

The Mean Excitation Energy for Stopping Power I, the Bragg Rule, and Chemical and Phase Effects. Application of a Statistical Treatment to the Determination of I for Chemically Bound Particles

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This article includes the following topics: (i) a concise, comprehensive summary of the stopping power theory; (ii) a critical analysis of mostly recent work on chemical bonding and phase effects on the mean excitation energy for stopping power; (iii) a presentation of the methods employed to determine the mean excitation energy; and finally (iv) the application of the statistical method for the calculation of the mean excitation energy of molecular hydrogen by following a new procedure that leads to a new value for the mean excitation energy of molecular hydrogen. This work is aimed at bringing this important field of research to the attention of chemists for future contributions to the solution of problems related to chemistry.

Introduction

The penetration of charged particles into matter has been the subject of numerous investigations since the time of the research of Bragg, Lenard, Rutherford, and Thompson on this topic,¹⁻³ both because of the interest it presents to basic research (e.g., in atomic, molecular, nuclear, and solid-state physics) and because of its important, present as well as potential, applications in fields such as radiobiology and medicine (charged particle beams for treatment of cancer),⁴⁻⁷ astrophysics, applied nuclear physics, applied solid-state physics, health physics, radiation physics, and radiation chemistry (cosmic rays, particle detectors, nuclear fusion assisted by ion beams, ion implantation, lithography, and ionizing-radiation effects on matter).⁸⁻¹⁶

Methods to determine the logarithmic mean excitation energy for stopping power, a quantity important to the study of the penetration of matter by charged particles, will be presented, and one of the methods will be applied for H₂ by use of a new approach.

Stopping Power

A quantity of great significance for the applications mentioned previously⁴⁻¹⁶ is the average amount of energy deposited per unit distance of penetration of homogeneous matter by a charged particle. When no bremsstrahlung or other resulting radiation escapes from the medium, this quantity of energy equals the average energy loss per unit path length of penetration into homogeneous matter by a charged particle, which is known as the stopping power of the medium (usually expressed in the following units of energy times inverse



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density of matter, MeV cm²/g) or the linear energy transfer (usually expressed in units of keV/μm or MeV/cm).

There have been several derivations of expressions for the stopping power that depend on the prevailing mechanism of interaction considered between the approaching Coulomb field of a moving charged particle and the particles of the target system, which, in turn, depends also on the magnitude of the velocity considered of the penetrating charged particle and, consequently, on the magnitude of the energy transferred per collision.

Bohr derived an expression for the stopping power¹⁷⁻¹⁹ using a semiclassical model for a fast-moving charged particle that interacts with atoms of the target matter traversed essentially through inelastic collisions with the electrons of the atoms, since the contribution

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of elastic collisions with the nuclei was shown by Darwin to be negligible.^{17,20a} In Bohr's treatment, the collision impact parameters and the frequencies of the bound atomic electrons were considered along with assumptions about the bound electrons in the target atoms, namely that the dimensions of their orbits, their displacements, their frequencies of oscillation, and their velocities (the latter with respect to the velocity of the incident charged particle) were all small. One form of Bohr's semiclassical expression for stopping power^{17,18} is

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} N \sum_{s=1}^{s=r} \ln \left[\frac{1.123mv^2}{n_s} \frac{vM}{e^2 z(M+m)} \right] \quad (1)$$

where E , M , v , and z are the kinetic energy, the mass, the velocity, and the charge (in au) of the impinging charged particle, m and e are the rest mass and the charge of an electron, N is the number of atoms per unit volume, and n_s is the (oscillation) frequency of the s th of r bound electrons per atom of the target matter. This expression holds quantum mechanically for nonrelativistic impinging charged particles with velocity much lower than the product^{19,21} of the electronic velocity at the ground state of the Bohr hydrogen atom ($e^2/\hbar = 2.1877 \times 10^8$ cm/s) times z .

Following incomplete attempts^{20b} for a quantum-mechanical expression, Bethe treated the problem of the determination of the electronic stopping power employing a quantum-mechanical procedure with the first Born approximation.^{20b-25} He considered the transfer of momentum as a result of inelastic scattering between a passing charged particle and the electrons of the atoms of the target matter and determined the total cross section for the excitation of an atom from the ground state to an excited state. The total sum of the product of each excitation energy, $E_n - E_0$, times the corresponding total excitation cross section, σ_n , times the number of atoms per unit volume, N , equals the electronic stopping power:

$$-dE/dx = N \sum_n (E_n - E_0) \sigma_n \quad (2)$$

For a heavy charged particle with a velocity larger than that of each electron in an atom or, alternatively, with the kinetic energy of the impinging particle much larger than the product of the ratio of its mass to that of an electron times the ionization potential of the electrons of the atoms of the target matter, Bethe finally derived the following expression²¹⁻²⁵ for the stopping power

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} N \sum_n f_{n0} \ln \left(\frac{2mv^2}{E_n - E_0} \right)$$

or

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \ln \frac{2mv^2}{I} \quad (3)$$

where Z is the number of electrons per atom of the target matter and I is the logarithmic mean excitation energy defined by

$$Z \ln I = \sum_n f_{n0} \ln (E_n - E_0) \quad (4)$$

where f_{n0} is the dipole oscillator strength for the transition from the ground state of energy E_0 to the state of energy E_n , and the rest were defined previously. The

validity of the nonrelativistic Bethe formula for the stopping power for fast heavy charged particles was extended for relativistic velocities by the work of Møller^{26,27} and Bethe^{21,23,28,29}

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \left[\ln \frac{2mv^2}{I} - \ln (1 - \beta^2) - \beta^2 \right] \quad (5)$$

where $\beta = v/c$ and c is the speed of light. Bohr extended the validity of his expression for the most probable energy loss by a charged particle, that is appropriate for electrons,²¹ in contrast to that for the average energy loss, that is appropriate for heavy charged particles,²¹ for relativistic velocities by finally subtracting $\ln (1 - \beta^2) + \beta^2$ from the logarithmic factor of that expression.¹⁸ Bloch³⁰ reported the corresponding expression for the average energy loss by relativistic heavy charged particles in a stopping medium of one-electron atoms according to Bohr's theory. It differs from the nonrelativistic expression by having $[\ln (1 - \beta^2) + \beta^2]/2$ subtracted from the logarithmic factor of eq 1 for $r = 1$ and $M \gg m$. For heavy charged particles at relativistic velocities, it has been shown that Bohr's semiclassical formula for the stopping power can take the slightly different form¹⁴

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \left[\ln \left(\frac{1.123mv^2}{\omega} \frac{v}{e^2 z} \right) - \ln (1 - \beta^2) - \frac{\beta^2}{2} + R_1 \right] \quad (6)$$

where R_1 represents very small additional terms¹⁴ and ω represents an average oscillation frequency for a bound atomic electron and equals²¹ I/\hbar , where I is the logarithmic mean excitation energy defined above and \hbar is Planck's constant divided by 2π . Bloch independently treated the scattering between a charged particle and the bound atomic electrons in a different quantum-mechanical way in which he also considered collision impact parameters and derived^{30,31} the following expression for the stopping power for a heavy charged particle:

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \left[\ln \frac{amv^2}{I} - \frac{1}{2} \ln (1 - \beta^2) - \frac{\beta^2}{2} + \psi(1) - \operatorname{Re} \psi \left(1 + i \frac{e^2 z}{\hbar v} \right) \right] \quad (7)$$

where $a = 2$ (in contrast to $|z| = 1$ and $a = g$, a "straggling" factor,³⁰⁻³³ for an incident electron), ψ designates the logarithmic derivative of the Γ function [$\psi(1) = \ln (1.123/2)$], and $\operatorname{Re} \psi$ designates the real part of ψ . Also, this expression is valid only for $v \gg (2.1877 \times 10^8 \text{ cm/s})z$. The Bloch formula is a general expression for the stopping power, that reduces to the Bohr formula for heavy charged particles in the form

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \ln \left(\frac{1.123mv^2}{\omega} \frac{v}{e^2 z} \right) \quad (8)$$

and the Bethe formula, eq 3, as a limiting case for the imaginary part in the argument ($e^2 z/\hbar v$) tending to a large number ($\gg 1$) and zero, respectively.^{14,21,30}

In the case of light charged particles (such as electrons and positrons) of low kinetic energy, where

bremsstrahlung is negligible and the energy loss of a charged particle per collision is essentially the result of inelastic collisions with the bound electrons of the stopping matter, the stopping power may be expressed by the Bloch formula for $|z = 1|$ and $\alpha = g$ defined above or approximately by the Bethe–Bloch formula after the change by $1/2$ in the energy transferred per collision due to the change in the reduced mass of the charged particle–bound electron system is considered, namely from m to $m/2$, in the argument of the logarithm^{21,28}

$$-\frac{dE}{dx} = \frac{4\pi e^4}{mv^2} NZ \ln \frac{mv^2}{I} \quad (9)$$

or by a less approximate expression than eq 9 for electrons

$$-\frac{dE}{dx} = \frac{4\pi e^4}{mv^2} NZ \ln \frac{mv^2}{2I} \left(\frac{e'}{2}\right)^{1/2} \quad (10)$$

where $e' = 2.718\dots$, the base of natural logarithms.^{21,23}

For relativistic electrons and positrons, additional expressions for the stopping power have been derived corresponding to that of eq 5 for heavy charged particles; for electrons,^{21,23,27,33–35} after a little algebraic modification so that mv^2 appears explicitly for comparison with previous expressions,

$$-\frac{dE}{dx} = \frac{2\pi e^4}{mv^2} NZ \left\{ 2 \ln \frac{mv^2}{I} - \ln [2b^4(b+1)] + b^{-2} - \frac{2b-1}{b^2} \ln 2 + \frac{1}{8} \left(\frac{b-1}{b}\right)^2 \right\} \quad (11)$$

where $b = (1 - \beta^2)^{-1/2}$, and for positrons^{34,36}

$$-\frac{dE}{dx} = \frac{2\pi e^4}{mv^2} NZ \left\{ 2 \ln \frac{mv^2}{I} + \ln \frac{2}{b^4(b+1)} - \frac{\beta^2}{12} \left[23 + \frac{14}{b+1} + \frac{10}{(b+1)^2} + \frac{4}{(b+1)^3} \right] \right\} \quad (12)$$

