Inelastic cross-sections and energy loss properties by non-relativistic heavy ions in zirconium dioxide

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A formalism for the inelastic cross-section for electronic collisions of protons and heavier ions in a material is developed based on a quadratic extrapolation of the experimentally based dipole oscillator strength distribution (DOSD) of the material into the energy momentum plane. The approach is tested by calculating various energy loss properties in zirconium dioxide. Mean free path, stopping power and continuous slowing down approximation (csda) range are predicted as a function of ion energy for various incident ions, with the stopping powers compared to experimental data to assess the effectiveness of the methodology. The DOSD is straightforwardly obtained from the experimentally measured energy loss function data below 80 eV and atomic photo-absorption cross-section data above 100 eV. Agreement between the results of the calculation for stopping power and the experimental data is within 10% for all ions when compared for energies greater than the Bragg peak. The discrepancy is larger below the peak due to limitations in the methodology, especially the failure to make corrections for the Barkas and higher order effects and the lack of charge cycling cross-section data.

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the dielectric response function \(\varepsilon(p, \gamma)\) for the medium in question. This complex function gives information on how a medium responds to a momentum, \(p\), or energy, \(\gamma\), transfer to it. When a fully stripped ion with incident energy \(E = MV^2/2\) enters a material the probability of the ion undergoing an energy loss per unit distance is given by [3]

\[
\tau(E, \gamma) = \frac{Z^2}{2\pi} \int \left[-\frac{1}{\varepsilon(0, \gamma)}\right] \delta(\gamma - \left(\gamma' + \frac{p^2}{2}\right)) \, dp \, d\gamma
\]  

(1)

where the reduced atomic units \(e = m_e = h = 1\) are used (and are used throughout this work) with \(e\) the electronic charge, \(m_e\) the electron mass, \(h\) Planck’s constant and \(M\) the reduced mass of the ion. The \(Z^2\) term in Eq. (1) distinguishes the expression for heavy ions from that for singly charged electrons and positrons, as noted in reference [9].

The probability of an energy loss event can be related to the inelastic collision cross-section by

\[
\sigma(E) = \frac{1}{N} \int \tau(E, \gamma) \, d\gamma
\]

(2)

with \(N\) being the number density of molecules in the medium. Furthermore,

\[
\sigma(E) = (N\mathcal{A}(E))^{-1}
\]

(3)

where \(\mathcal{A}\) is the mean free path of an ion in the medium. The stopping power, \(S(E)\), and \(csda\) range, \(R(E)\), are given by the two equations

\[
S(E) = \int \gamma \tau(E, \gamma) \, d\gamma
\]

(4)

\[
R(E) = \int \frac{1}{S(E)} \, dE
\]

(5)

Crucially, the expressions for the energy loss properties in a medium for an ion given above rely on \(\text{Im}[-1/\varepsilon(p, \gamma)]\), the imaginary part of the complex dielectric response function. This function is not available from experiment for most materials, however, the energy loss function (ELF) for optical data, where \(p = 0\), is much easier to obtain. Ashley has suggested an approximation to allow the evaluation of the energy loss properties, namely, the quadratic extension of the DOSD into the energy–momentum plane [2]

\[
\text{Im}[-1/\varepsilon(p, \gamma)] = \int \frac{Z^2}{2\pi} \text{Im} \left[\frac{1}{\varepsilon(0, \gamma)}\right] \delta(\gamma - \left(\gamma' + \frac{p^2}{2}\right)) \, dp \, d\gamma
\]

(6)

where \(\gamma'\) can be identified as a ‘binding energy’ associated with the molecules in the medium. This approximation allows us to use solely optical data in the previous Eqns. (1)-(5).

