Electronic stopping powers for low projectile velocities

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Previously we have discussed the shell corrections to electronic stopping which may be calculated from momentum distributions obtained from numerical atomic wave functions. In that case, the lower limit for particle velocity was determined by the largest orbital mean excitation energy for the system. Here we discuss the extension of these calculations to the kilovolt region of projectile velocity, and report stopping powers, stopping numbers, and shell corrections for various cases. Trends across the first two rows of the periodic table are discussed, and the low-velocity limiting behavior of the stopping power and stopping number is considered.

I. INTRODUCTION

Previously[1] we have described the calculation of electronic stopping powers based on a kinetic theoretical description[2] of projectile scattering from scatters with a velocity distribution obtained from a numerical atomic wave function. The calculation was restricted, however, by the requirement that projectile energies exceed the highest orbital mean excitation energy for the material in question. For most materials beyond the first row of the periodic table, this occurs at proton energies of several MeV (velocities of tens of atomic units), and excludes the region of the stopping power curve where its maximum is found, the kilovolt range of particle energies, and the limiting behavior of the stopping power as the projectile velocity tends to zero. In the present communication these calculations are extended to low projectile energies. We will, in Sec. II, present the outline of the theory and the method of calculation, and then discuss the low-energy shell corrections to the stopping power, the low-energy limiting behavior of the stopping power and its implications, and the relative orbital contributions to the stopping number.

II. MODEL AND COMPUTATION METHOD

In the standard development[3] of the theory of electronic stopping, the stopping power of a material is related to the stopping cross section $S(v)$,

$$-\frac{dE}{dx}=nS(v)\ , \tag{1}$$

where n is the particle density and

$$S(v)=\frac{4\pi e^4 Z_1^2 Z_2}{mv^2}L(v)\ . \tag{2}$$

Here v is the projectile velocity, and Z_1 and Z_2 are the nuclear charges of the projectile and target particles, respectively. For impinging protons, to which we will restrict ourselves, and in atomic units,

$$L(v)=\ln\left[\frac{2v^2}{I}\right]-\frac{C(v)}{Z_2}\ , \tag{3}$$

where relativistic, density, and the higher-order Barkas[4] (Z_1^3) and Bloch[5] (Z_1^4) corrections have been neglected. The mean excitation energy I has its usual meaning[1] and C/Z_2 in the total shell correction.

We have previously shown[1] that one obtains very good shell corrections to the stopping power if one treats the system in a shellwise fashion. We define orbital mean excitation energies I_k by requiring that the total mean excitation energy be split up as

$$\ln I=\frac{1}{Z_2}\sum_k w_k \ln I_k\ , \tag{4}$$

and that the corresponding orbital weights[6] are

$$w_k=\tfrac{1}{2}n_k(1+f_k)\ , \tag{5}$$

where the n_k are occupation numbers and the $n_k f_k$ are the total oscillator strengths of all optical transitions from shell k into unoccupied levels (continuum and discrete).[7] When one introduces these notions into Sigmund's kinetic theory[2] one obtains an expression for $L(v)$

$$L(v)=\sum_k L_k(v)\ , \tag{6}$$

which consists of shellwise contributions of the sort

$$L_k(v)=\tfrac{1}{4}\int_0^\infty dv_2\rho_k(v_2)v_2 \times\int_{|v-v_2|}^{v+v_2} dv_1 L_k^{(0)}(v_1)\left[1+\frac{v^2}{v_1^2}-\frac{v_2^2}{v_1^2}\right]\ , \tag{7}$$

where $\rho_k(v_2)$ is the electron velocity distribution in the kth orbital, normalized to unity, and $L_k^{(0)}(v)$ is the stopping number for a system where the scatterers are at rest.[1,2] Thus given an electron velocity distribution, a set of orbital mean excitation energies and weights, and a form for $L_k^{(0)}$, we should be able to calculate stopping numbers directly.

The electron velocity distributions used in the calculations reported here are obtained from the fast Fourier transform[8,9] of numerical Hartree-Fock *atomic* wave

functions generated by the Froese Fischer program[10] (MCHF77). The consistent sets of orbital mean excitation energies were, as in our previous work,[1] taken from the tables of Inokuti and co-workers.[11,12] It is thus a pure atomic theory. No solid-state effects are included.

