Low-energy proton stopping power of N_2, O_2, and water vapor, and deviations from Bragg's rule

Y. J. Xu and G. S. Khandelwal

Department of Physics, Old Dominion University, Norfolk, Virginia 23508

J. W. Wilson

NASA Langley Research Center, National Aeronautics and Space Administration, Hampton, Virginia 23665

A modified local-plasma model, based on the works of Lindhard and Winther, and Bethe, Brown, and Walske is established. The Gordon-Kim model for molecular-electron density is used to calculate stopping power of N_2, O_2, and water vapor for protons of energy ranging from 40 keV to 2.5 MeV, resulting in good agreement with experimental data. Deviations from Bragg's rule are evaluated and are discussed under the present theoretical model.

Recently, departures from Bragg's rule have been noticed in the theoretical calculations of the mean excitation energies of various molecular systems.[1,2] Analysis of the experimental data on energy loss of low-energy α particles in gases also indicates deviations from Bragg's rule.[3-5] In this paper, the stopping power theory of Lindhard and Winther,[6] and the local plasma theory of Lindhard and Scharff,[7] are used to perform calculations in the low-energy region. Modifications are introduced through a simplifying model which incorporates the effects of the shell corrections and of the screening of the projectile. The model is justified on the basis of fulfilling the more ambitious aim of obtaining the molecular stopping power. The Gordon-Kim[8] electron density model of molecular wave functions is utilized in the calculations. Such a model, as is known, allows a successful method of calculating chemical bond effects. Calculations done on N_2, O_2, and water vapor are found to be in fair agreement with experiments. Furthermore, departures from the Bragg's rule are noticed for all these systems.

The celebrated stopping-power formula for an energetic charged particle of charge ze and velocity v, traversing matter of charge number Z is given by

$$-\frac{dE}{dx} = \frac{4\pi z^2 e^4}{mv^2} NZL \ , \tag{1}$$

where m is the mass of an electron and N the number of atoms per unit volume of the medium.

The stopping number L of Eq. (1) has been a topic of considerable study. For instance, Lindhard and Winther have investigated the function L for a free-electron gas in the regions of low- and high-energy incident charged particles. These authors give for the high-energy case, the expression for L to order $1/v^2$ as

$$L = \ln Y - \frac{\langle T \rangle}{\frac{1}{2} mv^2} \ , \tag{2}$$

where $Y = 2mv^2/\hbar\omega_p$, the classical plasma frequency $\omega_p = (4\pi\rho e^2/m)^{1/2}$, ρ is the electron density, and $\langle T \rangle$, the average kinetic energy, is given by

$$\langle T \rangle = (\tfrac{3}{10}) mv_F^2 \ ,$$

where v_F is the Fermi velocity.

For the low-energy case, they give

$$L = \left(\frac{\chi^2}{3}\right)^{3/4} Y^{3/2} C_1(\chi) \ , \tag{3}$$

where

$$C_1(\chi) \frac{1}{2[1-(\chi^2/3)]^2} \left[\ln \frac{1+\frac{2}{3}\chi^2}{\chi^2} - \frac{1-\frac{1}{3}\chi^2}{1+\frac{2}{3}\chi^2} \right] \ ,$$

TABLE I. Proton stopping cross-section values (in units of 10^{-15} eV cm^2) per atom. These were obtained by dividing by two, the stopping cross section per molecule of the oxygen molecule.

E (keV)	Theoretical values of the present paper	Curve-fitted values, Andersen and Ziegler (Ref. 14)	Experimental results Reynolds *et al.* (Ref. 15)	Langley (Ref. 16)
40	15.89	14.6	15.2 ± 2.6	· · ·
80	17.48	17.0	17.25 ± 2.6	· · ·
100	17.43	17.0	17.17 ± 2.6	· · ·
300	11.84	11.9	11.99 ± 1.7	· · ·
500	8.92	8.8	8.84 ± 1.7	· · ·
1037	5.64	· · ·	· · ·	5.25
2591	2.97	· · ·	· · ·	2.85

TABLE II. Proton stopping cross-section values (in units of 10^{-15} eV cm^2) per atom. These were obtained by dividing by two, the stopping cross section per molecule of the nitrogen molecule.

