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Stopping Power of Molecular Target by Local Density Approximation

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abstract

The electric energy loss, depending on impact parameter, of swift ions in collisions with molecule and atom targets was theoretically investigated with the dielectric function method. The stopping power was calculated on the basis of Lindhard dielectric function with the local density approximation (LDA). Hereby we take into account the inner shell exitation, as well as the "plasmon" excitation. The molecular effect that the stopping power per atom of a molecular target is smaller than that of an atom was found for the nitrogen molecule target.

Introduction

The energy loss or the stopping power is important quantity on the atomic collision research. It is well known that the stopping cross section is propotional to the velocity v of the incident ion at low velocities and decreases as $(1/v^2)\log v^2$ at high velocities. For an atomic target, the stopping power formulae were obtained by Bethe and Bloch at high velocities and by Firsov at low velocities. There is no theoretical formula derived from the first principle in the intermediate velocities region. On the other hand, for the electron gas Lindhard, Ritchie and other theoreticians presented the stopping formulae, where the induced polarization of the media play an important role. A typical feature here is to be able to present the above mentioned velocity-dependences of the stopping power at low- and high-velocities. Those two asymptotic behaviors of the stopping power in the nonrelativistic region are connected smoothly in the elecrtron gas model, apart from the absolute values. In the electron gas , there are two excitation modes: one is the individual and the other is the collective excitation. At high velocities, the collective excitation mode makes an equal contribution to the stopping as the individual exitation mode. The experimental data of the stopping cross section of the various gases have presented by several group [1-4]. It is well-known that at high velocities Bragg's additive rule holds valid. Usually, the molecular effect was not taken into accunt there. At lower velocities, however, it well be expected. As far as the authors know, there was not any analysis on the molecular picture. Our motivation is to evaluate the stopping power of the molecular gases in the framwork of a relatively simple but a powerful model. The present method will be extended to the estimation of the related energy deposition phenomena.

We start with the brief description of the stopping power and the dielectric function with the local density approximation. After that, we compare the calculated results with the data. Finally the summary and the conclusion are described.

Stopping power formula by dielectric function

In general, the stopping powers is defined by the energy loss of a particle passing through path unit length as

$$S = -\frac{dE}{dx} \tag{1}$$

where E is the kinetic energy and x is the path length of a projectile. When the projectile moves in the target electron gas, the electric polarization is induced. This works as a resistant force i.e., the stopping power. Hence, the stopping power formula is rewritten as

$$S = -\frac{dE}{dx} = -\frac{1}{v}\vec{v}\,\nabla E = \frac{Z_1 e}{v}\vec{v}\vec{F}(\vec{R},t) \tag{2}$$

where $\vec{v}$ is velocity, $Z_1 e$ and $\vec{R}$ are the charge of the projectile and its position vector, $\vec{F}$ is the induced electric field and t is the time. In order to get the stopping power, the induced expression of the electric field should be found. To do so, we call Maxwell's equation

$$\nabla\vec{F}(\vec{r},t) = -4\pi\{\rho_{ext}(\vec{r},t) - \rho_{ind}(\vec{r},t)\},$$

$$\nabla\vec{D}(\vec{r},t) = -4\pi\rho_{ext}(\vec{r},t) \tag{3}$$

where ρ_{ext} is the external charge, ρ_{ind} is the induced electron density and $\vec{D}$ is the electric displacement. By solving above equations in the Fourier space with the definition

$$\vec{D}(\vec{k},\omega) = \epsilon(\vec{k},\omega)\vec{F}(\vec{k},\omega), \tag{4}$$

we have

$$\rho_{ind}(\vec{k},\omega) = \left\{1 - \frac{1}{\epsilon(\vec{k},\omega)}\right\}\rho_{ext}(\vec{k},\omega), \tag{5}$$

$$\vec{F}(\vec{k},\omega) = -i\vec{k}\frac{4\pi}{k^2}\rho_{ind}(\vec{k},\omega). \tag{6}$$

By Eqs.(5) and (6), the induced electric field is found to be

$$\vec{F}(\vec{k},\omega) = -i\vec{k}\frac{4\pi}{k^2}\left\{1 - \frac{1}{\epsilon(\vec{k},\omega)}\right\}\rho_{ext}(\vec{k},\omega). \tag{7}$$