For medium kinetic energies (e.g., larger than ≈ 100 keV for mesons and light nuclei or ions) eq 3, known as the Bethe or Bethe–Bloch formula, is used with the so-called “shell corrections” [$C/Z = (C_K + C_L + \dots)/Z$] to compensate for the lower contribution to stopping power of the electrons in the inner shells (K, L, etc.).^{14,24,29,37,38}

At high kinetic energies (e.g., for relativistic speeds for protons), another correction, the density effect correction, $\delta/2$, is applied to the Bethe–Bloch formula and to eq 11 and 12 to account for the decrease in stopping power because of the dielectric polarization of the stopping medium. The possibility of the decrease in the stopping power because of the polarization of the stopping medium was proposed by Swann.³⁹ Fermi^{40,41} investigated this phenomenon quantitatively with an approach based on classical electrodynamics in which the dielectric constant of the stopping medium was considered to be produced by electrons bound with a single frequency and damped in their motion. Fermi’s model showed a decrease in the stopping power of a medium in the condensed phase compared to that in the gaseous phase. Subsequently, Halpern and Hall^{42,43} showed the importance of considering different types of dispersion electrons instead of single-dispersion

electrons for the description of the dielectric constant of the stopping medium. They also determined density effect corrections⁴³ for several substances including metals. Fermi’s equations were extended for multidispersion bound electrons by Halpern and Hall,⁴³ Wick,⁴⁴ and Sternheimer.⁴⁵ Sternheimer^{45,46} extended the determination of the density effect correction for a large variety of substances and obtained a general expression for it. The resulting stopping power is reported to be expected to have a maximum error of $\pm 2\%$ and a most probable error of $\pm 1\%$ or less.^{14,45,46}

Kronig and Korringa^{47,48} derived an expression for the stopping power of metals for fast charged particles based on hydrodynamics by considering the disturbance on the charge density of the conduction electrons that were treated as a negatively charged compressible fluid on a positively charged ionic lattice of uniform charge density, that was equal in magnitude to that of the electronic fluid. Subsequently, Kramers⁴⁹ derived another expression for the stopping power of metals for α -particles by taking into consideration the polarization of the medium resulting from the interaction of the conduction electrons considered at rest with the electrons displaced by the charged particle. By employing the results of the quantum theory of dispersion of metals to calculate the dielectric constant and by following Bohr’s procedure for the stopping of fast charged particles by electrons elastically bound to equilibrium positions to calculate the energy transferred from an α -particle to a conduction electron, he arrived at an expression⁴⁹ for the stopping power that is very similar to Bohr’s formula, eq 8,

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} \rho \ln \left(\frac{1.123mv^2}{\omega'} \frac{v}{e^2 z} \right) \quad (13)$$

$$\omega' = \omega_p + 4\omega_c/\pi$$

where ω_c is a constant inversely proportional to the conductivity of the metal, ω_p is the plasma frequency, ρ is the number density of the conduction electrons, and the rest have their previous meaning. Since ω_c is of the order of $\approx 1\%$ of ω_p , ω' practically equals ω_p . The plasma frequency is given by

$$\omega_p = (4\pi e^2 NZ/m)^{1/2} \quad (14)$$

On taking the quantum-mechanical results of the stopping power due to bound electrons into consideration, Kramers derived the expression^{49,50}

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} \rho \ln \frac{2mv^2}{\hbar \omega_p} \quad (15)$$

Equation 15 leads to Kronig and Korringa’s expression for the stopping power of metals, in contrast to eq 13 that does not, if the coefficient of viscosity of the electron fluid in their model is set⁵⁰ equal to $3N\hbar/8$.

Additional treatments of the stopping power of metals based on collective electronic motion following the work of Kronig and Korringa,^{47,48} Kramers,⁴⁹ and Kronig⁵⁰ are the work of Bohr,⁵¹ Pines,⁵² Fröhlich and Pelzer,⁵³ and Hubbard.^{54,55} The latter work takes into consideration also effects due to the core electrons, binding effects of the conduction electrons, and damping effects.

The complete Bethe–Bloch formula with the density effect and shell corrections is

$$-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \left[\ln \frac{2mv^2}{I} - \ln(1 - \beta^2) - \beta^2 - \frac{C}{Z} - \frac{\delta}{2} \right] \quad (16)$$

At low kinetic energies, the electronic stopping power is determined on the basis of the theories of Lindhard⁵⁶⁻⁶⁷ and Firsov.⁶⁶⁻⁷⁴ At low kinetic energies (e.g., for less than 100 keV for first- and second-row nuclei) the velocity of the incident particle approaches that of the inner-shell electrons and thus they contribute less to stopping power. In addition, charge transfer (electron capture and loss) becomes important at low velocities and therefore the charge of the projectile becomes velocity dependent. At much lower kinetic energies (e.g., less than 10 keV for H⁺) the loss of energy due to momentum transfer to the nuclei becomes important (over 2%); therefore both nuclear and electronic stopping power should be considered.

Also in Lindhard's theory the electronic stopping power is expressed in terms of the dielectric constant, that is determined through a quantum-mechanical first-order perturbation treatment.⁵⁶ The electrons of the stopping medium are considered as part of a homogeneous free electron gas in the Coulomb field of the incident charged particle that is treated as a point charge. On integration, following the substitution of the derived expression for the longitudinal dielectric constant into the expression for the stopping power, an expression was found similar to the Bethe formula, eq 3, however, with the logarithm replaced by a dimensionless quantity $L(NZ, v)$. Various limiting cases have been explored; e.g., if the electrons are considered to be at rest, $L(NZ, v)$ becomes

$$L(NZ, v) = \ln \left\{ \frac{mv^2}{\hbar\omega_p} + \left[\left(\frac{mv^2}{\hbar\omega_p} \right)^2 - 1 \right]^{0.5} \right\} \quad (16a)$$

For large v , Lindhard's expression for the stopping power tends to Kramer's expression, eq 15. If there is a Fermi distribution of electron kinetic energies, L takes various forms depending on the magnitude of v . If the electron gas is considered inhomogeneous due to a nonuniform electron charge distribution (e.g., in an atom), L is averaged over the electron charge density (per atom).⁵⁷⁻⁵⁹ When the experimentally determined L for metals as a function of $v^2/v_0^2 Z$ (v_0 is the velocity in the hydrogen Bohr orbit, e^2/\hbar) was plotted, a universal curve was obtained⁵⁷ that approximately was valid for all the data. Lindhard and Winther⁶²⁻⁶⁷ derived further expressions for L for low (and high) velocities with respect to the electron Fermi velocity in the stopping medium.

At low kinetic energies, the electronic stopping power determined with Firsov's theory⁶⁶⁻⁷⁴ equals the inelastic energy losses per unit path length suffered by the impacting charged particle due to exchange of electrons between the charged particle and the stopping medium that causes the slowing down of the charged projectile. The electronic energy loss is determined from the momentum associated with the electron flux that penetrates a surface located at the position of minimum density between the target atom and the impacting charged particle. Firsov used the Thomas-Fermi atomic model for the determination of the required

electron density and mean speed. More recently⁷² the Hartree-Fock-Slater model has been used for both Firsov's and Lindhard's theories. Both theories predict direct proportionality between the electronic stopping power and the velocity of the charged projectile at low velocities.

Since no logarithmic mean excitation energy is directly involved in these expressions for low kinetic energies, they are not presented here. It should be mentioned that these two theories are applied also for moderate energies (nonrelativistic).

Recently, the effective charge theory^{75,76} (for an incident ion) has also been applied to the electronic stopping power for incident ions of intermediate and even low and high velocities.