E (keV)	Theoretical values of the present paper	Curve-fitted values, Andersen and Ziegler (Ref. 14)	Experimental results Reynolds et al. (Ref. 15)	Langley (Ref. 16)
40	17.20	16	17.1 ± 2.6	· · ·
80	18.41	17.9	18.5 ± 2.6	· · ·
100	17.79	17.7	17.9 ± 2.6	· · ·
300	10.85	11.2	11.2 ± 1.7	· · ·
500	8.10	8.1	8.08 ± 1.7	· · ·
1037	5.20	· · ·	· · ·	4.78
2591	2.71	· · ·	· · ·	2.56

with

$$\chi^2 = \frac{e^2}{\pi \hbar v_F}, \quad \hbar = \frac{h}{2\pi} \ .$$

Equation (2) for the L function warrants some discussion. First, one notes that the L function of Eqs. (2) and (3) are derived by Lindhard and Winther for a free-electron system. Transition to an atomic system of the first term of Eq. (2), as studied widely, is accomplished under the so-called local-plasma model in which density $\rho(\vec{r})$ is evaluated by using quantum-mechanical wave functions. The local-plasma model is equivalent to replacing the molecular dipole oscillator strengths by the corresponding classical plasma absorption spectrum. The adequacy of such a replacement was recently shown by Johnson and Inokuti[9] to be most accurate for evaluating atomic quantities associated with stopping power in spite of differences between the plasma spectrum and the actual oscillator strength distribution. A quantum-mechanical analog of the second term of Eq. (2) would be of interest. In this context, a result first derived by Brown would prove to be useful. Brown[10] studied the K-shell asymptotic stopping power of an hydrogenic system (with two K electrons) for a fast projectile, taking the maximum momentum transfer equal to $2mv$ as if the electron was free. The asymptotic stopping power equation obtained by Brown can be expressed in a form similar to the Eq. (2). The first terms of both these equations, since they involve the mean excitation energy, can be assumed essentially equivalent within the local-plasma approximation. He obtained for the second term in Eq. (2) for a hydrogenic system, the quantity $1/\eta_s$, where $\eta_s = \frac{1}{2}mv^2/Z_s^2 R$, where Z_s is the effective nuclear charge for the s shell ($s = K, L, \ldots$)

and R is the Rydberg constant. Walske,[11] on the other hand, took the upper limit for momentum transfer to be infinity, thus overestimating the nuclear momentum recoiling and obtained instead $2/\eta_s$. In reality, however, due to the recoiling of the nucleus the result should be expected to fall somewhere between $1/\eta_s$ and $2/\eta_s$. This fact will be incorporated later [see Eq. (6)] as a parameter which we later estimate. At the present, however, for the sake of simplicity, combining Brown's result for the K shell with Walske's result for the L shell,[12] but retaining the consistency with the free-electron model, we write the analogous second term (known as shell correction) for a hydrogenic system with Z electrons as

$$C = C_{K,\text{total}} + C_L = \frac{1}{\eta_K} + \frac{1}{\eta_L}\left(\frac{Z-2}{8}\right) , \tag{4}$$

which can be rewritten for a real atom as

$$C = \frac{1}{2}\frac{\langle T \rangle}{\frac{1}{2}mv^2}\phi(Z) , \tag{5}$$

where

$$\phi(Z) = Zf(Z)g , \tag{6}$$

and

$$\langle T \rangle = \frac{1}{Z}[Z_K^2 R + (Z-2)\frac{1}{4}Z_L^2 R] . \tag{7}$$

In the above, a coefficient $f(Z)$ has been introduced to distinguish a real atom from a hydrogenic one. The coefficient $f(Z)$ is known to be less than unity for L shells for low atomic number targets. The coefficient g is introduced

TABLE III. Proton stopping cross-section values (in units of 10^{-15} eV cm^2) per molecule for water vapor.

E (keV)	40	80	100	300	500
Theoretical values of the present paper	28.81	27.8	26.8	17.1	12.6
Reynolds et al. (Ref. 15)	25.0 ± 2.6	27.6 ± 2.6	27.3 ± 2.6	17.9 ± 1.7	13.0 ± 1.7

TABLE IV. Deviations from Bragg's rule in the case of oxygen molecule. ϵ (atomic), the atomic stopping cross section (in units of $eV \times 10^{-15}$ cm²/atom), was obtained from Eqs. (3) and (10). ϵ (molecule) is in units of $\frac{1}{2}$ $eV \times 10^{-15}$ cm²/molecule.

E (keV)	40	100	200	300	500	1037	100 000
ϵ (atomic)	17.44	17.48	14.65	12.15	9.1	5.72	0.1492
ϵ (molecule)	15.89	17.43	14.36	11.84	8.92	5.64	0.1476
Percentage deviation	8.9	0.3	2	2.6	2	1.4	1.1

to incorporate the effect due to the recoiling of the nucleus.

At this stage, it is appropriate to discuss various features associated with the low-energy projectiles and the low atomic number targets. First, in the low-energy region, the projectile's full charge z will not be operational in the stopping process due to electron capture that is influenced mainly by the outer shell electrons of the medium. Second, Walske has pointed out that the coefficients $f(Z)$ are unreliable for the low atomic numbers $Z \leq 30$ due to use of the hydrogenic wave functions.

