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Quasimolecule formation in the calculation of electronic stopping cross sections with the Firsov model

Dan N. Bernardo
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853-1301

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The Firsov model for calculating electronic stopping cross sections has been modified to take quasimolecule formation and charge polarization into account, since these effects are expected to become important at low collision energies. The cross sections predicted by the resulting molecular model (S_{mol}) were compared to those obtained using spherically symmetric free-atom electronic distributions (S_{free}). It is shown that $S_{\mathrm{mol}}/S_{\mathrm{free}}$ correlates with changes in electron density in the Firsov plane. Differences in the Firsov plane position and orbital contributions in the free-atom and molecular bases are also discussed.

I. INTRODUCTION

The importance of electronic energy losses and stopping cross sections in very-low-energy (several keV) collisions has been demonstrated in both theoretical[1] and experimental[2] studies. The models of Firsov[3] and Lindhard, Scarff, and Schiøtt[4] have been extensively used to calculate these quantities. Firsov's model is particularly interesting since it explicitly takes into consideration the electronic structure of both projectile and target. This semiclassical approach attributes the electronic energy lost during the collision to the momentum lost by the electrons as they cross an imaginary plane (the "Firsov plane") which lies between the two nuclei. It has been shown[5] that in the absence of adjustable parameters, electronic stopping cross sections obtained with the Firsov model can deviate from experimental values by as much as a factor of 2. In spite of this we think there is a need for calculating these cross sections at low energies where it is difficult to obtain or extrapolate[6] reliable experimental cross sections or deduce the charge state of the projectile (for use in other theories).

The original Firsov approach was based on the Thomas-Fermi electron gas atomic model; subsequent studies have dealt with the incorporation of more accurate approximations to the Hartree-Fock-Slater wave functions,[7-9] interatomic potentials,[10] and expressions for the flux across the Firsov plane[11] into the theory. Practically all these implementations and modifications have treated the colliding particles as isolated atoms with spherically symmetric electronic distributions, the exception being the treatment of molecular hydrogen targets.[12] At low collision energies the electronic velocities are greater than the nuclear velocities; one would expect charge polarization and quasimolecule formation to be present and become more important with decreasing energy. The inclusion of these two effects in the Firsov formalism should result in a model which provides a more realistic picture of low-energy atomic collisions. In addition, the contribution of quasimolecular formation to the discrepancies between theoretical and experimental heavy-atom electronic stopping cross sections has been cited but not quantitatively evaluated.[13]

In this study we shall modify the Firsov model (with Brice's expression for the flux[11]) to take these effects into account. The necessary modifications shall be shown, as well as predictions made with the resulting model. Differences between calculations involving free atoms and those done in a molecular basis shall be discussed. Calculations shall be confined to several ground-state diatomics representative of commonly used projectile-target combinations.

II. THEORY

A. Background

We shall briefly review the original Firsov theory[3] and modifications due to Brice.[11] In Firsov's theory the electronic energy loss in a collision is attributed to the momentum lost by electrons as they cross an imaginary plane (the "Firsov plane") which separates the two atoms. The electronic energy lost in a collision for a given impact parameter b is

$$\varepsilon(b)=m\int \phi_T(z_0)\mathbf{u}\cdot d\mathbf{z}_0\ , \tag{1}$$

where m is the electron mass, $\mathbf{u}$ is the relative velocity of and $\mathbf{z}_0$ the relative position vector between the two atoms (see Fig. 1), and ϕ_T is the total electronic flux across the Firsov plane. Integration is done over a single collision trajectory, which is dependent on b. For the collision of two isolated atoms, ϕ_T can be divided into contributions from the target and projectile electrons (subscripts t and p, respectively),

$$\phi_T=\sum_t \phi_t+\sum_p \phi_p\ . \tag{2}$$

The electronic stopping cross section is then

$$S_e=2\pi\int_{b_0}^{\infty}\varepsilon(b)b\,db\ , \tag{3}$$

where the minimum impact parameter b_0 is either used

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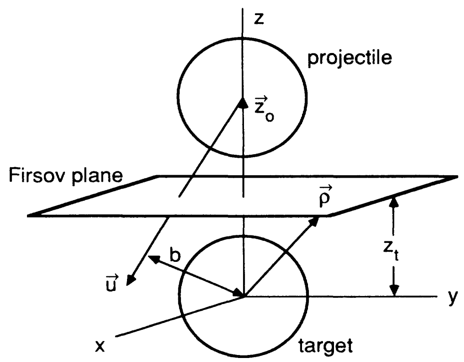

