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LETTER TO THE EDITOR

Triple photoionization of lithium near threshold

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Abstract
Solving the full classical four-body Coulomb problem numerically using a Wigner initial distribution, we formulate a classical-quantum hybrid approach to study triple ionization by single photon absorption from the Li ground state in the threshold region. We confirm the Wannier threshold law $\sigma \propto E^{\alpha}$, and we show that α determined in the interval between 2 and 5 eV deviates from the analytical threshold value of 2.16 which we find in the interval between 0.1 and 2 eV.

Triple photoionization of lithium is the most fundamental atomic process involving three bound electrons. It was only recently that Wehlitz *et al* succeeded in measuring the triple photoionization cross section down to 2 eV above threshold [1, 2]. Subsequent experiments have produced various double ionization cross sections, also very close to threshold. For lithium [3] and most recently beryllium [4], it was demonstrated convincingly that the double photoionization cross section has small oscillations superimposed on the rising smooth cross section. This has cast some doubt on the validity of Wannier's (classically derived) threshold law [5, 6] which predicts very close to threshold a power law behaviour of the cross section,

$$\sigma(E_\omega) \propto (E_\omega/I - 1)^{\alpha}, \tag{1}$$

where E_ω is the photon energy, I is the respective threshold energy and α is a characteristic exponent which is related to the stability of a classical fixed point of the N-electron dynamics [7].

For the present case of lithium triple ionization ($I = 7.478$ au), the experimental results reach only down to 2 eV above threshold [2]. The corresponding fit of the experimental data with equation (1) yields $\alpha_{\text{exp}} = 2.05$ close to the theoretical value of $\alpha = 2.16$ derived by Klar and Schlecht [8]. It is known from the well-studied two-electron escape case [9] that a Wannier exponent fitted to a cross section over an energy interval which is close but a finite distance away from threshold yields always a *smaller* α than the analytically predicted one. Hence, the experimental value is consistent with Wannier's prediction but not conclusive since one does not know what happens closer to threshold.

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The present classical study deals for the first time with the full four-body problem close to threshold and provides the triple photoionization (TPI) probability starting at $E = 0.9$ eV excess energy. We are able to confirm that, indeed, the Wannier threshold law with an exponent of $\alpha = 2.16$ is reached, but only for energies $E \equiv E_\omega - I < 2$ eV. By successively fitting finite energy intervals above the threshold I to our result, we can confirm the experimental result for α.

We formulate the TPI process from the Li ground state ($1s^2 2s$) as a two-step process [10, 11]. First, one electron absorbs the photon (photo–electron). Then, due to the electronic correlations, redistribution of the energy takes place resulting in three electrons escaping to the continuum. We express the above two-step process as

$$\sigma^{3+} = \sigma_{\rm abs} P^{3+}, \tag{2}$$

where $\sigma_{\rm abs}$ is the total absorption cross section and P^{3+} is the probability for triple ionization. In what follows, we evaluate P^{3+} and use the experimental data of Wehlitz [12] for $\sigma_{\rm abs}$. Physically interpreted, this relation splits the photon absorption ($\sigma_{\rm abs}$) from the subsequent energy redistribution in the three-electron system. The latter can lead to TPI, which we calculate in phase space formally from

$$P^{3+} = \lim_{t\to\infty} \int {\rm d}\Gamma_{\mathcal{P}^{3+}} \exp((t - t_{\rm abs}){\rm L}_{\rm cl})\rho(\Gamma), \tag{3}$$

with the classical Liouvillian $\mathtt{L}_{\rm cl}$ given by the Poisson bracket $\{H,\}$ [13], propagated from the time $t_{\rm abs}$ of photo absorption, with H the four-body Coulomb Hamiltonian. The primary electron absorbs the photon at the nucleus ($\mathbf{r}_1 = 0$), an approximation which becomes exact in the limit of high photon energy [14]. We note that no account is taken of the direction of polarization of the incident photon, since we currently consider electron orbitals that are spherically symmetric. Immediately after absorption, the phase space distribution of the remaining two electrons is the Wigner transform of the corresponding initial wavefunction $\psi(\mathbf{r}_1 = 0, \mathbf{r}_2, \mathbf{r}_3)$, where $\mathbf{r}_i$ are the electron vectors starting at the nucleus.