We have chosen $L_k^{(0)}$ to be the (orbital) Bethe term[13] without shell corrections

$$L_k^{(0)}(v)=\frac{w_k}{Z_2}\ln\frac{2v^2}{I_k} . \tag{8}$$

This should be a valid form as the Bethe formula derives from the first Born approximation, valid when the projectile velocity is large compared with the velocity of scatterers, an assumption which, in fact, holds for $L_k^{(0)}$ since, as explained after Eq. (7), $L_k^{(0)}$ is the stopping number for scatterers at rest. Indeed, this choice has been shown to give good results for C/Z_2 for swift particles.[1,2] There are, however, several other possibilities, such as the classical Bohr[14] expression

$$L^{(0)}=\ln v^3+\text{const} . \tag{9}$$

As it is expected that most stopping will be accomplished by the outer electrons in the case of low projectile velocity, we have chosen to implement the Bethe expression in a shellwise manner, that is,

$$L_k^{(0)}(v)=\frac{w_k}{Z_2}\ln\left[\frac{2v^2}{I_k}\right]\Theta(v-\alpha_k) , \tag{10}$$

where

$$\alpha_k=(I_k/2)^{1/2} . \tag{11}$$

It should be noted that even though $L_k^{(0)}(v)$ becomes zero for $v<\alpha_k$, there is still a contribution to the integral in Eq. (7) since v_1 becomes the integration variable. Thus we shall carry the integration down to low v, in contrast to previous work[1] where $L(v)$ was computed only for $v\geq\max\{\alpha_k\}$ for the atom in question.

In the case of high projectile velocities, $L(v)$ [cf. Eqs. (6) and (7)] can be expanded[1,2] in moments of averages of powers of the target electron velocity, and the expansion has been shown[1] to converge well in this limit. In the case of low projectile velocity, and for $v\leq\min\{\alpha_k\}$ an appropriate expansion can also be made:[2]

$$L_k(v)\cong\frac{w_k}{Z_2}\sum_{n=1}^{3}\frac{2}{2n+1}v^{2n+1}\langle v_2^{-(2n+1)}\rangle_{\alpha_k} , \tag{12}$$

where

$$\langle v^{-m}\rangle_{\alpha_k}=4\pi\int_{\alpha_k}^{\infty}v_2^{-m}\rho_k(v_2)dv_2 . \tag{13}$$

Thus

$$S_k(v)=8\pi w_k\left[v\frac{\langle v_2^{-3}\rangle_{\alpha_k}}{3}+v^3\frac{\langle v_2^{-5}\rangle_{\alpha_k}}{5}+\cdots\right] . \tag{14}$$

One would, then, since all terms in this series are positive, expect the stopping cross section to start off as a linear function of v and deviate in a positive manner at large v. Such deviations have indeed been reported[15] for low-energy stopping of heavy particles on gold foils.

We now have a framework in which we may compute electronic stopping properties. It should be noted, however, that we consider only the *electronic* stopping component of the total stopping at low projectile velocities. The nuclear stopping, which becomes important only at very low velocity, has been ignored and reactive scattering, stripping, screening, and the like, which may also become important at low projectile velocities, are not included either. There are several measurements and predictions against which we can test the results of this scheme,[16] some of which are presented below.

III. SHELL CORRECTIONS AND STOPPING NUMBERS

The experimental shell corrections[17] and the results obtained by this scheme for Ne, Ar, and Kr are presented in Figs. 1–3. In order to compare theoretical and experimental shell corrections, some account must be taken of the Barkas and Bloch terms, which are not included in the calculations. Using the notation of Besenbacher *et al.*,[17] one should compare experimental shell corrections $(C_2/Z_2)_{\text{expt}}$ to "apparent" theoretical shell corrections:

$$(C/Z_2)^*_{\text{theor}}=(C/Z_2)_{\text{theor}}-L^1-L^2 , \tag{15}$$

where the calculated values are $(C/Z_2)_{\text{theor}}$, and L^1 and L^2 are the Barkas and Bloch corrections, respectively. Equivalently, we have plotted $(C/Z_2)_{\text{expt}}+(L^1+L^2)$ and $(C/Z_2)_{\text{theor}}$.