When evaluating the expressions (1)-(5) of an ion interacting with the electrons in a medium the kinematic constraints of the situation must be considered to determine the bounds of integration. The ion with mass \(M\) and incident energy \(E = MV^2/2\) is assumed to collide with an electron at rest. The ion then leaves with energy \(MV_1^2/2\) and the electron has energy \(V_2^2/2\) with the contribution of \(\gamma'\) the ‘binding energy’ given to the system. According to energy conservation, we can say that \(MV_1^2/2 = MV^2/2 + V_2^2/2 + \gamma'\). We can also define the ‘energy loss’ as \(\gamma = (V_2^2 - V_1^2)M/2 > \gamma'\), which gives through simple rearrangement,

\[
V_1 = \sqrt{V^2 - 2\gamma/M}.
\]

(7)

For all possible energy losses, the value of \(\gamma_{\text{min}}\) is 0 while the maximum value of \(\gamma_{\text{max}}\) always corresponds to the minimum possible momentum transfer for a given energy transfer. By applying conservation of momentum, the following inequality for the minimum momentum transfer is defined

\[
\rho_{\text{min}} = M(V - V_1) < \rho.
\]

(8)

When combined with the definition for \(V_1\) above and the fact that \(\nu_2 = \sqrt{2(\gamma' - \gamma)}\), Eq. (7) becomes

\[
\gamma' < \gamma - M^2 \left(\frac{\nu^2}{M} - V\sqrt{V^2 - 2\gamma}/M\right) = \gamma_{\text{max}}.
\]

(9)

We can now apply a Taylor expansion to the square root terms in Eq. (8) as \(\gamma \ll MV^2/2\) for an ion colliding with an electron; giving

\[
\gamma'_{\text{min}} = 0 < \gamma' < \gamma - \gamma^2/2V^2 = \gamma_{\text{max}}
\]

(9)

Taking the right hand side of Eq. (9) allows us to determine the limits on energy transfer as

\[
\gamma_{\text{min}} = V^2 - V\sqrt{V^2 - 2\gamma} < \gamma < V^2 + V\sqrt{V^2 - 2\gamma} = \gamma_{\text{max}}.
\]

(10)

These inequalities, Eqns. (9) and (10), define the bounds of integration to a symmetric curve in the energy-transfer/binding-energy plane with allowable values under the curve; see the hashed area in Fig. 1.

Applying these constraints to Eq. (1) gives the following probability of energy loss,

\[
\tau(E, \gamma) = \frac{Z^2}{2\pi e E} \int_{\gamma_{\text{min}}}^{\gamma_{\text{max}}} \text{Im}[-1/\varepsilon(0, \gamma)] - G(\gamma, \gamma') \gamma' \, d\gamma
\]

(11)

where \(G(\gamma, \gamma') = \frac{1}{\gamma' - \gamma}\). From this we are able to define the inelastic cross-section and stopping power for electronic collisions as:

\[
\sigma(E) = \frac{Z^2}{2\pi e E} \int_0^{\gamma_{\text{min}}} \text{Im} \left[\frac{1}{\varepsilon(0, \gamma)}\right] \int \frac{1 + s - a) / (1 + s) \, d\gamma' \left[\frac{1]{1 - s - a) / (1 + s)}\right] \, d\gamma
\]

(12)

\[
S(E) = \frac{Z^2}{2\pi e E} \int_0^{\gamma_{\text{min}}} \gamma' \text{Im} \left[\frac{1}{\varepsilon(0, \gamma')}\right] \int \frac{1 + s - a) / (1 - s - a) \, d\gamma' \]

(13)

with \(a = \gamma/\sqrt{V^2}\) and \(s = \sqrt{1 - 2\gamma'V^2}\). From Fig. 1 it is clear to see that when evaluating total cross-sections \(\gamma_{\text{min}} = 0\) and \(\gamma_{\text{max}} = V^2/2\).

When modelling ion track structures, the simulations follow the trajectory of an ion collision by collision until the energy of the ion is less than a defined cut-off energy. The nature of a collision is determined from relative cross-sections for each type of collision at the energy of the ion, i.e. ionisation, excitation, vibration or...
elastic collisions. In the case of inelastic collisions, the differential inelastic cross-section is used to calculate energy loss via the so-called Y function [10]. This Y function corresponds to the ratio of the cumulative inelastic cross-section $\sigma(E)$ to the total inelastic cross-section $\sigma(E) = \sigma(E, E_{\text{max}})$ and is equivalent to the probability of an energy loss smaller than an energy $E$ [10]. Evaluation of the cumulative inelastic cross-section requires careful attention to the bounds of the integral in the $\gamma - \gamma'$ plane. As seen in Fig. 1, the bounds are defined by Eqs. (9) and (10) with a maximum value of $\gamma' = V^2/2$ when $\gamma = V^2$. For an energy loss in the range $0 < E < V^2$, the cumulative cross-section is given by