FIG. 1. Coordinate system and positions of colliding atoms and Firsov plane. The projectile passes the target with a relative velocity **u** and a distance of closest approach b. The location of the projectile is given by $\mathbf{z}_0$, while a point on the Firsov plane is denoted by $\boldsymbol{\rho}$. The distance from the target to the Firsov plane is z_t.

as an adjustable parameter or based on a given set of experimental conditions. Calculations in this paper shall use $b_0 > 2$ a.u. since low-energy collisions will be studied.

The Firsov approach has several additional computational degrees of freedom that affect S_e: (a) position and motion of the Firsov plane, (b) interatomic potential, and (c) flux across the Firsov plane. This plane serves as a boundary separating the "environments" of the two atoms. It is normally positioned perpendicular to the internuclear axis, at a point where the electrostatic potential is at its minimum. This location, when not used as a fitting or arbitrarily set parameter, can be based on the Kishinevskii equation[14]

$$z_t = \alpha_t z_0 ,\qquad \alpha_t = [1 + (Z_p/Z_t)^{0.167}]^{-1} , \tag{4}$$

where α_t is the fractional distance from the target atom, z_t is the distance from the target atom to the Firsov plane, and Z_p and Z_t are the atomic numbers of the projectile and target atoms, respectively. This equation was based on the superposition of free Thomas-Fermi atoms; in this study it shall be used to determine z_t in the free atom case. For molecules z_t will be based on molecular orbital (MO) calculations.

The commonly used rectilinear-trajectory approximation (zero potential) shall be used when examining the various details of the resulting model. This eliminates the effect of the collision pairs' atomic numbers on the collision trajectory and permits a clearer examination of the effect of MO formation in various collision pairs on the S_e. We shall also compare our theoretical predictions to experimental data in the absence of adjustable parameters. When making these comparisons two changes will be made: (a) the Biersack-Ziegler interatomic potential[15] shall be used, and (b) b_0 will be determined from experimental conditions. The reader is referred to the excellent paper by Cruz and co-workers[5] for the discussion and equations regarding these changes.

We shall use the quantum-mechanical approach proposed by Brice[11] in calculating the flux across the Firsov plane. Consider the system in Fig. 1 with the origin at the center of the target atom. Suppose $\boldsymbol{\rho}$ denotes a point on the Firsov plane and $\boldsymbol{\omega}$ denotes the plane's velocity with respect to the origin. The flux due to a wave function ψ_+ is given by the expression

$$\begin{aligned}\phi &= \int \frac{\hbar}{2im}(\psi_+^* \nabla \psi_+ - \psi_+ \nabla \psi_+^*) - \frac{\hbar k_0}{m}|\psi_+|^2 dA \\ &= \int \frac{1}{2m}\mathrm{Re}\left[\psi_+^* \left[\frac{\hbar}{i}\nabla\psi_+\right]\right] - \frac{\hbar k_0}{m}|\psi_+|^2 dA ,\end{aligned} \tag{5}$$

where $k_0 = m\omega_z/\hbar$ and the integration is over the Firsov plane. The last term takes the motion of the Firsov plane into account.

The net flux for a bound-state wave function is zero since Eq. (5) evaluates the flux in both directions across the Firsov plane. This makes it necessary to replace each electronic orbital wave function with its corresponding "partial wave function" (PWF). Brice defines the PWF as

$$\psi_+ = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{k_0}^{\infty} \varphi(\mathbf{k}) e^{-i\mathbf{k}\cdot\boldsymbol{\rho}} dk_z , \tag{6}$$

where $\varphi(\mathbf{k}) = \varphi(k_x, k_y, k_z)$ is the Fourier transform of the electronic wave function into momentum space. The PWF thus describes all those electrons with velocity $k_z > k_0$.

