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Interference effects in the electron and positron scattering from molecules at intermediate and high energies

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ABSTRACT

The independent atom model representation (IAM) in combination with the additivity rule (AR) is customary accepted as a good approximation to describe electron and positron scattering processes with polyatomic molecules at intermediate and high energies (typically above 100 eV). Within this approach, interference terms are not properly evaluated and are usually ignored in the cross section calculations. However, through a numerical solution of the Lippmann–Schwinger equation for three dimensional multicentre potentials we here demonstrate how interference terms can affect to the calculated differential and integral cross section values even at such relatively high energies. Practical corrections to the AR approach for both differential and integral electron and positron scattering cross section calculations from molecules are also proposed.

1. Introduction

In the last few years, experimental evidences of the efficiency of low energy electrons inducing damage to biomolecular systems have been presented in several publications [1–3]. Furthermore these damaging interactions are commonly resonant processes, such as vibrational excitation, charge transfer and electron attachment, which sometimes show selectivity and site-bond effects [4–6]. Examples of this behaviour were found in thymine where each of the H atoms may be selectively removed by electrons of a specific energy [7] or as a function of the electron donor kinetic energy in atom-molecule collision experiments [8]. The effective incorporation of these processes to radiation damage models would require an accurate description of all the radiation interaction sequence from the primary high energy beam until the generation of those low energy secondary species either electrons [9] or molecular radicals. A great part of this description relies on the knowledge of electron scattering cross sections with the molecular constituents of the medium over a broad energy range. Accurate ab initio methods are restricted to the low energy domain, say below 10–15 eV, so different approaches have been developed to obtain realistic cross section data at higher energies. In this context it is customary accepted that an independent atom representation (IAM) [10] is accurate enough for energies above 100 eV. This is a great simplification of the problem since for any biomolecular target its electron scattering cross sections can be represented as a coherent sum of those of its constituent atoms, typically C, N, O and H. This assumption motivated recent calculations for most biologically relevant molecules [11,12] providing data in which are based most of the radiation damage modelling procedures [13]. However, we demonstrate here that multiple scattering effects are not negligible even for so high energies and that interference terms could modify appreciable both the differential and integral calculated cross sections. In order to quantify the relevance of these interference terms, we used the procedure proposed by Polasek et al. [14] to solve the three-dimensional Lippmann–Schwinger equation for multicentre potentials. This procedure allows to propose some corrections to improve the AR approximation.

2. Calculation procedure

Within the IAM representation [10], electron and positron scattering cross sections by molecules can be derived from the approximated molecular scattering amplitude given by:

$$F(\theta) = \sum_{\text{atoms}} f_i(\theta) e^{i\mathbf{q}\cdot\mathbf{r}_i} \qquad (1)$$

where $\mathbf{q} = \mathbf{K}_f - \mathbf{K}_i$ is the momentum transfer, $\mathbf{r}_i$ are the atomic positions and $f_i(\theta)$ are the corresponding atomic scattering amplitudes. Assuming that each atom scatters independently, this expression

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would be valid when the interatomic distances are large in comparison with the associated wavelength of the projectile. In these conditions, and assuming that the optical theorem [10] applies for the approximate scattering amplitude given by Eq. (1), the total cross sections can be written as:

$$\sigma^{\text{total}}_{\text{molecule}} = \frac{4\pi}{k}\,\mathrm{Im}\,F(\theta=0) = \frac{4\pi}{k}\sum_{\text{atoms}}\mathrm{Im}\,f_i(\theta=0) = \sum_{\text{atoms}}\sigma^{\text{total}}_{\text{atom}\,i}, \tag{2}$$

where k represents the projectile momentum and $\sigma^{\text{total}}_{\text{atom}\,i}$ the total cross section of the ith atom.

The differential elastic scattering cross sections can be calculated from the above approximated amplitudes (1) by averaging their squared modulus over all the molecular orientations:

$$\frac{d\sigma^{\text{elastic}}_{\text{molecule}}}{d\Omega} = \sum_{i,j} f_i(\theta)f_j^*(\theta)\frac{\sin qr_{ij}}{qr_{ij}} = \sum_i |f_i(\theta)|^2 + \sum_{i\neq j} f_i(\theta)f_j^*(\theta)\frac{\sin qr_{ij}}{qr_{ij}}, \tag{3}$$

Here $q \equiv |\mathbf{q}| = 2k\sin\theta/2$ is the momentum transfer, r_{ij} is the distance between the i and j atoms and $\sin qr_{ij}/qr_{ij} = 1$ when $qr_{ij} = 0$. Considering only elastic processes is sufficient for our purposes. Therefore, in order to obtain the atomic scattering amplitudes $f_i(\theta)$, atoms will be represented by real scattering potentials. In these conditions, the total cross section (σ^{total}) will be coincident with the corresponding integral elastic cross section. Note that Eq. (3) is formed by two summatory functions being the first additive term the most relevant while the second summatory function accounts for the contribution of interference terms.

