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Valence structure effects in the stopping of swift ions

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Abstract

The valence structure of a material may affect the stopping of swift charged particles primarily via Z_2 structure, atom–molecule differences, gas–solid differences and metal–insulator differences. These material effects have a common physical origin and can therefore be considered from a unified point of view. Theoretical arguments focus on the effect of binding and orbital motion of the target electrons as well as projectile screening and Barkas–Andersen effect. Generally, valence effects depend on the atomic number, charge state and velocity of the projectile. Reference is made to recent calculations on the basis of binary stopping theory as well as experimental findings.

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1. Introduction

The slowing down of charged particles in matter is characterized primarily by the mean energy loss per path length and its variance (straggling),

$$\langle \Delta E \rangle = Nx \int T \mathrm{d}\sigma(T), \tag{1}$$

$$\langle (\Delta E - \langle \Delta E \rangle)^2 \rangle = Nx \int T^2 \mathrm{d}\sigma(T), \tag{2}$$

where Nx is the number of atoms per area in a thin layer of thickness x and $\mathrm{d}\sigma(T)$ the differential cross section for energy loss T.

Generally speaking, these quantities show a fairly smooth dependence on all parameters specifying the stopping material and the penetrating beam. Therefore, Thomas–Fermi or 'local-density' considerations have been successfully applied in quantitative estimates of stopping parameters [1,2]. Nevertheless, deviations from smooth behavior must be expected and have been found – or at least looked for – experimentally in particular in the stopping cross section $S = \int T \mathrm{d}\sigma(T)$. Focus has been on

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(1) Nonmonotonic variation with the atomic number Z_2 of the target material ('Z_2 structure'),
(2) Atom–molecule differences ('deviations from Bragg additivity'),
(3) Gas–solid differences,
(4) Metal–insulator differences and
(5) Nonmonotonic variation with the atomic number Z_1 of the ion beam ('Z_1 structure').

With the exception of the last phenomenon – which is not a subject of this note – these effects must originate primarily in the valence structure of the stopping material.

It is the purpose of the present note to discuss those four phenomena on a common ground. Qualitative considerations dominate, but reference is made to previous work on Z_2 structure [3] and deviations from Bragg additivity [4] on the basis of the binary theory of stopping [5,6]. It was found there – somewhat surprisingly – that deviations from smooth behavior do not only depend on the speed of the projectile but also on its atomic number and charge.

2. Qualitative considerations

Several target properties influence electronic excitation:

- Excitation spectrum and binding energies,
- Orbital velocities and
- Spatial distributions.

of the electrons. While these quantities are by no means independent, their influence on stopping parameters can to some degree be identified individually.

As far as filled electron shells are concerned, the above quantities are known to vary smoothly with atomic number, while nonmonotonic variations are found for unfilled shells. Therefore, if one looks for pronounced nonmonotonic behavior, attention needs to be paid to configurations where outer shells contribute significantly to stopping. That is the case in general for low-Z_2 materials and, for all materials, at low projectile velocities where excitation channels for inner target shells are closed.

Since straggling is much less sensitive to distant interactions – i.e. small energy transfers T – than the stopping cross section, valence effects in straggling must be less pronounced than in stopping. Therefore, this note focuses on the stopping cross section.

3. Light ions: Bethe limit

A convenient standard of reference for theoretical considerations is the simple Bethe formula for the stopping of a *swift point charge*,

$$S = \frac{4\pi Z_1^2 Z_2 e^4}{mv^2} \cdot L, \tag{3}$$

$$L = \log\frac{2mv^2}{I} + \text{relativistic terms}, \tag{4}$$

which is valid at velocities $v \gg Z_2^{2/3} v_0$, where v_0 is the Bohr velocity. Thomas–Fermi arguments [1] predict a smooth dependence of the mean logarithmic excitation energy (the 'I-value') on atomic number,

$$I \simeq Z_2 I_0, \quad I_0 \simeq 10\ \text{eV}, \tag{5}$$

but I-values extracted from experiment or calculated theoretically show an oscillatory behavior reflecting the valence structure [7]. This structure translates into the stopping cross section S. In view of the logarithmic dependence on I, the oscillation amplitude in S decreases with increasing projectile speed. Moreover, the oscillation amplitude of $I_0 = I/Z_2$ is found to decrease [8] with increasing Z_2.

