Eur. Phys. J. D (2015) 69: 9
DOI: 10.1140/epjd/e2014-50688-x

THE EUROPEAN PHYSICAL JOURNAL D

Regular Article

Calculated electron ionization cross sections of the alkali atoms and the hydrogen spin ionization asymmetry*

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Received 18 September 2014 / Received in final form 25 October 2014
Published online 8 January 2015 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2015

Abstract. This paper addresses two aspects of the electron-impact ionization of hydrogen and the alkali atoms Li, Na, K, and Cs. First, we show that the earlier observation that the detailed treatment of the 2 electrons in the final state of the hydrogen ionization process results in a cross section shape that is in excellent agreement with the cross section shape obtained from the semi-empirical Deutsch-Märk (DM) formalism can be extended to the "quasi one-electron" atoms Li, Na, K, and Cs. Second, we discuss specific aspects of the calculated hydrogen ionization spin asymmetry in light of some recent experimental observations.

1 Introduction

Atomic hydrogen with a single electron in the $(1s)$ orbital in its ground state, is the ideal target to study many aspects of electron-atom collision processes. There has been a wealth of literature on the interaction of an electron with an isolated H atom. We refer the reader to two comprehensive references for information regarding electron hydrogen collisions [1,2]. Electron impact ionization of hydrogen is a particularly interesting process, since it is the simplest 3-body collision complex in the exit channel (one proton and two electrons). In particular, spin considerations of the two outgoing electrons lead to a total spin of the 2-electron system of either 0 or 1, i.e. we can either have a singlet state ($S = 0$) or a triplet state ($S = 1$). This was discussed by Friedrich et al. [3,4]. More recently, Deutsch et al. [5] discussed the convergence of top-down (deductive) and bottom-up (inductive) approaches to the calculation of electron impact ionization cross for hydrogen (and helium). They highlighted the fact that the detailed treatment of the 2 electrons in the final state of the hydrogen ionization process as described by Friedrich et al. [3,4] results in a cross section shape that is in excellent agreement with the cross section shape obtained from the semi-empirical DM formalism [5–8]. They also commented on some aspects of the hydrogen ionization spin asymmetry, i.e. the relative contributions of the singlet and the triplet final state to the total ionization cross section as a function of energy.

Here we extend the previous discussion of the hydrogen ionization cross section shapes to the alkali atoms, which may be considered "quasi one-electron" atoms (a single $(ns)^1$ valence electron outside of completely filled shells) and we address certain aspects of the ionization spin asymmetry for hydrogen in the framework of our approach.

2 Theoretical background and ionization cross sections

2.1 Theoretical background

The DM formula for the total single electron ionization cross section σ of an atom is [5–8]:

$$\sigma(u) = \sum_{n,l} g_{nl}\pi r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u)[\ln(c_{nl}u)/u] \qquad (1)$$

where r_{nl} is the radius of maximum radial density of the atomic subshell characterized by quantum numbers n and l (column 1 in the tables of Desclaux [9]) and ξ_{nl} is the number of electrons in that subshell. The sum extends over all atomic subshells labelled by n and l. The weighting factors g_{nl} were originally determined from a fitting procedure [5,6]. The "reduced energy" u is given by $u = E/E_{nl}$, where E refers to the incident energy of the electrons and E_{nl} is the ionization energy in the (n,l) subshell. The energy-dependent quantities $b_{nl}^{(q)}(u)$ were introduced in an effort to merge the high-energy shape of the ionization

* Contribution to the Topical Issue "Elementary Processes with Atoms and Molecules in Isolated and Aggregated States", edited by Friedrich Aumayr, Bratislav Marinkovic, Stefan Matejcik, John Tanis and Kurt H. Becker.

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cross sections, which follow an energy dependence given by the Born-Bethe approximation [10], with the DM cross sections at low impact energies. The function $b_{nl}^{(q)}(u)$ in equation (1) has the explicit form

$$b_{nl}^{(q)}(u) = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2 \tag{2}$$

where the 4 quantities A_1, A_2, A_3, and p are constants that were determined (in conjunction with the constant c_{nl}) from reliable measured cross sections for the various values of n and l [5–8]. The superscript "q" refers to the number of electrons in the (n,l) subshell and allows the possibility to use slightly different functions $b_{nl}^{(q)}(u)$ depending on the number of electrons in a given (n,l) subshell. We note that, at high impact energies (as u approaches infinity), the first term in equation (2) goes to zero and $b_{nl}^{(q)}(u)$ becomes a constant, which, in turn, ensures the high-energy behavior of the cross section as predicted by the Born-Bethe theory [10].

