The status of theoretical L-subshell ionization cross sections for protons

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Abstract

Accuracy of PIXE analyses depends on inner-shell ionization cross sections. These cross sections are often calculated in the ECPSSR theory; results of its variant (that uses DHS wavefunctions) are employed in the GUPIX package. While the ECPSSR theory agrees well with massive compilations of K x-ray production, it deviates systematically from L-subshell data – in particular, L₁ and L₂ cross sections. Various modifications of the ECPSSR theory and their results are reviewed versus the empirical database from Orlic for 0.3–3.5 MeV protons on 45 ≤ Z ≤ 92 targets. Comparison with this database does not give a clear choice between the ECPSSR and the ECPSSR with all modifications. Independently of the chosen theory and because of the increasing scatter in the data with the decreasing proton energy, PIXE packages that may rely on reference cross sections for L₁ x-ray production in lanthanides by 0.2–MeV protons could err by an order of magnitude in the determination of the concentration of these elements. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is no theory that gives good predictions for L-subshell ionization cross sections by ions below 1 MeV/u, even by the lightest ions – protons. There are no systematic coupled-state calculations that would set a benchmark to test perturbation theories for such collisions. Thus an assessment of the status L-subshell ionization theory is limited to the ECPSSR theory [1] vis-

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ECPSSR effects [1], from tables [4] or published codes [5]. Massive collections of x-ray production cross sections for K- [6] and L-shell [2] have been normalized to the ECPSSR. As illustrated in Fig. 1, the ECPSSR underestimates L-subshell – especially L2 and L1 – ionization data for less than 1-MeV protons. A number of modifications to this – called classical by the Naples group [7] – ECPSSR have been suggested; often by that group as seen most recently in Balsamo et al. [8]. Results of the ECPSSR and its modifications are presented via the Orlic database in Section 2, and Section 3 concludes with questions about the outcome and validity of such a comparison.

2. Normalization of empirical cross sections to the classical ECPSSR and modified ECPSSR

First-order perturbation theories such as the binary encounter approximation (BEA) [9], the straight-line trajectory semiclassical approximation (SCA) [10] and, equivalent to it, the plane wave Born approximation (PWBA) [11], are in reasonable agreement with the measured cross sections for L-subshell ionization by protons of a few MeV and higher energies. The ECPSSR theory improves upon this agreement and attempts to extend it to lower energies; it goes beyond the first-order theories by accounting for the projectile’s energy ($E$) loss and its Coulomb ($C$) deflection from the straight-line path and by applying a perturbed-stationary state (PSS) description of the L-shell electron with the relativistically ($R$) increased mass. The importance of the ECPSSR effects grows when protons are slow enough to ionize the L shell electron predominantly at impact parameters within the L shell.

Inner-shell ionization is a sum of direct ionization to the target’s (atomic number $Z_2$) continuum and electron capture to unoccupied states on the projectile (atomic number $Z_1$). In the following, First Born stands for the sum of the PWBA for direct ionization [11] plus the Oppenheimer–Brinkman–Kramers (OBK) of Nikolaev for electron capture [12]; ECPSSR will denote direct ionization [1] plus electron capture [13]. When $Z_1/Z_2 \ll 1$, as is the case in L-subshell ionization of elements with $Z_2 \geq 49$ by protons, the electron capture contributes no more than 1% to these sums. Hence the scaling of the First Born cross sections is practically identical to the scaling of $\sigma_{S}^{PWBA}$, where $S = K, L_1, L_2, L_3, M_1, \ldots, M_5$. 

Fig. 1. Empirical cross sections from Orlic’s database for L-subshell ionization in $Z_2 = 45, 74, 83$ and 92 atoms by 0.3–3.5 MeV protons [2] normalized to the ECPSSR theory [1]. In all figures the size of the symbol increases with $Z_2$. 
When evaluated with the screened hydrogenic wavefunctions, for which $Z_{2S} = Z_2 - s$ (where Slater's screening constant $s = 4.15$ for the $L_i$ subshells) and $\theta_S = \text{observed binding energy}/\frac{1}{2}(Z_{2S}/n)^2$, $g^{\text{PWBA}}_S \propto Z_i^2 F_S(\xi_S, \theta_S)/Z_{2S} \theta_S$. With the projectile velocity $v_1$ relative to the $S$-shell electron velocity $v_{2S} = Z_{2S}/n$, the dimensionless $\xi_S = 2v_1/v_{2S} \theta_S$ is a measure used to distinguish slow ($\xi_S < 1$) and fast ($\xi_S > 5$) collisions; for all elements and their shells, ionization cross sections peak in the intermediate collision regime at $\xi_S \approx 3$.