$$
\sigma(E, E_{\text{max}}) = \frac{Z^2}{2 \pi EN} \int_{0}^{E_{\text{max}}} \ln[-1/\epsilon(0, \gamma')] \ln\left(\frac{b - q(x_0)}{ab}\right) d\gamma'
$$

where $b = E/V^2$. However, when $V^2 < E < 2V^2$ evaluating the integral is more complicated as we have to consider the appropriate "region of integration". The most straightforward approach is to subtract the "missing" cross-section due to energy losses in the range $E$ to $E_{\text{max}}$ from the total cross-section, that is to determine the following

$$
\sigma(E, E_{\text{max}}) = \sigma(E, E_{\text{max}}) - \frac{Z^2}{2 \pi EN} \int_{0}^{E_{\text{max}}} \ln[-1/\epsilon(0, \gamma')] \ln\left(\frac{(1 + s - a)b}{(b - q(x_0)(1 + s)}\right) d\gamma'
$$

(15)

The probability of an energy loss from $E$ to $E + dE$ is given by the differential Y function, $dY/dE$. This quantity is analogous to the differential energy loss distribution for a particle at the energy in question. Since the Y function is independent of the charge and of the mass of the ion, depending only on its velocity, all ions at the same specific energy will have the same differential energy loss distribution. Heavy ion energy differential Y functions show peaks at the same energy of the DOSD and ELF, however with differing relative magnitudes. This is due to the underlying relationship between the three quantities.

Examination of Eqs. (11)–(15) reveals that the charge of the ion in the target material influences the energy loss properties of the ion in the material. Furthermore, this dependence on ion charge has significant implications for understanding radiation effects since as the ion passes through the material and slows down, it will capture electrons from the target material, changing its net charge. This captured electron can also be lost back to the medium. The gain and loss of electrons cycles the ion’s charge, affecting the rate of energy loss and the associated properties. Ideally, ion and material dependent charge cycling cross-sections should be (measured and) used in the interpretation of the energy loss and radiation track structure; however, the effects of charge cycling on the energy loss properties of ions are frequently approximated using an empirical approximation for the mean or the effective charge obtained by fitting experimental data.

The mean charge of an ion defined by charge exchange experiments is

$$
\bar{q} = \sum_{q=0}^{n} qF_q
$$

(16)

with $F_q$ the fraction of ions in a given charge state determined by charge cycling cross-sections and $n$ the number of different charge states for an ion.

Several empirical expressions exist to approximate the mean equilibrium charge state of projectiles in materials, for instance Schiwietz et al. suggest [11],

$$
q_{\text{mean}} = \frac{Z(8.29x + x^4)}{(5.16x + 7.4x^2 + x^3)}
$$

(17)

with the scaling variable $x = C_1 \left(\frac{V}{1.54c_2}\right)^{1-1.83/z}$

(18)

where

$$
c_1 = 1 - 0.26\exp\left(-\frac{Z_t}{11} - \frac{(Z_t - Z)^2}{9}\right)
$$

(19)

$$
c_2 = 1 + 0.030\nu\ln(Z_t)
$$

(20)

and

$$
\bar{v} = Z^{-0.543}/v
$$

(21)

with $Z_t$ being the “nuclear” charge of the target material and $v$ the Bohr velocity.

As with any empirical model, specifying the mean or effective charge based on fitting to experimental data is only appropriate for the experimental systems originally considered and is only valid over the energy ranges considered. Furthermore, these empirical fits will incorporate discrepancies between theory and experiment that do not arise from charge exchange. Sigmund recently stated that the empirical methods used to account for the cycling of an ion’s charge lack rigorous theory and that a better method should be found to predict mean charge states [12]. In addition, according to the formalism presented here the stopping power, $S_{\text{max}}$, of a material for an ion with fully stripped charge $Z$ should be related to the stopping power of a proton with the same velocity, $S_{\text{proton}}$, by

$$
S_{\text{max}} = S_{\text{proton}} \sum_{q=0}^{n} q^2F_q = <q^2> S_{\text{proton}}
$$

(22)

where $<q^2>$ is the mean squared charge. By definition, the mean of a distribution is not equal to the distribution’s root mean square so the use of (the square of) this parameter is not even a mathematically satisfactory substitute for the charge state cross-sections of an ion in a material.