There are additional corrections to the Bethe-Bloch formula for effects^{14,67,77} like, e.g., the "z³ or Barkas effect",⁷⁹⁻⁸² which accounts for differences in stopping power between positive and negative incident particles, effects due to higher Born approximations, and other effects. Some of these effects have been taken into account in expressions that contain fitting parameters for the determination of stopping power at low,⁸³⁻⁸⁵ intermediate,^{83,86} and high^{83,87} energies. Plots of the stopping power as a function of the atomic number of the stopping medium that show oscillations depending also on the kinetic energy of the incident ions and tables with numerical results for the stopping power of each element and the range of ions have been reported.^{67,83,87-93a}

There has been also considerable research of importance to various fields on other aspects associated with the stopping power of a medium, e.g., the electron capture,^{93b} and the emission and the energy and spatial distribution of secondary, etc., electrons from ionization of various stopping media by low to high energy charged particles.^{93c}

The Logarithmic Mean Excitation Energy

A common feature of the presented quantum-mechanical expressions of the stopping power, even of some forms—e.g., eq 6 and 8—of the Bohr formula, is the presence of the logarithmic mean excitation energy, I , of the particles that compose the stopping medium, which, in fact, have been considered to be noninteracting atoms as in a dilute gas. Consequently, knowledge of I is required to determine the average energy loss of high-velocity charged particles traversing a stopping material, expressed either as stopping power of the medium, $-dE/dx$, or as stopping cross section, $-(1/N) dE/dx$ (in units of eV·cm² per particle). Further, once I and the stopping power of a medium have been determined, additional quantities of interest can be determined like the range

$$R(E_i \rightarrow E_f) = \int_{E_f}^{E_i} (-dE/dx)^{-1} dE \quad (17)$$

that is the average distance of penetration traveled by equienergetic charged particles of initial kinetic energy E_i until their energy is decreased to E_f in the medium and the energy "straggling" and the range "straggling", namely the fluctuations in the energy loss and in the range.^{21,24,93d}

In this work a new procedure is reported to determine this important quantity for basic and applied research

and for various other applications,⁴⁻¹⁶ the logarithmic mean excitation energy. This procedure is applied to chemically bound particles, in contrast to noninteracting atoms.

Determination of the Logarithmic Mean Excitation Energy

The logarithmic mean excitation energy has been determined for a variety of stopping substances from the experimentally determined absolute or relative (with respect to a reference stopping medium like air, Cu, or Al) stopping power by employing the Bethe-Bloch formula, eq 16, for large-velocity charged particles^{21,24,94-96} at appropriate kinetic energies where corrections to the formula are negligible or at lower kinetic energies by considering some of the corrections.^{34,82c,97} However, the use of corrections introduces additional uncertainty, since not all of them are very accurately known and some of them require knowledge of I for their accurate determination. For chemical compounds for which there are no experimental measurements of stopping power, the logarithmic mean excitation energy has been determined empirically from the experimental stopping power of the constituent atoms of the chemical compound with the application of an additivity relation that was first postulated by Bragg and Kleeman^{1,98} and is called the Bragg additive law,⁹⁹ Bragg's additive rule,²⁹ or simply the Bragg law or Bragg's rule.^{14,21,100,101} The Bragg additivity rule can be expressed as

$$S_{A_iB_mC_n} = lS_A + mS_B + nS_C \quad (18)$$

where S_A , S_B , and S_C designate the stopping power of the atoms A, B, and C and $S_{A_iB_mC_n}$ designates the stopping power of the three-element polyatomic molecule $A_iB_mC_n$ composed of lA , mB , and nC atoms, respectively. If the stopping power in eq 18 is expressed in terms of the Bethe formula, eq 3, or in terms of the complete Bethe-Bloch formula, eq 16, if the corrections are assumed to be appropriately additive, the expression of Bragg's additivity rule for the logarithmic mean excitation energy is obtained

$$\begin{aligned} N_{\text{mol}} Z_{A_iB_mC_n} \ln I_{A_iB_mC_n} &= \\ lN_{\text{mol}} Z_A \ln I_A + mN_{\text{mol}} Z_B \ln I_B + nN_{\text{mol}} Z_C \ln I_C & \\ \text{or} & \\ Z_{A_iB_mC_n} \ln I_{A_iB_mC_n} &= \\ lZ_A \ln I_A + mZ_B \ln I_B + nZ_C \ln I_C & \end{aligned} \quad (19)$$

where N_{mol} designates the number of molecules $A_iB_mC_n$ per unit volume occupied by the chemical compound and Z and I , as before, designate the number of electrons and the logarithmic mean excitation energy of each particle, whether it is a molecule or an atom. Equation 19 can be generalized for any complex chemical species

$$Z \ln I = \sum_{i=1}^n \alpha_i Z_i \ln I_i \quad (20)$$

where

$$Z = \sum_{i=1}^n \alpha_i Z_i \quad (20a)$$

designates the total number of electrons of the complex chemical species and α_i designates the number of times each of the n particles (atoms or ions) with Z_i electrons is contained in the complex chemical species.

The Bragg additivity rule as applied by Bragg and Kleeman^{1,98} does not necessarily mean that chemical binding effects of atoms in a compound or interparticle effects in condensed phases can be ignored, contrary to such an apparent interpretation.¹⁰² It should be noted that the "atomic" stopping power used for key atoms like H, N, O, and "air atoms" was empirical, in fact, proportional (half^{31,98,100}) to the experimental value for H_2 , N_2 , O_2 , and "air molecules",^{1,100} consequently, a contribution of chemical binding effects has already been included indirectly. Similarly, possible intermolecular and polarization effects may have been included in the "atomic" stopping power data from condensed phases. The possibility of a different additivity for the stopping power between solids and gases of various molecular complexity has already been pointed out by Bragg and Kleeman.^{1a} Of course the range of validity of Bragg's rule lies within the experimental uncertainty for stopping power. The latter, as quoted earlier in this work, is expected to be within $\pm 2\%$ according to Sternheimer and Peierls.⁴⁶ Thompson^{14,103} reported deviations from Bragg's additivity rule for stopping power for 270-MeV protons of the order of 2% for compounds with hydrogen and within $\approx 1\%$ for compounds with C, N, and O. Recently uncertainty of 0.5% was reported.^{82c} Of course, the corresponding percent deviations from the Bragg rule for the logarithmic mean excitation energy are higher in magnitude by a logarithmic factor

$$\frac{dI}{I} = -\frac{dS}{S} \ln \frac{2mc^2\beta^2}{I(1-\beta^2)\exp(\beta^2)} \quad (21)$$

as can be shown by differentiating the Bethe-Bloch formula, eq 16, with no shell and density effect corrections considered. Since mc^2 equals 511.0 keV and β equals 0.6301 for 270-MeV protons, the value of the logarithmic factor for $I = 300$ eV is approximately 7.3. An interesting case of a discrepancy from Bragg's rule for the mean excitation energy is the discrepancy between the value of I of 328 eV determined by fitting the stopping power formula of eq 16 to the observed range in Ilford G5 emulsion^{29,104} and the value of I of 300 eV^{29,105,106} determined from the Bragg rule by employing the values of the logarithmic mean excitation energy for Ag, Br, I, C, N, S, H, and O.²⁹ However, also this deviation of I by $\leq 10\%$ is within the expected maximum experimental error for stopping power and within the expected deviation from the Bragg rule that had been estimated not to exceed 1-2% from additional earlier work.^{21,100,107,108}

However, even larger deviations from the Bragg additivity rule for stopping power were reported in earlier work¹⁰⁹ for NO with protons of 30-600 keV as the incident particles. Below 150 keV, Bragg's rule was found¹⁰⁹ to hold for none of several diatomic, triatomic, and polyatomic gaseous compounds tested.

More recent experimental work in the gas state¹¹⁰⁻¹¹⁸ and in the condensed state¹¹⁸⁻¹²⁸ and theoretical work^{120b,129-131} revealed additional cases of larger than 1-2% deviations from the Bragg additivity rule for stopping power and the mean excitation energy.^{120b,129,131} They have been ascribed (i) to chemical bonding of the target atoms, despite some uncertainty, even in the 1970s, as to whether chemical bonding had any effect¹³² on stopping power and (ii) to phase effects^{118,121,133-140} that cause, e.g., the stopping power of a medium in the gas state to be larger than that in the condensed state.

This change in the stopping power between the condensed and the gaseous state is in agreement with the early prediction of Swann,³⁹ based on the effect of the polarization of the stopping medium, and the results of the subsequent work for moderate and high energies by Fermi^{40,107} and others⁴²⁻⁴⁵ mentioned here previously in the Stopping Power section. However, this decrease in the stopping power in the condensed state is contrary to a later theoretical conclusion¹⁰⁰ that the stopping power of a medium is lower in the gas state than in the condensed state because of a claimed decrease¹⁰⁰ in I in the condensed state and similarly contrary to such reported early experimental results, e.g., higher stopping power¹⁰⁰ for H₂O vs. H₂O vapor and for D₂O ice¹⁴¹ vs. H₂O vapor for incident¹⁴¹ H⁺ of ≈ 90 to ≈ 590 keV that are in conflict also with subsequent measurements on H₂O ice¹³⁵ and H₂O^{136a} vs. H₂O vapor. Finally, this decrease in the stopping power in the condensed state is also contrary to a statement in more recent work^{132b} that there is no difference between the stopping power of solids and gases.

