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# Electron capture in the ion-cluster collision: effect of the electronic interaction

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**Abstract.** We investigate the electron capture occurring in the collision between an ion $A^+$ and a cluster $A_n$ ($n = 5$). The process has been modelled within the Hubbard Hamiltonian,which takes into account the intrasite $U$ electron correlation. An exact procedure has been numerically applied which involves all the excited states to examine the time evolution of the system during the collision. We have applied the model to the sodium case. We have investigated the time evolution of the electron population during the collision on the projectile *versus* the kinetic energy of the projectile. It displays some oscillations which means that the electron exchanges between the ion and the cluster occurs alternatively in one direction and the other. We also vary $U$ and examine its influence on the dynamics of the oscillation of the average population. Finally the cross section is derived *versus* the energy and $U$.

**PACS.** 36.40.-c Atomic and molecular clusters – 36.40.Cg Electronic and magnetic properties of cluster – 34.70.+e Charge transfer

## 1 Introduction

Most of our understanding about the electronic properties of metal cluster over the past years comes from the studies of the cluster response weakly perturbated by an external electric fields [1].

Charge transfer represents one of the fundamental atomic interaction in the elementary ion-atom reaction [2] and complex ion surface interactions [3], which are important in the surface science and catalysis.

Recently an urge activity has been devoted to the intermediate case of ion-cluster collision [4–8]. Some study involves dissociative and non dissociative electron capture. But in general, the fundamental events accompanying cluster collision include simultaneous and mutually coupled electronic transitions (charge transfer, excitation, ionization) and energy transfer in nucleus degrees of freedom (vibration, fragmentation, ...).

More recently has been carried out more studies devoted to metal cluster electronic response at a time scale for which nuclear motion are frozen by using femtosecond laser [9] or keV collisions with atom and protons [4,10] in order to desentangle electronic properties from nuclear motion.

So some works [5] have investigated the collisional charge transfer between singly charged free cluster $A_n^+$ ($A$ = Na, Li, K) and atomic target $X$ ($X$ = Cs, Na) *versus* a collisional velocity in energy range of 1-10 keV such that:

$$A_n^+ + X \rightarrow A_n + X^+ \tag{1}$$

leading to the determination of the charge transfer cross section $\sigma$. $\sigma$ appears to be highly dependent with the cluster size.

Another recent experiments [11] have been reported on the dissociative and non dissociative electron capture cross section, but for medium velocity collision of carbon cluster $C_n^+$ ($n < 5$) with helium. For the range of velocity the dissociative part has been found to be the largest one in all cases increasing with $n$. In order to explain the quite large branching ratios for dissociation, it is very interesting to notice that the multielectron process of capture-projectile excitation has been invoked [11].

Recent calculations have been devoted to the collision described by the previous equation (1). Knospe *et al.* have calculated the energy dependence of the cross section for $4 < n < 11$, for $A$ = Na and $X$ = Cs using the so-called non-adiabatic quantum molecular dynamics (Na-QMD) [12]; as for Martin *et al.*, they have investigated the electron capture and excitation in the proton-Na$_n$ ($n$ = 8, 20, 40, 92) within the impact energy range 40-500 eV in the framework of the Kohn-Sham formalism with a local-density approximation which includes exchange, correlation and a self-interaction correction [13].

The present article deals with the consequences on the dynamical evolution due to the electronic excitation given by the strongly large screened Coulombic perturbation during the collision leading to non-adiabatic behaviour as for example the possibility during the the electron capture

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of a charge exchange from the projectile to the target and reversely from the target to the projectile. The article illustrates the collision of the cluster $X_5$ with an ion $X^+$. For example $X$ could be the sodium.