In slow collisions, $F_S(\xi_S, \theta_S)$ becomes independent of $\theta_S$ so that upon multiplication by $Z_{2S}^2$ the First Born ionization cross sections – which vary by orders of magnitude with $Z_2$ in the 0.1–4.0 MeV range of proton energies that is of interest to PIXE practitioners (Fig. 2(a) for the $L_3$ subshell) – merge into an essentially (neglecting slight $\theta_{L_3}$ dependence) single curve as a function of $\xi_{L_3}$. That single curve is drawn in Fig. 2(b) for comparison with the ECPSSR cross sections [1], which just as the empirical cross sections [2] in Fig. 2(c) also appear to scale as a function of $\xi_{L_3}$ once multiplied by $Z_{L_3}^2$. Ratios of empirical-to-the First Born cross sections reveal systematic and large dependence on $Z_2$; while for uranium they drop abruptly by more than a factor of 4 below $\xi_{L_3} \approx 0.3$, for rhodium they fall gradually starting already around $\xi_{L_3} = 1.5$ (Fig. 3(a)). By contrast, the normalization of empirical cross sections to the ECPSSR appears to be $Z_2$-independent and about half of the data is in excellent (within 10% which is less than the 20% uncertainty typically cited for L-shell measurements) agreement with this theory (Fig. 3(b)). The kink seen at $\xi_{L_3} \approx 0.4$ points to a 35% underestimate of the data by the ECPSSR in the worst case scenario. For all $Z_2$, this kink is also clearly around the same $\xi_{L_3}$ in Fig. 2 of Campbell et al. [3] who displayed the Orlic data-to-ECPSSR values in three ranges of $Z_2$. Ratios of measured-to-ECPSSR cross sections for $L\alpha$ ionization by protons should be essentially identical with the ratios for $L_3$ ionization; although analyzed versus $\xi_{L_3}^R$ rather than $\xi_{L_3}$, indeed the presence of the kink is evident in such ratios [14].

The overall good agreement between the data and the ECPSSR notwithstanding, or perhaps be-

![Fig. 2. L$_3$ ionization cross sections for 22 \leq Z_2 \leq 92 as a function proton energy in the First Born theory [11,12], and multiplied by $Z_{L_3}^2$ as a function of the reduced velocity variable $\xi_{L_3}$ according to the First Born (fitted curve) and the ECPSSR [1] theories, and based on Orlic’s database for 0.3–3.5 MeV protons on 45 \leq Z_2 \leq 92 elements [2].]
cause of that kink, it is interesting to examine the effects of various modifications of the ECPSSR.

2.1. W: Wavefunction modification

The ECPSSR cross sections are calculated by an appropriate scaling of the PWBA cross sections evaluated with the nonrelativistic screened hydrogenic (SH) wavefunctions and with a minimum momentum transfer $q_{0S}$ that neglects the energy-loss effect. Chen and Crasemann produced PWBA cross sections calculated with relativistic Dirac Hartree Slater (DHS) wavefunctions and with the exact $q_{0S}$ [15]. They are denoted here as $\sigma_{S}^{\text{EPWBA}}$ (HS). Fig. 4(a) shows, for the L3-subshell, a wavefunction factor

$$W \equiv \frac{\sigma_{S}^{\text{EPWBA}}(\text{HS})}{\sigma_{S}^{\text{EPWBA}}(\text{SH})}$$

by which the ECPSSR based on SH wavefunctions should be multiplied to account for a switch to a HS description of the target atom.