The estimates of the Barkas and Bloch corrections as a function of velocity were taken from Besenbacher *et al.*,[17] and are obtained from qualitative theoretical considerations and thus include some uncertainties.[18] In addition, there is some scatter in the data, of the order of 0.05. On the whole, however, the agreement is good. The theoreti-

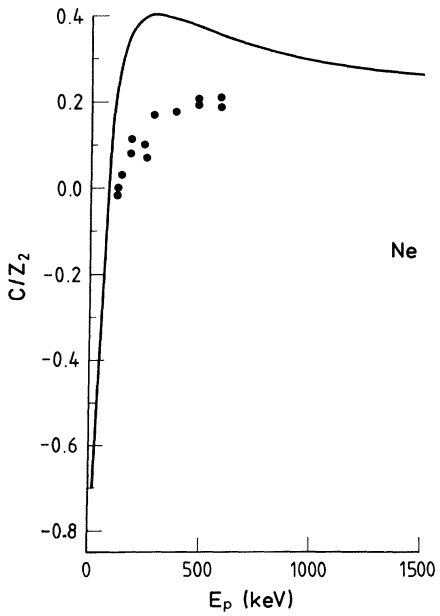

FIG. 1. Shell correction for Ne (——) as calculated in this work and experimental data (●) from Besenbacher *et al.* (Ref. 17) vs projectile energy in proton keV.

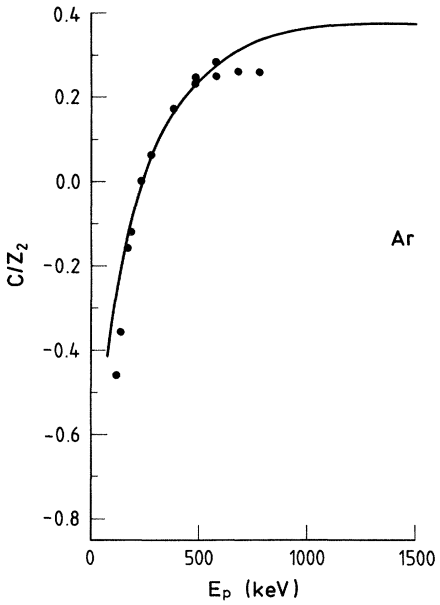

FIG. 2. Shell correction for Ar (——) as calculated in this work and experimental data (●) from Besenbacher *et al.* (Ref. 19) vs projectile energy in proton keV.

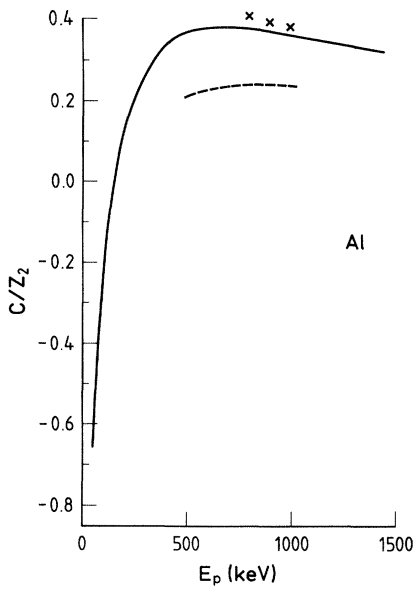

FIG. 4. Theoretical shell corrections for Al as calculated in this work (——) and by Bonderup (Ref. 19) (— — —) vs projectile energy in proton keV. Experimental points (×) are from Andersen *et al.* (Ref. 20).

cal results presented here are also in good agreement with those of Bonderup.[19] Although the low-energy data are not so extensive for aluminium, a similar plot (Fig. 4) shows agreement with the experimental data of Andersen *et al.*[20] in the several hundred kilovolt range. The experimental data are more reliable for Al than for the three other atoms since for Al the Barkas and Bloch corrections are determined experimentally by varying Z_1 of the projectile. The results of Bonderup are also presented for comparison.