Similar conclusions hold for atom–molecule and gas–solid differences [9]. Chemical binding implies increased excitation energies and hence larger I-values for compounds and solids compared to isolated atoms, and hence a lower stopping cross section per target atom [10,11]. The Bragg additivity rule ignores this difference.[1]

[1] Empirically, deviations from Bragg additivity are not always negative as claimed here [12]. This can occur when stopping cross sections of elemental solids instead of atomic gases are used in the comparison.

Metals differ from insulators primarily in the lowest electronic excitation level. A general statement about the I-value – which represents an integral over the entire excitation spectrum – is not obvious. This is consistent with the fact that no evidence has been found for metal–insulator differences *in the Bethe regime*.

4. Bare heavy ions: Bohr limit

According to Bohr's kappa criterion [13], the classical Bohr formula [14]

$$L = \ln \frac{Cmv^3}{Z_1 e^2 \omega}; \quad \omega = \frac{I}{\hbar}, \tag{6}$$

with $C = 1.1229$ must be superior to Eq. (4) at relative energies up to $0.1 \cdot Z_1^2$ MeV/u. This has the immediate implication that with increasing atomic number Z_1 of the ion, the argument of the logarithmic stopping number L decreases, thus causing *enhanced* Z_2 structure as well as atom–molecule and atom–solid differences. In other words, at a given velocity, valence effects are expected to be more pronounced for heavy than for light projectiles within the range of validity of Eq. (6).

Fig. 1 shows some evidence in support of this feature. Z_2 structure is observed for 0.5 and 1.0 MeV/u alpha particles [8] and lead ions [15]. The data for He lie in the Bethe regime. Structure seems to be more pronounced at the lower of the two energies – as expected – but the difference is small. The measurements with lead ions fall clearly into the Bohr regime, and much more pronounced structure is indeed found at both energies, again with a somewhat greater effect at the lower energy as expected. However, lead ions carry electrons in this energy regime, and therefore, Bohr's formula cannot provide a quantitative estimate. More compelling evidence could be gained by performing similar experiments at energies about an order of magnitude higher.

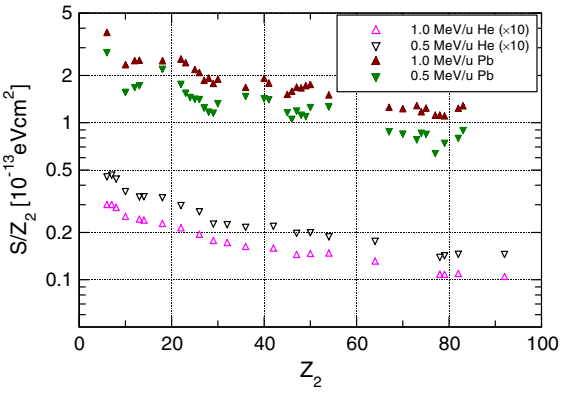

Fig. 1. Stopping cross section per target electron for 1.0 and 0.5 MeV/u Pb [15] and He [8] ions versus atomic number of the target material, from [3].

Measurements on deviations from Bragg additivity have been performed mostly with protons and alpha particles. Measurements with *bare heavy ions* to confirm or reject the trend toward more pronounced valence effects would be desirable.

5. Projectile screening

According to Bohr [13], swift ions carry electrons at energies up to $\simeq 0.025 Z^{4/3}$ MeV/u. In this energy regime the projectile interacts with the target electrons via *screened* Coulomb interaction. This results in a smaller contribution from distant interactions to stopping while the significance of close collisions is essentially unaffected.