It is evident from the above observations that some sort of crude estimate of the quantity C is on order. This is justified since the usual incorporation of these effects involves the fitting with the experimental data. The inclusion of the effect of projectile's effective charge should decrease the stopping number of all the elements: for Li the most and for Ne the least. In order to incorporate this effect and the other problem of the need for an accurate value of the coefficient $f(Z)$ as stated above, it is reasonable as a first approximation to assume a semiempirical constant value of the quantity $\phi(Z)$ equal to half the total number of electrons in noble-gas atoms. Such a division should overestimate shell corrections for lithium and beryllium in decreasing fashion and underestimate that for helium, neon, carbon, nitrogen, oxygen, and fluorine also in a decreasing manner. Such a change in shell corrections is indeed what is needed as almost entirely compensating the effect of the effective charge of the projectile on the stopping power. Since, in this paper we are interested in the atoms with atomic number below 10 this assumption implies that

$$\phi(Z) = \begin{cases} 1 & \text{for } Z \leq 2 \ , \\ 5 & \text{for } 3 \leq Z \leq 10 \ . \end{cases} \tag{8}$$

Implicit in the above partition of ϕ is the fact that the quantity C no longer represents the so-called shell corrections only, but presumably also some other effects including that due to the projectile's effective charge as well as due to the

neglect of the higher-order terms in Eq. (2). One can now write Eq. (5) as

$$\frac{C}{Z} = \begin{cases} \dfrac{1}{2} \dfrac{\langle T \rangle}{\frac{1}{2}mv^2} \dfrac{1}{Z} & \text{for } Z \leq 2 \ , \\ \dfrac{1}{2} \dfrac{\langle T \rangle}{\frac{1}{2}mv^2} \dfrac{5}{Z} & \text{for } 3 \leq Z \leq 10 \ , \end{cases} \tag{9}$$

where $\langle T \rangle$ by virial theorem is just the average kinetic energy of the electron and should be averaged over all the Z electrons in the atom.

In order to make a transition to an atomic system, we assume the above results and accordingly replace Eq. (2) with

$$L = \begin{cases} \ln Y - \dfrac{3^{1.5}}{10 \chi Z} \dfrac{1}{Y} & \text{for } Z \leq 2 \ , \\ \ln Y - \dfrac{3^{1.5}}{2 \chi Z} \dfrac{1}{Y} & \text{for } 3 \leq Z \leq 10 \ . \end{cases} \tag{10}$$

The low- and high-energy L functions should now be combined to determine the appropriate dependence of the stopping power on energy. To do this, we used Eqs. (3) and (10) for our desired results after replacing ω_p by $\gamma \omega_p$ in them, where nonconstant values of γ were obtained from Ref. 2. Bonderup,[13] had combined Eqs. (2) and (3) and assumed a constant value of γ equal to $\sqrt{2}$. Unlike Bonderup, we tried to preserve the continuity between the low-energy stopping number function given by Eq. (3) and the high-energy function given by Eq. (10). In this way, stopping number values for a system can be obtained given the velocity of the projectile and the density $\rho(\vec{r})$.

For a diatomic molecule, the Gordon-Kim model gives the density as

$$\rho_{\text{molecule}} = \rho_a(\vec{r}) + \rho_b(\vec{r} - \vec{R}_{ab}) \ , \tag{11}$$

where $\rho_a(\vec{r})$ is the atomic ground-state density. R_{ab} is the

TABLE V. Deviations from Bragg's rule in the case of nitrogen molecule. ϵ (atomic), the atomic stopping cross section (in units of $eV \times 10^{-15}$ cm²/atom), was obtained from Eqs. (3) and (10). ϵ (molecule) is in units of $\frac{1}{2}$ $eV \times 10^{-15}$ cm²/molecule.

E (keV)	40	100	200	300	500	1037	100 000
ϵ (atomic)	19.33	18.57	14.32	11.46	8.53	5.30	0.1340
ϵ (molecule)	17.20	17.79	13.75	10.85	8.10	5.20	0.1319
Percentage deviation	11	4.2	4.00	6.1	5.0	1.9	1.3

TABLE VI. Deviations from Bragg's rule in the case of hydrogen molecule $\epsilon(2\times\text{atomic})$, the atomic stopping cross section (in units of $\text{eV}\times 10^{-15}$ cm^2/atom), was obtained from Eqs. (3) and (10). ϵ (molecule) is in units of $\text{eV}\times 10^{-15}$ cm^2/molecule.

E (keV)	100	200	300	500	800	1037	2591
$\epsilon(2\times\text{atomic})$	12.7	8.13	6.1	4.17	2.89	2.36	1.11
ϵ (molecule)	11.43	7.53	5.71	3.93	2.75	2.24	1.07
Percentage deviation	10	7.4	6.4	5.8	4.8	5.1	3.6

distance between the two atoms, which is known to be 1.094 Å for N$_2$ and 1.207 Å for the O$_2$ molecule. Equation (11) was generalized for water vapor including its partial ionic bond nature and neglecting the overlap between the two H atoms. The distance between the O and H nuclei was taken equal to 0.958 Å.