This assumes that $\sigma_{S}^{\text{EPWBA}}(\text{SH})$ – the PWBA corrected for the $E$ and $R$ effects according to the ECPSSR prescription – accounts for the Chen and Crasemann’s use of the exact $q_{0S}$ and relativistic wavefunctions. While the ECPSSR’s treatment of the energy-loss effect is – as verified by comparison with the EPWBA [16] or ECPSSR [4] tables that had been generated with the exact $q_{0S}$ – solid, the ECPSSR’s account for the relativistic effect does not just simulate relativistic nature of the target atom. It also depends on the $\xi_{S}$ of the collision. The main trend, nevertheless, of the $W$ factor in Fig. 4(a) is due to the change from the SH to HS wavefunctions. The ratio curves in Fig. 6 of Sarkadi and Mukoyama [17] that reflect the
changes caused by the replacement of nonrelativistic hydrogenic wavefunctions with DHS wavefunctions exhibit indeed the same trends as \( W \) for L subshells. In fact, it is noted in [17] that “for the L\(_3\) subshell, in the contradiction with expectations, the increasing deviations between the two theories with decreasing (reduced) velocity \( (\zeta_L) \) means that the use of more realistic wave functions would destroy the nice agreement (with experimental cross sections)”. This is indeed seen in Fig. 4(b) where the kink in the ratio of empirical-to-ECPSSR was raised to a 50% after the ECPSSR had been multiplied by the \( W \) factor of Eq. (1). If plotted versus proton energy, this ratio would have overlapped with Fig. 3 of Campbell et al. [3] that displays the ratio of the reference cross sections to the ECPSSR–DHS cross sections [15] which are employed as the theoretical ionization cross sections in the GUPIX package.

2.2. UA: United Atom modification

In the ECPSSR, \( \theta_S \Rightarrow \zeta_S \theta_S \), where the PSS function \( \zeta_S = 1 + (2Z_l/Z_{2S}\theta_S)[g_S(\zeta_S) - h_S(\zeta_S)] \), was derived in the Separated Atom (SA) picture as a first-order perturbation of the S-shell electron binding energy; the \( 0 < g_S(\zeta_S) \leq 1 \) accounts for the increase in the binding that increases with decreasing \( \zeta_S \) as the projectile penetrates deeper into the S shell and \( h_S(\zeta_S) \) accounts for the decrease in the binding at intermediate \( \zeta_S \) where the projectile polarizes the S shell in its passage outside the S shell. In the very slow collision limit of \( \zeta_S \to 0 \), with \( h_S = 0 \) and \( g_S \to 1 \), \( \zeta_S = 1 + 2Z_l/Z_{2S}\theta_S \), the binding energy should have been the binding energy of the United Atom (UA), \( \frac{1}{2}(Z_l + Z_{2S})^2\theta_{S,UA}^2/n^2 \) so that \( \zeta_S \) ought to be

\[
\zeta_{UA}^S = (1 + Z_l/Z_{2S})^2\theta_{S,UA}^2/\theta_S.
\]

Note that with \( \theta_S < 1 \) and \( Z_l \ll Z_{2S}, \zeta_{UA}^S = [1 + 2Z_l/Z_{2S} + (Z_l/Z_{2S})^2]\theta_{S,UA}^2/\theta_S < 1 + 2Z_l/Z_{2S}\theta_S \). Hence \( \zeta_{UA}^S \) truncates the increase of the binding energy in the \( \zeta_S \to 0 \) limit. Since the decrease in the binding energy yields greater cross sections, in that limit \( \sigma_{S,ECPPSR}^{UA} \) evaluated with \( \zeta_{UA}^S \) of Eq. (2) \( > \sigma_{S,ECPPSR} \) of the ECPSSR.

Following Laegsgaard et al. [18], the UA binding energy has been used in approximate calculations for all \( \zeta_S \) as a matter of convenience or, as in [5,15], because of unpublished \( \zeta_{Mi}^S \)’s. Compounded by the neglect of the polarization effect at intermediate collisions, the indiscriminate use of the UA binding energy results in smaller cross sections than in the ECPSSR outside the slow collisions range where the UA picture is clearly untenable.

