Double-Ionisation Processes and Electronic Structures*

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The electron momentum distribution of a given target can be extracted, under impulsive conditions, from the simple ionisation processes relevant to Compton collisions. This document classifies and investigates the physical mechanisms of double ionisation, in connection with the target electronic structure.

Key words: Double-ionisation processes; Scattering cross-section; Electron scattering, inelastic; Electronic structure.

I. Introduction

All notations make use of Hartree atomic units. Questions involving antisymmetrisation procedures will be left as an exercise. The discussion will focus on ionisation by electron impact.

With the detection of three outgoing electrons in coincidence, recent measurements [1] of the so-called (e, 3e) processes have brought a new interest to the study of double ionisation mechanisms by electron (or, similarly, by photon) impact. The Auger effect is one of them. It is known to represent the result of a specific electronic rearrangement in the target that occurs after the (simple) ionisation of a deep level, or, alternatively, corresponds to a shake-off resonant process. It may thus be classified as an (e, 2e + e') effect [2], since the energy of the e' electron is strictly fixed and its emission is governed by lifetime mechanisms.

A natural approach to double ionisation mechanisms consists of relating the double ionisation to the simple ionisation processes. Studies of (e, 2e) processes represent a well-established field [3]. At sufficiently high incident energies (first Born approximation) and owing to the difficulty of building a final ionised state of the target strictly orthogonal to its intitial state, the simpler theoretical descriptions consider two regimes:

- the *Compton regime*, where *one* target electron suffers a collision of the Compton type (energy-momentum conservation), the other electrons being spectators. This electron is ejected with a final asymptotic momentum $\boldsymbol{k}_e$ close to $\boldsymbol{k}$ [$\boldsymbol{k}=\boldsymbol{k}_i-\boldsymbol{k}_s$, momentum transfer] and a Doppler spreading due to its initial velocity distribution $\varrho(\boldsymbol{p})$ in the target.
- the *dipole regime*, at sufficiently small momentum transfer; the plane wave $\exp(i\boldsymbol{k}\boldsymbol{r}_\mu)$ associated to the ejection of the μth electron is replaced by $[i\boldsymbol{k}\cdot\boldsymbol{r}_\mu]$, the first effective contribution in its Taylor expansion.

Finally, the main theoretical problem to be solved in the (e, 2e) scattering models consists in a perfect description of the *electron path of the ejected electron* in the field of the remaining ion and, at lower incident energies, of the path of both outgoing electrons. In that sense, several attempts – and their generalization to (e, 3e) problems (Brauner, Briggs, and Klar [4], Dal Cappello et al. [5]) – handle some properly chosen hypergeometric functions in place of the plane waves used in the common impulse theories. They were proved quite successful in reproducing the absolute measurements of (e, 2e) differential cross-sections. However, and as a consequence, when the experimental conditions do not meet *the conditions* (the Bethe ridge) *required for an impulse collision*, the simple relationship allowing an interpretation of (e, 2e) measurements in terms of target electronic velocity distributions is generally lost. A deconvolution procedure can be used (i.e. via perturbative treatment [6]) to correct the major distortions resulting from these post-collisional effects. It is also important to emphasise here the basic difference between the short-range interactions producing the so-called Compton defects [7] observed in the energy-loss spectra of the scattered particles and the long-range effects prevailing into (e, 2e) and (e, 3e) processes in the case of non-impulse conditions.

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II. Basic Mechanisms in a Simple or a Double Ionisation

A preliminary identification of the basic ionisation mechanisms can be carried out directly from the total cross-section [8] or alternatively from the generalised oscillator strength [9], and their properties. Indeed, the integrated differential cross-sections fulfil a number of sum-rules. The *sum-rules related to the successive moments in energy-loss* of the scattered particle have a specific interest here.

