, \tag{1}$$

$$(z-\omega_C)G_{CA}=V_{CA}G_{AA}+\sum_F V_{CF}G_{FA}\,, \tag{2}$$

$$(z-\omega_F)G_{FA}=\sum_C V_{FC}G_{CA}\,, \tag{3}$$

where Γ is the rate of decay (autoionization width) of $|2s^2\rangle$. Solving Eq. (3) for G_{FA} and substituting into Eq (2), we obtain

$$(z-\omega_C)G_{CA}=V_{CA}G_{AA}+\sum_F \frac{|V_{FC}|^2}{z-\omega_F}G_{CA}\,. \tag{4}$$

Following the standard procedure, we set $z=\omega_C+i\eta$ in the denominator $z-\omega_F$ in the right-hand-side of Eq. (4); and in the limit $\eta\rightarrow +0$, the sum over F separates into a real and an imaginary part, the first leading to the shift and the second to the width of state $|C\rangle$. It is the width that is essential to our argument here. It comes from the δ function arising in the limit $\eta\rightarrow +0$ and results in the expression

$$\gamma_C=2\pi\int\sum_l|\langle K_0 l|\mathbf{e}\cdot\mathbf{r}|2s\rangle|^2 d\Omega_{K_0} \tag{5}$$

with $\mathbf{e}$ being the polarization vector of the radiation, where the integration over Ω_{K_0} extends over the complete solid angle, while K_0 corresponds to the energy E_0

$=E_{2s}+\hbar\omega$. Introducing γ_C into Eq. (4), it can be written as

$$(z-\omega_C+\tfrac{1}{2}i\gamma_C)G_{CA}=V_{CA}G_{AA}$$

from which we can obtain an expression for G_{CA}. Substituting that expression into Eq. (1), we have

$$(z-\omega_A)G_{AA}=1+\sum_C \frac{|V_{CA}|^2}{z-\omega_C+\frac{1}{2}i\gamma_C}G_{AA}-\tfrac{1}{2}i\Gamma G_{AA}\,. \tag{6}$$

We will again approximate the sum over C by its value at $z=\omega_A$ and will retain explicitly only its imaginary part, which is finally written as

$$-\frac{\gamma_A}{2}=-\frac{\gamma_C}{2}\int\sum_l \frac{|\langle Kl|\mathbf{e}\cdot\mathbf{r}|2s\rangle|^2}{(E_K-E_1)^2+\frac{1}{4}\gamma_C^2}dE_K\,d\Omega_K$$

$$=-\pi\int\sum_l |\langle K_1 l|\mathbf{e}\cdot\mathbf{r}|2s\rangle|^2 d\Omega_{K_1}\,, \tag{7}$$

where $E_1=\hbar\omega-(E_{2s}-E_{2s^2})$. K_1 corresponds to the energy E_1.

Using Eq. (7) with Eq. (6), we obtain

$$G_{AA}=\frac{1}{z-\omega_A+\frac{1}{2}i\bar{\gamma}_A}\,,\quad \bar{\gamma}_A=\gamma_A+\Gamma\,, \tag{8}$$

which combined with the expressions for G_{CA} and G_{FA}, enables us to express G_{FA} as

$$G_{FA}=\frac{V_{FC}V_{CA}}{(z-\omega_F)(z-\omega_C+\frac{1}{2}i\gamma_C)(z-\omega_A+\frac{1}{2}i\bar{\gamma}_A)}\,, \tag{9}$$

where we can write

$$V_{FC}V_{CA}\approx\langle Kl|\mu|2s\rangle\langle K'l'|\mu|2s\rangle\ \ (\mu=\mathbf{e}\cdot\mathbf{r})\,. \tag{10}$$

The photoelectron energy spectrum corresponds to the spectrum of final states of the two-photon two-electron transition. As such, it is given by $\lim_{t\to\infty}|U_{FA}(t)|^2$ and $U_{FA}(t)$ is obtained as the inverse Laplace transform of $G_{FA}(z)$. From Eq. (9) it is evident that the three poles of $G_{FA}(z)$ lead to an expression for $U_{FA}(t)$ which consists of a linear combination of three exponentials, two of which decay as $t\to\infty$. After some straightforward algebraic manipulations, the photoelectron energy spectrum for double-electron emission can be written as

$$|U_{K,K'}|^2=\frac{|\langle Kl|\mu|2s\rangle|^2|\langle K'l'|\mu|2s\rangle|^2}{[(E_{K'}+E_K-E_{2s^2}-2\hbar\omega)^2+\frac{1}{4}\bar{\gamma}_A^2][(E_K-E_0)^2+\frac{1}{4}\gamma_C^2]}\,. \tag{11}$$

We must at this point elaborate on the various levels of approximation in the description of the state $|2s^2\rangle$ and their consequences on the photoelectron spectrum. The approximation adopted above is crude (but not unphysical). The energy E_{2s^2} would then be given by $2E_{2s}+\langle 2s^2|1/r_{12}|2s^2\rangle$ which is different from the correct energy, but also different from $2E_{2s}$. As long as $E_{2s^2}\neq 2E_{2s}$ we shall have $E_1\neq E_0$ and the electron spectrum will exhibit two peaks [see Eq. (11)]. An even more crude approximation would be to neglect the term $\langle 2s^2|1/r_{12}|2s^2\rangle$, which corresponds to two noninteracting electrons leading to $E_{2s^2}=2E_{2s}$ (see Fig. 1) and therefore to a single-electron peak, since in that case $E_1=E_0$. Although unphysical for He, this latter approximation to the energy represents the correct limit for $Z\to\infty$. Both of the above are unacceptable, even as zeroth-order approximations, for He.