Although various schemes had been suggested to bridge the united and separated atom treatments of the binding effect [19], Vigilante et al. [20] were the first to merge the UA and SA accounts for this effect within an ECPSSR approach. Fig. 5 shows how \( \zeta_{S,UA}^S \) of Eq. (2) truncates the increase in the binding energy obtained with \( \zeta_S = 1 + (2Z_l/Z_{2S}\theta_S)[g_S(\zeta_S) - h_S(\zeta_S)] \). Here, the ECPSSR is modified to UA–ECPSSR via the \( \zeta_{S,UA}^S \Rightarrow \zeta_{S,UA}^S \) replacement where

\[
\frac{\zeta_{S,UA}^S}{\zeta_S} = \begin{cases} \frac{\zeta_{UA}^S}{\zeta_S} & \text{when } \zeta_{UA}^S \leq \zeta_S \text{ for slow collisions} \\ \frac{\zeta_{UA}^S}{\zeta_S} & \text{when } \zeta_S \leq \zeta_{UA}^S \text{ for intermediate and fast collisions} \end{cases}
\]

This joining the united and separated atom formulas as they are derived and valid in the complementary collision regimes. Fig. 6 demonstrates that this modification brings the theory to a closer agreement with the data; although it lowers the kink by just a few percent for heavy targets, it cuts the difference between the data and the theory in half for the lightest target.

2.3. IS: Intra Shell coupling modification

Arguing that the ionization of one subshell is not independent from the ionization of the other subshells, Sarkadi and Mukoyama calculated the redistribution of the vacancies induced by the projectile via intra-shell (IS) transitions in the same collision [17 and references cited therein]. This modification was parametrized as multiplicative correction factors given by Eqs. (12)–(15) in [17] involving universal functions of \( \zeta_{i}^L \). Unfortunately, these functions were limited to the \( 0.2 \leq \zeta_{i}^L \leq 0.8 \) range. As seen in Fig. 7(a), however, for...
the \( L_3 \) ionization the IS modification decreases the ECPSSR cross sections only in the middle of this \( \xi_{L3} \) range and does so by merely a few percent for heavy targets and about 10% for the lightest target. In effect, for the \( L_3 \) subshell, the IS coupling and UA modifications tend to offset each other so that Fig. 7(b) for experiment/theory ratios almost duplicates Fig. 4(b).

2.4. QC: Quantum Coulomb deflection modification

In the ECPSSR, the Coulomb deflection obtains from a leading factor – \( \exp(-\pi d q_{0S}) \), where \( d \equiv Z_1 Z_2 / A v_1^2 \) is the half distance of the closest approach with \( A \) being the reduced mass of the projectile–target system – that Brandt et al. [21] extracted from the ratio of classical (in the treatment of the projectile) calculations of Bang and Hansteen [10] with a hyperbolic trajectory to the straight-line SCA. The ratios of the cross sections induced in an inner shell of the same target by deuterons to those by protons of the same velocity (the isotope effect) offered a very sensitive test of the Coulomb deflection factor since the energy-loss effect was very well accounted for in the ECPSSR and the PSSR effects plus a host of uncertainties, including those of the fluorescence yield and the detection system, cancelled out in this ratio. Measurements of the isotope effect appeared to confirm the validity \( \exp(-\pi d q_{0S}) \) [22], although there were indications that especially for larger \( Z_2 \) the Coulomb deflection factor was smaller [23]. According to the monopole approximation in the classical formulation of Bang and Hansteen [10] this factor...
should have been significantly smaller than \( \exp(-\pi dq_{05}) \) [24]. The isotope effect data for the ionization of L subshells agreed with the monopole approximation [25].

Yet, the Naples group has continued to revisit over the last decade [7,8,26] another treatment of the Coulomb deflection effect. Lapicki and Losonsky [27] had extracted a quantum Coulomb deflection factor QC from the Coulomb-to-plane wave functions ratio taken at the impact parameter \( p_0 \) at which impact parameter dependent probabilities for ionization peak; in the straight-line SCA this impact parameter is of the order of \( q_{05}^{-1} \). For present calculations, QC is evaluated according to Eq. (11) of [27] and it is assumed that \( p_0q_{05} = 1 \). It is evident from Fig. 8 that, relative to the classical \( C = \exp(-\pi dq_{05}) \), in very slow collisions of \( \xi_{L3} < 0.25 \) the QC factor gives dramatically smaller cross sections. This is consistent with the monopole approximation and supports those who criticized [24] the \( \exp(-\pi dq_{05}) \) factor as improperly extracted from [10]. Unfortunately, the Orlic database does not extend to these very slow collisions for a resolution of this dispute.