The molecular stopping power for protons was obtained by averaging the stopping number over $\bar{r}$ for N$_2$, O$_2$, and water vapor molecules. Hartree-Fock wave functions were employed in these calculations.

Table I lists the results of this paper, together with Andersen-Ziegler curve fitted results,[14] and two sets of experimental data for the O$_2$ molecules. Table II lists these values for the N$_2$ molecule. In Table III, the results of this paper for water vapor are compared with the available experimental data for energies ranging from 40 to 500 keV. Good agreement, within 10%, is found with the experimental data.

In order to discuss the departures from Bragg's rule, it would be relevant to cite a systematic study carried out in a series of experiments at Baylor University.[3-5] The study revealed that for low-energy projectiles there may exist a deviation from Bragg's rule depending on the physical state, but most importantly, on the chemical structure of the compounds. The confusing status of the dependence on the chemical structure can best be described by citing these studies in chronological order. First, in 1971 the Baylor group[3] summarized that the compounds with single and double bonds should obey Bragg's rule. The compounds containing triple-bond structure were found to deviate from Bragg's rule by as much as 12.8% (α particles of energy between 0.3 and 2.0 MeV often were the projectiles). In particular, these authors indicated that the molecular hydrogen (single-bonded molecule) should obey Bragg's rule. Later in 1972, the Baylor group[4] critically looked again on their previous conclusions. They indicated that perhaps the hydrogen atomic stopping cross section may be considerably

different than one-half of the molecular stopping cross section and thus should cause considerable deviations. However, the Baylor group in 1974,[5] recognizing the difficulty of obtaining atomic cross sections experimentally, based their analysis on the existence of some modified, but unique atomic stopping cross sections.

It is therefore imperative that in order to discuss the deviations from the Bragg's rule, one must have access to the atomic and molecular stopping cross sections. We calculated both the atomic and the molecular stopping cross sections as a function of projectile energy of the molecules O$_2$, N$_2$, and H$_2$. These results together with the deviations from Bragg's rule are exhibited in Tables IV–VI. One sees that the deviations from Bragg's rule become small as incident energy increases—in agreement with observations made by many workers including those at Baylor University. It is to be noted that N$_2$ is a triple-bonded, O$_2$ is an approximately double-bonded (from the bond energy point of view), and H$_2$ is a single-bonded molecule. The maximum deviations from Bragg's rule for energy 100 keV and above are 6.1%, 2.6%, and 10%, respectively, for these molecules. Thus, the deviation depends on the chemical structure. When the Gordon-Kim model is used, the overlap of electron density determines the deviation or molecular binding effects. For instance, for the hydrogen molecule, the distance between nucleons is very small, equal to 0.74 Å. It is expected that the overlap of electron density is large, thus explaining the considerable deviation from the Bragg's rule. The stronger the bond energy, the shorter the distance will be. It is interesting to note that single-, double-, and triple-bonded carbon molecules have internuclear distances equal to 2.94, 2.52, and 2.24 in Bohr units, respectively. We may thus expect that the triple-bonded carbon will have more deviation from Bragg's rule than the single-bonded carbon.

[1]J. W. Wilson and E. Kamaratos, Phys. Lett. 85A, 27 (1981).

[2]J. W. Wilson and Y. J. Xu, Phys. Lett. 90A, 253 (1982).

[3]P. D. Bourland and D. Powers, Phys. Rev. B 3, 3635 (1971).

[4]D. Powers, W. K. Chu, R. J. Robinson, and A. S. Lodhi, Phys. Rev. A 6, 1425 (1972).

[5]A. S. Lodhi and D. Powers, Phys. Rev. A 10, 2131 (1974).

[6]J. Lindhard and A. A. Winther, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 34, No. 4 (1964).

[7]J. Lindhard and M. Scharff, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 27, No. 15 (1953).

[8]R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972).

[9]R. E. Johnson and M. Inokuti, Comments At. Mol. Phys. (to be published).

[10]L. M. Brown, Phys. Rev. 79, 297 (1950).

[11]M. C. Walske, Phys. Rev. 88, 1283 (1952).

[12]M. C. Walske, Phys. Rev. 101, 940 (1955).

[13]E. Bonderup, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 35, No. 17 (1967).

[14]A. H. Andersen and J. F. Ziegler, Hydrogen Stopping Power and Ranges in all Elements (Pergamon, New York, 1977).

[15]H. K. Reynolds, D. N. F. Dunbar, W. A. Wenzel, and W. Whaling. Phys. Rev. 92, 742 (1953).

[16]R. A. Langley, Phys. Rev. B 12, 3575 (1975).