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Calculating electronic stopping power in materials from first principles☆

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ABSTRACT

From the early models of electronic stopping power to the current first principles simulations, the techniques evolved to increase the range of validity and to reduce empiricism. Thanks to a combination of theoretical advances provided by Time Dependent Density Functional Theory and the development of numerical codes, it is currently possible to predict electronic stopping power for realistic materials by performing direct simulations of the electron excitation processes beyond linear response, and including electronic band structure effects. Electronic stopping power is an important quantity used to predict and understand the effects of particle radiation in matter. First principles calculations of electronic stopping power can be applied to any atomistic system, solids, liquids and alloys. This review aims to help graduate level students and researchers immerse themselves into state-of-the-art techniques to computationally model and calculate electronic stopping power.

1. Introduction

Stopping power is a measure of the ability of a material to slow down energetic particles that travel in its interior. Given a certain type of energetic particle and a target material, stopping power is the amount of kinetic energy lost in relation to the thickness of material traveled. Stopping power is an important quantity used to predict and understand the effects of particle radiation in matter, ion ranges [1], the energy deposited, and ultimately the damage produced by energetic particles in diverse contexts, such as nuclear technology [2] and medicine [3]. The phenomenon of stopping power also gives us a glimpse on how matter reacts far from equilibrium, and in particular on the nature of the dynamic interaction between ions and electrons.

Stopping power is a general concept, although the term is normally utilized for charged particles (ions or electrons), interacting coulombically with the material medium. The stopping power depends on the type of charged particle or projectile (usually some ionized atom), the target material or host (phase, density and temperature conditions), and, all other things being equal, it depends on the kinetic energy (typically in keV or MeV) or equivalently in the velocity of the charged particle (typically in Å/fs or $a_0 E_h/\hbar$). In crystalline materials, there is an additional dependency on the relative orientation of the crystal with respect to the main projectile velocity direction [4]. This orientation dependency is natural if we think of the stopping power as an effect that arises from interactions taking place at atomic scales, specifically by a collection of sequential or simultaneous many-body Coulomb collisions.

Microscopically, this energy loss is the effect of a retarding force due to collisions with particles that compose the material. Therefore, stopping power is dimensionally a force and commonly expressed in units of energy over distance (for example, in electronvolt per angstrom eV/Å or hartree per Bohr radius E_h/a_0).

Our understanding of materials at the atomic scale consists in modeling, at different levels of detail, the dynamics and structure of atoms (ions) and electrons. Due to the vastly different individual masses, ions and electrons behave very differently. Many properties of materials can be explained to an acceptable degree by using the theory of classical mechanics for the ions and of quantum mechanics for electrons [5,6].

At normal conditions for a material, its ions move relatively slowly, with characteristic particle thermal and sound velocities in excess of 10^3 m/s, while electrons are relatively fast, with effective Fermi velocity v_F (for valence or conduction electrons) in the order of 10^6 m/s. Naturally, this defines two regimes for the stopping process (Fig. 1): One at low velocity, the *nuclear stopping* regime; in which the charged particle mainly loses energy through an effective interaction with the host ions (while the electrons respond instantaneously without undergoing noticeable excitations), and another regime at high velocity, the *electronic stopping* regime; in which the charged particle loses energy by partially screened Coulomb interactions with the electrons while the host ions simply have no time to react due to their large inertia (mass). In both regimes, the charged particle interacts equally with electrons and ions (through Coulomb forces), the main difference is the precise dynamical process involved in the energy loss (screened lattice excitations *vs.* electronic excitations, respectively).

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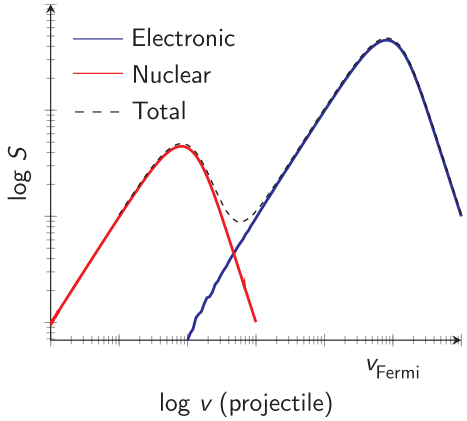

Fig. 1. Qualitative picture of stopping power as a function of projectile velocity. At high velocities, when the projectile travels at speeds comparable to those of the electrons, the electronic stopping power dominates. At low velocity nuclear stopping becomes relatively more important depending on the type of projectile.

As long as the effective atomic interactions are known, nuclear stopping can be modeled by classical ion-ion interactions. Pure nuclear stopping is, from a theoretical standpoint, a solved problem; in practice, all the difficulties that remain are reduced to the calculation of the effective interactions (e.g. *ab initio* potentials [7] and ZBL potentials [8]). Meanwhile, electronic stopping power requires a different level of description and modeling.

In this brief review, my aim is to help graduate level students and researchers immerse themselves into state-of-the-art techniques to computationally model and calculate *electronic stopping power*; giving a glimpse of the type of capabilities that these techniques provide.