The effective charge of an ion in a material is usually defined as the implied non-integer "charge state [of an ion at a given energy] required to reduce calculated Bethe-Bloch stopping [powers] to agree with experimental stopping values" [13]. Specifically, the effective charge is defined by relating the experimental stopping power of an ion with fully stripped charge $Z$ in a material, $S_{\text{max}}$, to the experimental stopping power of a proton with the same velocity,

$$
q_{\text{eff}}^2 = S_{\text{max}}/S_{\text{proton}}
$$

(23)

where the charge state of the "hydrogen ion" is taken to be one at all energies. The parameter $q_{\text{eff}}$ is usually determined by considering the stopping of many ions in many materials and determining an empirical fit. This approach results in a single expression which is presumed to be target independent.

A variety of different expressions for effective charge, $q_{\text{eff}}$, have been proposed [11,14–18] and are discussed straightforwardly in Ziegler [18]. These expressions are generally based on Bohr’s postulate that heavy ions stripping will depend on the electron orbital velocities relative to the ion’s velocity; electrons with orbital velocities less than the ions velocity can be deemed to be stripped [19]. The first to suggest an exponential relationship to velocity was Northcliffe [17], who proposed an empirical effective charge of

$$
q_{\text{eff}} = Z \left(1 - 1.85\exp\left(-\frac{2V}{v}\right)\right)^{1/2}
$$

(24)
relating the effective charge to the velocity of the incident ion with respect to the Bohr velocity. As more data has become available more accurate parameterisations over a greater number of ions and energies were suggested, for example Pierce and Blann [16] suggested

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\frac{0.95 V_f}{v_B Z^2 \gamma} \right] \right)$$

with $V_f$ the relative velocity of the incident ion to the electrons in the medium as described in [16]. Ziegler has made a study of hundreds of datasets including light and heavy ions in many different materials [18] and obtained the following parameterisation,

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\frac{0.95 V_f}{v_B Z^2 \gamma} - 0.07 \right] \right) + \left( \exp \left[ -\frac{0.95 V_f}{v_B Z^2 \gamma} - 0.07 \right] \right) \left( \frac{v_B/v_f}{2} \right)^2 \ln \left[ 1 + \left( \frac{2.4 V_f}{a_0 v_B} \right)^2 \right]$$

with $v_f$ the fermi velocity of the target. This expression includes a treatment of the screening of an ion by unstripped electrons, with the parameter $A_i$ being a screening length to describe the electrons associated with the ion and $a_0$ the Bohr radius [18]. The screening length $A_i$ details how the electronic distribution changes size as the amount of ionisation changes (as a function of energy) [18].

In the particular case of helium, Ziegler has suggested the following parameterised equation for the effective charge of

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\sum_{i=0}^{5} a_i \ln |E_{\text{EEL}|}^2 \right] \right)^{1/2}$$

where $Z = 2$, with $a_i$ being a set of empirically fitted parameters and $E_{\text{EEL}}$ the energy of the incident helium ion [18]. The fitted parameters are:

- $a_0 = 0.2865$, $a_1 = 0.1266$, $a_2 = -0.001429$, $a_3 = 0.02402$, $a_4 = -0.01135$, $a_5 = 0.001475$. The two equations suggested by Ziegler, Eqs. (25) and (26) will be used in this study to describe effective charge.

In this study, stopping power is used merely as a way to challenge the suitability of the formalism developed with the ultimate goal being to employ the formalism to produce cross-sections for use in track structure simulations. The choice of effective charge over mean equilibrium charge formalisms is not of primary concern; future iterations of this code may explore this dependence further.

### 3. Results and discussion

Construction of dipole oscillator strength distributions relies on the availability of experimental refractivity and absorption data in the very low energy range (0–100 eV), and frequently there is the need for interpolation between the available data and photon cross-sections at higher energies. The differential DOSD of a material, $f(\gamma)$, at energy $\gamma$ is related to the energy loss function $\text{Im}[1/(0, \gamma)]$ by the equation:

$$f(\gamma)/\gamma = \frac{2m}{\hbar^2 e^2 N} \text{Im}[1/(0, \gamma)]$$

with $m$ the electron mass, $e$ its charge, Planck’s constant $\hbar$ and $N$ the number density of molecules of the medium. The energy loss function is related to $n$ and $k$, the frequency dependent refractive index and extinction coefficient of the medium, respectively, through the complex dielectric response function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and the energy loss function