On the other hand, in the range of \( \xi_{L3} \) where the database is available, relative the \( \exp(-\pi dq_{05}) \) the QC factor yields greater cross sections — progressively so with the decreasing \( \xi_{L3} \) up to a factor of 1.5 at \( \xi_{L3} = 0.3 \) (Fig. 8(a)). The near-perfect agreement between the data and the ECPSSR has been destroyed by the QC factor at this value of \( \xi_{L3} \). The bothersome kink at \( \xi_{L3} = 0.4 \) and its shoulder at higher \( \xi_{L3} \), however, were completely erased. For these \( \xi_{L3} \), the modified ECPSSR

Fig. 7. IS modification factor [17], and empirical cross sections normalized to IS–ECPSSR–W and divided by this factor.

Fig. 8. QC deflection modification factor [27], and empirical cross sections normalized to IS & UA–ECPSSR–W and divided by this factor. This is Orlic’s database [2] normalized to the ECPSSR with all modifications.
theory is in remarkably good agreement with the data (Fig. 8(b)).

Figs. 9 and 10 compare the empirical cross sections with the ECPSSR, display the results of its modifications discussed above, and show the ratio of the empirical cross sections to the ECPSSR theory that incorporates all of these modifications for L_2 and L_1 subshells. The ECPSSR

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Fig. 9. L_2 ionization: empirical cross sections [2] normalized to the ECPSSR [1], its modification factors, and Orlic's database [2] normalized to the ECPSSR with all these modifications.
underestimates the data essentially in the same way for all \( Z_2 \), increasingly so with the decreasing \( \xi_{L1} \); in the very slow collisions at \( \xi_{L1} = 0.25 \) the data rise above the theory by factors of 3 for \( L_2 \) and 2 for \( L_1 \) subshells. The ECPSSR theory with all its modifications substantially eliminates these large discrepancies; it agrees with most of the data within 20%, and all the data within a 50% margin.

Fig. 10. \( L_1 \) ionization: empirical cross sections [2] normalized to the ECPSSR [1], its modifications factors, and Orlic’s database [2] normalized to the ECPSSR with all these modifications.
3. Conclusions

The fact that the ECPSSR theory for \( L_2 \) and \( L_1 \) ionization is in considerably larger disagreement with the database than for \( L_3 \) is traced to inherently larger errors in the experimental cross sections extracted from the L x-ray spectrum. The peaks associated with the \( L_2 \) and \( L_1 \) subshells are significantly weaker than the major peaks that involve the \( L_3 \) subshell; Fig. 11 shows the \( L_3 \) subshell as indeed the major contributor in L-shell ionization for all \( Z_2 \) and proton energies. \( L_2 \) is the weakest contributor to L-shell ionization below 1 MeV; especially so for heavier elements that account for the steep rise of the data-to-ECPSSR ratio (Fig. 9(a)). Exceptionally strong reduction of this ratio by the IS redistribution of vacancies may not be meaningful when \( L_2 \) related lines are just a few percent in the L-shell spectrum. Very good agreement between \( L_1 \) data and the ECPSSR with all modifications may also be somewhat accidental; the data themselves could have been systematically underestimated because the common practice of neglecting the natural line shapes in the L-shell spectrum analysis – this is particularly so in the case of \( L_\gamma \) peaks [28]. Hence the status of theoretical cross sections for PIXE analyses is primarily as good as their agreement with the \( L_3 \) database. Aside from a 35\% underestimate of the data at \( \xi_{L_3} = 0.4 \) by the ECPSSR and the overestimate of the data in slower collisions by its modified version, IS & UA–EQCPSSR–W, both theories provide reliable (to within the experimental uncertainties of the data) cross sections for PIXE packages. Both theories give essentially the same and excellent results above 1 MeV; they start to differ to a significant extent from the data obtained with the several hundred keV proton beams.