## 2 The model

The present article deals with the study of the electron capture described by:

$$X_n + X^+ \rightarrow X_n^+ + X. \tag{2}$$

We consider that the atom $X$ is an alcaline atom such that in the process, every atom of the cluster gives only one s type electron, so the initial electronic configuration of the cluster is the $(3\uparrow; 2\downarrow)$ one. We have chosen for the cluster geometry: the pyramid with a square base. In the following we illustrate the process for the sodium case. The cluster is modelled with the Hubbard Hamiltonian which has been intensely used to described the magnetism [14]:

$$H = -\sum_{i,j,\sigma} t c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{3}$$

$c^{\dagger}_{i\sigma}$ $(c_{j\sigma})$ is the creation (annihilation) operator of an electron with spin $\sigma$ at lattice site $i(j)$. $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$ is the number operator. The first term describes the hopping from site $i$ to site $j$ between two nearest neighbor. The second term describes the on-site interaction between electrons. For small clusters like $\mathrm{Na}_5$, an exact solution can be achieved using a numerical approach (an exact diagonalisation procedure) to obtain the exact groundstate.

Owing to the fact that the ionization potential of Na is larger than the cluster one, in an adiabatic point of view when $\mathrm{Na}^+$ is close to $\mathrm{Na}_5$ a transfer of an electron is occurring from the cluster to the projectile $\mathrm{Na}^+$. But in the following we shall show that this point of view is not true due to the excitation in the cluster which allows also the transfer from the projectile to the cluster.

To study the electron capture,we are looking at an exact time evolution in the full Hilbert space which is a sum of the 3 subspaces $\{(\mathrm{Na}_5, \mathrm{Na}^+), (\mathrm{Na}_5^+,\mathrm{Na}), (\mathrm{Na}_5^{++}, \mathrm{Na}^-)\}$.

The collision process is described by adding to the Hubbard Hamiltonian a coulomb interaction $V(t)$:

$$V(t) = \sum_{r,s,\sigma} V_{r,s}(t)(c^{\dagger}_{r\sigma} c_{s\sigma} + c^{\dagger}_{s\sigma} c_{r\sigma}) \tag{4}$$

with the following term $V_{r,s}(t)$ for instance in the $(\mathrm{Na}_5, \mathrm{Na}^+)$ subspace

$$V_{r,s}(t) = -\frac{e^2}{4\pi\epsilon_o} \int \phi^*_r(\boldsymbol{r}) \phi_s(\boldsymbol{r}) \frac{d\boldsymbol{r}}{\mid \boldsymbol{r} - \boldsymbol{R}(t) \mid} \tag{5}$$

where $\boldsymbol{R}(t)$ is the $\mathrm{Na}^+$ position.

The exact time evolution is obtained with the following procedure: firstly by an exact diagonalisation to derive the groundstate at the beginning of the process, the next step is the propagation of the wave function using the *Schrödinger* equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi. \tag{6}$$

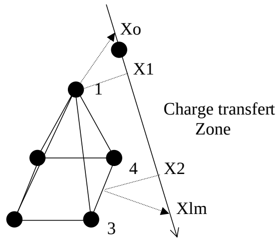


**Fig. 1.** Geometry of the projectile trajectory analyzed in the article.

## 3 Results

In the following we report the time evolution of the capture charge population on the projectile $n(t)$ for different correlation $U$ term. Let us focus firstly on the behavior for one projectile direction: the one which is parallel to a triangle face and contained in the median plane of this face. This trajectory is completely defined by a length $d$ which may be called the impact parameter, representing the distance from the trajectory to the face. Practically, the projectile is mainly interacting firstly with the atom 1 at the top of the pyramid then it interacts with two other atoms (atoms 4 and 5) see figure 1.