An atomic orbital (AO) in the Cartesian coordinate system can be represented by a combination of Gaussian functions[16]

$$\Gamma_k = \Theta_k \sum_j d_{j,k} \exp(-\beta_{j,k} r^2) , \tag{7}$$

$$\Theta_k = x^{l_k} y^{m_k} z^{n_k} , \tag{8}$$

where $d_{j,k}$ and $\beta_{j,k}$ are constants. The latter determines the orbital's radial extent. The exponents in Θ depend on the azimuthal symmetry of the AO, e.g., $\Theta = 1$ for an s-type orbital and $\Theta = y$ for a p_y orbital. The Fourier transform and the inverse transform [Eq. (6)] are applied to the AO's to obtain the corresponding atomic PWF's.

B. Calculations in a molecular basis

The Firsov formalism shall now be modified to take molecular orbital formation into account. A molecular orbital can be represented by a combination of atomic orbitals,

$$\psi_\lambda = \sum_k c_{k,\lambda} \Gamma_k , \tag{9}$$

where $c_{k,\lambda}$ are the coefficients ($c_{k,\lambda} \in \mathbb{R}$) of the λth MO. Since the coordinate system has been defined in such a way that the z axis is always normal to the Firsov plane (Fig. 1), the transformations need only be applied to the molecular orbitals' z component to obtain the corresponding PWF. The flux for this MO can be calculated as

$$\phi_\lambda=\int\frac{1}{2m}\mathrm{Re}\left[\frac{\hbar}{i}\left[\sum_j c_j\Gamma^*_{j+}\right]\left[\sum_k c_k\nabla\Gamma_{k+}\right]\right] -\frac{\hbar k_0}{m}\sum_{j,k}(c_j\Gamma^*_{j+})(c_k\Gamma_{k+})dA\ , \tag{10}$$

where the index λ has been omitted from the right-hand side coefficients for clarity.

The nonlinear dependence of S_e on the projectile velocity has been observed for some systems;[6] it is interesting to note that Eqs. (5) and (6) do provide for a nonlinear relationship between S_e and **u** (through k_0). However, most calculations involving the Firsov approach do not take the motion of the Firsov plane into account (i.e., $k_0=0$). This leaves S_e dependent on **u** only through Eq. (1), the linear dependence of which is consistent with most experimental findings at low energies. To simplify the computations we have elected to set $k_0=0$ in all molecular as well as free-atom calculations. This condition allows use of the following relation for the flux of a bound-state orbital (atomic or molecular):

$$\phi(0,\infty)=-\phi(-\infty,0)\ , \tag{11}$$

where

$$\phi(a,b)=\mathrm{Re}\left[\psi^*_+(a,b)\left[\frac{\hbar}{i}\nabla\psi_+(a,b)\right]\right]\ , \tag{12}$$

$$\psi_+(a,b)=\frac{1}{(2\pi)^{3/2}}\times\int_{-\infty}^{\infty}dk_x\int_{-\infty}^{\infty}dk_y\int_a^b\varphi(\mathbf{k})e^{-i\mathbf{k}\cdot\rho}dk_z\ . \tag{13}$$

Equation (11) facilitates calculation of the flux in both free-atom and molecular cases. In the coordinate system specified in Fig. 1, the electronic flux for the free-atom case [Eq. (2)] becomes

$$\phi_T=\sum_t\phi_t(0,\infty)-\sum_p\phi_p(-\infty,0) \tag{14}$$

$$=\sum_t\phi_t(0,\infty)+\sum_p\phi_p(0,\infty)\ . \tag{15}$$

A similar expression can be obtained for the molecular case. Let the indices t,u represent orbitals centered on the target atom and p,q the orbitals on the projectile. Equation (10) can be written as