Here, as the external charge is assumed to be a point charge, one has

$$\rho_{ext}(\vec{k},\omega) = 2\pi Z_1 e\delta(\omega - \vec{k}\vec{v}). \tag{8}$$

Therefore, from Eqs.(2), (7) and (8), the stopping power is reduced to

$$S = \frac{Z_1^2 e^2}{\pi v^2}\int_0^\infty d\vec{k}k\int_{-kv}^{kv} d\omega\ \omega\ i\left\{1 - \frac{1}{\epsilon(\vec{k},\omega)}\right\}. \tag{9}$$

As shown in the next section, the real part of the inverse dielectric function is an even function of ω and the imaginary part is an odd function with respect to ω. Then the stopping power finally becomes

$$S = \frac{2Z_1^2 e^2}{\pi v^2}\int_0^\infty \frac{dk}{k}\int_0^{kv} d\omega\ \omega\ \mathrm{Im}\left\{1 - \frac{1}{\epsilon(\vec{k},\omega)}\right\}. \tag{10}$$

We remark that the imaginary part of the dielectric function can only contribute to the electronic stopping power.

Dielectric function

We consider the system of the free electrons moving in the uniform positive background. The Hamiltonian of this system is written as

$$\mathcal{H} = \sum_i -\frac{\hbar^2}{2m_e}\Delta_i + \frac{1}{2}\sum_{i(\neq)j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - V_0 \tag{11}$$

where $\vec{r}_i$ is the position vector of the i-th electron and Δ_i denotes the Laplace operator with respect to $\vec{r}_i$. V_0 is the interaction potential between the free electrons and the uniform positive backround. If we express the second term in Eq.(11) in the Fourier space, one obtains

$$\mathcal{H} = \sum_i -\frac{\hbar^2}{2m_e}\Delta_i + \sum_{k(\neq 0)}\frac{2\pi e^2}{k^2}\rho_k^\dagger \rho_k, \tag{12}$$

where $\rho_k = \sum_j e^{-i\vec{k}\vec{r}_j}$ is the density fluctuation operator. Here we drop the constant terms of no interest.

The interaction potential $\mathcal{H}_{ind}$ between the external charge and the free electrons is also expressed in the Fourier space as

$$\mathcal{H}_{ind} = -\lim_{\delta\to 0}\sum_{k,\omega}\frac{4\pi e^2 Z_1}{k^2}\rho_k^\dagger \rho_{ext}(\vec{k},\omega)e^{i\omega t}e^{\eta t}, \tag{13}$$

where η is the positive infinitesimal because the interaction is introduced adiabatically. With Eqs.(11) and (13), the induced charge density in the electron gas is obtained within the perturbation

$$\rho_{ind}(\vec{k},\omega) = -\frac{4\pi e^2 Z_1}{\hbar k^2}\rho_{ext}(\vec{k},\omega)\sum_n\left\{\frac{|\langle\phi_n|\rho_k^\dagger|\phi_0\rangle|^2}{\omega - \omega_{n0} + i\eta} - \frac{|\langle\phi_n|\rho_k|\phi_0\rangle|^2}{\omega + \omega_{n0} + i\eta}\right\}, \tag{14}$$

where ϕ_0 and ϕ_n are the wavefunctions of an initial state $|0>$ and a final excited state $|n>$, E_0 and E_n are the energy in an initial state and a final state, and $\omega_{n0} = (E_n - E_0)/\hbar$. By substituting Eq.(14) into Eq.(5), the inverse dielectric function is

$$1 - \frac{1}{\epsilon(k,\omega)} = \frac{4\pi e^2}{m_e}\sum_n\frac{f_{n0}}{\omega_{n0}^2 - \omega(\omega + 2i\eta)}, \tag{15}$$

where f_{n0} is the oscillator strength of the form $f_{n0} = (2m_e/\hbar k^2)\omega_{n0}|\langle\phi_n|\rho_k|\phi_0\rangle|^2$. Using a mathematical relation:

$$\frac{1}{x + i\eta} \longrightarrow \wp(1/x) - i\pi\delta(x) \qquad (\eta \to 0_+),$$

the inverse dielectric function can be divided into the real part and the imaginary part.