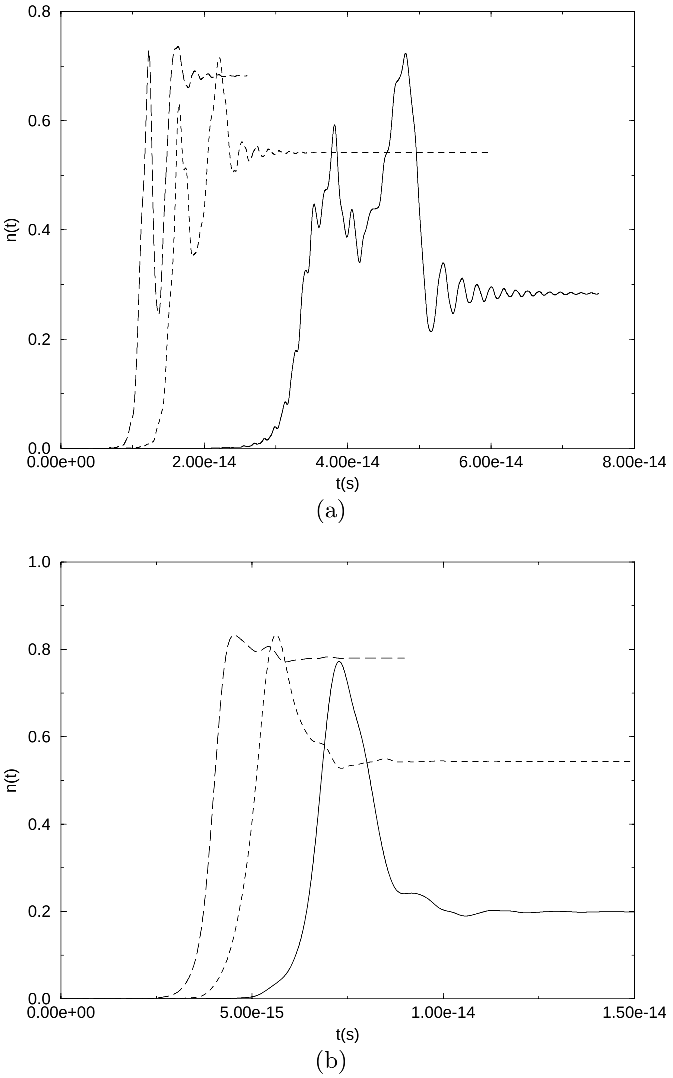
For $U < 2.4$ eV the $(3\uparrow; 2\downarrow)$ has a degenerate groundstate. To avoid all problem in the discussion only the time evolution dependence with the projectile energy only for $U > 2.4$ eV: *i.e.* $U = 3.6$ eV and 5.5 eV.

In figure 2, the time evolution of the electron population on the projectile $n(t)$ is displayed for different $\mathrm{Na}^+$ energy $E$. One important feature is the $n(t)$ oscillations. It means that during some moments the cluster is electron acceptor and during others electron donor.

Let us see how the $E$ dependence of the $n(t)$ curves can be understood for $U = 3.6$ eV or 5.5 eV. For these large $U$ values the electrons in the molecule are less mobile and the hole created on an atom does not leave it rapidly.

All the curves exhibit an interaction zone $x_o < x < x_{lm}$ where $x_o$ $(x_{lm})$ are the position of the projectile approximatively distant of 3.5 Å of atom 1 (atoms 4 and 5). The projectile begins to be filled smoothly from the position $x_o$. For low $E$ ($E = 100$ eV), $n(t)$ has two mains peaks (fig. 2a) corresponding to the projectile positions $x_1$ and $x_2$ defined respectively as the projections at the atom 1 and of the two interacting atoms 4 and 5 on the trajectory (fig. 1). Let us notice that in the $x_{lm}$ region $n(t)$ has damping oscillations around an average value, this phenomena is linked with the electron excitation.