$$\begin{aligned}\phi_\lambda=&\int\frac{1}{2m}\mathrm{Re}\left[\frac{\hbar}{i}\sum_{t,u}c_tc_u\Gamma^*_{t+}(\nabla\Gamma_{u+})\right]dA\\&+\int\frac{1}{2m}\mathrm{Re}\left[\frac{\hbar}{i}\sum_{p,q}c_pc_q\Gamma^*_{p+}(\nabla\Gamma_{q+})\right]dA\\&+\int\frac{1}{2m}\mathrm{Re}\left[\frac{\hbar}{i}\sum_{t,p}c_tc_p(\Gamma^*_{t+}\nabla\Gamma_{p+}+\Gamma^*_{p+}\nabla\Gamma_{t+})\right]dA\ ,\end{aligned} \tag{16}$$

where the last term represents the flux due to the overlap of atomic orbitals centered on different atoms. Integration after reversing the order of the sums and integrals yields

$$\phi_\lambda=\sum_{t,u}\phi_{tu}+\sum_{p,q}\phi_{pq}+\sum_{t,p}\phi_{tp}\ . \tag{17}$$

The "overlap flux" can be treated as the average of the fluxes of electrons with $k_z>0$ and those with $k_z<0$:

$$\begin{aligned}\phi_\lambda=&\sum_{t,u}\phi_{tu}(0,\infty)-\sum_{p,q}\phi_{pq}(-\infty,0)\\&+\frac{1}{2}\left[\sum_{t,p}\phi_{tp}(0,\infty)-\sum_{t,p}\phi_{tp}(-\infty,0)\right]\\=&\sum_{t,u}\phi_{tu}(0,\infty)+\sum_{p,q}\phi_{pq}(0,\infty)+\sum_{t,p}\phi_{tp}(0,\infty)\ .\end{aligned} \tag{18}$$

Thus the electronic flux need only be evaluated in the positive z direction for both free-atom and molecular cases. It is Eqs. (15) and (18) which are used to evaluate the electronic fluxes in the free-atom and molecular cases. The results are then used in Eqs. (1) and (3) to obtain the corresponding electronic stopping cross sections S_e. In the free-atom and molecular bases these cross sections shall be denoted by S_{free} and S_{mol}, respectively. Using this approach the contribution each orbital makes to the electronic stopping cross section can also be determined from its contribution to the flux.

In keeping with Firsov's original concept of the plane separating the environments of the two atoms, the total (i.e., electronic plus nuclear) electrostatic potential shall be used in calculating S_e for a molecule. Since the determination of these electrostatic potentials is a routine part of many MO computations we have placed the Firsov plane at the total electrostatic potential minimum.

Molecular-orbital calculations using a 6-31G* basis set[17,18] were performed at the self-consistent-field (SCF) and configuration-interaction (CI) levels with GAMESS,[19] an *ab initio* quantum chemistry program. The same basis set was used to construct the corresponding spherically symmetric free-atom wave functions. Since the greatest electronic energy losses occur at small b, the change of variables $s=1-b_0/b$ was done in Eq. (3). Equations (1) and (3) were numerically evaluated with 15- to 24-point Gauss-Legendre quadratures; the accuracy of and uncertainty in the integrations were checked by analyzing their convergence.

III. RESULTS AND DISCUSSION

Differences in the fractional distance α_t in the free-atom and molecular bases were first investigated. Figure 2 shows α_t for several collision pairs at $z_0=1$ and 3 a.u. The points correspond to α_t in the molecular basis. At a given ratio Z_p/Z_t, these values for α_t are tightly grouped at small z_0, and this distribution slightly broadens with increasing z_0. The solid line is the value of α_t for the free-atom basis as calculated from the Kishinevskii equation [Eq. (4)]. This equation cannot be expected to (and indeed does not) predict the position of the Firsov plane in a diatomic molecule. In this figure it can be seen that the position of the Firsov plane in the molecular basis is

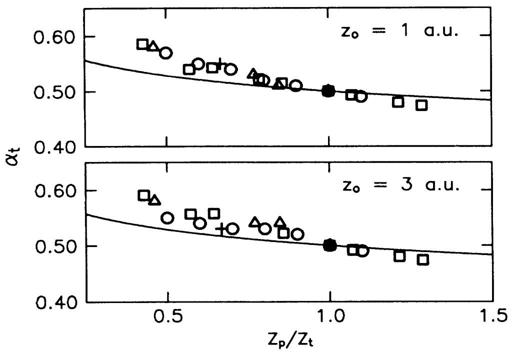

FIG. 2. Comparison of fractional distance α_t in free-atom and molecular bases. Its relation to Z_p/Z_t is shown at two internuclear separations. Points represent α_t based on the total electrostatic potential minimum from MO calculations. Results for several projectile-target combinations are presented. The targets are represented as follows: □, silicon; ○, neon; △, aluminum; +, carbon. Solid line is α_t as predicted by the Kishinevskii equation [Eq. (4)].

