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  Tomoko Ohyama-Yamaguchi and Atsushi Ichimura
Electron localization among three moving centers:
Coulomb explosion with slow highly charged ions

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Abstract. The three-center Coulombic over-the-barrier model is developed for the Coulomb explosion of a homonuclear diatomic molecule in collisions with a slow (∼10 eV/amu) highly charged ion. A conventional two-step picture of multiple electron transfer followed by Coulomb explosion is far from appropriate because the molecule BC sets out to dissociate before the ion A approaches the closest distance. We treat the formation of a quasimolecule ABC and its decay into the three moving atomic ions, where two possible processes are considered for population in an atomic site B as ABC → BC → B and ABC → AB → B. It is shown that the contribution from the second process is crucial in a slow collision. Charge-asymmetric fragmentation between sites B and C observed in a triple-coincidence measurement is suggested to reflect the bond elongation during a collision. Collisions of Kr⁸⁺ + N₂ are analyzed.

1. Introduction
Much attention has been drawn to the Coulomb explosion of molecules in a variety of collision processes on the basis of the momentum imaging technique. In particular, Kaneyasu and coworkers [1, 2] have made a triple coincidence measurement in a coplanar geometry for N₂ molecules colliding with slow (10 – 170 eV/amu) Kr⁸⁺ ions. They employ an experimental setup where the fragment ion pair N²⁺⁺N²⁺ is detected ‘back-to-back’ in transverse to the beam axis and in coincidence with the scattered ion. The most remarkable aspect in their measurement is unequal strengths of charge-asymmetric (Q ≠ Q’) fragmentation between the near and far sites relative to the point of closest approach on a projectile trajectory. For a given charge pair (Q, Q’), the asymmetry parameter A = (Pₗ – Pᵋ)/(Pₗ + Pᵋ) is obtained through the coincidence populations Pₗ ≡ P[Qᵋ > Qₗ] and Pᵋ ≡ P[Qᵋ < Qₗ]. The experiment indicates a positive asymmetry A > 0; the far site is populated more by the higher charge than by the lower charge. This asymmetry was interpreted to arise from electron polarization by the projectile in the course of dissociation, and qualitatively supported by a microscopic calculation with the time-dependent density functional theory [1].

In a former paper [3], we tried to analyze the charge-asymmetric fragmentation with a three-center Coulombic over-the-barrier model. The model was originally developed by the present authors for describing molecular orientation effects in multiple electron transfer [4, 5], on the basis of a previous two-center Coulombic over-the-barrier model for ion-atom collisions [6]. For simplicity, however, we took a conventional but questionable two-step picture of electron removal.
followed by Coulomb explosion. In this process, the charge asymmetry is only caused by residual electrons in the molecule. They are localized into two atomic sites on the way of fragmentation, while polarized by a receding projectile. Although leading to a correct sign of $A$, this effect is found to be negligibly small unless an unrealistic assumption is made, i.e. that the projectile stays near the point of closest approach even when the multiple electron transfer has been completed. Furthermore, the experiment [1, 2] indicates a remarkable enhancement of the asymmetry as the collision velocity $v$ decreases. These points need to be clarified.

In this paper, we further examine the dynamics of the charge-asymmetric fragmentation without taking the two-step picture. We develop the three-center Coulombic over-the-barrier model so as to describe an inseparable process of electron transfer and Coulomb explosion, and so as to take full account of the three-center nature in the electron localization among three moving (one scattered and two dissociating) atomic ions.

Atomic units are used throughout the paper unless otherwise stated.

2. Three-center Coulombic over-the-barrier model

We address collisions of a slow ($v \ll 1$) highly charged ion $A^{q+}$ with a homonuclear diatomic molecule BC. They are treated as the formation and decay of a triatomic quasimolecule $ABC^{q+}$,

$$A^{q+} + BC \rightarrow ABC^{q+} \rightarrow A^{(q-r)+} + B^{n+} + C^{r+c+},$$

where $r = r_B + r_C$ is the total number of removal electrons. The probability of producing a pair of charge states $(r_B, r_C)$ is calculated for an incident trajectory with the velocity $v$ and the impact parameter $b$. According to the model by Niehaus [6], many-electron dynamics is described by a sequence of quasimolecule formations of respective electrons in numerical order of ‘rank’ $t$ ($= 1, 2, \ldots$) in the way in of a collision, and by a sequence of their decays in reverse order in the way out. The $t$-th electron is assumed to be initially bound in the molecule with its $t$-th ionization potential; an electron correlation effect is taken into account in this procedure. The critical nuclear configuration for the electron delocalization (localization) on the way in (way out) is determined along a given trajectory by a classical over-the-barrier criterion, i.e., by a condition that a diabatic electron energy $E$ coincides with the potential height $U$ at a saddle point. Both the electron energy and the potential saddle point are varied with the nuclear configuration described by three scalar variables, $R$, $d$, and $\cos \alpha = \mathbf{R} \cdot \mathbf{d}$, where two relative position vectors are defined as $R = R_A - (R_B + R_C)/2$ and $d = (R_B - R_C)/2$ among three nuclear positions, $R_A$, $R_B$ and $R_C$. In contrast to the previous applications [4, 5], the bond length $2d$ is not fixed to be the equilibrium distance but allowed to be elongated during a collision because of the Coulomb repulsion between dissociating ions.