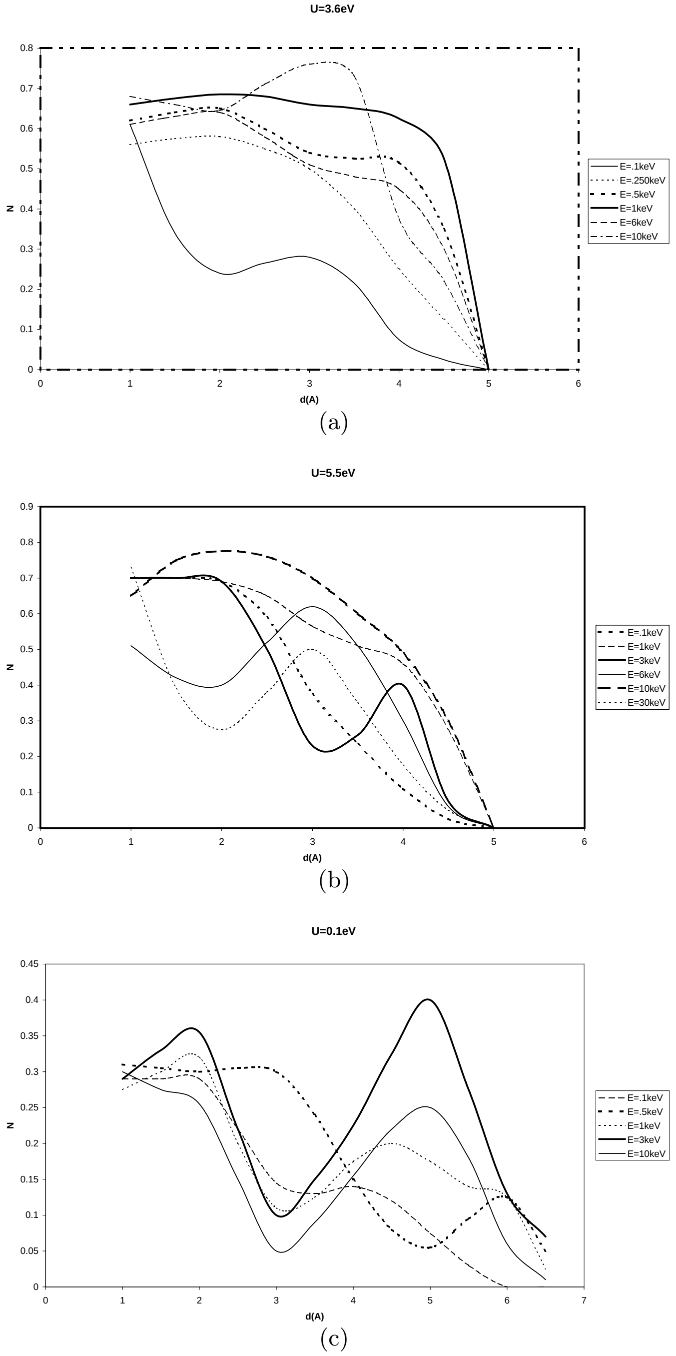
At low energy $E = 100$ eV and $E = 500$ eV (fig. 2a) the incident ion behaves first as an acceptor of electrons coming mainly from the atom 1, then as a donor to the



(a)

(b)

**Fig. 2.** Time evolution of the electron projectile population $n(t)$ *versus* the time $t$(s) for $U = 3.6$ eV, for an impact parameter $d = 3$ Å for the trajectory described in figure 1 and for different projectile energy $E$: (a) $E = 100$ eV (solid line), $E = 500$ eV (dashed), $E = 1$ keV (long dashed); (b) $E = 3$ keV (solid line), $E = 6$ keV (dashed) and $E = 10$ keV (long dashed).


U=3.6eV

U=5.5eV

U=0.1eV

(a)

(b)

(c)

**Fig. 3.** Captured electron projectile population $N$ *versus* the impact parameter $d$(Å) of the trajectory described in figure 1 for different kinetic projectile energy $E$ and for different $U$: (a) $U = 3.6$ eV, (b) $U = 5.5$ eV, (c) $U = 0.1$ eV.

atom 1 since the projectile motion is slow. In a second step it arrives in the vicinity of atoms 4 and 5 and behaves here again as an acceptor then as a donor. The main difference between the two curves is that at 500 eV the second donor process is less efficient. This is likely due to the excitation of the cluster electrons which increases with the suddenness of the process. This excitation partly prevents the electron transfer to the cluster.