different from that in the free-atom basis when two different atoms are colliding. (For the collision of identical atoms, $Z_p/Z_t=1$ and $\alpha_t=0.5$ in both bases.)

The importance of electron correlation in the calculation of electronic stopping cross sections was next determined. Cross sections obtained using configuration-interaction wave functions were compared with values resulting from self-consistent-field wave functions. Some cross sections are shown in Table I: In most cases (B_2, C_2, and Ne_2 being representative of these) the differences between the CI and SCF results were comparable to the uncertainties in the integrations. It was only for O_2 that a significant difference in the two kinds of cross sections was observed.

An estimate of the extent of quasimolecule formation and charge polarization is necessary if one wishes to examine its effect on the electronic stopping cross section. One such parameter is the electron density in the region of the Firsov plane, which we shall designate as Λ. To measure its change the following definitions in the free-atom and molecular bases will be used:

$$\Lambda_{\text{free}}=\int_{b_0}^{\infty}\int\left[\sum_t|\Gamma_t|^2+\sum_p|\Gamma_p|^2\right]_{z=z_t(b)}dA\,db\ ,$$
$$\Lambda_{\text{mol}}=\int_{b_0}^{\infty}\int\sum_\lambda|\psi_\lambda|^2_{z=z_t(b)}dA\,db\ . \tag{19}$$

TABLE I. Comparison of a few molecular electronic stopping cross sections based on SCF and CI ground-state wave functions. Different collision velocities and minimum impact parameters were used for each collision pair.

Collision pair	S_{mol} (10^{-14} eV cm^2/atom) SCF	CI
B+B	0.77±0.02	0.78±0.02
C+C	1.44±0.03	1.42±0.03
O+O	1.08±0.03	1.02±0.03
Ne+Ne	1.62±0.03	1.60±0.03

For the free-atom basis the target and projectile atomic orbitals ($\Gamma_{k,t}$ and $\Gamma_{k,p}$, respectively) are centered at points corresponding to the positions of the nuclei used in the MO calculations. The first integration is performed over the Firsov plane at position Z_t for a given internuclear separation; the result is then evaluated over the range of impact parameters.

The ratios $S_{\text{mol}}/S_{\text{free}}$ and $\Lambda_{\text{mol}}/\Lambda_{\text{free}}$ for several projectile-target combinations are compared in Fig. 3. Changes in the electronic stopping cross sections roughly correlate with the extent of charge polarization into the Firsov plane region as measured by Λ_{mol} and Λ_{free}. For example, the repulsive interaction in Ne+Ne decreases Λ and S_e, while polarization of charge into the internuclear region (as in C+C) increases both. These results are consistent with those of Brice and Cruz,[12] who used the Firsov treatment in calculating S_e for molecular hydrogen targets. It was found that decreasing the internuclear distance R_{mol} within the target molecule drew charge away from the region between the molecule and the incoming projectile. This resulted in decreased values of S_e. The same relation between R_{mol} and S_e was obtained by Geertsen, Oddershede, and Sabin[20] using the polarization propagator formalism.