$$\begin{aligned} Re\left\{\frac{1}{\epsilon(\vec{k},\omega)}\right\} &= 1 + \frac{4\pi e^2}{\hbar k^2}\sum_n|\langle\phi_n|\rho_k|\phi_0\rangle|^2\wp\left(\frac{2\omega_{n0}}{\omega^2 - \omega_{n0}^2}\right), \\ Im\left\{\frac{1}{\epsilon(\vec{k},\omega)}\right\} &= \frac{4\pi e^2}{\hbar k^2}\sum_n|\langle\phi_n|\rho_k|\phi_0\rangle|^2\{\delta(\omega - \omega_{n0}) - \delta(\omega + \omega_{n0})\}. \end{aligned} \tag{16}$$

We can see from this equation that the real part is an even function of ω and the imaginary part is an odd function. By this relation, one realizes that Eq.(9) may be rewritten by Eq.(10).

Dielectric function and individual excitation

Lindhard have calculated the dielectric function of the electron gas at T=0 [K]. In this model the electron gas in the ground state receives a momentum $\hbar\vec{k}$ from the external electric field and is excited out of the Fermi sphere. Since the electrons occupy the momentum space in the Fermi sphere, the momentum of an excited electron is allowed to range

$$\hbar k_F < \hbar p < \hbar(k_F + k), \tag{17}$$

where k_F is the Fermi wave number. Therefore, the oscillator strength becomes

$$f_{0n} = \frac{2m_e}{\hbar k^2}\omega_{n0}|\langle\phi_n|\rho_k|\phi_0\rangle|^2 = \frac{2m_e}{\hbar k^2}\omega(\vec{p}+\vec{k},\vec{k})n_{p\sigma}(1-n_{\vec{p}+\vec{k}\sigma}), \tag{18}$$

$$\omega(\vec{p}+\vec{k},\vec{p}) = \frac{\hbar(\vec{p}+\vec{k})^2}{2m_e} - \frac{\hbar p^2}{2m_e}, \qquad n_{\vec{p}\sigma} = \begin{cases} 1 & (p \leq k_F) \\ 0 & (p > k_F), \end{cases}$$

where $\hbar\omega(\vec{p}+\vec{k},\vec{p})$ is the energy transfer and $n_{\vec{p}\sigma}$ is the Fermi-Dirac distribution function. Then, the dielectric function is reduced to

$$1 - \frac{1}{\epsilon(k,\omega)} = \frac{4\pi e^2}{\hbar k^2}\sum_p \frac{2\omega(\vec{p}+\vec{k},\vec{p})(1-n_{\vec{p}+\vec{k},\sigma})n_{\vec{p},\sigma}}{\omega(\vec{p}+\vec{k},\vec{p})^2 - \omega(\omega+i\eta)}. \tag{19}$$

By calculating the above equation, we obtain the Lindhard dielectric funcion as

$$\epsilon(k,\omega) = \epsilon_R(k,\omega) + i\epsilon_I(k,\omega), \tag{20}$$

$$\epsilon_R(z,u) = 1 + (\chi^2/z^2)f_1(z,u), \quad \epsilon_I = (\chi^2/z^2)f_2(z,u), \tag{21}$$

$$f_1(z,u) = \frac{1}{2} + \frac{1}{8z}\{1-(z-u)^2\}\ln\left|\frac{z-u+1}{z-u-1}\right| + \frac{1}{8z}\{1-(z+u)^2\}\ln\left|\frac{z+u+1}{z+u-1}\right|, \tag{22}$$

$$f_2(z,u) = \begin{cases} \dfrac{\pi u}{2} & (z+u<1\text{のとき}), \\ \dfrac{\pi}{8z}\{1-(z-u)^2\} & (|z-u| \leq 1 \leq z+u\text{のとき}), \\ 0 & (|z-u|>1\text{のとき}). \end{cases} \tag{23}$$

where z, u, χ are the reduced dimensionless parameters, $z = k/2k_F$, $u = \omega/v_F k$, $\chi^2 = v_0/\pi v_F$.