It should be noted that long ago chemical bonding and the phase of the target matter were suggested to have an effect on stopping power and on the validity of the Bragg additivity rule both by experiments^{98,100,142} and by calculations.^{107,108}

Already in 1936 Förster⁹⁸ reported results of an experimental investigation with α -particles that was undertaken specifically to examine the effect of chemical bonding on stopping power in view of the already reported deviations from Bragg's rule (e.g., for compounds of H), which, however, needed⁹⁸ additional confirmation from experiments of higher accuracy. Following Bragg and Kleeman,¹ Förster⁹⁸ used the definition of the relative stopping power in a gaseous medium (which is actually the ratio of the reduced or total range of a charged particle in the air over that of the charged particle in the gaseous medium; for the condensed state the densities and the atomic weights are included). Thus, from the experimentally determined ranges in a gaseous mixture of 2 parts H₂ and 1 part O₂ and in H₂O vapor of the same mass formed by combustion of the previous gaseous mixture, it was found⁹⁸ that the stopping power for the H₂O vapor was lower than that for the H₂ and O₂ mixture by 3%—corrected¹⁰⁰ to 2.4%. If this reported difference in stopping power (2.4%) is ascribed to a shift in I because of chemical bonding, the resulting shift¹⁰⁷ in I determined from eq 21 for α -particles of ≈ 4 MeV is $\approx 8\%$ —as also reported by Platzman.¹⁰⁰ This is in fair agreement with the difference in recent values of I calculated¹³¹ for H₂O (71.62 eV) and for H₂ + 0.5O₂ (69.06 eV). Thus, these values support such a shift in I for H₂O as in Förster's data contrary to an early suggestion.¹⁰⁰ However, some, if not all, of these values of I may be further improved. Also, subsequent experiments¹⁰⁹ with H⁺ showed that $\epsilon_{\text{H}_2} + 0.5\epsilon_{\text{O}_2}$ was higher than $\epsilon_{\text{H}_2\text{O vapor}}$, however, only for >200 keV—energy of 200 keV for H⁺ corresponds to energy of 800 keV approximately for α -particles of equal velocity; ϵ designates the stopping cross section. Recent experimental values of ϵ for H₂O vapor^{135,136a} are lower than the calculated^{136a} ones, with the Bragg rule value of 67.9 eV for I , for α -particles of 0.5–2.5 MeV. In view, however, of the way I was calculated, these values can apply to $\epsilon_{\text{H}_2} + 0.5\epsilon_{\text{O}_2}$ and thus indicate deviations as in

Förster's results. Nevertheless, there is still uncertainty regarding the accuracy of the values of I and the exact values of the effective charge^{14,82b} on the α -particle to be used. However, it should be noted that above 2.5–8.0 MeV the measured values^{136a} of $\epsilon_{\text{H}_2\text{O vapor}}$ get progressively lower than the calculated values,^{136a} thus indicating an opposite deviation even in the energy region of Förster's results.^{98,100} The disagreement between the recent^{135,136a} experimental values of $\epsilon_{\text{H}_2\text{O vapor}}$ dictates special caution, though.

The very recent experimental results on water and^{136b} its vapor, that were subsequently found, support the lower¹³⁵ values of $\epsilon_{\text{H}_2\text{O vapor}}$ below 1 MeV in disagreement with the higher^{136a} ones. It should be noted that the experimental I values^{136b} of 79 eV for water and 71 eV for water vapor were recently revised to ≈ 68 eV and ≈ 60 eV, respectively,^{136c} and the theoretical I value for water vapor¹³¹ of 71.62 eV, mentioned also later in this work, is challenged.^{136c}

Similarly for 5.3-MeV α -particles ϵ_{NO} was found to be greater and $\epsilon_{\text{N}_2\text{O}}$ lower than the corresponding sums of ϵ_{N_2} and ϵ_{O_2} in early work¹⁴² supported qualitatively by later work¹⁰⁹ for H⁺ at lower energies. However, subsequent application of empirical corrections reportedly eliminated earlier deviations¹¹⁰ from Bragg's rule for several compounds including N₂O except for NO¹¹⁰ and H₂O.^{110,113} An investigation of the reported deviations for H₂O has been under way.¹⁴³

In the energy region of validity of Bethe's formula, eq 3, already the theoretical values of I for elements calculated by Brandt¹⁰⁸ to be larger in the condensed state than in the gas state (free atoms), indicated a phase effect. Similarly, the different values of I calculated¹⁰⁸ for free atoms and molecules of the same element suggested a chemical bonding effect. Of course, the quantitative extent of these predicted effects depends on the nature of the particular elements involved and on the degree of the approximation of the calculations.

As a result of the chemical bonding effects, the importance of the stopping power per atom, for lower velocities of incident charged particles, is questioned¹²⁸ and the usefulness of the stopping power per (organic) group^{113,128} of atoms and per bond¹²⁸—that bonds two atoms in a molecule or radical—is supported,¹²⁸ the latter especially for covalent compounds of C and H.

However, for protons at higher energies (e.g., >2 MeV) penetrating, e.g., metal oxides,^{122,144} the Bragg additivity rule is reported to hold, which may indicate a smaller chemical effect on I for these compounds that causes practically no change to the stopping power, particularly at higher velocities at which the logarithmic factor in eq 21 reaches larger values and reduces the shift¹⁰⁷ in stopping power brought about by the shift in I in the energy region of validity of eq 21. Of course, more information on ϵ for metals and metal oxides as already suggested¹¹³ will be useful. Similarly for ⁴He ions of kinetic energy above ≈ 1.0 MeV the stopping power data reported¹³⁴ for the gaseous and the solid state of O₂, Ar, and CO₂ agree within the experimental error (2–3%). With these experimental data on solid O₂ the calculated stopping power for WO₃ is reported¹⁴⁵ to agree well with experimental results and calculations from tabulations¹⁴⁶ for gaseous oxygen, but not for solid oxygen. Similarly, the measured stopping power values

for solid BaCl_2 and BaF_2 are reported¹⁴⁵ to agree with the Bragg rule values determined with data for chlorine and fluorine in the gaseous state, but not in the solid state. Also, recent stopping power ratios of several materials, measured with respect to water for 60-MeV positive and negative pions, agree¹⁴⁷ within 0.6% with corresponding values calculated from the Bethe–Bloch formula, eq 16, and Bragg's additivity rule. In addition, it may be possible that the reported deviation from Bragg's rule for the stopping power of H_2O can be eliminated.¹⁴³

Definitely, accuracy in stopping power of at least $\leq 1\%$, that is needed also for additional applications,^{148,149} will further unravel the extent of shifts in stopping power due to chemical bonding and phase difference from the accompanying experimental error and artifacts as already pointed out long ago.⁹⁸

A recent indication of the possible magnitude of expected deviations from the Bragg additivity rule is the reported difference between the calculated logarithmic mean excitation energy from a Hartree–Slater oscillator strength distribution for atomic nitrogen,¹⁰¹ 76.91 eV, and that from a semiempirical oscillator strength distribution for molecular nitrogen,¹⁵⁰ 82.1 eV, that was considered by the researchers to certainly support the Bragg rule.¹⁰¹

The first theoretical determination of the logarithmic mean excitation energy was performed by Bethe for the hydrogen atom ($I_{\text{H}} = 1.105$ multiplied by its ionization potential,²² $I_{\text{H}} = 1.103$ multiplied by its ionization potential²³) over 50 years ago.^{22,23,96} It is interesting that this value for I_{H} is still found to be accurate: 14.99 eV,¹⁵¹ 14.98 eV.¹³¹ This determination was based on direct calculation with the defining equation for I , eq 4. In 1932 Bethe²⁸ reported also values for I_{H_2} (15 eV), I_{N_2} (35 eV), I_{Fe} (60 eV), I_{Ag} (170 eV), and I_{Pb} (250 eV) that were expected to be uncertain by approximately $\pm 30\%$ due to the uncertainty of the dipole oscillator strengths of the forbidden transitions according to the Pauli principle. Mano,⁹⁶ who fitted his experimental range results to the Bethe–Bloch formula very precisely by using $I_{\text{H}_2} = 16$ eV, reported⁹⁶ that Bethe gave the value of $I_{\text{H}} = 14.9$ eV for the H atoms and accepted the value of $I_{\text{H}_2} = 15$ eV for the H_2 molecules, whereas Williams proposed the value of $I_{\text{H}_2} = 17.5$ eV.^{23,96,152} Williams adopted this value for I_{H_2} (actually initially^{152a} 1.1×16 eV; this value—17.6 eV—is quoted also by Bethe²³ to lead to agreement with experimental results) “in conformity with the value for atomic hydrogen, viz., 1.1 multiplied by its ionization potential”.¹⁵² This value of I_{H_2} led to a ratio for stopping power for H_2 and He that was found to be compatible with the ratio of the values of experimental stopping power for H_2 and He. Platzman later proposed the value of $1.2 \times 15.43 \approx 19$ eV for I_{H_2} .^{29,100} Bloch³¹ proposed an approximation in the frame of the statistical Thomas–Fermi atomic model, that does not include the exchange and the electron–spin interaction, for the calculation of the stopping power that essentially consisted in setting I equal to $ZuR/2\pi$ in the Bethe formula, eq 3, where R is the Rydberg energy (13.606 eV) and u is a dimensionless constant for all stopping particles, the value of which was determined empirically with eq 3 from the experimentally determined stopping power for gold ($Z = 79$). The determined value of u was 6.04. By using

the resulting value of $\approx 13Z$ for I , Bloch calculated values of the stopping number, B ,

$$B = Z \ln(2mv^2/I) \quad (22)$$

for several gaseous and metallic elements that deviated $\leq 12\%$ from the experimentally determined stopping numbers, whereas the values of B calculated by Bethe with the then available values of I showed much higher—up to 97%—deviations for each of the substances considered, including hydrogen (97% for gold).³¹ Recently the value of u was determined¹⁵³ nonempirically, thus leading to the value of 4.95 for the ratio I/Z , which is in gross disagreement with reliable values for I . It should be noted that already by 1937 it had been pointed out by Jensen^{108,154} from theoretical work that considered also the interaction of spin between electrons, in contrast to Bloch's model, that I/Z was expected to be higher for low Z elements than for higher Z elements. Jensen^{108,154} proposed another approximate relation for I based on a statistical model of the atom according to which the electron cloud is uniformly distributed inside a sphere as in the Sommerfeld conduction electron gas in a metallic sphere

$$I = \kappa Z(1 + \alpha Z^{-2/3}) \quad (23)$$

where the constants κ and α ($\alpha \leq 1$) must be determined experimentally. More recent information shows that after some oscillations at low Z , for high Z (e.g., $Z \geq 30$) I/Z tends to ≈ 10 eV.^{29,45,101,155,156}