At medium energy $E = 1$ keV (fig. 2a), the figure shows that the first peak is more resolved which shows that all the first interaction (acceptor and donor phases are more efficient). We think that as the velocity increases the atoms 4 and 5 are partly associated with atom 1 in the first interaction, which will increase the amplitude of the exchanges. There appears a second interaction with atom 4 and 5 where the acceptor phase from the aggregate to the projectile is favorized while the reversed process almost disappears. This feature is certainly due to the large excitation of the cluster electrons which in the second interaction, tends to favorize the departure of electron from the the aggregate and simultaneously electrons and prevents them to go back to the aggregate.

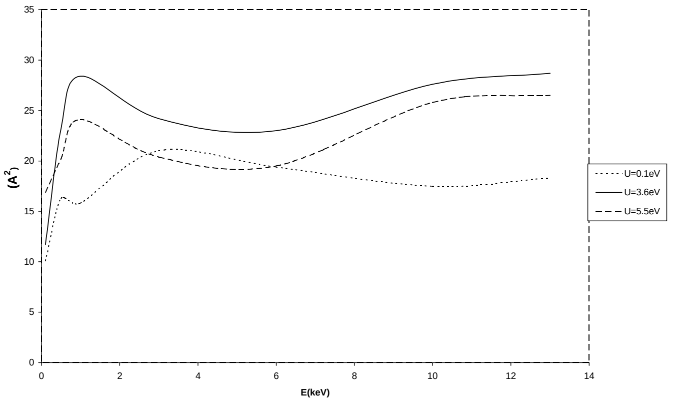


**Fig. 4.** Capture cross section $\sigma(\text{Å}^2)$ *versus* the projectile energy $E$(keV) for $U = 3.6$ eV, $U = 5.5$ eV and $U = 0.1$ eV.

At larger energies $E = 3$ keV, 6 keV and 10 keV (fig. 2b) the incident particles sees the three atoms 1, 4 and 5 almost at the same time. Consequently there is only one event (peak) with an acceptor phase which is almost the same for the three energies and a donor phase which decreases as $E$ increases because the atom, at the time when the donor phase would begin, is more and more far from the whole cluster. One may predict at even larger energies ($E > 30$ keV), the amplitude of the acceptor phase would also decrease and the capture tends to zero.

In figure 3, the electron population $N$ on the projectile at the end the process (*i.e.* the captured charge) is reported for different kinetic energy $E$ *versus* the different impact parameters $d$ of the previous trajectory described in figure 1 and for $U = 3.6$ eV (fig. 3a), $U = 5.5$ eV (fig. 3b), $U = 0.1$ eV (fig. 3c). For $U = 0.1$ eV, an average on the different states due to the electronic degeneracy has been done. The behavior of $N$ with $d$ and $E$ is not trivial a understanding need to keep on the analyze previously done on the time dependence of the projectile population $N$. However we can done two remarks, for $U = 3.5$ eV and 5.5 eV $N$ is larger than for $U = 0.1$ eV this result is linked with the fact that when the projectile is at the closest position from the cluster the effect of the electronic correlation is to decrease the charge excitation (*i.e.* to have a uniform electron density in the molecule formed by the cluster and the projectile). Another fact is that the electron transfer occurs for $U = 0.1$ eV at larger impact parameter, it means that the electron are more mobile.

Finally let us report the cross section of the process for different $U$ values. $U$ has the tendency of increasing the cross section but for large $U$ the effect is decreasing certainly due to the fact that the electrons are less mobile. The cross section displays some resonance for $E = 1$ keV. The $\sigma$ value is about 20-25 Å$^2$ between 1-10 keV and is smaller than the one obtained for the collision between ionized cluster and a atom.

## 4 Conclusion

This calculation has shown the importance of the excitation during the collisions leading to non-adiabatic process, in particular the fact that the cluster has sometime an acceptor character and other time a donnor one. It will be interesting to examine the dependence of the cluster size on the cross section.

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