Plasmon excitation

The collective excitation induced in the electron gas is called the plasmon excitation. The dispersion relation of the plasmon $\omega = \omega(k)$ is obtained from $\epsilon(k,\omega(k)) = 0$. Let us consider only the real part of the dielectric function. By the denominator and the numerator in *log* are expanded in terms of $u \pm z$ for $u > z + 1$, Eq.(22) becomes

$$f_1(z,u) = \frac{1}{3}\frac{1}{z^2 - u^2} - \frac{1}{5}\frac{z^2 + 3u^2}{(z^2 - u^2)} + \frac{4z^2}{15}\frac{1}{(z^2 - u^2)^3} + \cdots . \tag{24}$$

In the region of $u > z + 1$, the imaginary part of the dielectric function automatically vanishes. Then, from

$$\epsilon_R = 0 = 1 + f_1(z,u), \tag{25}$$

we obtain the plasma dispersion function

$$u^2 = \frac{\chi^2}{3z^2} + \frac{3}{5} + z^2, \qquad \omega^2 = \omega_p^2 + \frac{3v_F^2}{5}k^2 + \frac{\hbar^2}{4m_e}k^4 \equiv A^2, \tag{26}$$

where ω_p and v_F is the plasma oscillation frequency and the Fermi velocity, respectively. It is generally known that the oscillator strength should satisfy the sum rule:

$$\sum_n f_{n0} = n.$$

By substituting ω_{no} into Eq.(15) and using the sum rule, the imaginary part of the inverse dielectric function is

$$Im\left\{\frac{-1}{\epsilon(\vec{k},\omega)}\right\} = \frac{\pi\omega_p^2}{2\omega}\frac{1}{2\pi}\frac{2\eta}{(\omega^2 - A^2)/(4\omega^2) + \eta^2}. \tag{27}$$

Using the mathematical equation

$$\delta(x) = \lim_{\eta \to 0}\frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-\eta|k|}e^{ikx} = \frac{1}{2\pi}\frac{2\eta}{x^2 + \eta^2},$$

Eq.(27) becomes

$$Im\left\{\frac{-1}{\epsilon(\vec{k},\omega)}\right\} = \frac{\pi\omega_p^2}{2A}\delta(\omega - A). \tag{28}$$

By substituting Eq.(28) into Eq.(10), we finally get the stopping power of the plasmon is

$$S = \frac{Z_e^2 e^2 \omega_p^2}{2v^2}\ln\frac{k_c}{k_-}, \tag{29}$$

$$k_- = \{2(v^2 - 3v_F^2/5) - 2\sqrt{(v^2 - 3v_F^2/5)^2 - \omega_p^2})\}^{1/2}.$$

Here, the upper limit of k, k_c is the crossing point between the plasma dispersion curve and the line of $z = u + 1$. On the other hand, the lower limit k_- is the crossing between the plasma dispersion and the curve $\omega = vk$. The total stopping power is obtained as the sum of the contribution of the individual excitation and the plasmon excitation.

Local density approximation-LDA

The stopping power is formulated by the dielectric function method. In order to predict the stopping power especially at high velocities, we would like to adopt the local density approximation (LDA), because of taking into account the inner-shell excitation. This method is valid in the high-velocity cases. So far, we know the gaseous LDA and the solid LDA [5]. If it can be assumed that the number density $\rho(\vec{r})$ of the electron varies smoothly as the function of a position $\vec{r}$, we can replace ρ (this is constant) by the local density $\rho(\vec{r})$. Hence, If we define the local Fermi velocity $v_F(\vec{r}) = (\hbar/m_e)[3\pi^2\rho(\vec{r})]^{1/3}$ and the local plasma frequency $\omega_p(\vec{r}) = [4\pi e^2\rho(\vec{r})/m_e]$, the stopping power formula of the atomic LDA is

$$S = \frac{4\pi Z_1^2 e^2}{m_e v^2} N \int_0^\infty d\vec{r}\rho(\vec{r})L(\vec{r}) \tag{30}$$

where $L(\vec{r})$ is the local stopping number. N denotes the number density of the target atoms. The stopping power of the dielectric function is only the contribution of the outer-shell electrons, the LDA stopping power should include the contribution of the inner- and the outer-shell excitation.The electron density of the atomic LDA approaches zero at distance far from the nucleus. Note that in the LDA total energy loss, the contribution of all trajectories is independent of the molecular orientation. This is because each volume element contributes to the energy loss independently, and the total energy loss is a simple sum of these contributions. Here we can assume that the coulomb deflection are neglected.