Radiation effects in materials is a challenging scientific problem [9], since it ranges from the behavior of electrons and atoms under non-equilibrium damage events to the macroscopic impact of those defects, spanning length and time scales that range over many orders of magnitude [2]. Electronic stopping power is one aspect of the radiation effects, that sits at the smallest time (fs) and length scale (nm).

2. History and analytic models

The calculation of electronic stopping power predates the inception of quantum mechanics, and it is intimately related to its development. For example, the Rutherford landmark experiment (1911), where the deflection of alpha particles passing through a thin gold film was measured, can be viewed as a stopping power experimental setup [10]. In this crucial experiment, the structure of the atom was probed and the coulombic nature of the interaction between the charged particle and a relatively massive central nucleus was revealed. By extension, the coulombic nature of the electrons bound to atoms was also accepted. Other historical reviews are available in the literature [11,12]; the review presented here simply paves the way for the following sections that describe the theory and results of the new methods for the calculation of electronic stopping power.

The early models of the atom and the electrons therein were entirely or partially classical [13], and the first stopping power models for atoms in solids were no different. After the early attempts of Rutherford [10], Thomson [14], and Darwin [15], Hans Bethe (1930) derived an electronic stopping power model by imagining the material as a collection of classical electrons that, in this picture, are somehow not bounded and initially static [16,12]. In this model, the interaction between the projectile and the material's electrons produce a sequence of binary Coulomb collisions in which the projectile loses energy, since each collision transfers energy to the host electrons. Each binary collision is elastic (for the system projectile-electron); however, since the projectile always finds new electrons at rest which to push forward, the final result looks like an inelastic effect producing an average retarding force on the projectile.

Coulomb scattering (Rutherford scattering) is characterized by long range interactions and by formally diverging cross sections. This makes Bethe's picture impractical to apply directly, since the incoming projectile would simultaneously interact with all electrons in the material, and stopping power would result to be a diverging quantity. In the real system, several phenomena conspire against this divergence. First, the interaction is many-body; electrons dynamically screen each other defining a length scale (Debye length) that cuts-off the long range interaction. Second, electrons are not free particles; there is a minimum excitation energy (I) required for the electrons to be freed from their discrete (e.g. quantum) bound states. Collectively, these types of cutoffs are called Coulomb logarithms [17]. The former cutoff is important in plasmas, the latter is more important in materials.

Taking into account the minimum excitation energy, the Bethe formula for the electronic stopping power S as a function of velocity v resulted in:

$$S(v) = \frac{4\pi n}{m_e v^2} Z^2 k_e^2 e^4 \log\left(\frac{2m_e v^2}{I}\right). \tag{1}$$

However crude, the Bethe formula sets up the language commonly used to describe electronic stopping power [12]. First, the stopping is in direct relation to the density of electrons n and the charge of the projectile $|Z|$. Second, it establishes an inverse proportion with v^2 at large velocities, which is the correct non-relativistic limit (m_e and e are the mass and charge of the electron, $k_e = \frac{1}{4\pi\varepsilon_0}$ is the Coulomb's constant.) The formulation can be straight forwardly extended to relativistic regimes [12] and it is derived purely classically, except for the quantity I. I (with units of energy) could introduce effectively the physics of screening and quantum mechanical effects. The formula diverges (to negative values!) when $v < \sqrt{I/2m_e}$, defining its own lower bound for the range of validity.

For the low velocity limit, a separate formula was found by Fermi and Teller (1947) [18]

$$S(v) = Z^2 \frac{2v}{3\pi} m_e \frac{k_e^2 e^4}{\hbar^3} \log(\pi \hbar v_F k_e e^2). \tag{2}$$

The expression is linear in v and, therefore, must breakdown presumably near $v \gtrsim v_F$, yet for the first time it takes into account the degenerate nature of electrons.

Ambiguities appear when these formulas are interpreted to be applied to a real material. For example, n can be interpreted to be the *all-electron* density or just the *valence-electron* density; and Z could be the charge of the bare ion (atomic number) or some charge resulting from partial ionization (effective charge). Additionally, these two quantities could be functions of the velocity themselves ($Z(v)$ and $n(v)$); as it is expected that the number of participating electrons and the effective charge changes continuously with the velocity [19]. These parameters, in the context of analytic models, are usually flexibly or empirically interpreted for different experiments and regimes.

Historically, models evolved to increase their range of validity of the model and to reduce this empiricism, culminating in the *first principles* calculations of the electronic stopping power that I will describe in the next section. The first milestone in this path was the general linear-response treatment by Lindhard (1963) [20,21]. In his seminal papers, Lindhard demonstrated that the retarding force can be calculated from the interaction of a moving ion with the density perturbation that itself produces in an electron gas. The Lindhard stopping formula for the homogeneous electron gas depends on a linear dielectric response ε [22].

$$S(v) = 2Z^2 \frac{e^2}{\pi v^2} \int_0^\infty \frac{dk}{k} \int_0^{kv} \omega d\omega \Im\left(\frac{-1}{\varepsilon(k,\omega)}\right) \tag{3}$$