$$\text{Im}[1/(0, \gamma)] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

by

$$\varepsilon_1 = n^2 + k^2$$

and

$$\varepsilon_2 = 2nk$$

where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary components of the dielectric response function, respectively. For energies above 100 eV, $n$ is close to one and $k$ is small, so $\varepsilon_1$ tends to $n^2$ and $\varepsilon_2$ to $2k$. Consequently, the energy loss function, $\text{Im}[-1/(0, \gamma)]$, is determined solely by $k$ and we are able to assume that the core electrons are localised and summing atomic absorption cross-sections is an acceptable substitute for optical data for compounds. In the following, atomic absorption cross-sections for energy above 100 eV are taken from Veigele [20]. When experimental measurements of the energy loss function do not reach up to 100 eV (which is usual), the available data is interpolated using a log ($f_0$) vs $E$ plot between the two energy ranges.

Partial energy loss functions for ZrO$_2$ derived from experimental data by Frandon et al., Prieto et al., McComb, and Tahir et al. are shown in Fig. 2 [21–24]. The energy loss functions of Frandon et al. and of McComb extend to 50 and 60 eV, respectively, while that of Prieto et al. and Tahir et al. covers a wider energy range, extending up to 80 eV.

The four sets of data are very similar, although that of Tahir et al. appears to be shifted by a couple of eV to higher energy than the other data. There are key transitions at 14, 26 and 41 eV (discussed in detail in reference [23]); however, the absolute strengths of the peaks differ. The lowest energy maximum at around 14 eV, which has been described as a ‘bulk plasmon’ contribution, is the dominant peak in the ELF of Prieto et al. and Tahir et al., but is much smaller in the data sets of McComb and of Frandon et al. where the 26 eV maximum corresponding to the O 2p→Zr 4d transition is larger. The maximum at 41 eV, identified as the Zr 4p resonance peak, is larger in the data set of Frandon than those of Prieto et al., Tahir et al. and Frandon et al. [23].

The energy loss function of Prieto et al. [23] is used in this study primarily as it requires less interpolation to the point at which photon absorption cross-section data is available and the locations of the dominant features match the energies of the same features in Frandon et al. and McComb. The DOSD of ZrO$_2$ has been formulated up to 1 MeV. The complete differential DOSD obtained is shown in Fig. 3. Peaks corresponding to the three transitions

![Fig. 2](image-url)
identified in the energy loss function remain, but the relative strengths differ as the $\gamma^{-1}$ weighting in Eq. (27) reduces the importance of the peaks at lower energy.

According to the Fano sum rules [25], the ‘effective number of electrons which may receive energy from an energy transfer from an incident electron’ [2] is calculated by integrating the DOSD:

$$Z_{\text{eff}} = \int_{E_0}^{E_{\text{max}}} f(E) dE.$$  

(30)

In the case of ZrO\textsubscript{2}, there are 56 electrons, and the raw DOSD developed here and shown as a broken line in Fig. 3 gives a value of $Z_{\text{eff}} = 50.41$ electrons at 1 MeV, which is not correct. Rather than simply renormalizing the raw DOSD to reproduce the sum rule, the component of the DOSD derived from the energy loss function of Prieto et al. was rescaled (increased) and the interpolation to the well-known atomic absorption cross-sections repeated. The dependence of $Z_{\text{eff}}$ on the magnitude of an energy transfer is shown in Fig. 4 for both the raw and modified DOSD. Obviously, the modified DOSD data gives the correct asymptotic value of 56 electrons. Modification of the DOSD increases the “heights of the steps”, i.e. the number of electrons that can be influenced by a given energy transfer. The step changes can be considered as relating to the energy levels of the electrons in the ZrO\textsubscript{2} crystal. At least for the core electrons, these step changes correspond well to the binding energies for the atomic Zr and O components. The binding energies for the various atomic orbitals are highlighted in the figure [26]. Energy transfers below about 40 eV affect only the outer 16 ‘bonding’ electrons of the oxide. For energy transfer up to 100 eV, a further 6 electrons corresponding to the 2 s electrons from oxygen (2 sets of 2 for the 2 oxygen atoms in ZrO\textsubscript{2}) and 4 s electrons from zirconium are influenced. Further sharp discontinuities are apparent at 200 and 2000 eV and reflect the remaining inner-shell electrons, culminating in the final Zr 1 s core electrons experiencing effects for energy transfers above 20 keV.