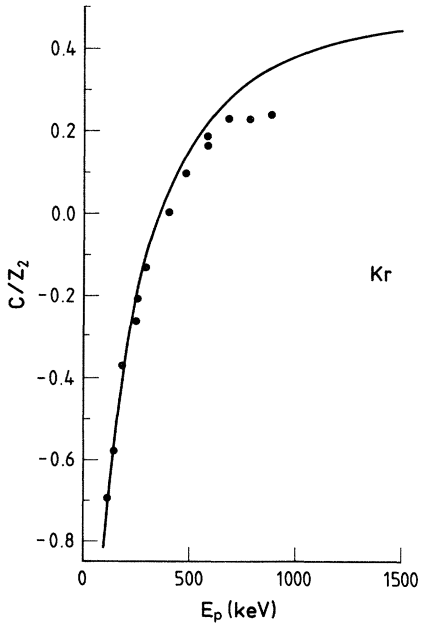

FIG. 3. Shell correction for Kr (——) as calculated in this work and experimental data (●) for Besenbacher *et al.* (Ref. 17) vs projectile energy in proton keV.

The low-velocity limiting behavior of the stopping number $L(v)$ and the stopping cross section $S(v)$ can be obtained from the low-velocity expansion given in Eqs. (12) and (14). Thus if we denote the quantities calculated by a two-term expansion with a tilde, we see

TABLE I. Range of validity of the low-velocity expansion of $S(v)$ in Eq. (17).

Atom	v_{10}[a]	I_k[b]
H	0.3	0.551
He	0.7	1.427
Li	0.1	0.121
Be	0.2	0.269
B	0.4	0.424
C	0.5	0.771
N	0.5	1.201
O	0.6	1.714
F	0.7	2.310
Ne	0.8	2.990
Na	0.1	0.090
Mg	0.1	0.163
Al	0.2	0.178
Si	0.3	0.326
P	0.3	0.504
S	0.5	0.947
Cl	0.4	0.712
Ar	0.5	1.211
K	0.1	0.059
Ca	0.1	0.099
Br	0.3	0.725
Kr	0.4	0.875

[a]See text for definition; velocity in a.u.
[b]The smallest I_k for the atom; in a.u.

TABLE II. Orbital contribution to $S(v)$ at low projectile velocity for Al.

	% orbital contribution				
v^a	1s	2s	2p	3s	3p
0.5	0.02	0.47	1.38	52.19	45.94
1.0	0.03	0.81	2.23	54.12	42.81
1.5	0.07	1.65	4.22	53.01	41.05
2.0	0.12	3.00	7.14	51.28	38.46
2.5	0.19	4.65	10.62	49.02	35.52
20.0	6.14	11.90	44.68	22.56	14.72

[a]In a.u.

$$\tilde{S}(v)=\sum_k \tilde{S}_k(v) , \tag{16}$$

$$\tilde{S}_k(v)=\frac{8\pi w_k}{3}v\langle v_2^{-3}\rangle_{\alpha_k}+\frac{8\pi w_k}{5}v^3\langle v_2^{-5}\rangle_{\alpha_k} . \tag{17}$$

The moment integrals were done by Simpson's-rule integration of the numerical orbital velocity density $\rho_k(v)$.[1,8] A correction is made when α_k falls between two grid points. A linear interpolation scheme using only the two "neighboring" grid points is used. The maximum correction occurs when α_k is large compared to the maximum in $\rho_k(v)$, i.e., for H for which the correction is about 1%.

The expansion, Eq. (17), should be valid only for low projectile velocities, that is, the projectile need have low velocity compared to the lowest orbital electron velocity,

$$v_{\text{proj}} \ll (2E_k^{\text{kin}})^{1/2}=\langle v_k\rangle , \tag{18}$$

where k refers to the highest-energy (valence) orbital, and E_k^{kin} is the kinetic energy of a k-shell electron. Thus the expansion should be valid only in the projectile (proton) energy range of a few decades of kilovolts, or velocities of a fraction of an atomic unit. The peak in proton stopping powers is typically in the 100 kilovolt range, so the power expansion is valid only considerably below this energy. Indeed, if we ask for the velocity (v_{10}) at which $S(v)$ [calculated directly via Eqs. (2), (6), (7), and (9)] and $\tilde{S}(v)$ [from Eqs. (13), (16), and (17)] differ by approximately 10%, it appears that the expansion quite quickly deviates from the correct result (see Table I). It is clear that the deviation is governed by the lowest mean ionization potential I_k of the atom, and that the lower this is, the more restricted is the ambit of validity of the expansion. As the orbital mean excitation energy varies across each period, so does the range of validity of the expansion, with the greatest range occurring at the rare-gas end of each period. The greatest range comes at Ne, and even here the expansion is valid only to a projectile energy of approximately 25 proton keV.