The effective interaction range for a point charge is characterized by Bohr's adiabatic radius

$$a_{\mathrm{ad}} = \frac{v}{\omega}. \tag{7}$$

This quantity is largest for interactions with the outermost target shells. Hence, it is the contribution of the valence electrons to stopping that is most dramatically reduced by projectile screening. In other words, valence effects tend to decrease with increasing screening and hence to counteract the difference between Bethe and Bohr stopping mentioned above.

Experimental evidence to support these features is mainly indirect. While direct tests on the range of validity of Bragg additivity have been performed only with light ions, the mere assumption of Bragg additivity is known to allow reasonable predictions of stopping forces for heavy ions in numerous compounds [16]. Recent examples – using only theoretical input – have been given in [4].

Pronounced Z_2 structure is found in Fig. 1 despite heavy screening for lead ions. This does not necessarily imply a contradiction: measurements with bare ions as suggested above might well show an even more pronounced Z_2 structure.

Gas–solid differences have been found for heavy ions [17–19], but the stopping force in the solid is found to *exceed* that of the gas, while a valence effect would suggest the opposite because of increased binding in the solid. Indeed, this gas–solid difference is commonly ascribed to the well-known difference in equilibrium charge state of such ions [20].

6. Lower projectile speed

A more appropriate form of Eqs. (4) and (6) is

$$L = \sum_j f_j L_j, \tag{8}$$

where f_j is the oscillator strength of the jth shell ($\sum_j f_j = 1$). The stopping number L_j of the jth shell depends on the respective I-value I_j.

Let us initially retain the logarithmic form of L_j in Eqs. (4) and (6). Then, as the argument of the logarithm for the innermost shell approaches 1, that excitation channel becomes closed, and the stopping cross section is determined by the remaining shells. This tends to *enhance* valence effects on a relative scale.

However, L_j does not retain its logarithmic form, and additional physics enters via shell and Barkas–Andersen corrections.

6.1. Shell correction

The shell correction is determined primarily by the orbital motion of the target electrons. Its relative magnitude increases with decreasing speed, and it changes sign near the point where the logarithmic approximation approaches zero (Fig. 2).

The leading term in an asymptotic expansion reads [21,22]

$$\Delta L_j \sim -\frac{\langle v_e^2 \rangle_j}{v^2}, \tag{9}$$

where $\langle v_e^2 \rangle_j$ is the mean-square orbital velocity of an electron in the jth target shell. This quantity increases with increasing binding and hence increasing I_j. Since this contribution is negative, it *enhances* the effect of the I-value.

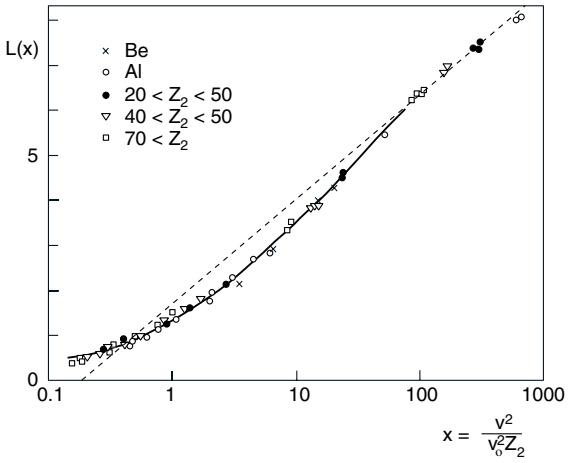

Fig. 2. Stopping number L for protons for a variety of materials. If Eq. (5) were valid, points would lie on one curve, from [2].