To confirm the acceptability of the modification of the DOSD, the mean excitation energy, $I_{\text{eff}}$, given by the second moment sum rule,

$$Z_{\text{eff}} \ln(I_{\text{eff}}) = \int_{E_0}^{E_{\text{max}}} f(E) \ln(E) dE$$  

(31)

was also calculated for ZrO\textsubscript{2} using the raw and the modified DOSD. Table 1 compares the asymptotic values of $Z_{\text{eff}}$ and $I_{\text{eff}}$ obtained using the raw and modified DOSD with the value obtained by applying Bragg additivity and values available elsewhere in the literature. The raw DOSD leads to a predicted value for $I_{\text{eff}}$ which is significantly larger, almost twice, the value found by using Bragg’s rule, 295 eV [27]. The modified DOSD yields a mean excitation value of 327 eV, which is much closer to the value obtained using Bragg additivity and is in good agreement with the value of 313 eV in reference [28] calculated using the energy loss function of Frandon et al.

The use of data from Prieto et al. rather than the data of Frandon et al., McComb or Tahir et al. does not significantly alter the energy loss function or the derived DOSD. The formalism developed here to calculate cross-sections and energy loss properties avoids the construction of a generalised oscillator strength distribution. It is not necessary to explicitly consider outer electron orbitals, as is necessary in other methods [28]. The flexibility lent to the model by avoiding this step means this approach to calculating electronic collision cross-sections is much swifter and more straightforward than others in the literature and can be applied to even the most complex materials.

The most important test of any model is comparison with the available experimental data. There is relatively little data on the energy loss properties of ions in ZrO\textsubscript{2}. The largest volume of experimental and theoretical data is for the stopping power of ZrO\textsubscript{2} for various ions [29–31]. Figs. 5–7 shows stopping powers calculated with the formulation described here using the DOSD derived above. The figures make a comparison with the available data (either experimental or from other modelling studies). Generally, good agreement is found. In all cases, the Bragg peak (the

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**Table 1**

<table>
<thead>
<tr>
<th>Source</th>
<th>Mean excitation energy (eV)</th>
<th>No. electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work modified DOSD</td>
<td>327</td>
<td>56</td>
</tr>
<tr>
<td>Present work raw DOSD</td>
<td>578.4</td>
<td>50.41</td>
</tr>
<tr>
<td>Bragg additivity</td>
<td>295</td>
<td>56</td>
</tr>
<tr>
<td>Behar et al. [29]</td>
<td>377</td>
<td>56</td>
</tr>
<tr>
<td>Abril et al. [28]</td>
<td>312.8</td>
<td>56</td>
</tr>
</tbody>
</table>
maximum of the stopping power vs ion energy curve) occurs at around the same energy as found elsewhere, about 0.1 MeV/u for lighter ions and rising to 0.3 MeV/u for heavier ions.

Fig. 5 compares experimental data for the stopping power of ZrO₂ for protons and helium ions with predictions from the formalism presented here and other calculations in the literature. For protons at energies higher than the Bragg peak (>0.2 MeV/u), there is a good agreement between all of the calculations and the experimental data; however, where there is no experimental data available, below the Bragg peak, the three calculations differ with the method presented here, predicting a smaller stopping power than the other studies. The discrepancy between the formalism presented here and the SRIM experimental data is within 6% at high energies and falls to 12% at lower energies, close to the Bragg peak.

The experimental data for helium ions are in good agreement for specific energies above 0.2 MeV/u; however, there is a significant discrepancy between the available experimental data in the region of the Bragg peak below specific energies of 0.2 MeV/u. As was found for protons, the calculations are in good agreement at high energy, for ion energies greater than 1 MeV/u where the helium ion will be fully stripped. At lower energies, where the helium ion will not be fully stripped, the predictions of the calculations differ. This difference is most evident in the two calculations of this study: the two different empirical approximations for the effective charge give significantly different predictions for the stopping power. Eq. (26), the helium specific effective charge proposed by Zeigler, gives much better agreement with the experimental data than the Eq. (25). This discrepancy reflects the fact that the former is significantly more tailored than the latter, resulting from fitting 287 data sets for specifically helium ions in solid materials, rather than formulating the equation over all ions. The phase of the material is important due to a density effect, which drastically alters the charge exchange cross-sections in a material [12]. The experimental stopping powers measured by Zhang et al. [32] are in excellent agreement with the predictions of SRIM; however, the measurements at all energies by Behar et al. [29] agree more closely with the predictions of the formalism presented here.