Bohr developed a statistical treatment of stopping power for metals mentioned previously, in which the electrons were considered as an ensemble of oscillators with different excitation probabilities. In his work he estimated also values of I for metals, e.g., 45 eV for^{51,57} I_{Li} and 60 eV for^{51,98b} I_{Be} . However, by 1960, the only accurate calculations of the logarithmic mean excitation energy done by direct summation according to eq 4 were only those of H and He. At that time Dalgarno^{82b,150,157–160} proposed a method of determining I based on the semiempirical calculation of the slope of the function

$$S(k) = \sum_n f_{n0}(E_n - E_0)^k \quad (24)$$

for k , a real number, tending to zero:

$$\ln I = [(d/dk) \ln S(k)]_{k=0} \quad (25)$$

$S(k)$ was approximated by

$$S(k) = [a + bk + ck^2 + d \ln(2.5 - k)]^k S(0) \quad (26)$$

and I was determined finally from

$$I = (a + d \ln 2.5)R \quad (27)$$

where R is the Rydberg energy as before. The constants a , b , c , and d were determined from the Thomas–Reiche–Kuhn sum rule that sets $S(0)$ equal to Z and from additional sum rules^{157–163} for the oscillator strengths. E.g., for $k = -2$, $S(-2)$ equals $\alpha/4$, where α is the static dipole polarizability in units of the cubed Bohr radius. In this way values for I_{Li} (38.8 eV) and I_{Be} (66.1 eV) in close agreement with available experimental values were obtained,¹⁵⁷ as well as new values for I_{H} (14.8 eV) and I_{He} (41.7) that agreed with those from the direct summation of eq 4, 15.0 and 41.5 eV, respectively.^{157–160} Later values for molecular hydrogen¹⁶¹ (18.4 eV) and nitrogen¹⁵⁰ (82.1 eV) were deter-

mined with the same method. Subsequent to the determination of I_{Li} and I_{Be} , the same procedure was applied^{164a} to calculate I for Ne, Ar, and Kr. Later I_{He} was recalculated^{101,164b} (39 eV).

The semiempirical method of summations, based on $S(k)$ was also applied for the determination of the mean excitation energy for energy straggling^{29,164a} I_1 defined by

$$\ln I_1 = \sum_n (E_n - E_0) f_{n0} \ln (E_n - E_0) / \sum_n (E_n - E_0) f_{n0} \quad (28)$$

where the symbols have the same meaning as in eq 4 and the summation over n includes also integration over the continuum. In terms of $S(k)$, I_1 was determined from

$$\ln I_1 = (d/dk) \ln S(k)|_{k=1} \quad (29)$$

for Ne, Ar, and Kr.^{164a} From a similar equation to eq 25 and 29, however, with $k = -1$, the corresponding quantity I_{-1} is obtained that is related to the cross section for electronic excitation due to inelastic scattering for fast charged particles with atoms and molecules.

In addition, I_{He} (42.0 eV),¹⁶⁵ I_{He} (42.1 eV),¹⁶⁶ and I_{Li} (33 eV)¹⁶⁷ were recalculated from the dipole spectrum of He and Li that was determined with the application of a variational procedure to the solution of the linear equation that describes the response of these atoms to a time-dependent dipole perturbation. Also, I_{He} was determined.¹⁶⁶ The new value of I_{Li} is in much better agreement with additional values^{101,159} of I for free Li.

The method was extended¹⁶⁸ by constructing a model of the complete spectrum of dipole oscillator strengths for H_2 from experimental and theoretical data that was consistent with the sum rules for parallel, f^{\parallel} , and perpendicular, f^{\perp} , oscillator strengths for parallel and perpendicular transitions, respectively. I was defined by

$$\ln I = \frac{1}{2} [\sum_n f_{n0}^{\parallel} \ln (E_n - E_0) + \sum_m f_{m0}^{\perp} \ln (E_m - E_0)] \quad (30)$$

This method led to the value¹⁶⁸ of 18.6 eV for H_2 that is in good agreement with the previous value¹⁶¹ of 18.4 eV, yet still smaller than the value of 19.5 (± 0.5) eV calculated previously by Garcia¹⁶⁰ along with those of I_{H} , I_{He} , and I_{Li} with the method of sums $S(k)$, using eq 25.

The variational¹⁶⁵ method was further extended and modified¹⁶⁹ and was applied to H_2 . It led to the value¹⁶⁹ of 18.2 eV for I_{H_2} . The method of sums was also later applied to H_2 and led to a value¹⁷⁰ of 19.52 eV for I_{H_2} for clamped nuclei and to 19.21 eV for thermal averaging¹⁷⁰ over rotational levels for the ground vibrational state of H_2 . These values are higher than those of Dalgarno;^{161,168} however, they are in good agreement with Garcia's value.¹⁶⁰ Values of I for He (40.8 eV) up to Na (112.2 eV) were also calculated^{171a} by using approximate generalized oscillator strengths. This latter formulation was recently applied for I values for positive ions of Al and Au.^{171b}

More recently several investigators used oscillator strength spectra and the method of moments^{101,131,151,172-179} to calculate I along with other quantities, e.g., the following: I_{He} (38.82 eV),¹⁰¹ I_{Li} (34.02

eV),¹⁰¹ I_{Be} (38.62 eV),¹⁰¹ and I for several other elements;¹⁰¹ I_{H} (15.03 \pm 0.15 eV),¹⁷² I_{H_2} (18.73 \pm 0.19 eV),¹⁷² and I for all the noble gases except Rn;¹⁷² I_{H_2} (19.2 eV)¹⁷³ and I_{Ar} .¹⁷⁴ Inokuti and co-workers^{101,175,176} employed nonempirical calculations of various moments of electric dipole oscillator strength distributions (df/dE) to determine values for the mean excitation energy for stopping power, I , and for energy straggling,²⁹ I_1 . They employed a Hartree-Slater central potential model and calculated df/dE explicitly from the dipole matrix elements between initial and final electronic states for the entire spectrum. They obtained values for I for all free atoms from helium through strontium. I and I_1 were determined from^{101,172,177}

$$\ln (I/R) = L(0)/S(0) \quad (31)$$

and

$$\ln (I_1/R) = L(1)/S(1) \quad (32)$$

where

$$S(k) = \int \left(\frac{E}{R}\right)^k \frac{df}{dE} dE \quad (33)$$

and

$$L(k) = \frac{dS(k)}{dk} = \int \left(\frac{E}{R}\right)^k \ln \left(\frac{E}{R}\right) \frac{df}{dE} dE \quad (34)$$

The values 0, 1, and -1 for k are associated with stopping power, straggling, and electronic excitation due to inelastic scattering of fast charged particles, respectively. The integrals represent also summations over discrete spectra. Meath and co-workers^{131,151,178,179} used also the above approach with both experimental data and available accurate theoretical dipole oscillator strength distributions and determined I and I_1 for several atoms and molecules including H_2 (19.26 eV), O_2 (95.02 eV), N_2 (81.84 eV), H_2O (71.62 eV) and hydrocarbons. Also, these results^{131,151,178} show an increase in I for diatomic molecules compared to that for atoms, apparently due to chemical bonding effects.

Recently calculated values of the mean ionization potential of several elements were reported¹⁸⁰ to be generally close to experimental values of I of the same elements.

In condensed phases, the mean excitation energy has also been defined in terms of the complex dielectric response function

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (35)$$

where the angular frequency ω equals E/\hbar , where E designates energy and \hbar Planck's constant divided by 2π . The expression for I is^{14,29,175,181-183}

$$\ln I = (2/\pi\omega_p^2) \int_0^\infty \omega \text{Im} [-1/\epsilon(\omega)] \ln (\hbar\omega) d\omega \quad (36)$$

where ω_p is the plasma frequency given by eq 14. Here $\omega \text{Im} [-1/\epsilon(\omega)]$ corresponds to $Z^{-1} df/dE$ which is included in eq 31 implicitly. This definition accounts for collective effects in addition to shifts in energy levels of the atoms due to chemical bonding and other interatomic interactions in the condensed phase.

Additional semiempirical expressions for I were developed^{184,14} in the 1960s following Jensen's expression,^{108,154} eq 23:

$$I_{\text{adj}} = 12Z + 7 \text{ eV} \quad (37)$$

for $I_{\text{adj}} < 163 \text{ eV}$ or $Z < 13$, and

$$I_{\text{adj}} = 9.76Z + 58.8Z^{-0.19} \text{ eV} \quad (38)$$

for $I_{\text{adj}} \geq 163 \text{ eV}$ or $Z \geq 13$, where I_{adj} is defined¹⁸⁵ by

$$I_{\text{adj}} = I \exp(C/Z)_{\beta=1} \quad (39)$$

Equation 38 was proposed by Sternheimer¹⁸⁴ and applied both for¹⁸⁴ I_{adj} and for^{46,186} I (both equations for I_{adj} , eq 37 and 38, are ascribed to Sternheimer in ref 14). The following expressions for I were determined¹⁸⁷ empirically from the analysis of experiments:

$$I \text{ (eV)} = 11.2 + 11.7Z \quad (Z \leq 13) \quad (40)$$

$$I \text{ (eV)} = 52.8 + 8.71Z \quad (Z > 13) \quad (41)$$

Additional computations of lower and upper bounds^{188,189} of I and of values^{82b} of I and I_1 for atoms were done in the late 1960s and in the 1970s. A variational procedure¹⁸⁹ was used for the bounds of I_H and the method of sums^{188,82b} for the bounds¹⁸⁸ of I_H , I_{He} , I_{Ne} , I_{Ar} , and I_{Kr} and for values of I and I_1 . Values of I for all the noble gases except Rn were reported^{82b} again.