2.2 Ionization cross section of the alkalis Li, Na, K, and Cs

Here we extend the previous discussion of the hydrogen ionization cross section [5] to the alkali atoms. The DM formula for a specific subshell (n,l) has the form:

$$\sigma_{nl}(u) = g_{nl}\pi r_{nl}^2 \xi_{nl}\{[A_1 - A_2]/[1 + (u/A_3)^p] + A_2\} \times [\ln(c_{nl}u)/u] \tag{3}$$

which we can write as:

$$\sigma_{nl}(u) = g_{nl}\pi r_{nl}^2 \xi_{nl} f_{DM}(u). \tag{3a}$$

All constants A_1, A_2, A_3, c_{nl}, and p for H and for the valence electron of the alkali atoms are identical [5,8], so that the cross section values for the various atoms are solely determined by the product $g_{nl}\pi r_{nl}^2$, since $\xi_{nl} = 1$ and the shape of the cross sections for H and the alkalis is determined by the $(ns)^1$ $(n = 1, 2, 3, \ldots)$ valence electron configuration.

For hydrogen, the product $g_{nl}E_{nl} = g_{1s}E_{1s}$ has a value of 38.20 eV [5,8] which results in $g_{1s} = 2.81$ for $E_{1s} = 13.60$ eV. Using $r_{1s} = a_0$, the Bohr radius and $\xi_{nl} = 1$, one finds [5]:

$$\sigma_{1s}(u) = 2.81\pi a_0^2 f_{DM}(u). \tag{4}$$

The recent work by Friedrich et al. [3,4] has shed some new light on the energy shape of the hydrogen ionization cross sections based on a more rigorous treatment of the (indistinguishable) scattered and the ejected electrons involving integration of the time-dependent Schrödinger equation in the framework of the one-dimensional s-wave model. Since the total electron spin S of the 2-electron system can either be 0 (singlet, $S = 0$) or 1 (triplet, $S = 1$), these authors calculated the singlet and triplet probabilities, $P^{S=0}$ and $P^{S=1}$, respectively, as well as the spin-averaged probability $P_{av} = 1/4(P^{S=0} + 3P^{S=1})$ [4]. They normalized the dimensionless quantities obtained from the s-wave model, so that the maximum of the calculated cross section coincides with the maximum of the experimentally determined value [11]. We can express the H ionization cross section σ_{FR} in this model as:

$$\begin{aligned}\sigma_{FR} &= 1/4\sigma_0 \left(P^{S=0} + 3P^{S=1}\right) \\ &= 2.53 \left(\pi a_0^2\right) \left(P^{S=0} + 3P^{S=1}\right) = 2.53 \left(\pi a_0^2\right) f_{FR}(u)\end{aligned} \tag{5}$$

using $\sigma_0 = 10.1\pi a_0^2 = 8.88 \times 10^{-20}$ m^2 and abbreviating the sum $(P^{S=0} + 3P^{S=1})$ as $f_{FR}(u)$. A comparison of (4) and (5) suggests that we may view the factor 2.53 in (5) as a spin-averaged weighting factor (averaged over the $S = 0$ and $S = 1$ final states; see Ref. [5] for details), which we denote by g_1^*. If we also recall that the product $g_{1s}E_{1s} = 38.20$ eV (using $g_{1s} = 2.81$ and $E_{1s} = 13.60$ eV), we find from the relation $g_{1s}^*E_{1s}^* = 38.20$ eV a corresponding E_{1s}^* value of 15.10 eV, which, in turn, can be interpreted as a spin-averaged ionization energy for hydrogen.

We now show, similar to what was found for hydrogen [5], that the function f_{FR}(u) is also suitable to describe the $(ns)^1$ partial ionization cross section shapes for the alkalis and that the resulting cross section shapes are in excellent agreement with those obtained from the DM formalism. We re-write σ_{FR} in a formal fashion similar to the DM cross section

$$\sigma_{FR}(u) = \pi r_{ns}^2 g_{ns}^* f_{FR}(u) \tag{6}$$

where the factors g_{ns}^* are the equivalent of the weighting factors g_{ns} in the DM formula. If we assume that the relation $g_{1s} = 1.11g_{1s}^*$ for hydrogen, also holds for other values of n, i.e. $n = 2$, 3, 4, and 5 (for, respectively, Li, Na, K, and Cs), we can determine the corresponding values of the g_{ns}^* factors for the alkali atoms (see Tab. 1). Table 1 also lists all other values of the weighting factors g_{ns}, the product $g_{ns}E_{ns}$ $(= g_{ns}^*E_{ns}^*)$, and the energies E_{ns} and E_{ns}^* required for the calculation of the ionization cross sections for Li, Na, K, and Cs according to formulas (6) and (4). For reasons of completeness, we also include the corresponding constants for H in Table 1. Figure 1 shows the four calculated $(ns)^1$ partial ionization cross sections for Li, Na, K, and Cs according to formulas (4) and (6). We note that for each target the cross section of formula (6) was normalized to the corresponding DM cross section at the maximum. The agreement between the two cross