Other factors such as the velocity or momentum distribution of the electrons can also influence changes in S_e. Suppose one considers the electron flux as a classical effusion process. Such a treatment was used in Firsov's original model[3] (using Thomas-Fermi atoms), and was modified by Cheshire and co-workers[7] to utilize more accurate Hartree-Fock atomic wave functions. The flux due to a wave function Γ_k at a given internuclear separation z_0 can be written as

$$\phi_k(z_0)=\langle v_\perp\rangle_k\int|\Gamma_k|^2dA\ , \tag{20}$$

where $\langle v_\perp\rangle_k$ is the average of the electronic velocity that is normal to the Firsov plane, and the integration is carried out over the Firsov plane. From electron momentum distribution studies[21] it is known that $\langle v_\perp\rangle_k$ decreases upon charge polarization into the internuclear re-

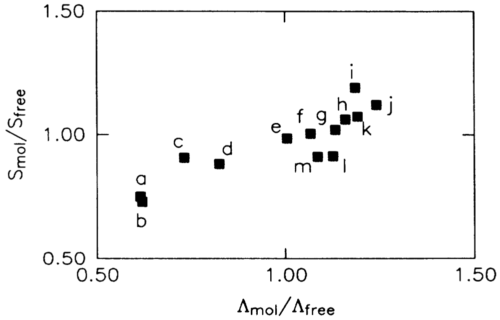

FIG. 3. Effect of charge polarization (as measured by $\Lambda_{\text{mol}}/\Lambda_{\text{free}}$) on changes in electronic stopping cross section. Several collision pairs are shown (label = projectile + target): a=F+Ne; b=Ne+Ne; c=O+Ne; d=F+F; e=O+O; f=Be+Be; g=Al+Al; h=Ne+Si; i=N+N; j=C+C; k=B+B; l=O+Si; m=O+C.

TABLE II. Atomic orbital contributions to S_{free} for some second-row homonuclear diatomics (with $b_0=2.5$ a.u., $v=0.25$ a.u.).

Collision pair	Atomic orbital contribution (%) 1s	2s	2p+3d	Number of electrons in orbital[a] 1s	2s	2p+3d
N+N	0	39	61	4	4	6
O+O	0	33	67	4	4	8
F+F	0	27	73	4	4	10
Ne+Ne	0	22	78	4	4	12

[a] Sum of electrons in two identical orbitals since the system is composed of two identical atoms.

gion. This means that two main competing effects are present: an increase in electron density about the plane (leading to an increase in S_e) is accompanied by a decrease in electron momentum perpendicular to the Firsov plane (which tends to decrease S_e). If momentum effects were largely responsible for changes in the cross sections then one would observe increases in charge polarization into the Firsov plane to be accompanied by decreases in S_e. The results in Fig. 3 show that the reverse is true, indicating the importance of electronic density effects. Thus, within the framework of the Firsov formalism, changes in the electron density as reflected in $\Lambda_{\text{mol}}/\Lambda_{\text{free}}$ can be used as the primary indicator of changes in $S_{\text{mol}}/S_{\text{free}}$. This is again in agreement with the findings of Brice and Cruz[12] for molecular hydrogen targets.

One might expect chemical bond formation between collision partners to increase Λ_{mol} and S_{mol} relative to the free-atom values. Figure 3 shows that $S_{\text{mol}} > S_{\text{free}}$ for the multiply bonded C_2 and N_2. For other cases (single or no bonds between collision partners) no general relation is evident. For example, the molecular electronic stopping cross sections for F+F and O+C are less than the free-atom values, even though these two pairs form stable diatomic molecules. It is interesting to note that electronic densities around the Firsov plane resulting from the superposition of the free-atom values can be greater than the corresponding molecular values, even in cases where chemical bonds are formed.

One difference between the free-atom and molecular bases in the Firsov framework is the effect of additional electrons in a sequence of elements on the electronic stopping cross sections. Consider the set of second-row homonuclear diatomics from N to Ne shown in Table II. As one progresses through the sequence, a pair of electrons is added to the outermost set of orbitals, which in this case is composed of the 2p and 3d orbitals. It can be seen that each incremental pair of electrons contributes to S_{free}. For the molecular case, it is only the electrons in bonding orbitals which make significant contributions to S_{mol}. The same set of diatomics is shown in Table III; although the number of electrons increases as one proceeds through the sequence these additional electrons form the antibonding orbitals and so make no contribution to S_{mol}. Practically all electronic energy lost in the collision comes from the electrons which make up the bonding molecular orbitals; the contributions to S_{mol} by these electrons is independent of the electronic population of the antibonding orbitals.