The discussion is reduced to the case of atomic scattering only and neglects possible exchanges between incident and target electrons. The following definitions and properties are easy to verify, as a consequence of the optical theorem

$$\sigma_{\text{exact}} = 2\pi k_i^{-1} \langle \exp(i\boldsymbol{k}_i \boldsymbol{r}_0)\, \Psi_i(1 \ldots N)| \qquad (1)$$
$$\cdot\, V\, \delta[K + V - E_i - (\Delta_0 + k_i^2)/2]\, V\, |\exp(i\boldsymbol{k}_i \boldsymbol{r}_0)\, \Psi_i\rangle .$$

V represents the interaction potential $V = -Z/r_0 + \sum_\mu 1/r_{0\mu}$, for an atomic target of Hamiltonian K in a fixed initial state such as $K\,|\Psi_i\rangle = E_i\,|\Psi_i\rangle$. The respective momentum and energy of the incoming electron are represented by $\boldsymbol{k}_i$ and $k_i^2/2$.

Equation (1) is an exact analytical expression. However, this expression is difficult to calculate without any further approximation. The first Born approximation is the simplest approach at medium energies of the incoming particle. It can be obtained by the neglect of V in the δ-function. [Besides, further corrections to the first-Born propagator will consist in performing a Taylor expansion of $\delta(\varepsilon + V)$ in powers of V].

After use of Bethe's formula (Fourier transform of $1/r$ terms), the previous expression thus becomes

$$\sigma_{\text{Born1}} = 4 \int \mathrm{d}\boldsymbol{k}_s / k_i\, k^4 \langle \Psi_i |\, [Z - \sum_\nu \exp(-i\boldsymbol{k}\boldsymbol{r}_\nu)]$$
$$\cdot\, \delta(K - E_i - \Delta E)\, [Z - \sum_\mu \exp(i\boldsymbol{k}\boldsymbol{r}_\mu)]\, |\Psi_i\rangle \qquad (2)$$

with $\Delta E = (k_i^2 - k_s^2)/2$. ΔE hence represents the target energy gain (or the expectation value of the operator $(k_i^2 + \Delta_0)/2 = \Delta E_{\text{op}}$).

Moreover, an evaluation of differential scattering properties (such as angular and energy distributions of the outgoing particles, in the specific case of ionisation) usually requires the knowledge of the final target states $|\Psi_f\rangle$. In order to avoid this difficulty, our purpose will consist in looking for *properties that depend on the initial state* $|\Psi_i\rangle$ only. A good example is given by the calculation of successive moments of ΔE_{op},

$$\{\Delta E^n\} \propto 2\pi k_i^{-1} \langle \exp(i\boldsymbol{k}_i \boldsymbol{r}_0)\, \Psi_i |\, V (\Delta E_{\text{op}})^n \qquad (3)$$
$$\cdot\, \delta[K + V - E_i - (\Delta_0 + k_i^2)/2]\, V\, |\exp(i\boldsymbol{k}_i \boldsymbol{r}_0)\, \Psi_i\rangle .$$

Since the first-Born treatment consisted in the neglect of V in the δ-function, cf. (1), a similar approximation can be applied to (3). Some useful properties – such as the Bethe sum-rule $\langle \Delta E \rangle_{\text{Born1}}$ – can be derived in this framework. The ΔE_{op} moments thus become

$$\langle \Delta E^n \rangle_{\text{Born1}} \propto \int k^{-4} k_s\, \mathrm{d}k_s \langle \Psi_i |\, \sum_\nu \exp(-i\boldsymbol{k}\boldsymbol{r}_\nu) (\Delta E_{\text{op}})^n$$
$$\cdot\, \delta(K - E_i - \Delta E) \sum_\mu \exp(i\boldsymbol{k}\boldsymbol{r}_\mu)\, |\Psi_i\rangle , \qquad (4)$$

with the well-known results [8, 9]

$$\langle \Delta E \rangle_{\text{Born1}} = k^2/2;$$
$$\langle (\Delta E - k^2/2)^2 \rangle_{\text{Born1}} = \langle (\boldsymbol{k} \cdot \boldsymbol{p})^2 \rangle = (2E_i/3) \cdot k^2 . \qquad (5)$$

The first result in (5) simply says that, under a given momentum transfer k, the energy lost by the incoming particle just corresponds to $k^2/2$ (Bethe's sum-rule). At sufficiently large k the energy-loss spectra exhibit a Compton line. This line spreads according to the (initial) kinetic energy distribution in the scatterer (second sum-rule).