Table 1. Values for the weighting factors g_{ns} and g_{ns}^*, the "reduced" weighting factors $g_{ns}E_{ns}$ and the ionization energies E_{ns} and E_{ns}^* for hydrogen and the alkalis Li, Na, K, and Cs required for the calculation of the ionization cross sectiosn of these atoms.

	g_{ns}	g_{ns}^*	$g_{ns}E_{ns}$	E_{ns}	E_{ns}^*
H $(1s)$	2.81	2.53	38.20	13.60	15.10
Li $(2s)$	2.23	2.00	12.00	5.39	6.00
Na $(3s)$	1.91	1.72	9.80	5.14	5.70
K $(4s)$	1.72	1.55	7.40	4.31	4.79
Cs $(5s)$	1.39	1.25	5.40	3.89	4.32

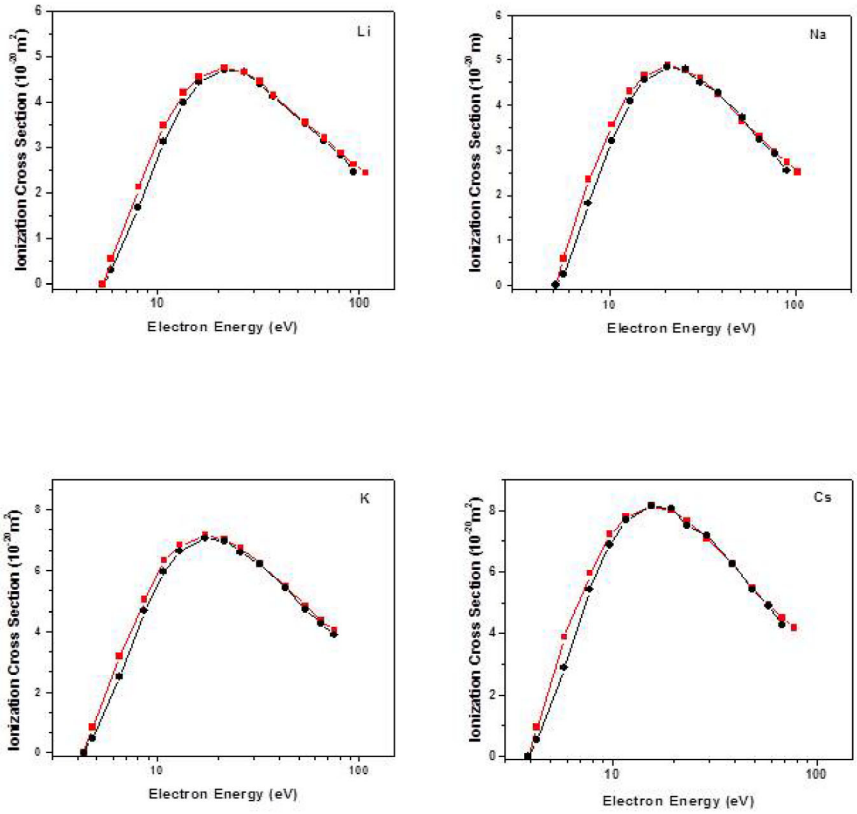

Fig. 1. Calculated $(ns)^1$ partial electron-impact ionization cross section for Li, Na, K, and Cs ($n = 2,3,4$, and 5) as a function of electron energy. The filled squares represent the DM cross section (see e.g. [5]), whereas the filled circles denote the cross section based on the formalism by Friedrich et al. [3,4].

sections for each alkali atom is excellent, better than 5% except at energies below 10 eV where the DM cross sections lies consistently about 20% higher than the cross section based on the formalism of Friedrich et al. [3,4]. This very good agreement in the cross section shapes affirms the earlier observation for hydrogen that detailed treatment of the 2 electrons in the final state of the ionization process of a quasi one-electron atom carried out by Friedrich et al. [3,4] supports the results of $(ns)^1$ partial cross section shapes for the alkali atoms obtained from the semi-empirical DM formalism.