It is impossible to choose definitively which theory, the ECPSSR (Fig. 1) or IS & UA–EQCPSSR–W (Fig. 12), is better because the Orlic database becomes progressively more thinner and prone to greater scatter with larger errors and more erratic fits at its 300–400 keV limits. Overall, the QC factor is the most critical modification. We are forced to repeat what was stated originally: “the scatter (of the data) does not allow to decide whether the (quantum) refinement of Coulomb deflection is warranted” [27] or similarly concluded 15 years ago by Harrigan and Cohen [29]. In fact, fitting subsets of Orlic database measured at 400 keV and below can lead to diametrically different conclusions about the ECPSSR and its modifications vis a vis the experiment. Reis and Jesus [30] fitted the empirical-to-ECPSSR ratios for \( L_1 \) x-ray production to a polynomial in a single
variable; they relied on a subset of the Orlic database limited to the $62 \leq Z_2 \leq 71$ targets. This polynomial is redrawn in Fig. 13 for $Z_2 = 62$ and 70 as functions of $\xi_{L_1}$ and proton energy. The curves show that instead of underestimating the data, the ECPSSR overestimates the cross sections measured in the 150–200 keV range by as much as a factor of 12! The ECPSSR with all modifications rises by more than a factor of 16 above the fitted data. The conversion of x-ray production-to-ionization cross sections with larger $L_1$-subshell fluorescence yield [31] than used in [30] and generally accepted $\omega_1$ [32] for the $62 \leq Z_2 \leq 71$ elements could lower the fitted ratios of Reis and Jesus by about 5%, or in the extreme case of $^{64}$Gd by almost 30% [33]. For these lanthanides bombarded by 150–200 keV protons, based on a heuristic equation (A3) in [34], the enhancement of $\omega_1$ due to multiple L and outer shell ionization would lower experimental ionization cross sections even further by several percent. Both ECPSSR and ECPSSR with all modifications would definitely overestimate the selected data in the 150–200 keV range by an order of magnitude.

This dichotomy is particularly perplexing from the perspective of Fig. 1 in [7] that shows the empirical/ECPSSR ratio for the identical set of targets as in [30]. As the proton energy decreases, in agreement with the general trend exhibited at comparable $\xi_{L_1}$ by the Orlic database for the heavier targets, these data rise above the ECPSSR by as much as a factor of 2 at 250 keV. In sharp contrast, at this energy the fit of Reis and Jesus [30] places the measured $L_1$ x-ray production cross section in ytterbium a factor of 2 below the ECPSSR (see Fig. 13).

Gauged by the reference cross sections (Orlic database) utilized in the GUPIX, the reliance on the peaks associated with $L_1$-subshell vacancy production and the ECPSSR would overestimate the concentration of all elements typically by some 30%, or in the worse case scenario by a factor of 2 for uranium if the sample was bombarded by 400-keV protons. This, however, might be a misleading conclusion. On the basis of the Reis and Jesus fit, the ECPSSR theory would have underestimated the concentration the $Z_2 = 62–71$ trace elements in a sample irradiated with 150–200 keV protons by one order of magnitude! With the modified ECPSSR, the factor of 2 discrepancy in detection of $L_1$ x-rays induced from U by 400-keV protons would be eliminated but the production of such x-rays in the selected rare-earth elements by 150–200 keV protons would still be overestimated.

Fig. 12. Empirical cross sections from Orlic’s database for L-subshell ionization in $Z_2 = 45, 74, 83$ and 92 atoms by 0.3–3.5 MeV protons [2] normalized to the ECPSSR theory with all modifications as reviewed here.
by one order of magnitude. If the data fitted by Reis and Jesus are correct, then small (below 300 keV) accelerator users who detect a peak associated with an L₁ hole and who might rely on a PIXE package that employs the ECPSSR, modified or not, for theoretical ionization cross sections would have underestimated the presence of lanthanides in their samples by one order of magnitude. On the other hand, if the cross sections measured in [7] are correct, the concentration of the very same elements could have been overestimated by a factor of 2.

References

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