The explicit calculation of these two moments (order 1 and 2) shows clearly *that their values come strictly from a one-electron process*, i.e. from the terms $\sum_{\mu=\nu} \sum \exp(-i\boldsymbol{k}\boldsymbol{r}_\nu)\, \delta(\ldots) \exp(i\boldsymbol{k}\boldsymbol{r}_\mu)$ in (4).

It is then highly interesting to discuss the contribution of the remaining terms ($\nu \neq \mu$) to $\langle \Delta E \rangle_{\text{B1}}$ and $\langle \Delta E^2 \rangle_{\text{B1}}$. The corresponding results for these expressions strictly vanish in both cases. As a consequence, such contributions are essential to the elastic scattering factor. Although corresponding to a bielectronic operator in (4), they *cannot* be considered as the signature of a double ionisation mechanism, except perhaps at very small momentum transfer.

In other words, the basic idea to introduce, in the quantum theory of the Compton effect, a *second-order density matrix* [8] in place of the first-order density matrix $\Gamma(\boldsymbol{p}\,|\,\boldsymbol{p}) = \varrho(\boldsymbol{p})$ (which corresponds to the terms with $\nu = \mu$), is not consistent with the sum-rules relative to the first-Born assumptions.

The second-order density matrix contributions

$$\int \Gamma(\boldsymbol{p}_1 + \boldsymbol{k}, \boldsymbol{p}_2 - \boldsymbol{k}\,|\,\boldsymbol{p}_1, \boldsymbol{p}_2)\, \delta(\ldots)\, \mathrm{d}\boldsymbol{p}_1\, \mathrm{d}\boldsymbol{p}_2 \qquad (6)$$

(corresponding to the case $\nu \neq \mu$) cannot simply represent the result of a second ejection along the $(-\boldsymbol{k})$

direction, prepared by some – internal – correlation process.

Such a mechanism (a shake-off process that would be basically different from the Auger mechanism, itself relevant to the case $v=\mu$) leaves a problem with (5), which is consistent only in the limit of very small momentum transfer (or very low energies of both ejected electrons in a double ionisation).

A similar conclusion may also be deduced from direct calculations [10] relative to the transition matrix elements of the first-Born (monoelectronic) scattering operator $\sum_{\mu} \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_{\mu})$. These matrix elements represent the "vertical" description of a double ionisation. Such terms are found to vanish when they are calculated in the Hartree-Fock frozen-core model. The calculation of these transition matrix elements requires *fairly correlated* functions to describe the target properties as well as the post-collisional interaction of the outgoing electrons and the remaining ion.

The sum-rule properties indicate that a double ionisation mechanism rather corresponds to the next contribution in the Born expansion (i.e. a second-Born effect, with at least two successive collisions between the incident particle and the target electrons). A simple estimate of such contributions will consist in replacing $\Delta E = K - E_i$ by the "exact" $\Delta E \simeq K + V - E_i$, a correction where V is replaced by V^2 – or alternatively $\exp(i\boldsymbol{k}\boldsymbol{r}_{\mu})/k^2$ by $\pi\exp(i\boldsymbol{k}\boldsymbol{r}_{\mu})/2k$, which correspond respectively to the Fourier transforms of $1/r$ and $1/r^2$ – in order to reproduce the second-Born effects.