2.3 Hydrogen ionization spin asymmetry

We now address the H ionization spin asymmetry A, a dimensionless quantity defined as:

$$A = \left(\sigma^{S=0} - \sigma^{S=1}\right) / \left(\sigma^{S=0} + 3\sigma^{S=1}\right) = \left(\sigma^{S=0} - \sigma^{S=1}\right) / \sigma_I \quad (7)$$

where σ_I is the spin-averaged total ionization cross section, which can be determined in experiments using unpolarized targets and projectiles. The quantity A, therefore, contains information about the difference in the singlet ($\sigma^{S=0}$) and triplet ($\sigma^{S=1}$) channel due to electron exchange. A value of $A = 1$ indicates that only singlet ionization is present, whereas pure triplet ionization yields a value of $A = -1/3$. If equal contributions of singlet and triplet ionization are present, the value of A goes to 0.

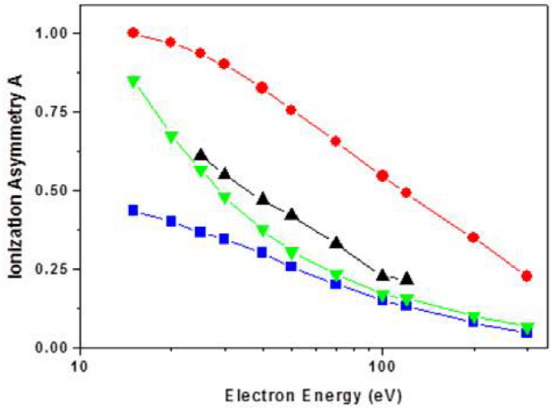

Fig. 2. Hydrogen ionization spin asymmetry A as a function of electron energy. The solid circles represent the results of the DM calculation based on the results of reference [4], the filled triangles and inverted triangles denote the calculation of, respectively, Ochkur [15] and Peterkop [14], and the filled square are experimental data [12,13].

Figure 2 shows our results for the spin asymmetry A based on the calculations of the probabilities $P^{S=0}$ and $P^{S=1}$ from reference [4], together with some experimental

data and the predictions of various calculations [12–15]. We summarize the results shown in Figure 2 as follows:

1. For all impact energies from threshold to 300 eV, our calculated spin asymmetry as well as the results of other calculations and experiments, which terminate at impact energies between 100 eV and 300 eV, remain positive, with our calculated values lying consistently above all other curves by as much as a factor of 3 at some energies.
2. Our calculated spin asymmetry starts at a value of 1, i.e. indicates a dominance of the singlet contribution (and the absence of the triplet contribution) at the ionization threshold and begins to decline for higher energies, particularly above about 20 eV, which indicates the increased contribution due to the presence of a triplet contribution as the impact energy increases. Our data are different from essentially all other data shown in Figure 2, which indicate a value of A of less than unity at threshold, i.e. roughly around 0.5 based on the data from references [12,13]. One might argue on the basis of the fact that the singlet cross section has a lower ionization threshold compared to the triplet cross section that A must be equal to 1 at threshold, since only the singlet ionization cross contributes for energies below the triplet ionization threshold.

Both experimental determinations and theoretical calculations of the hydrogen ionization spin asymmetry A are extremely challenging at very low electron energies close to threshold. For instance, Bray et al. [16,17] explicitly state that their Convergent Close-Coupling (CCC) approach has problems in the regime of very low energies close to threshold. Willliams et al. [18] carried out single-, double-, and triple-differential cross section measurements at low impact energies highlighting details of the hydrogen electron-impact ionization in the energy regime near threshold. Their results indicate that the Wannier threshold law [19] holds for energies within 1 eV of the ionization threshold, but that deviations begin to become noticeable at 15.6 eV, i.e. for energies about 2 eV above threshold.

The calculations of Friedrich et al. [3,4] show a slightly lower ionization threshold for the singlet contribution vs. the triplet contribution, e.g. 13.6 eV vs. 15.1 eV for H (and correspondingly smaller differences for the alkalis) as shown in Table 1. Figure 3 shows our calculated singlet ($\sigma^{S=0}$) and triplet ($\sigma^{S=1}$) contributions to the H ionization cross section as well as a function that represents $3\sigma^{S=1}$, which allows us to calculate the spin asymmetry A, for energies from threshold to more than 10^5 eV. The cross section curves have been constructed in three energy ranges using different methods:

1. For energies from threshold to 300 eV, we used the values as reported directly by Friedrich et al. [4].
2. In the energy range from 300 eV to 4 keV, we extrapolated the cross sections by normalizing the calculated total H ionization cross section relative to the measured cross section [20].
3. For energies above 4 keV, the calculated cross sections are the result of an extrapolation using the Bethe high-energy cross section shape.