Turning now to more realistic descriptions, our development in this paper is consistent with perturbation theory with $1/Z$ as a parameter. In the zeroth order, we must diagonalize the total Hamiltonian of the atom within the degenerate manifold of the two hydrogenic configurations $2s2s$ and $2p2p$ (with $Z=2$). The resulting lowest-energy eigenvector exhibits a dominant $2s^2$ character (77%) with an energy of -0.7540 a.u. and will be labeled here as $2\tilde{s}^2$. In that case, we have $E_{2\tilde{s}^2}>2E_{2s}$ which leads to two peaks in the electron spectrum. They merge into one in the limit $Z\to\infty$.

Even within the above approximation, there is no possibility of transition through correlated channels ($nl,n'l'$ with $n,n'>2$), since the overlap between the single-particle hydrogenic wave functions ϕ_{2s} or ϕ_{2p} and any other Coulomb function is zero. Therefore our development [Eqs. (1)–(11)], although complicated by the appearance of new intermediate and final states due to the presence of the $2p2p$ configuration in $2\tilde{s}^2$, remains valid. The two situations ($2s^2$ and $2\tilde{s}^2$ representations) are presented in Fig. 1.

The first level of approximation that allows transitions

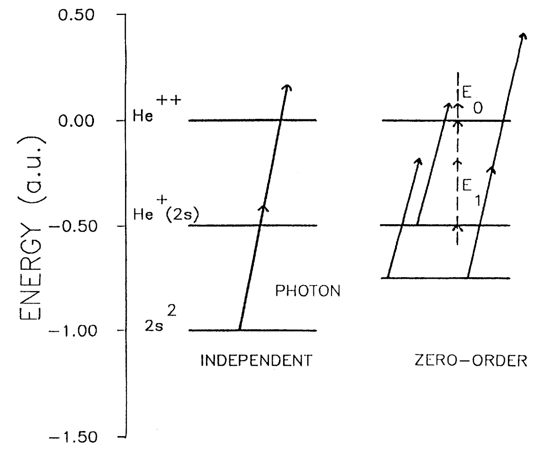

FIG. 1. A schematic diagram of the levels involved in double-electron ejection. The figure on the left (independent) represents the case where the initial state $|2s^2\rangle$ is represented by a product of two hydrogenic ϕ_{2s} functions. On the right (zero order), the initial state is calculated through a configuration-interaction method within $2s2s$ and $2p2p$; as a consequence it is shifted upward. E_0 and E_1 correspond to the position of the peak in Fig. 2.

through correlation in virtual intermediate states is a representation of $2\tilde{s}^2$ including configurations beyond the $n=2$ degenerate manifold. Consider, for example, a representation of the form

$$|2\tilde{s}^2\rangle=\sum_{n=2}^{\infty}\alpha_n|2sns\rangle+\sum_{n=2}^{\infty}\beta_n|2pnp\rangle\,,$$

where again we assume hydrogenic $(Z=2)$ single-particle wave functions (or equivalently we could choose two configurations, $2s^2$ and $2p^2$, optimized with some screened charge Z^* different from 2). Clearly, states of the form $nsKp$ and $npKl$ $(l=0,2)$ with $n>2$ can serve as virtual intermediate states, thus leading to a continuous distribution of photoelectron energies. It should also be clear that the channel $|2\tilde{s}^2\rangle\rightarrow|2sKp\rangle\rightarrow|K'pKp\rangle$ will dominate followed in importance by $|2\tilde{s}^2\rangle\rightarrow|2pKl\rangle\rightarrow|K'l'Kl\rangle$ $(l'=0$ or $2)$. Both of these channels contribute to the same two peaks which will usually rise above the continuum background, since the configurations ns and np (for $n>2$) will appear with smaller coefficients. It is worth noting that a similar situation arises when the continuum is evaluated with a screened charge $Z^*\neq 2$.