At these low collision velocities most of the stopping is due to the valence orbitals $2s+2p+3d$ for the free-atom basis, and $\sigma_g 2s+\sigma_g 2p+\pi_u 2p$ for the molecular case. These results are in general agreement with those of Sabin and Oddershede[22] and Cruz, Cisneros, and Alvarez[23] for the free-atom basis.

The significance of the differences in S_{mol} and S_{free} can be seen in the comparison of experimental data with theoretical values. Figure 4 shows the experimental S_e's for C+C over a range of energies,[24] and compares these to the predicted S_{mol} and S_{free}. The theoretical electronic stopping cross sections are closer to the experimental values when quasimolecule formation is included in the calculations. As mentioned in Sec. II A, in making these comparisons the Biersack-Ziegler potential was used in the calculation of the collision trajectories, and b_0 was determined from the experimental configuration. These two measures, in addition to the process of locating the

TABLE III. Molecular orbital contributions to S_{mol} for some second-row homonuclear diatomics (with $b_0=2.5$ a.u., $v=0.25$ a.u.).

Collision pair	Molecular orbital contribution[a] (%) $\sigma_g 2s$	$\sigma_u^* 2s$	$(\sigma_g 2p+\pi_u 2p)$	$(\pi_g^* 2p+\sigma_u^* 2p)$	Number of electrons in orbital $2\sigma_g 2s$	$\sigma_u^* 2s$	$(\sigma_g^* 2p+\pi_u 2p)$	$(\pi_g^* 2p+\sigma_u^* 2p)$
N+N	27	1	72	0	2	2	6	0
O+O	27	2	70	1	2	2	6	2
F+F	28	0	71	1	2	2	6	4
Ne+Ne	30	0	70	0	2	2	6	6

[a] Contributions from $\sigma_g 1s$ and $\sigma_u^* 1s$ are negligible and are not shown.

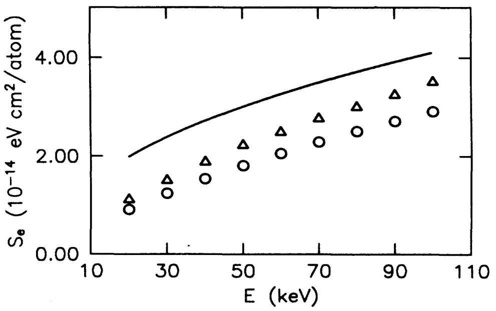

FIG. 4. Comparison of theoretical electronic stopping cross sections with experimental values for C+C at several collision energies: Solid line, experimental values from Ref. 24; ○, cross sections based on free-atom wave functions; △, cross sections based on molecular wave functions.

Firsov plane at the total electrostatic potential minimum, constituted an attempt to place these usually adjustable parameters on a realistic basis. It must also be pointed out that the modifications in this study do not incorporate any collision velocity dependence into the extent of charge polarization, i.e., the extent to which molecular orbitals are formed is assumed to be complete over the collision velocities of interest. Since charge polarization (and differences in S_{mol} and S_{free}) are greater with decreasing internuclear separation, the smaller impact parameters at higher energies lead to greater differences in S_{mol} and S_{free}.

IV. CONCLUSIONS

Modification of the Firsov model to take quasimolecule formation and charge polarization into account requires molecular orbital calculations at several internuclear separations. The operations necessary to obtain the molecular PWF's and electronic stopping cross sections are analogous to those used for the free-atom case, except for the additional treatment of terms resulting from the overlap of orbitals centered on different nuclei.

Calculations were carried out for several collision pairs involving second- and third-row elements. It was found that the Kishinevskii equation cannot predict the position of the Firsov plane in the molecular basis.

Correlation was observed between changes in the electron density in the internuclear region and the electronic stopping cross section. It was found that, in the molecular basis, electrons in antibonding orbitals made negligible contributions to the cross section. Formation of multiple chemical bonds between collision partners resulted in $S_{\text{mol}} > S_{\text{free}}$, but no general relation between the absence or formation of single bonds and S_e was seen.

Theoretical electronic stopping cross sections for C+C were calculated in the absence of adjustable parameters and compared to the experimental values. The inclusion of quasimolecule formation brought about an improvement in the agreement of these quantities.

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