Electron density

In order to study the molecular effect, we calculate the LDA stopping power of a N atom and a N_2 molecule. The electron density of a N atom is determined from the Roothaan-Hartree-Fock wavefunction by Clementi and Rotti [6]. The wavefunction for 1s, 2s and 2p states are as follws:

$$\begin{aligned}
\phi(1s) &= 0.93780\chi_1 + 0.05849\chi_2 + 0.00093\chi_3 - 0.00170\chi_4 + 0.00574\chi_5 + 0.00957\chi_6, \\
\phi(2s) &= -0.21677\chi_1 - 0.00846\chi_2 + 0.17991\chi_3 + 0.67416\chi_4 + 0.31297\chi_5 - 0.14497\chi_6, \\
\phi(2p) &= 0.26639\chi_7 + 0.52319\chi_8 + 0.27353\chi_9 + 0.01292\chi_{10},
\end{aligned} \tag{31}$$

$$\begin{aligned}
\chi_n &= 2^{-1/2}\{2 \times \xi_n\}^{1/2}\ exp(-\xi_n r)\ Y_{00}(\theta,\phi) \qquad (n = 1,2), \\
\chi_n &= 2^{-1/2}\{2 \times \xi_n\}^{3/2}\ r\ exp(-\xi_n r)\ Y_{00}(\theta,\phi) \qquad (n = 3 \sim 6), \\
\chi_n &= 2^{-1/2}\{2 \times \xi_n\}^{3/2}\ r\ exp(-\xi_n r)\ Y_{10}(\theta,\phi) \qquad (n = 7 \sim 10),
\end{aligned} \tag{32}$$

where $\xi_1 = 6.45739$, $\xi_2 = 11.17200$, $\xi_3 = 1.36405$, $\xi_4 = 1.89734$, $\xi_5 = 3.25291$, $\xi_6 = 5.08238$, $\xi_7 = 1.16068$, $\xi_8 = 1.70472$, $\xi_9 = 3.03935$, $\xi_{10} = 0.01292$ and Y_{00} and Y_{10}, are spherical hermonics. In this paper the electron density is aussmed to be spherically symmetric so that we take Y_{00} and Y_{10} to be $(4\pi)^{-1/2}$. Figure 1 shows the spatial density of the electrons in a N atom. The spatial electron density in a N_2 molecule can get from the sum of the electron densities of two N atoms, where the interatomic distance is $2.068(a.u.)$[7].

Results and discussion

Figure 2 shows the LDA stopping cross sections per atom of the N atom and the N_2 molecule for a proton. The solid curve and the broken curve denote the N_2 molecular target and the N atom, respectively. The symbols ○, ×, △ and + denote the experimental data of Ormrod, Phillips, Reyolds and Bichsel, respectibely. It shows that while the data are larger than the

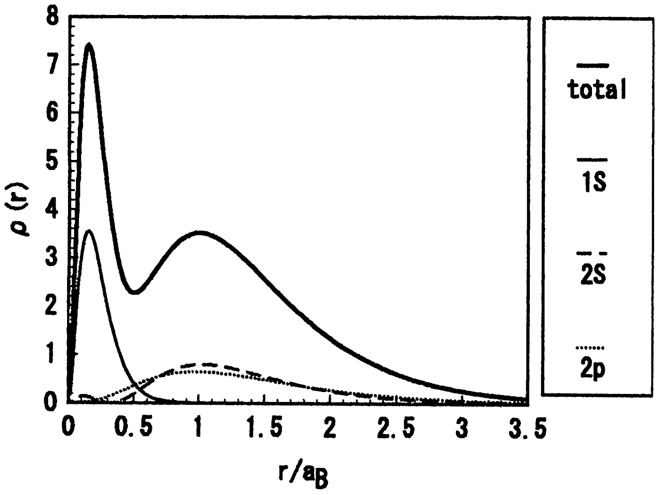

Fig.1. The probability density of the electron in a nitrogen atom. The solid, the broken and the dotted lines denote the probability density of 1s, 2s and 2p, respectively. The abscissa is given in terms of the variable r/a_B. (a_B is the Bohr radius)