While one failing in the energy loss formalism developed here has already been highlighted, specifically the use of an effective empirical charge rather than target dependent cross-sections, there is a significant secondary failing at low energies below about 0.1 MeV/u. This failing is the breakdown in the approximation used in developing the formalism, specifically the quadratic extension of the DOSD into the energy momentum phase space. It is well known (e.g. from studies of liquid water [3]) that this approximation is not adequate at low incident ion energies where relatively large momentum transfers are possible, as the quadratic expansion does not accurately reproduce the general oscillator strength distribution.

The prediction of the formalism developed here for the dependence of the stopping power of ZrO₂ for oxygen ions on their energy is shown in Fig. 6. At high energies, the predictions of our formalism are again in good agreement with those of a SRIM calculation. The only available experimental data are for ion energies close the Bragg peak. While the SRIM calculation agrees with the experimental data, our calculation underestimates the experimental data by 20.7% at 0.4 MeV/u. In addition, the energy dependence predicted by our calculation has a considerably wider Bragg peak than shown by the experimental data and the predictions of SRIM.

Fig. 5. Comparison of stopping powers of ZrO₂ for protons and helium ions. Open symbols are experimental data for from [29] for protons (○) and helium ions (●). Filled symbols (●) are experimental data from helium ions from [32]. The solid lines refer to the predictions of this study, with the black line for helium ions from Eq. (25) and the grey line from using Eq. (26) to calculate effective charge. The black dotted lines show the predictions of the SRIM code [18]. The grey dashed line is the prediction for protons from Abril et al. [28]. The grey dashed line shows the predictions of Behar et al. [29] for helium ions.

Fig. 6. Stopping powers of ZrO₂ for O ions. Experimental data are taken from the studies of Msimanga et al. (●) and Zhang et al. (○) [31,32]. The solid black line shows the prediction of this study and the dashed line the prediction of a SRIM calculation. Thin solid lines are the predictions of the formalism from this study with specific charge states (as labelled).

Fig. 7. Ion energy dependence of the stopping power of ZrO₂ for Mg and Al ions. Experimental data are taken from the studies of Msimanga et al.: Mg (○), Al (●) [31,32]. The solid lines show the predictions of this study and the dashed line the predictions of SRIM calculations.
The origins of this broadening lie in the empirical expression used for the effective ion charge, Eq. (25). The figure also shows the predicted ion energy dependence of the stopping power of ZrO₂ for O ions in each of the eight possible charge states. As expected the Bragg peak for each of the ion states occurs at the same ion energy, 0.14 MeV/u. This energy is significantly lower than the energy at which the experimental Bragg peak occurs (0.3–0.4 MeV/u) as well as the energy range of the broad Bragg peak calculated using an effective ion charge given by Eq. (25) (0.3–1 MeV/u).

Fig. 7 shows the ion energy dependence of the stopping power of ZrO₂ for magnesium and aluminium ions. The figure reveals similar trends to those highlighted in Fig. 6 for oxygen ions; however, the discrepancy between the predictions of our calculations and the experimental data (and the predictions of the SRIM code) decrease with ion mass, i.e. in the order O > Mg > Al. It is quite clear that one of the principal sources of this discrepancy is the treatment of the charge of the ion in the material, which is clearly inadequate.

First order perturbation theories often consider stopping power to be proportional to $Z^2$. However for heavy ions at intermediate energies higher order corrections to classical first order perturbation theory must be considered [14]. Higher order corrections to the stopping power, i.e. in $Z^2$ and $Z^3$ known as the Barkow-Anderson and Bloch corrections respectively, are not taken into account in the current formulation. These corrections will have large effects on heavy ions at low velocities. So, whilst the predictions for protons and helium are not significantly affected, the calculations presented for magnesium and aluminium ions will underestimate the experimental data. The next iterations of the formalism must address this challenge.