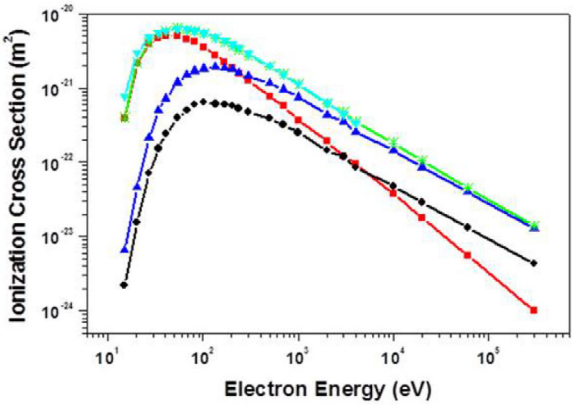

Fig. 3. Calculated singlet ($\sigma^{S=0}$, filled squares) and triplet ($\sigma^{S=1}$, filled circles) contributions to the H ionization cross section as well as a function that represents $3\sigma^{S=1}$ (filled triangles). Also shown are the total cross section (filled inverted triangles) constructed from the singlet and triplet cross sections and the experimentally determined cross section from reference [20] (filled diamonds). See text for further details.

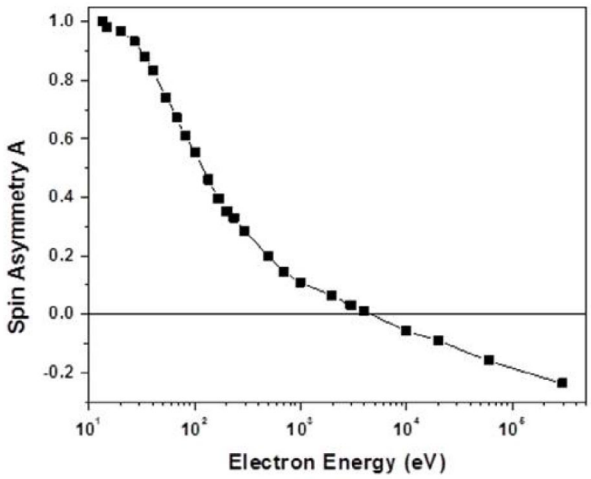

Fig. 4. Calculated hydrogen ionization spin asymmetry A as a function of electron energy using the DM formalism from threshold to 30 keV.

The resulting spin asymmetry A from threshold to energies well above 10^5 eV is shown in Figure 4. The curve starts at $A = 1$ at threshold (pure singlet contribution) and remains flat for about 1.5 eV until the triplet contribution begins to show its presence. With increasing energy, the curve declines monotonoically and cross the zero-line ($A = 0$, equal singlet and triplet contributions) around 3000 eV. For even higher impact energies, the curve stays negative indicating an increasing dominance of the triplet contribution and seems to approach its lower limit of $A = -1/3$ (absence of any singlet contribution) at energies well above a few times 10^5 eV.

However, the above picture may be too simplistic as discussed by Greene and Rau [21], who took a closer look at the Wannier threshold law [19] for the double escape of two electrons from a positive ion. They argued that the inclusion of dynamical considerations and the highly

correlated motion of the two escaping electrons at very low energies might cause A to be less than unity immediately above threshold. Obviously, more detailed calculations and high-precision experiments would be highly desirable to shed more light on this issue.

3 Summary

We showed that the excellent agreement between the ionization cross section shape for the electron-impact ionization of hydrogen taking into account the singlet and triplet contributions in the exit channel and the cross section shape obtained from the semi-empirical DM formalism can be extended to the partial $(ns)^1$ ionization cross section shapes of the alkali atoms Li, Na, K, and Cs.

Stimulated by the recent very detailed experimental near-threshold single-, double-, and triple-differential ionization cross section studies of Williams et al. [18], we also calculated the hydrogen ionization spin asymmetry in the framework of the DM formalism using the spin-resolved cross sections as introduced by Friedrich et al. [3,4]. In support of the experimental data of Williams et al. [18], our calculation confirms a dominance of the singlet ionization channel for incident energies from threshold to about 2 eV above threshold, which, in turn, is manifested in a value of the spin asymmetry of $A = 1$. Our calculations are extended to impact energies of up to 30 keV, where the spin asymmetry begins to approach its high-energy limit of $A = -1/3$.

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