It should be noted that the calculations^{108,190} of I by Brandt in the 1950s for free and chemically bound atoms mentioned earlier in this work were based on Jensen's expression^{108,154}. The values of I for free atoms from eq 23 were subsequently multiplied by a correction factor accounting for "valence shell"—chemical bonding and interparticle interaction—and polarization effects to derive the values of I for molecules in the gaseous and condensed states and for metals. For molecules, e.g., for H_2 , this factor was reduced¹⁹⁰ to the square root of the ratio of the polarizability of H in the free atomic state and in H_2 ; hence, from I_H (14 eV) the value¹⁰⁸ of 18 eV was calculated for I_{H_2} .

In 1953 Lindhard and Scharff⁵⁷⁻⁵⁹ reported the development of a statistical model based on an inhomogeneous free electron gas mentioned earlier in the Stopping Power section. This model led to the approximate determination of I by employing the "local plasma approximation". In this approximation it was assumed that the collective modes of longitudinal interaction between electrons in the electronic cloud characterize the dynamical behavior of an atom in the stopping medium instead of the individual electronic transitions in the atom. Therefore, the logarithm in the quantum-mechanical stopping power expression of Kramers,^{49,50,57} eq 15, based on a homogeneous electron gas was averaged⁵⁷ with respect to the nonuniform total electron cloud distribution in an atom of the stopping medium over the space coordinates. The resulting integral was set equal to the dimensionless quantity L mentioned previously under Stopping Power after a constant parameter was also introduced⁵⁷

$$L = Z^{-1} \int \rho(\vec{r}) \ln \left[\frac{2mv^2}{\gamma \hbar \omega_p(\vec{r})} \right] d^3\vec{r} \quad (42)$$

L was related to the stopping number B given by eq 22 as follows:

$$L = B/Z \quad (43a)$$

or

$$L = \ln(2mv^2/I) \quad (43b)$$

Consequently, from eq 42 and 43 the expression for I in terms of $\rho(\vec{r})$ and $\omega_p(\vec{r})$ was obtained according to the local plasma model.

$$Z \ln I = \int \rho(\vec{r}) \ln [\gamma \hbar \omega_p(\vec{r})] d^3\vec{r} \quad (44)$$

or

$$I = \gamma \exp \left\{ Z^{-1} \int \rho(\vec{r}) \ln [\hbar \omega_p(\vec{r})] d^3\vec{r} \right\} \quad (45)$$

for

$$\int \rho(\vec{r}) d^3\vec{r} = Z \quad (46)$$

where $\rho(\vec{r})$ is the local electron number density at distance $|\vec{r}|$ from the origin, γ is a constant, and $\omega_p(\vec{r})$ is the plasma frequency corresponding to $\rho(\vec{r})$, i.e.,

$$\omega_p(\vec{r}) = [4\pi e^2 \rho(\vec{r}) / m]^{1/2} \quad (47)$$

In an alternate⁵⁸ semiempirical formulation that treats the oscillator strength density $g(\omega)$ explicitly, L was set equal to

$$L = Z^{-1} \int_0^{2mv^2/\hbar C} g(\omega) \ln(2mv^2/\hbar\omega) d\omega \quad (48)$$

with

$$\int g(\omega) d\omega = Z \quad (49)$$

where the effective frequency ω is the averaged orbital frequencies of the electrons in the independent-particle model and C is a positive constant that is intended to exclude the contribution to stopping power by high frequencies that makes the value of the logarithm negative. In this statistical treatment the cut-off value of ω was approximately set equal to 1 for low kinetic energies. The effective frequency was expressed as a function of the local electron density $\rho(\vec{r})$ included in $\omega_p(\vec{r})$ in eq 47

$$\omega = \gamma \omega_p(\vec{r}) \quad (50)$$

and the oscillator strength density was also expressed in terms of $\rho(\vec{r})$ with eq 48 applied not to the entire space of the electron cloud but to a volume element instead so that the number of electrons in the volume element will be equal to the oscillator strength associated with the same element.

$$g(\omega) d\omega = 4\pi \rho(r) r^2 dr \quad (51)$$

or

$$g(\omega) d\omega = \rho(\vec{r}) d^3\vec{r} \quad (52)$$

Equations 48–52 lead to eq 42 and 44. The constant γ was introduced to adjust the contribution from the collective modes of longitudinal electronic oscillations to the effective frequency as is shown by eq 50. The value of γ was expected⁵⁷ to approach the value of 1 for light substances, where the polarization in an atom is not so important and it was assumed to be equal to 2^{0.5} for heavier substances. With γ set equal to 1 Lindhard and Scharff⁵⁷ obtained values of I with eq 44 for some elements in the gaseous state including H_2 ($I_{H_2} = 16 \text{ eV}$) using atomic Hartree wave functions and in the solid state that were in close agreement with the corresponding experimental values of I that were accepted

then. With γ set equal to $2^{0.5}$ they calculated⁵⁷ values of the ratio I/Z for Ar and atomic Hg with $\rho(\bar{r})$ from the Hartree atomic model, which were compared to the I/Z values from the Thomas-Fermi and Lenz-Jensen statistical models of the atom.

They expected that estimates of I for molecules and solids, where chemical binding enters, would not be very accurate because the most loosely bound electrons would be involved. However, on the basis of their results they suggested⁵⁷ that the shift in I due to chemical binding or due to deviations from the statistical model for different atoms could be estimated from eq 44 by introducing the appropriate shift in $\rho(\bar{r})$. The change in I was expected⁵⁷ to be comparable to the corresponding change in I due to the uncertainty in the values of the constant γ .

Later Brandt¹⁹¹ applied eq 44 of the local plasma model for the determination of values of I . He proposed to approximate γ by

$$\gamma(\bar{r}) = [1 + \omega^2(\bar{r})/\omega_p^2(\bar{r})]^{1/2} \quad (53)$$

where the ratio of ω over ω_p relates the contribution of the one-electron independent-atom modes to that of the collective modes of electronic excitation in the electron cloud. For $\omega = 0$ γ equals 1 according to eq 53. Brandt¹⁹¹ showed using hydrogenic wave functions that I and γ for atoms could be determined from the corresponding values of I and γ for each electronic shell, γ_n and I_n , using eq 44

$$\ln I = Z^{-1} \sum_n Z_n \ln(\gamma_n I_n) = \ln \prod_n (\gamma_n I_n)^{Z_n/Z} = \ln(\bar{\gamma} \bar{I}) \quad (54)$$

and determined¹⁹¹ the values of I for the K and L shell, I_K and I_L

$$I_K = 0.893 N_K^{1/2} Z_K^{3/2} r y \quad (55)$$

$$I_L = 0.151 N_L^{1/2} Z_L^{3/2} r y \quad (56)$$

N and Z refer to number of electrons in the shell and the effective charge. The corresponding expression for the K shell for the independent-particle model determined by Bethe^{21,24} and co-workers is

$$I_K = \lambda Z_{\text{eff}}^2 r y \quad (57)$$

In all these expressions the energy units are rydbergs (13.606 eV). The constant λ in eq 57 equals²¹ 1.102.

Brandt¹⁹¹ also pointed out the analogy between eq 54 with I_n and γ_n from the statistical model of the atom with a corresponding expression for the model of the independent atom, eq 4.

Brandt finally extended the local plasma model by applying eq 44 to the determination of I for the molecule of LiH and for the LiH crystal using appropriate $\rho(\bar{r})$ for these cases.¹⁹¹ In preliminary calculations¹⁹¹ he had determined I values with the Bragg rule for the LiH crystal, considered to be composed of a mixture of Li, H, Li⁺, and H⁻ corresponding to the mean charge distribution in the LiH crystal.

Lindhard and Scharff extended⁵⁸ the calculations of I values with eq 44 of their model to several elemental gases and metals. They used $\gamma = 2^{0.5}$ and atomic Hartree wave functions to determine $\rho(\bar{r})$ for gases. The values obtained were compared with values of I determined semiempirically by measuring the maximum (S_m) in stopping cross sections plotted as a function of the

energy of incident protons. The relation used at the maximum is

$$L_m = S_m(v^2/v_0^2 Z)_m \quad (58)$$

The agreement was close for Al and heavier elements including noble gases.