In general, close to threshold the ionization probability does not depend on the details of the initial wavefunction [5]. Hence, we approximate it as a simple product of hydrogenic orbitals $\phi_i^{Z_i}(\mathbf{r}_i)$ with effective charges Z_i to facilitate the Wigner transformation. Z_i are chosen to reproduce the known ionization potentials I_i, namely for the 2 s electron $Z_3 = 1.259$ ($I_3 = 0.198$ au) and for the 1 s electron $Z_2 = 2.358$ ($I_2 = 2.780$ au). We use atomic units throughout the paper if not stated otherwise. The Wigner distribution W conserves energy only in the mean [15]. Near $E = 0$, however, energy conservation is vital. Therefore, the Wigner distributions for the individual electron orbitals $\phi_i^{Z_i}(\mathbf{r}_i)$, $W_{\phi_i^{Z_i}}$, are restricted to their respective energy shell, leading to the initial phase space distribution

$$\rho(\Gamma) = \mathtt{N}\,\delta(\mathbf{r}_1)\delta(\varepsilon_1 + I_1 - \omega) \prod_{i=2,3} W_{\phi_i^{Z_i}}(\mathbf{r}_i, \mathbf{p}_i)\delta(\varepsilon_i + I_i), \tag{4}$$

where $\epsilon_i, i = 1, 2, 3$, are the individual electron energies. The advantages of the Wigner distribution as an initial phase space distribution over other distributions as well as the reasons for restricting the Wigner distribution of the hydrogenic orbitals on their respective energy shell are discussed in [16].

With $\rho(\Gamma)$ from equation (4) the initial phase space volume to be sampled reduces significantly, although regularized coordinates [17] are required to avoid problems with electron trajectories starting at the nucleus. Other than that, the integral in equation (3) is evaluated with a standard Monte Carlo technique which entails following classical trajectories in phase space (CTMC) [16, 18–20]. The projector $\mathcal{P}^{3+}$ indicates that we integrate only

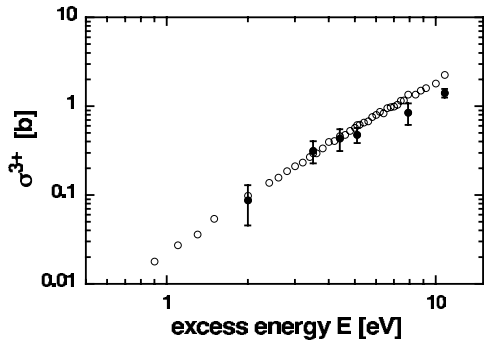

Figure 1. TPI cross section obtained by multiplying the TPI probability from the present calculation with the total photo cross section from [12] (○) in comparison to the experiment [2] (•).

over those parts of phase space that lead to TPI. Triple ionization is decided by propagating trajectories long enough so that the individual electron energies $\epsilon_i, i = 1, 2, 3$, are positive and stable within a margin that guarantees that all three electrons are very far away from the nucleus and each other. A similar approach to the one described above was successfully used to describe the knockout mechanism for the double ionization of He from the ground [21], the $2^{1,3}$S excited states [22] and the double ionization of H_2 [23].

We also note that generally, not only close to threshold, the classical TPI trajectories provide information as to how energy is redistributed from the primary photo electron to the other two electrons, which is analysed in detail in [24].

Figure 1 shows the TPI cross section σ^{3+} resulting from the probability P^{3+} in connection with equation (2). We find very good agreement with the experimental results. Thus, our classical approach with an approximate initial quantum wavefunction captures the relevant correlations among the three electrons which mainly form after the photo absorption at lower excess energies. Let us note that the reason why we currently consider energies of 0.9 eV and above is the numerical difficulty involved in computing P^{3+}. Specifically, in order to obtain 10^3 TPI trajectories at $E = 0.9$ eV one has to evolve 10^{10} trajectories with the CTMC method. One may be tempted to see a slightly different slope of the experimental curve compared to the theoretical one in figure 1. Concerning the theoretical curve, this may be due to the fact that we employ a 'high energy' approximation for the photo absorption, namely that the photon is absorbed by an electron that is sitting initially in the nucleus ($\mathbf{r}_1 = 0$). In the future, we may relax this approximation by using a photon-frequency-dependent assumption for $r(\omega)$ of the photon–electron as described in [25]. However, given the present accuracy of the experiment near threshold, the slope of the experimental curve is somewhat uncertain as well, see error bars in figure 1. Luckily, these experimental and theoretical difficulties do not hamper the present goal of analysing the behaviour of the cross section towards threshold, $E \to 0$. We want to investigate whether the Wannier power law for σ^{3+} is really approached in the limit of vanishing threshold energy. To this end we have fitted $\sigma^{3+} = \sigma_0(E/I)^\alpha$, where σ_0 and α are fit parameters while I is the triple ionization potential. For the closest energy interval to threshold we could reach, 0.9 eV$\leqslant E \leqslant 2$ eV, $\alpha_{\text{theo}} = 2.15$ is very close to the analytical value of $\alpha = 2.16$, as figure 2 reveals. We then apply the fit, keeping the lower limit of the energy interval constant, $E = 0.9$ eV, and increasing the upper energy limit until we reach $E = 4.0$ eV (α_{exp} is obtained in the range 2–5.1 eV = 3.1 eV). Subsequently, we shift the 3.1 eV interval to higher excess energies to obtain α as a function of the upper limit of the energy range [26].