calculated two LDA curves around the peak velocities, the data are smaller than the LDA curves at low velocites. Comparing two LDA curves, the molecular one yields the lower values than the atomic one. We call this the molecular effect. This effect appears around the peak energy down to the low energies. This is due to the increase of binding of the electrons in the molecular by the overlap of the atomic electron density.

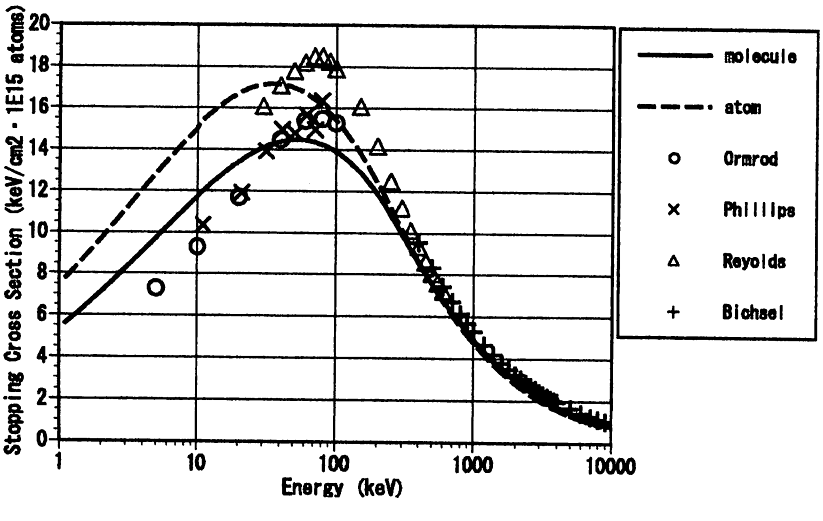

Fig.2. The stopping cross section per atom of a nitrogen gas. The solid and the broken lines denote the molecule LDA and the atom LDA, respectivery. The symbols ○, ×, △ and + denote the experimental data of Ormrod, Phillips, Reyolds and Bichsel, respectively. The abscissa is the kinetic energy of an incident proton.

Kabachnik[8] performed a similar calculation for the energy loss of a He^{2+} ion traversing N_2 molecular target as to the case where the ion is incident both along the molecular axis direction and the perpendicular direction, respectively. They used the Lindhard formula approximated in the high velocities and the electron density of MOLPRP code. As far as, they considered the straggling. Figure 3 shows a contour plot on the deposited energy (in eV) calculated by Kabachnik[8] for collisions of He^{2+} ions with N_2 molecular at the incident energy of 2 MeV. The outermost solid line corresponds to an energy loss of 10 eV. Other lines are drawn in steps of 20 eV(a) or 15 eV(b). The innermost line corresponds to an energy loss of 170 eV(a) and 85 eV(b).

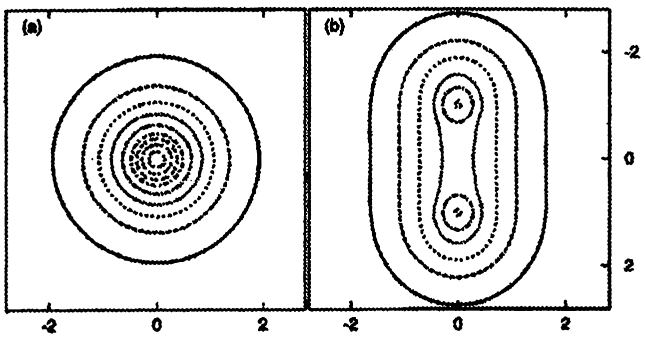

Fig.3. The deposited energy (in eV) for the collision of a He^{2+} ion with a N_2 molecule at the energy loss of 2 MeV by Kabachnik [8]. The outermost solid line corresponds to an energy loss of 10 eV. Other line are drawn in the steps of 20 eV (a) or 15 eV (b). The innermost line corresponds to an energy loss of 170 eV (a) and 85 eV (b).