Later Bonderup¹⁹² determined I values for several elements semiempirically from experimental stopping power values using the following relation with Al as the reference standard

$$I = I_{\text{Al}}(Z/Z_{\text{Al}}) \exp(L - L_{\text{Al}}) \quad (59)$$

The I values were in agreement with experimental values. Later eq 44 was used to determine I for atoms with¹⁹³ $\gamma = 1$ and¹⁹⁴ $\gamma = 2^{1/2}$ and for K and L shells.¹⁹³ So far, eq 44 of the local plasma approximation had been applied to calculations of the logarithmic mean excitation energy of chemical elements by employing an electron number density for the atom of every element considered to determine $\rho(\bar{r})$ and $\omega_p(\bar{r})$ with the exception of the calculations for LiH¹⁹¹ and elemental solids where less approximate expressions for $\rho(\bar{r})$ were used.^{57,58,93,195} The values of I calculated in this way for atoms were subsequently compared^{158,93,194,195} with the experimental results for molecules in the gas phase or elements in the condensed phase, in addition to atoms of the noble gases, and lately these values of I have been scaled^{93,195} to fit the corresponding empirical and experimental values. However, chemical bonding and interparticle interactions had not been explicitly accounted for^{193,194} except for LiH and some elemental solids mentioned previously. Recently, eq 44 of the local plasma approximation was employed to determine I for molecules¹⁹⁶ (e.g., $I_{\text{H}_2} = 18.9$ eV) by expressing the local electron number density for each atom in the molecule according to the Gordon-Kim¹⁹⁷ electron gas model of molecular binding. Correction factors were derived to account for the change in atomic I values because of the chemical binding between two atoms. The electron number density for each atom was determined with lowest order Slater orbitals.¹⁹⁸ Subsequently, the determination of I was extended to partially ionic compounds¹⁹⁹ like LiH and LiF by using Hartree-Fock-Slater atomic wave functions¹⁹⁹ for the atoms and ions contributing to the total electron density.

Last year I proposed²⁰⁰ that eq 44 of the local plasma approximation be applied with the use of accurate electronic wave functions that account for chemical binding to describe the local electron number density in the gas phase and in the solid phase for ionic solids and especially for metals. In this work such a new application of the local plasma approximation to determine I of gas-phase molecules is described. It consists in employing available very accurate molecular electronic wave functions to determine the required local electron number density of diatomic and small polyatomic molecules. Once the values of I for diatomic molecules are determined, one can obtain approximate values of I , perturbed by the chemical bonding, for atoms, and subsequently values of I for polyatomic molecules by applying Bragg's additivity rule for I . It would be very interesting and very important for various applications⁴⁻¹⁶ to compare the values of I obtained in this way with those to be obtained by using available molecular electronic wave functions for small poly-

atomic molecules and radicals and those that have been obtained by experimental and other theoretical models.

Additional Results and Discussion

It was decided^{200c} to utilize available molecular electronic wave functions that take chemical bonding into account explicitly to determine the local electron number density in a covalently bonded molecule and subsequently the value of the molecular logarithmic mean excitation energy according to eq 44 of the local plasma model in view of its great simplicity compared to using the models that require knowledge of the electronic dipole oscillator strengths (or distributions). The local electron number density, $\rho(\vec{r})$, for a diatomic molecule with n electrons in a stationary state is defined by

$$\rho(\vec{r}) = \sum_{i=1}^n \int |\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots, \vec{r}_i, s_i, \dots, \vec{r}_n, s_n; R)|^2 \times \delta(\vec{r} - \vec{r}_i) d^3\vec{r}_1 ds_1 d^3\vec{r}_2 ds_2 \dots d^3\vec{r}_n ds_n \quad (60)$$

where \vec{r}_i and s_i are the space and spin coordinates of the i th electron, R is the internuclear distance of the diatomic molecule, and $\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots, \vec{r}_i, s_i, \dots, \vec{r}_n, s_n; R)$ designates the time-independent electronic wave function of the system of n electrons.

In these first calculations for a homonuclear diatomic molecule with eq 44, the molecular electronic wave functions employed were as follows: (i) the earliest electronic wave function for H_2 , the electronic wave function with 13 terms for H_2 at its equilibrium internuclear distance (1.4 bohr) of James and Coolidge,²⁰¹ that was reported to yield a dissociation energy of 4.697 eV compared with the present experimental value of 4.75 eV; (ii) a more recent molecular electronic wave function for H_2 at its internuclear equilibrium distance (1.4 bohr) with a three-term closed-shell correlation function by Kolos and Roothaan²⁰² that is reported to yield a dissociation energy of 4.6955 eV; and (iii) another accurate molecular electronic wave function for H_2 with 12 terms by Kolos and Roothaan²⁰³ that yielded a dissociation energy of 4.7397 eV at 1.4 bohr internuclear distance. The use of these molecular wave functions led to the computation of $\rho(\vec{r})$ with eq 60 and, with eq 44 of the local plasma approximation for $\gamma = 1$, to the computation of the values 20.3, 19.5, and 20.2 eV for I_{H_2} , respectively. These numbers are expected to be correct within less than 5% error as a result of approximations and possible nonconvergence to the correct values.

In order to determine the correct value for I_{H_2} the value of γ has to be determined. Once the value of γ has been determined, the correct value of I is proportional to the value of I for $\gamma = 1$, $I_{\gamma=1}$, as follows from eq 45

$$I = \gamma I_{\gamma=1} \quad (61)$$

Instead of determining γ_n for each atomic shell, as in Brandt's work,¹⁹¹ by comparison of I_n from this model with accurate values from another model,¹⁷⁵ effective values of γ for atoms were determined by direct comparison of atomic I values from this model with those from the method of moments of the oscillator strength distribution.¹⁰¹ It has been reported^{101,176} that eq 44 led to low values of I for atoms with¹⁹³ $\gamma = 1$ and to values of I for atoms¹⁹⁴ with $\gamma = 2^{1/2}$ that were higher by

TABLE I. Values of the Constant γ for Atoms Obtained with Various Electronic Wave Functions for Atoms of Several Elements

atom	γ_{SL}	γ_{HF-HS}	γ_{HFS}	$\gamma_{\text{exact w/f}}$
H (1)				1.235
He (2)	1.03 (1)	1.12 (3)	1.09 (7)	
Li (3)	1.27 (7)	1.24 (3)	1.29 (6)	
Be (4)	1.20 (5)	1.19 (8)	1.22 (6)	
B (5)	1.21 (0)	1.22 (2)	1.24 (7)	
C (6)	1.18 (2)	1.21 (8)	1.24 (0)	
N (7)	1.14 (7)	1.20 (5)	1.22 (4)	
O (8)	1.13 (3)	1.19 (0)	1.22 (7)	
F (9)	1.10 (4)	1.17 (6)	1.22 (0)	
Ne (10)	1.07 (5)	1.16 (0)		

20–30% compared to the corresponding atomic values obtained with the method of moments of electronic dipole oscillator strength distributions.^{101,176} Therefore, the effective value of γ for atoms that counterbalances the shift in the effective frequency in eq 50 with respect to the plasma frequency turns out to be between 1 and 2 for all atoms up to Sr for which accurate values of I have been calculated.¹⁷⁶

Of course, here not an atom but a covalently bonded molecule is treated. Nevertheless, a similar approach, namely, to consider the value of 19.26 eV from the model of moments^{131,157,178} with semiempirical data as the correct value for I_{H_2} and to determine γ for H_2 from the ratio of I for the two models, perhaps an easy way out, was dismissed as being a priori prejudicial to either model. I decided to examine the theoretical results for I of atoms more closely instead.

Table I shows effective values of γ for atoms calculated from the ratio of the accurate values of I as determined from the model of moments¹⁰¹ over those from the local plasma model using (i) electron densities determined with Slater orbitals¹⁹⁸ (SL), in this work, (ii) electron densities tabulated by Herman and Skillman, based on Hartree–Fock wave functions (HF–HS),²⁰⁴ from previous work,^{194,93} and (iii) electron densities determined with Hartree–Fock–Slater orbitals (HFS), in this work. The latter orbitals were determined by Clementi and Roetti.²⁰⁵

Discussion and Conclusion

The difference between the SL and HFS atomic γ values in Table I is ascribed to the differences in the wave functions used. Possibly, the same is true for the HF–HS values of γ .

The calculations with Hartree–Fock wave functions, along with SCF (self-consistent field) wave functions, however to a limited sense, lead to values for quantities like, e.g., electron densities that are considered valid to “second order” as a result of the early investigations of Brillouin,^{206–208} and Møller and Plesset.²⁰⁹ Therefore, the Hartree–Fock–Slater (HFS) γ values in Table I are considered to be the most reliable. These atomic γ values show practically no difference between γ for the lighter atoms and γ for the heavier atoms with the exception of He and to some extent Li, contrary to the early assignment⁵⁷ of the value of 1 for the light atoms and of $2^{1/2}$ for the heavy atoms. The lower γ for He may be due to a slight underestimation of I_{He} as already indicated by Dehmer et al.¹⁰¹ Indeed this value¹⁰¹ of I_{He} is about 9% smaller than the closest experimental value,¹⁰¹ while for other noble gases the corresponding difference from experimental values is about a few

percent. Incidentally, the value of I_{He} determined with the local plasma model¹⁹⁴ is shown smaller by $\approx 10\%$ in Figure 9 of ref 101, and this slight misrepresentation has apparently been carried over in Figure 4 of ref 14.