It is important to notice that the above Eqs. (2) and (3) are not compatible, i.e. the integration of the differential cross section values in Eq. (3) does not give the total cross sections of Eq. (2). Both differ by the integrated contribution of the interference terms, $\sigma^{\text{interference}}$, which in general does not vanish and is given by:

$$\sigma^{\text{interference}} \equiv \int d\Omega \sum_{i\neq j} f_i(\theta)f_j^*(\theta)\frac{\sin qr_{ij}}{qr_{ij}} \tag{4}$$

This is a consequence of the approximate nature of the molecular scattering amplitude ($F(\theta)$) given by Eq. (1), and means that it does not satisfy the optical theorem. In other words

$$\int d\sigma^{\text{elastic}}_{\text{molecule}}/d\Omega \neq \sum_{\text{atoms}}\int d\sigma^{\text{elastic}}_{\text{atom}\,i}/d\Omega \tag{5}$$

and therefore the optical theorem for the molecular scattering amplitude seems to fail. However, maintaining the interference

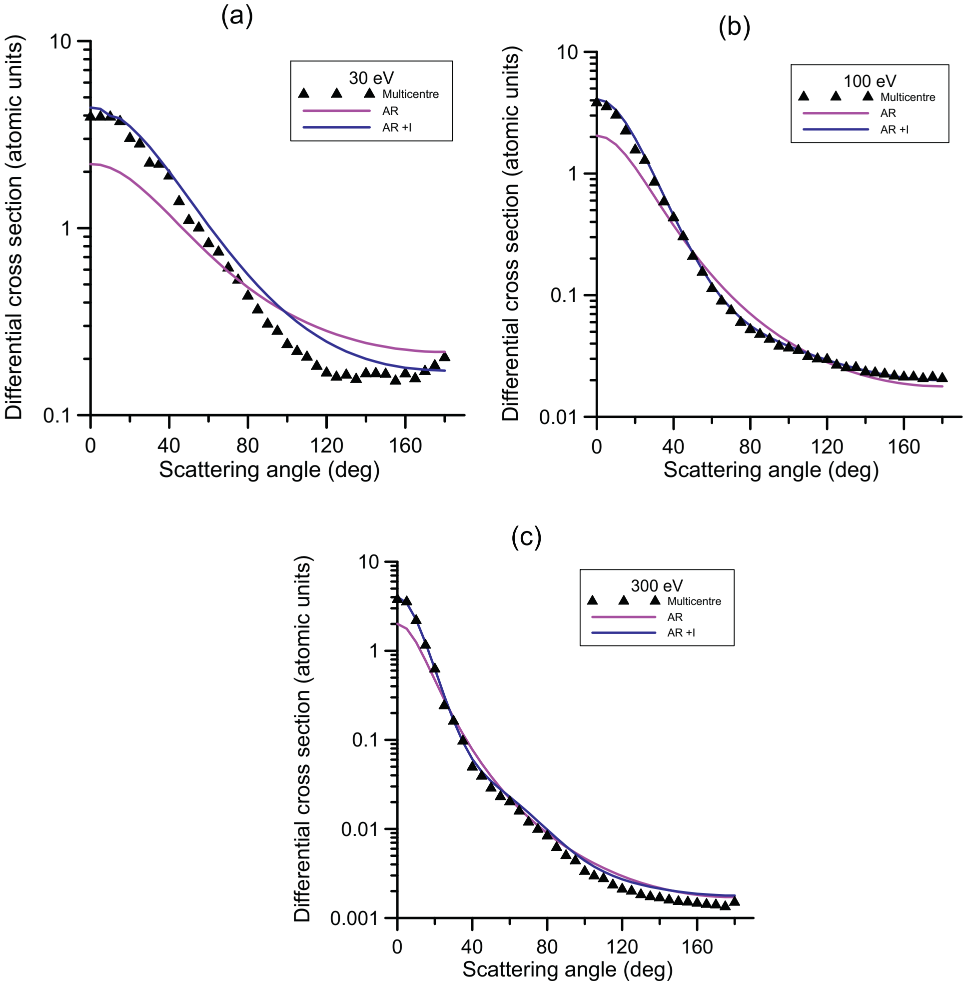

Figure 1. Differential electron scattering cross section from H_2 at (a) 30 eV, (b) 100 eV and (c) 300 eV incident energies. ▲, present multi-centre calculation; ▬, additivity rule (AR); ▬, additivity rule including interference terms (AR + I).