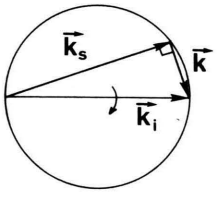


Fig. 1

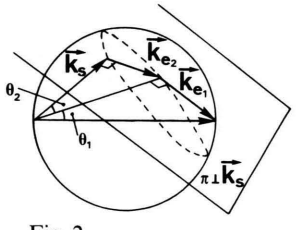
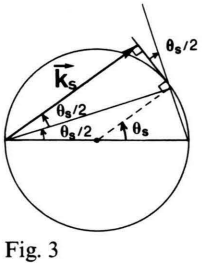


Fig. 2



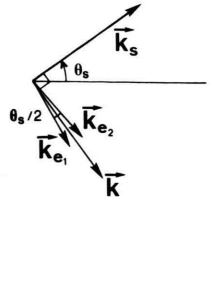


Fig. 3

Then $\langle\Delta E\rangle_{B2} \simeq \pi k/2$ [and $\langle\Delta E^2\rangle_{B2} \simeq \langle\Delta E\rangle^2_{B2}$, in a.u.], a result that will give the *order of magnitude of the conditions allowing* a double ionisation as the result of two successive (Compton) collisions. The momentum transfer required in that case would be rather large, in accordance with the (double) ionisation energy.

III. Angular Distributions in a Double Ionisation

The corresponding cross-sections are fivefold differential (3 angles, 2 energies – or energy losses – to be selected). The highest probability to observe such a double ionisation can be deduced from the following simple arguments used to define the impulsive situation (see Fig. 1):

$$\boldsymbol{k}_i = \boldsymbol{k}_{s1} + \boldsymbol{k}_{e1}; \quad \boldsymbol{k}_{s1} = \boldsymbol{k}_s + \boldsymbol{k}_{e2},$$
$$k_i^2 = k_{s1}^2 + k_{e1}^2; \quad k_{s1}^2 = k_s^2 + k_{e2}^2$$

with finally $\boldsymbol{k} = \boldsymbol{k}_{e1} + \boldsymbol{k}_{e2}$, $2\Delta E = k_{e1}^2 + k_{e2}^2$.

When $\boldsymbol{k}_i$ and $\boldsymbol{k}_s$ (or $\boldsymbol{k}$) are fixed, the origin of $\boldsymbol{k}_{e1}$ belongs to a sphere that admits $\boldsymbol{k}_i$ as a diameter. The end of $\boldsymbol{k}_{e2}$ (the origin of $\boldsymbol{k}_{e1}$) is also found in a plane π perpendicular to $\boldsymbol{k}_s$. This plane and the sphere then intersect along a certain circle (Fig. 2).

It is interesting to note that this intersection *may reduce to a single point*, a situation that can be expected to reduce the angular dispersions of ejected electrons to a high degree and *thus to optimise the counting rates*. It is easy to prove that the required condition is $\theta_1 = \theta_2 = \theta_s/2$, in a coplanar geometry (Fig. 3). For a fixed θ_s, k_s must be adjusted to

$$k_s = k_i(1+\cos\theta_s)/2$$

(to be compared with $k_i\cos\theta_s$ in the usual Compton process), and

$$\Delta E = k_i^2[1 - \cos^4(\theta_s/2)]/2,$$

adjusted to $\pi k/2 = \pi \cdot k_i \cdot \sin(\theta_s/2)$.

Such a geometry predicts the ejection of two electrons with approximately the same momentum $k/2$ (Fig. 4). This description is completely independent of their initial positions, and some strong post-collisional effects may be expected for that geometry.

It is clear that this "optimised" kinematics *no longer fulfils the first-order moment* (generalised Bethe sum-rule) in a simple way, but the remaining difference may accomodate the required energy for the double ionisation.

As a conclusion, the description of the double ionisation processes seems to provide a very *selective test* on the quality of the correlated wave functions used to represent the target system. Since double ionisation processes do not seem to meet impulse conditions prevailing in the simple ionisation, all possible models must also fit properly the ejection trajectories of two electrons that are strongly correlated in the exit channel as well as in the target.

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