The inelastic mean free path and csda range of protons and helium ions in ZrO₂ at a variety of energies in the range 0.1–3.2 MeV are listed in Table 2. The mean free path, which reflects the average distance between electronic energy transfers for an ion with the specified energy, is inversely dependent on the inelastic collision cross-section through Eq. (3). For energies covering the region of the Bragg peak, i.e. ~0.1 MeV/u for protons and ~0.3 MeV/u for helium ions, the mean free path is comparable to or smaller than the distance between the ionic constituents of the ZrO₂ crystal lattice, ~2 × 10⁻⁸ cm from [33], implying that every crystallographic ion in the radiation particles path will be ionised (or undergo electronic excitation).

**Table 2**

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Fig. 8. Comparison of the mean free path of a helium ion calculated for an effective charge given by Eq. (26) with that for $^4$He⁺ and $^4$He⁺⁺. The solid lines show the predicted values using the effective charge approximation, the dashed line the predictions for $^4$He⁺ and the dotted line the predictions for $^4$He⁺⁺.

Fig. 8 examines the effect of ion charge on mean free path, comparing the mean free path of a helium ion calculated for an effective charge given by Eq. (26) with that for single, and doubly charged ions, $^4$He⁺ and $^4$He⁺⁺ respectively. The higher mean free path values are found for $^4$He⁺ meaning that, for a given energy, a singly charged incident ion is less likely to ionise or excite the material than a doubly charged ion. Ions considered to be fully stripped in ZrO₂ would result in a more dense interaction track. The csda ranges listed in Table 2 are obtained by integrating the calculated stopping power according to Eq. (13) to a minimum cut-off energy of 25 keV/u. In the calculations for helium ions reported in Table 2, the effective charge of the ion was incorporated using Eq. (26). As the trajectory of an ion is close to linear until nuclear collisions become an important attenuation pathway, the ranges correspond to the penetration of the proton or helium ion at the specified energy into ZrO₂.

The differential Y functions in ZrO₂ for 0.5 MeV protons and a variety of heavier ions of energy of 0.5 MeV/u are shown in Fig. 9. The distributions are clearly the same and independent of ion charge. The most probable energy loss is approximately 15 eV. Calculations for other energies (not included here) reveal that this value is more-or-less independent of the ion's energy.
The differential Y function shows maxima at the same energies as the ELF and the DOSD of ZrO₂. The relatively higher density of the differential Y function for low energy transfers compared to the DOSD reflecting the range of non-zero momentum transfers possible.

The mean energy loss per inelastic collision for protons at a range of incident ion energies is shown in Table 3. As the differential Y function for a given ion velocity is independent of the incident ion, the mean energy loss of an ion only depends on the velocity of the ion and not the ion type. (This behaviour is specified by the equation defining the ratio of the cumulative cross-section to the total cross-section, which depends only upon $E/M$, i.e. upon $V$.) As the maximum possible energy transfer, given by $4E/M$ in the reduced units used here, the mean energy transfer increases gradually with ion energy (velocity).

4. Conclusions

An approach for calculating the inelastic cross-sections of ions in materials based on the differential dipole oscillator strength of the material is presented. As the DOSD is dependent on phase and on crystallographic structure, this formalism naturally incorporates effects on the energy loss processes due to phase and crystallographic structure. The DOSD for monoclinic ZrO₂ has been constructed and its validity demonstrated by calculating the zero distance, $r_0$, and first Fano sum rules to give the effective number of medium electrons which may receive energy from an energy transfer, $Z_{eff}$, and the mean excitation energy, $E_{exc}$. The DOSD has been used to predict energy loss properties in order to evaluate this formalism. Specifically the stopping power, mean free path and cgsa range protons and helium ions in ZrO₂ as well as the stopping powers of a variety of heavier ions are considered. Comparison of the predictions with available experimental stopping powers and other calculations in the literature shows good agreement especially at ion energies greater than the Bragg peak. Failings of the approach developed are highlighted: the inadequate treatment of the effective charge of the ion; the breakdown of the formalism for evaluation the probability of the ion undergoing an energy loss per unit distance, $\tau(E, \gamma)$, from the DOSD at low energies ($<0.1$ MeV/u) and the lack of incorporation of higher order effects. Challenges in these areas will be considered before the use of these inelastic cross-sections in track structure simulations however this paper describes a novel formulation of these cross-sections for heavy ions in materials.

Acknowledgements

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Table 3

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