In Fig. 5 we present the deviation of $\tilde{S}(v)$ from $S(v)$ for the orbitals of Al, and it is apparent that the outer orbitals, those with the lowest $I_k(\alpha_k)$ deviate first. However, it is just those outer obitals which contribute most to $S(v)$, as can be seen in Table II. In general, nearly 90% of the stopping at low velocity is due to the valence shell. As ex-

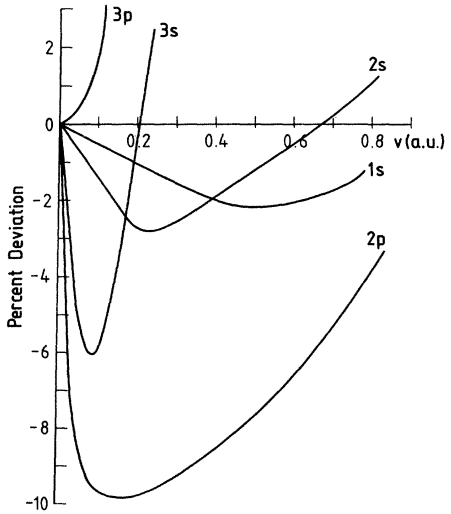

FIG. 5. Percent deviation of the two-term expansion $\tilde{S}(v)$ [Eq. (17)] from $S(v)$ for the shells of Al, calculated as $100[\tilde{S}(v)-S(v)]/S(v)$.

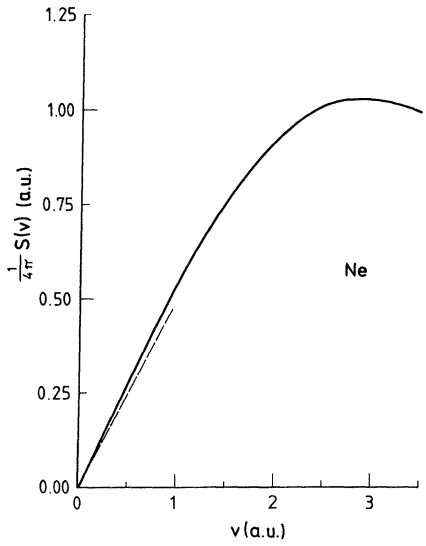

FIG. 6. Stopping cross section, $(1/4\pi)S(v)$ vs v for Ne. Linearity is indicated by the dashed line.

pected, the inner shells contribute more to the high-velocity stopping, as can be seen from the single large-velocity ($E_p = 10$ MeV) entry in the table.

As discussed in connection with Eq. (14) one might expect $S(v)$ to start as a linear function of v and thereafter to experience positive deviations from linearity. Moak *et al.*[15] have indeed found such deviations in some heavy-ion work, but the question remains as to whether or not the effect is general. Because of the poor range of validity of the low-velocity expansion [Eq. (17)], it can serve no predictive value here. It does serve to indicate, however, that such an effect might be most likely found in cases where the range of validity is largest, since it is here that the v^3 terms may have had a chance to grow to a significant fraction of the linear terms in $S(v)$. A full calculation not utilizing the power-series expansion on Ne is presented in Fig. 6, and indeed a small positive deviation from linearity is observed before the maximum ($E_p = 100$ keV). For aluminium, on the other hand, the expansion has a very short range of validity (see Table I) and (Fig. 7) no positive deviation from linearity is observed. One need beware in comparing with experiment, as the present results apply to atoms, and one finds sizable gas-solid differences in low-energy stopping.[21,22]

IV. Z_2 OSCILLATIONS

The oscillations of $S(v)$ at constant v with the atomic number of the target particle is a well-known phenomenon[23,24] and is apparently due to an oscillatory behavior in both I_k and in the velocity (momentum) density of the outer electrons, which contribute most to the stopping number and cross section[1] (see also Table II). The orbital I_k determines the lower limit of the velocity moment integrals in the expansion formula [Eq. (7)] via