6.2. Barkas–Andersen correction

The Barkas–Andersen correction[2] accounts for terms uneven in the atomic number Z_1 of the projectile. The leading term is governed by the parameter

$$\frac{Z_1 e^2 \omega_j}{m v^3}, \tag{10}$$

i.e. the correction is positive for positively-charged projectiles and increases with increasing binding. Thus, it *opposes* the effect of the shell correction. The relative significance of the two corrections depends on Z_1 and Z_2. For light ions the shell correction tends to dominate, while for heavy ions the two corrections tend to be comparable in magnitude and thus may result in a rather small total correction [24].

For negatively-charged projectiles the Barkas–Andersen correction changes sign and hence *enhances* the effect of the shell correction. Therefore, valence effects should be particularly pronounced

[2] Addition of H.H. Andersen's name to Barkas' follows a recent recommendation [23].

for antiproton stopping which, for this reason, must be the preferred option to study these effects experimentally. This conclusion is strengthened further by the fact that antiprotons do not carry electrons. Hence, the screening effect, shown above to give rise to diminished valence effects, is absent in antiproton stopping.

7. A note on low-velocity stopping

There is common agreement on the fact that at projectile speeds well below the stopping maximum, excitation of valence electrons tends to dominate. While this implies that this regime is of interest in the present context, measurements are difficult, and theoretical concepts designed for higher velocities tend to break down [23].

Metal–insulator differences are of particular interest in this energy regime, where it is the lowest excitation levels that are expected to govern the stopping force.

Recent measurements were performed with protons and antiprotons on LiF [25,26]. Although there are differences between the proton data of the two groups, there is agreement on the absence of a threshold effect.

In the velocity range of those experiments, down to ~1 keV/u, the projectile speed is considerably lower than that of the valence electrons in the target. Hence, the maximum energy transfer in a single collision with a target electron is given by

$$T_{\max} \simeq 2mvv_e \quad \text{for } v \ll v_e, \tag{11}$$

where v_e is a characteristic speed of the valence electrons.

In a conductor, v_e may be identified with the Fermi velocity, and since there is no energy gap, the ion transfers energy to conduction electrons even at very low speed. For insulators, on the other hand, it has been suggested that a major drop should occur as $T_{\max}$ passes below the lowest excitation level.

While we do not intend to deny the possibility of a threshold effect, a simple classically-based argument indicates that such a threshold could well lie at a considerably lower speed, the reason being that a bound electron can be hit several times by a slow ion. Therefore, the total energy picked up from the ion may well exceed $T_{\max}$.

For simplicity, consider a one-dimensional system with an electron bound harmonically, resonance frequency ω and oscillation amplitude $A = v_e/\omega$, v_e being the velocity amplitude. An ion passing by at a speed v interacts with the electron over a time interval $\tau \sim 2A/v$. The total number of interactions is, therefore, given by

$$2\tau \cdot \frac{\omega}{2\pi} \simeq \frac{2}{\pi}\frac{v_e}{v}. \tag{12}$$

While considerable caution is indicated with regard to further going conclusions from such a simple, classical and one-dimensional estimate, it is clear that energy losses exceeding $T_{\max}$ as given above cannot be excluded on the basis of an argument based on free binary collisions.

8. Summary

Explicit claims made in this note refer to swift ions, i.e. projectile speeds above the Bohr velocity. While it makes little sense to compare the magnitude of Z_2 structure with that of deviations from Bragg additivity, trends are predicted to be very similar for the two phenomena.

- As a rough guide, if one is interested in studying pronounced valence effects, experiments ought to be performed with antiprotons or with weakly-screened ions such as protons or heavier ions at velocities $v > Z_1^{2/3}v_0$ but not much higher.
- Conversely, if one is interested in minimizing valence effects, screened ions should be employed. Very little direct evidence appears available to experimentally support this central feature.
- Ionic compounds or ionic crystals such as LiF are particularly suitable candidate materials because of small Z_2 and large differences in binding energies. The main challenge here is getting experimental stopping data on the elements.
- For the study of gas–solid differences, antiprotons ought to be particularly useful to separate valence from charge-state effects which seem to dominate for positive ions.

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