Since in Table I even for larger atoms than H the effective γ value is ≈ 1.22 —with the exception of He and to a lesser extent of Li—it may be considered not untenable to ascribe a similar value of γ to light molecules like H_2 since, in addition, no distinction between atoms and molecules was made by Lindhard and Scharff in their model.⁵⁷ Incidentally, this assignment may appear to be somewhat related to an assigned similar proportionality between the corresponding ionization potential and the I value for H and for H_2 that was introduced long ago by Williams^{152a} when he proposed that the I_{H_2} value should be higher than 15 eV, the value which Bethe²⁸ had proposed, namely $I_{\text{H}_2} \approx 1.1 \times \text{IP}$, in similarity with Bethe's expression for the I value for H, $I_{\text{H}} = 1.10 (3) \times \text{IP}$, mentioned earlier in this work under Determination of the Logarithmic Mean Excitation Energy. Nevertheless, in this work this assignment was based both on the results for γ for several atoms and on the similarity of H and H_2 in some ways. After all, the local electron density difference is small—albeit extremely important to chemical bonding—between molecules and their constituent^{210–213} atoms (or ions) compared to the local electron density of the constituents of the molecule in all areas, except in the inter-nuclear region, where, however, the electron density is many times smaller compared to that around the nuclei. As for the nuclear charge distribution both in a molecule and in the constituent atoms (or ions) the distribution deviates similarly from that of a uniform fixed background of positive charge assumed in the statistical models. Therefore, the shift in the effective frequency in eq 50 in going from the independent-particle model to the statistical atomic model may be considered approximately equal to the shift from the independent-molecule model to the statistical “molecular” model. Such an assignment, i.e., $\gamma \approx 1.2$, would certainly lead to a value of I for H_2 well over 20 eV. Indeed, if the value of 19.5 eV is accepted for I_{H_2} with $\gamma = 1$, the value for $\gamma \approx 1.2$ would yield 23.4 eV. Of course, this value is based on the static electron density at the equilibrium nuclear distance. However, when the effect of the internal motion^{214–218} of the molecule on the electron density is taken into account, this figure may become somewhat lower, roughly ≈ 23 eV, in view of the already reported¹⁷⁰ decrease of I_{H_2} from 19.52 to 19.21 eV when thermal averaging over rotational levels at the ground vibrational level of H_2 was taken into account in the calculation of I_{H_2} with the method of sums, $S(k)$, mentioned earlier in this work.

There are several estimates and experimental values^{219–238} of I_{H_2} in addition to the values mentioned earlier in this work. A summary of previously reported values of I_{H_2} is shown in Table II. It is interesting that the originators⁵⁷ of this statistical model treated the case of molecular hydrogen using an atomic wave function, however, with Z set equal to 1.2 to account for chemical bonding and γ set equal to 1. The value of 16 eV that they obtained⁵⁷ compared excellently with the experimental values accepted⁵⁷ at that time. Nevertheless, the value of 16 eV for I_{H_2} was lower in relation to the theoretical values.^{57,100,152}

Certainly the value of ≈ 23 eV for I_{H_2} agrees with none of the previously reported theoretical values in Table II. However, it is within,²³² or a little higher than,^{229,230,238} the upper limit of some of the reported experimental values^{229,230,232,238} in Table II when the reported experimental error is considered.

It may be of interest to note that already the theoretical values of $I_{\text{H}_2\text{O}}$ for vapor (71.62 eV)^{131,151,175,178} and for liquid (75 eV)^{181,175} have been disputed,^{136c} and the values for I_{Al} determined^{200b} by employing experimental plasmon data and a more accurate wave function for solid Al, at my suggestion, are appreciably lower compared to the accepted values. However, the position of this researcher is that definitely more work is needed to assess the significance of these values, including the I_{H_2} value and especially the I_{Al} values.

Further Research

More work is in progress to determine values of I for several other molecules and to further investigate this very interesting development regarding the value of I_{H_2} . It may lead to reconsideration of accepted values of I for H_2 and for other molecules or atoms that have been determined relative to I_{H_2} with Bragg's additivity rule and finally to revision of accepted values, if supported by additional evidence.

Further applications of the local plasma model with wave functions that take into account chemical bonding and interparticle interaction, if present, explicitly are the investigation of the determination of additional mean excitation energies, e.g., for straggling, I_1 , for electronic excitation, I_{-1} , and for the Lamb shift (of atomic energy levels), I_2 . All four I_k 's mentioned above can be regarded¹⁷⁷ as special cases of

$$\ln I_k = [d \ln S(x)/dx]_{x=k} \quad (62)$$

where $S(x)$ was defined previously in this work in eq 24, for a discrete spectrum, and eq 33 for a continuum.

Additional possible applications of the present procedure are the calculation of “shell” corrections from experimental stopping powers and I values for molecules, etc., calculated with the local plasma model—as for H_2 —by using eq 16 and the accurate determination of the effective frequency by determining γ more accurately or by modifying ω_p , e.g., by considering more terms to increase the order of accuracy.^{52,239}

In view of the encouraging results that have been obtained so far by various investigators^{57,58,191,193–196,199} with eq 44 of the local plasma model, it is plausible to expect further work to explain its success. It has already been pointed out by Inokuti and co-workers¹⁷⁶ that there may be an analytical quantitative derivation of eq 44. In the transition between eq 4 for I according to the independent-particle model and eq 44 according to the statistical treatment of a particle, in this work of a molecule, the averaging with respect to the dipole oscillator strength has been replaced by the averaging over the electron cloud density and the discrete transition energies have been replaced by $\hbar\omega_p$, where ω_p is associated with disturbances of the entire electron cloud density that show oscillatory time behavior, i.e., the plasma oscillations.²⁴⁰ It has been shown also in a quantum-mechanical perturbation treatment of an electron gas^{239,52} that $\hbar\omega_p$ is approximately the funda-

TABLE II. Values of the Logarithmic Mean Excitation Energy for Stopping Power of H_2 from Theoretical Calculations, Experiments, and Estimates Based on Theoretical or Experimental Data

ref ^a	I_{H_2} , eV	
	theory	experiments
Bethe (28, 96) 1932	15	
Blackett (94) 1932		(90), 15 (cor)
Williams (152, 96) 1932	17.5, 17.1	
Mano (96) 1933		16.0
Hirschfelder/Magee (219) 1948		17.93
Platzman (100, 29) 1950	19	
Bakker/Segré (220) 1951		15.6 (from $-CH_2-$ for $I_{Al} = 150$)
Bogaardt/Koudijs (221) 1952		17.1 \pm 0.3
Thompson (103, 222) 1952		18.2 (for liquid H_2 for $I_{Cu} = 279$) (ref 222)
		21.7 (renormalized to $I_{Cu} = 306$) (ref 222)
		21.9 (renormalized to $I_{Cu} = 314$) (ref 223)
		22.2 (renormalized to $I_{Cu} = 320$) (ref 224)
		22.3 \pm 1.6 (renormalized to $I_{Cu} = 322$ and $I_{water} = 75$) (ref 225)
Lindhard/Scharff (57) 1953	16	
Brolley/Ribe (185, 222, 226) 1961		19
Brandt (190) 1956	15	18
Brandt (108) 1958	18	
Zrellov/Stoletov (227, 222) 1959		15 (for $I_{Cu} = 305$)
Riezler/Schepers (228) 1961		16.5
Kramer-Agehev/Mash. (102, 229) 1961		14 \pm 7 (for 635–651 MeV)
Martin/Northcliffe (230) 1962		18.3 \pm 2.6
Barkas/Berger (184) 1964	19	
Berger/Seltzer (231) 1964	18.7	
Dalgarno/Williams (161) 1965	18.4	
Palmer (232) 1966		20 \pm 3 (at 2.5 MeV), 17 \pm 0.7 (at 3–7 MeV), 21.5 \pm 2 (at 8 MeV)
Garcia (160) 1966	19.5 \pm 0.5	
Bichsel (155) 1968		18
Victor/Dalgarno (168) 1969	18.6	
Kamikawai et al. (169) 1969	18.2	
Turner et al. (233) 1970		18.2
Garbincius/Hyman (234) 1970		20.4 \pm 0.9 (for liquid H_2)
Bonderup/Hvelplund (235) 1971		19.4
Bichsel (236) 1972		19.2
Langhoff/Yates (172) 1972	18.73 \pm 0.19	
Ford/Brown (170) 1973	19.52, 19.21	
Gerhart (173) 1975	19.2	
Andersen/Ziegler (83) 1977		18.8
Zeiss et al. (131, 151, 178) 1977	19.26	
Besenbacher et al. (237) 1979		17.6
Janni (238) 1980		20.4
Ahlen (14) 1980	18.5 \pm 0.2	
Ziegler (93a, 195) 1980		19
Wilson/Kamaratos (196) 1981	18.9	
Seltzer/Berger (225) 1982	19.2 \pm 0.4	
Kamaratos (200c) 1983	\approx 23	

^a Entries in this column are in the following form: researcher (ref) year.

mental quantum of energy of the collective oscillations in the electron gas, the plasmon energy. It should be noted that long ago a free electron gas model was applied to individual molecules in addition to the condensed state of matter to treat the electron density of π -electrons and the diamagnetic anisotropy of aromatic molecules^{241–243} and to determine energy states and account for observed spectra of large organic molecules.^{244–256} Araki²⁵⁶ reported that the frequency of the absorption maximum in carotenoids decreases as the molecular length increases and ultimately converges to a limit that corresponds to the plasma frequency of the π -electrons. Therefore, the excitation energy converges to the energy of the plasma oscillation $\hbar\omega_p$. More recently, calculations on ethene indicated²⁵⁷ a collective singlet state at about 50 eV. However, no experimental evidence has been obtained.²⁵⁸

The results on atoms and molecules obtained with this statistical model that takes the collective longitudinal electronic excitation into account support further investigation of collective effects in molecules to establish which of these effects are indeed real and which

are just apparent and, in the latter case, what their cause is.

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Since that time the validity of previously reported I values for metallic Al (163–169 eV) including the previous theoretical I value¹⁸³ has been disputed²⁵⁹ in a new theoretical determination of the I value for metallic Al and a new I value for it in the range of 145–150 eV has been reported.²⁵⁹

Recent investigation of several experimental results for the stopping power of H_2 over the last \approx 20 years has

shown support^{200c,260} to a large extent for a value of over 20 eV for I_{H_2} .

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