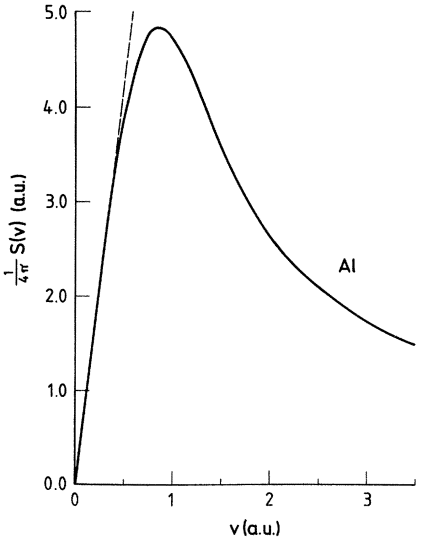

FIG. 7. Stopping cross section, $(1/4\pi)S(v)$ vs v for Al. Linearity is indicated by the dashed line.

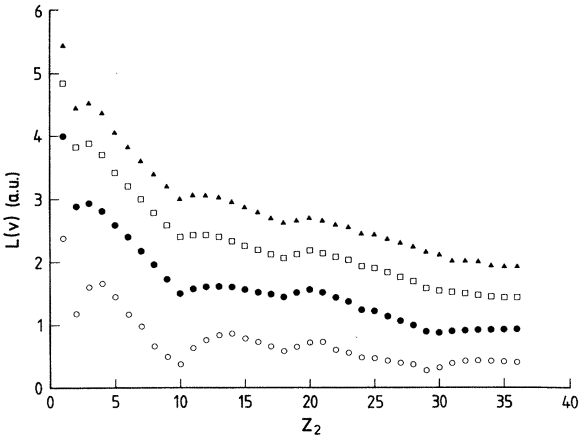

FIG. 8. Stopping number $L(v)$ vs Z_2 the atomic charge of the target atom, at projectile velocities of 2 a.u. (○), 4 a.u. (●), 6 a.u. (□), and 8 a.u. (▲).

$L_k^{(0)}$ [Eq. (10)]. In any case, the variation in I_k as one progresses across the periodic table would be expected to give rise to oscillations which decrease in amplitude as the velocity increases. In Fig. 8 we present $L(v)$ vs Z_2 for four projectile velocities in the 100 kilovolt range, and the structure is as expected. If we compare (Fig. 9) Z_2 oscillation in the whole atom mean ionization potential I [see Eq. (4)] with the Z_2 structure of $L(v)$ it is seen that the variation in $L(v)$ parallels that in I.

V. CONCLUDING REMARKS

We have presented here a computational scheme which is based on Sigmund's[2] kinetic theory of stopping and which utilizes high quality, quantum-mechanical, electron velocity distributions for the scatterers. From this, we extract low-velocity electronic stopping cross sections and shell corrections. These seem to reproduce both the qualitative and quantitative experimental results reasonably well.

The moment expansion of $S(v)$ at low velocity is shown to have a low range of validity ($v < v_0$), but it does indicate that positive deviations from initial linearity[15] of $S(v)$

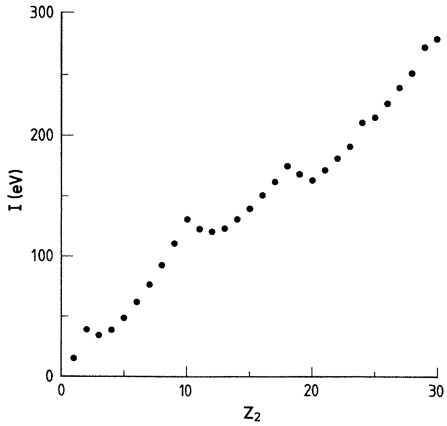

FIG. 9. Total mean excitation energy (from Inokuti, Ref. 11) vs Z_2.

are possible. Calculations not utilizing the series expansion show that Ne might indeed show this behavior, while it is not expected for atomic Al. Since I_k for the valence shell, as shown by Shiles *et al.*,[25] is considerably larger for metallic Al than for atomic Al, the validity range of the low-velocity expansion is extended considerably for the metal and it is plausible that *metallic* Al may show a positive deviation from linearity at low velocities. Finally, we find that the oscillations of $L(v)$ with Z_2 for constant v parallel those in I.

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