In this calculation, Kabachnik presented that the stopping cross section is 32.4×10^{-15} ($eVcm^2$/atom) and the exprimental data[9] is 37.4×10^{-15}($eVcm^2$/atom). Using our LDA model, we also calculated the energy loss of a He^{2+} ion for a N_2 molecule and compared with Kabachnik's. Figures 4 and 5 show our calculated results. The values of contour steps are the same with Kabachnik's. But it is the different point that those innermost contours correspond to an energy loss of 150 eV(fig.4) and 85 eV(fig.5). And the stopping cross section is 27.2×10^{-15}($eVcm^2$/atom). Our result is smaller than Kabachnik's result. This is due to the straggling.

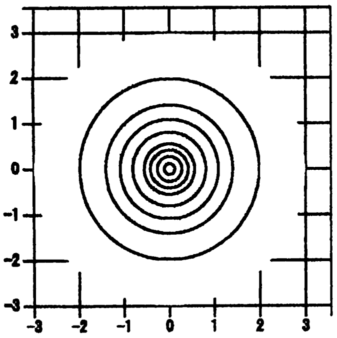

Fig.4. The energy loss of a He^{2+} ion for a N_2 molecule along the molecular axis.

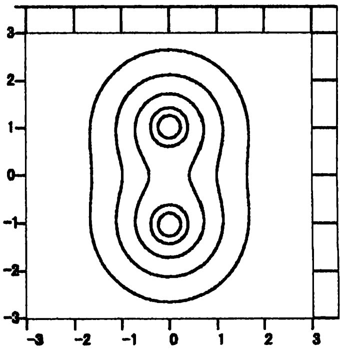

Fig.5. The energy loss of a He^{2+} ion for a N_2 molecule along perpendicular to the molecular axis.

In the dielectric function method, the atomic LDA energy loss tends to be overestimated at low velocities. Therefore, the theoretical result of the stopping cross section is larger than the experimental data at the low velocities, but at high velocities the theoretical result agrees with experimental data. In spite of a slight overestimation, our result shows a clear difference between atomic target and molecular target.

Since the electron density of the molecule is greater than that of the atom, the molecule LDA stopping per atom is smaller than the atom LDA on the whole. The cotribution of the energy loss of the particle passing through interatomic region is suppressed because of the local Fermi velocity. The electron density is enhanced there. This enhancement works strongly at low and intermediate velocities, but does not work so much at high velocities. Therefore, the molecuar effect appears at the low velocities, but doesn't appear at high velocities.

In this calculation, we use the overlap of the statistical electron densities. However, one might think that it is significantly different from the quantum-mechanical electron density. To check it, we compare in fig.6 the present and the quantum-mechanical electron density of a N_2 target [10]. As shown in figure, the statistical electron density well approximates the quantum-mechanical one. Then our analysis can be considered to be well reasonable within the employed model.

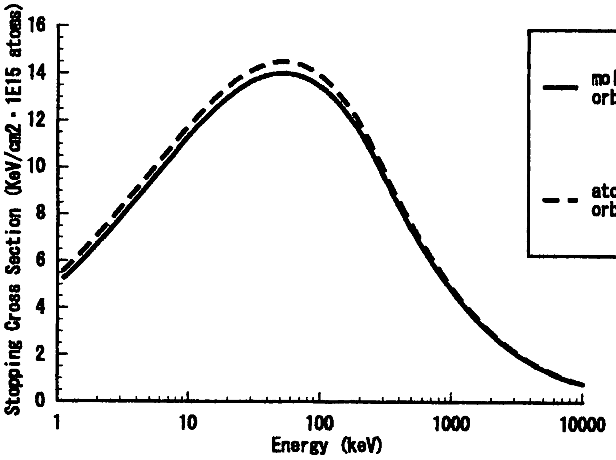

Fig.6. Comparing the stopping power of a N_2 molecule for the electron density with the molecule orbital and with the atom orbital for the proton-N_2 molecule collision.

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