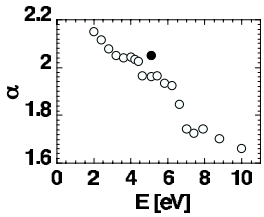

Figure 2. The Wannier exponent α, obtained by fitting finite energy intervals to equation (1), see text. The filled circle is the experimental value from [2].

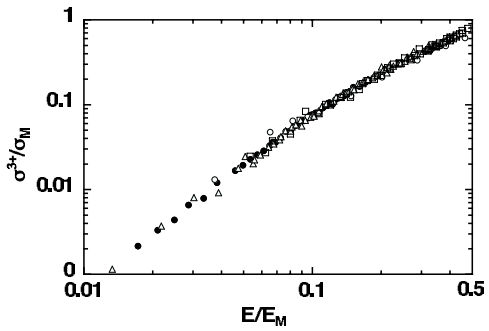

Figure 3. TPI cross section in scaled coordinates [27] for lithium (this work, •), and from the experiments on lithium ([2], ○), neon ([26], △) and argon ([26], □).

Figure 2 illustrates that the Wannier exponent fitted to the cross section over an energy interval which is close but a finite distance away from threshold yields a *smaller* α than the analytically predicted one. Hence, the fit to the experimental data (filled circle in figure 1) is consistent with Wannier's theory and in good agreement with our present theoretical result. The strong variation of the Wannier exponent in figure 2 also indicates that the threshold region where Wannier's threshold law applies is certainly less than the energy range shown in figure 2.

Secondly, we explore if the triple photoionization cross sections for different atomic elements have a similar shape close to the threshold region. We use the shape formula for the TPI cross section [27],

$$\sigma^{3+} = \sigma_M x^\alpha \left(\frac{\alpha + 7/2}{\alpha x + 7/2} \right)^{\alpha+7/2}, \tag{5}$$

to obtain a dimensionless cross section σ/σ_M as a function of the dimensionless excess energy $x = E/E_M$ with E_M, σ_M as fitting parameters and with α set to its analytical value of 2.16. Equation (5) reproduces, by construction, for Coulomb complete break-up processes, the Wannier threshold law and the cross section for high excess energies. In figure 3, one sees that the experimental data for Li, Ar and Ne fall on top of the theoretical data from figure 1.

It has been argued that a secondary power law, or at least additional structure in the TPI cross section, could originate from the very different binding energies for the electrons in the lithium atom with its $1s^2 2s$ configuration in contrast to neon and argon, which both contribute three electrons from a single shell to ionization (2p and 3p, respectively) [2]. The present calculation does take into account the difference in binding energy and spatial extension of the respective orbitals. We find our results to be consistent with a smooth change of the TPI cross section for the ground state of Li. Hence, one may conclude from the agreement of our

lithium calculation regarding the shape of the ionization cross section with neon and argon that the different binding energies do not strongly influence the shape of the cross section.

In summary, in the framework of a quantum-classical hybrid approach, we have analysed triple photoionization of lithium near threshold using a Wigner initial distribution and a classical propagation of the three electrons in time. We can confirm that the total cross section grows from threshold with a power of $\alpha = 2.16$ in accordance with Wannier's threshold theory. In addition, using the shape formula, we find our results to be consistent with a smooth change of the triple ionization cross section for the Li ground state.

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