We describe the single electron dynamics using a three-center Coulombic potential $U(r) = -q_A/r_A - q_B/r_B - q_C/r_C$ with ion core charges $q_A$, $q_B$, and $q_C$, where $r_A = |r - R_A|$ etc. This potential has two saddle points, $r_H$ and $r_L$, which are characterized by their relative heights as $U_H > U_L$ with $U_H = U(r_H)$ and $U_L = U(r_L)$. A classically allowed region of electron position $r$ is defined by a condition that $U(r) < E$. According to the energy $E$, the allowed region is divided into one, two or three simply connected $r$ domains each of which contains some of the three Coulomb centers. The nuclear configuration space $(R, d, \cos \alpha)$ is divided into three domains, $D_{A-BC}$, $D_{B-CA}$ and $D_{C-AB}$ because the electron moves around over two of the three centers when $U_H > E > U_L$. Boundaries between the nuclear domains are given by the equi-height condition of two saddle points, $U_L(R/d, \cos \alpha) = U_H(R/d, \cos \alpha)$.

The formation and decay processes of a three-center quasimolecule evolves as illustrated in Figs. 1 and 2. The initial asymptotic configuration ($R \gg d$) belongs to $D_{A-BC}$, where the higher saddle point is located outside the molecule BC while the lower inside. In a covalent molecule such as $N_2$, valence electrons are delocalized over two sites B and C, hence initially $U_H > E > U_L$; the quasimolecule is formed in the same domain $D_{A-BC}$. However, the quasimolecule may decay
in another domain $D_{C-AB}$ if the molecule sets out to dissociate before the projectile recedes from it. Therefore, eventual populations in the near (B) and far (C) atomic sites are generally contributed from two possible processes I and II, one via $D_{A-BC}$ and another via $D_{C-AB}$. In respective processes, the populations are calculated from branching probabilities at critical nuclear configurations with $E = U_H$ and with $E = U_L$ along a given trajectory $(R(\tau)$ and $d(\tau)$ with time $\tau$). The branching probability is estimated through a ratio of phase space volumes,

$$p^\beta_s = \frac{\rho^\beta_s}{\rho^\beta_s + \rho^\gamma_s}, \quad \rho^\beta_s,\gamma_s = \int_{\beta,\gamma} d^3 p d^3 r \delta(U_s - p^2/2 - U(r; q_A, q_B, q_C)),$$

where a suffix ‘s’ represents H or L according to the higher or lower saddle point, which divides the available phase space into two separable regions $\beta$ and $\gamma$.

### 3. Results and Discussion

We apply the present model to collisions of Kr$^{8+}$ + N$_2$ at velocities of $v = 0.01 - 0.08$ (i.e. 2.5 - 160 eV/amu) and consider 10 covalent electrons in the N$_2$ molecule. We assume a linear trajectory of incidence with the impact parameter of $b = 3$, together with a dissociation trajectory retaining the initial orientation of $\alpha = 0$.

Time evolution $d(\tau)$ of half the bond length is shown in Fig. 3, where the horizontal scale is taken $\nu \tau$, representing the projectile position along the linear trajectory. It is assumed that the $t$-th electron is removed from the molecule when the projectile reaches the $t$-th critical distance on the way in and that the molecule is dissociated through the Coulomb repulsion between charges $t/2$ and $t/2$. Also plotted is a boundary between nuclear domains $D_{A-BC}$ and $D_{C-AB}$ for an electron with rank $t = 6$. This boundary is obtained with effective ion-core charges $(q_A, q_B, q_C) = (8, 3, 3)$ through the evolution of potential heights at two saddle points (see Fig. 4). They cross each other, depending on the velocity $v$; the points of crossing form the boundary. It is seen from Fig. 3 that the nuclear configurations asymptotically belong to $D_{A-BC}$ on the way in ($\tau < 0$) regardless of the velocities. On the way out ($\tau > 0$), however, relevant domains depend on the velocity: both $D_{A-BC}$ and $D_{C-AB}$ are competing at $v = 0.08$, while only $D_{C-AB}$ is involved for $v \leq 0.04$. At the lower velocities, the localization into the near site (B) is contributed exclusively from the process II indicated in Fig. 1.
Figure 3. Time evolution \( d(\tau) \) of half the bond length for collision velocities of \( v = 0.01, 0.02, 0.04 \) and \( 0.08 \) (- - - -), half the equilibrium bond distance (——) and a boundary of nuclear domains \( D_{A-BC} \) and \( D_{C-AB} \) for an electron with rank \( t = 6 \) (——).

Figure 4. Evolution of two saddle points, \( U_1 \) and \( U_2 \), for an electron with rank \( t = 6 \) for collision velocities of \( v = 0.02 \) and 0.08 when molecular bond elongation is allowed (- - - -) and when the equilibrium bond distance is retained (——).

Figure 5. Evolution of branching probabilities at higher and lower saddle points with a collision velocity of \( v = 0.02 \) for electrons with rank \( t = 2, 4 \) and 6, for which the effective charges are taken as \( (q_A, q_B, q_C) = (8, t/2, t/2) \). The probability \( p^\beta = \rho^\beta / (\rho^\beta + \rho^\gamma) \) is indicated by \( \beta/(\beta + \gamma) \) (see Eq. (2)).

Branching probabilities at higher and lower saddle points are calculated with Eq. (2) and shown in Fig. 5 for \( v = 0.02 \). At this velocity, the quasimolecule decays exclusively in domain \( D_{C-AB} \). Hence, the near site B is populated as \( ABC \rightarrow AB \rightarrow B \) while the far site C as \( ABC \rightarrow C \). It is seen from the figure that the probability in branching \( ABC \rightarrow AB \) is almost one and that the probability in \( AB \rightarrow B \) is \( 0.1 \sim 0.2 \). Hence, the population is \( 0.1 \sim 0.2 \) at site B, while extremely small \( (\ll 0.1) \) at site C. This mechanism, due to the bond elongation during a collision, may lead to a crucial contribution to a large charge-asymmetry \( A \) observed in slow collisions [1,2]. We leave a systematic analysis in this direction to a future work.

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