RESULTS AND CONCLUSIONS

We analyze now the mechanism of double ionization, starting from the zero-order case described above. After a development similar to Eqs. (1)–(11), one can show that

$$|U_{K,K'}|^2\approx\frac{1}{4\pi^2}\frac{\gamma_C\gamma_A^C}{[(E_{K'}+E_K-E_{2\tilde{s}^2}-2\hbar\omega)^2+\frac{1}{4}\gamma_A^2][(E_K-E_0)^2+\frac{1}{4}\gamma_C^2]}\,. \tag{12}$$

$\gamma_A=\sum_{C'}\gamma_A^{C'}+\Gamma$ ($\gamma_A^{C'}$ is the partial width of $2\tilde{s}^2$ due to the coupling with all possible channels C'). Also we define $\Delta=E_{2\tilde{s}^2}-2E_{2s}$, in terms of which $E_{2\tilde{s}^2}+2\hbar\omega=2E_0+\Delta$. We have evaluated this spectrum in the case of two-photon double ionization of the $2\tilde{s}^2$ state. The parameters (energy and widths) have been calculated for $\hbar\omega=0.53$ a.u. We have used techniques which go beyond the zero-order approximation in order to evaluate accurately the position of $2\tilde{s}^2$ $(-0.7780$ a.u.). Thus the resulting spectrum can be compared to experimental results when available. We will discuss these techniques in a subsequent paper. The electron spectrum presented in Fig. 2 has been calculated for the dominant final state $KpK'p$ (then the dominant intermediate states are of the type $2sK'p$).

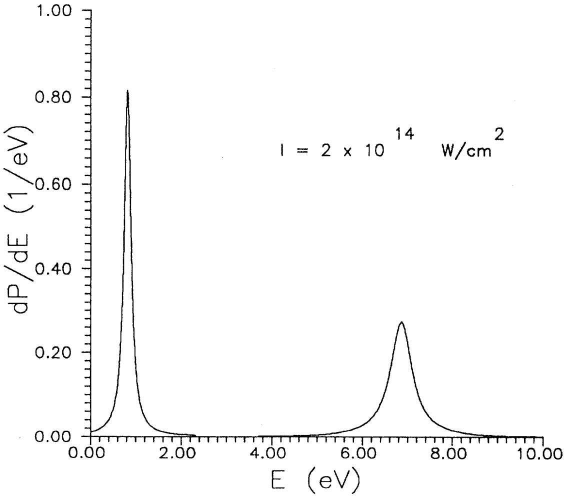

FIG. 2. Electron spectra calculated for an intensity $I=2\times10^{14}$ W/cm^2. The energy and autoionizing width Γ of the initial state are -0.7780 a.u. and 0.467×10^{-2} a.u., respectively. Also, the intensity-dependent quantities are $\gamma_A=0.0144$ a.u. (total width of the initial state) and $\gamma_C=0.00686$ a.u. (width of the $2s$ state of He$^+$). Note that the autoionizing width Γ is included in γ_A; it corresponds to a decay of the levels $2\tilde{s}^2$ toward the adjacent $1sKs$ continuum.

Before continuing with our discussion we assume that from here on the term "correlation" will be associated to the corrections which go beyond the zero-order approximation (such as the inclusion of screening effects as discussed above).

We have thus found that on the basis of very general considerations, the two-photon double-electron energy spectrum will exhibit two prominent peaks separated in energy by the amount $\Delta=6$ eV, which represents the energy difference between the true $2\tilde{s}^2$ state and the independent-particle energy of that state. In the limit of complete independent particles in the initial state, we would have only one peak. To put this result in the proper perspective, let us recall that single-photon double-electron ejection cannot occur at all without correlation at least in the initial state. Stated plainly, one photon cannot eject two independent electrons. As a consequence, the double-electron energy spectrum has a continuous distribution with a more or less pronounced minimum at the equipartition of kinetic energy between the two electrons. Two (or more) photons, on the other hand, can eject two independent electrons. If correlation is excluded, the double ejection can proceed through uncorrelated intermediate states to an independent-particle final state. Under those conditions, the energy spectrum will exhibit two well-separated peaks and not a continuous distribution. The importance of this conclusion lies in that we expect those two peaks to dominate the spectrum even when correlations are included. In that case, these two peaks will appear on top of a continuous distribution of energies resulting from direct two-electron transitions through correlation in the intermediate states. Note that the widths of the two peaks (in Fig. 2) are unequal for two reasons. First, $\gamma_A\neq\gamma_C$, because the transition from $2\tilde{s}^2$ is broadened not only by the photoabsorption but also by autoionization which contributes a width Γ added to γ_A. Second, the effective width of the peaks shown in Fig. 2 is the result not of a single Lorentzian but of a convolution.

Additional questions pertinent to double-electron ejection are whether the electrons are emitted "simultaneously" or sequentially and what measurement can provide an answer. These questions are pertinent to the more general problem of multiple-electron ejection under multiphoton ionization [5–7]. On the basis of the above results, it is evident that as long as the two peaks dominate, there is no way of distinguishing sequential from simultaneous. Two electrons emitted through uncorrelated channels can do so simultaneously or follow each other at any time. They are, however, emitted independently and the question of simultaneity is essentially irrelevant. It becomes relevant and meaningful only when correlation is involved. An attempt to measure such simultaneity must therefore focus on photoelectron energies away from the above dominant peaks, assuming that the continuum part of the spectrum is sufficiently large to be detectable. At this point, we must also note that a coincidence experiment where the ejected electron and the He^{2+} ion are observed simultaneously will not make a distinction between uncorrelated and correlated processes. From preliminary results we have on direct double-electron ejection through correlated channels, we expect the latter to be detectable as a low background between the peaks outside of their widths. This will be discussed fully in a future paper.

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