Maximum Entropy Theory of Recoil Charge Distributions in Electron-Capture Collisions

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A generalized Fermi-Dirac distribution is derived and applied to charge-state distributions in single collisions between multiply charged ions and rare-gas atoms. It relates multiple electron loss in single-electron capture to multiple ionization in multiphoton absorption and discloses inner-shell vacancy formation in double- and triple-electron capture.

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In the transfer ionization[1] process

$$A^{q+}+B\rightarrow A^{(q-k)+}+B^{n+}+(n-k)e \qquad (1)$$

the ionization of $n-k$ electrons occurs simultaneously with the capture of k ($k\geq 1$) electrons leaving a recoil ion B^{n+}. The large number of accessible final states makes the direct quantum mechanical approach unfeasible and the need for statistical methods is evident. Müller, Groh, and Salzborn[2] recently applied Russek's evaporation model[3,4] to the calculation of multiple ionization probabilities for processes of type (1) ($k=2,3$) for a variety of multiply charged ions ($2\leq q\leq 15$) with typical energy $10q$ keV colliding with rare-gas atoms.[5] They found a remarkable agreement with experiment[5] though using a form[3] of the model which assumes that the recoil ions may still be in autoionizing states at detection. This assumption is, however, incorrect, since the flight times[5] are much larger than the lifetimes of these states.

In order to avoid this type of limitation of specific models and to obtain a minimally prejudiced recoil charge-state distribution for processes of type (1) we use the maximum entropy principle (MEP).[6,7] This, together with Dirac-Fock ionization energy calculations, reveals, contrary to Ref. 2, definite nonstatistical features caused by inner-shell vacancy formation in multiple-electron capture by projectiles with q around six. The single-electron–capture distributions, not considered in Ref. 2, are shown to be statistical and to have the same origin as those arising from outer-shell multielectron stripping[8] in multiphoton absorption. This has never been demonstrated explicitly although ionization by fast collisions and electric fields has been related to multiphoton transitions.

In applying MEP we introduce the recoil charge n as the stochastic variable, and the multiple-electron loss in reaction (1) is assumed to occur in the outermost subshell of B. The prior distribution is given by a counting of available many-electron final states. According to the exclusion principle the number of final manifolds of electron states which pertain to the loss of n electrons out of N is $M=\binom{N}{n}$. Summing over n gives $N_0=2^N$ manifolds, each containing an infinite number of states describing the captured and ejected electrons plus photons. Thus the recoil ion is assumed stable against further ionization.

For small kinetic energies of the projectile A the capture of k electrons leads to distributions for which

$$\sum_{n=k}^{n_0}\sum_{\kappa=1}^{M}p(\kappa,n)=1, \qquad (2)$$

where $p(\kappa,n)$ is the probability of a state with recoil charge n within a manifold and n_0 ($k\leq n_0\leq N$) is the maximum number of electrons which can be ionized by the energy released in the capture. In contrast to fast collisions n_0 in Eq. (2) depends on the collision energy only[2,5] through

$$\Delta E(q,k)\geq\sum_{\nu=1}^{n_0}I_\nu(B), \qquad (3)$$

where $I_\nu(B)$ is the νth ionization energy and where $\Delta E(q,k)=E(A^{q+})-E(A^{(q-k)+})$ is the maximum energy which the projectile A makes accessible to B in a capture collision changing q to $q-k$. The probability $P_k(n_0,n)=\sum_\kappa p(\kappa,n)$ for observing a recoil ion which has lost n electrons has then the following prior form:

$$P_k^0(n_0,n)=\binom{N}{n}\left[\sum_{n=k}^{n_0}\binom{N}{n}\right]^{-1}. \qquad (4)$$

According to MEP[6] the most probable charge distribution can be determined by maximizing the information-theoretical entropy

$$S = -\sum_{n=0}^{N}\sum_{\kappa=1}^{M} p(\kappa,n)\ln p(\kappa,n) \tag{5}$$

subject to normalization and additional constraints. These are taken to be the average residual charge

$$\sum_{n=0}^{N}\sum_{\kappa=1}^{M} p(\kappa,n)n_\kappa = \langle n\rangle \tag{6}$$

and the average excitation energy

$$\sum_{n=0}^{N}\sum_{\kappa=1}^{M} p(\kappa,n)E_{n\kappa} = \langle E\rangle, \tag{7}$$

where $E_{n\kappa}$ is the average energy required to produce a recoil ion with charge n_κ. The maximization of Eq. (5), subject to Eqs. (2), (6), and (7), using the variational method based on the Lagrange multiplier technique[6] leads to

$$P_k(n_0,n) = \binom{N}{n}\exp\Gamma_n\left[\sum_{n=k}^{n_0}\binom{N}{n}\exp\Gamma_n\right]^{-1}, \tag{8}$$

where $\Gamma_n = \lambda n + \lambda' E_n$ is assumed to be independent of the magnetic quantum numbers of the residual $N-n$ electron state, i.e., $E_{n\kappa} = E_n$. The Lagrange parameters λ and λ' are uniquely[6] determined by Eqs. (6) and (7).

For $k=0$ and $n_0 = N$ Eqs. (2), (6), and (7) are analogous to the subsidiary conditions that are used in the derivation of the nonequilibrium Fermi-Dirac distributions. This is seen by expressing $E_{n\kappa}$ in Eq. (7) as a sum of one-electron excitation energies ϵ_ν, where each ν specifies vacancy quantum numbers in κ. The variational procedure yields then in counterdistinction to conventional derivations[10] even for *finite* $n_0 = N$ the distribution function $\langle n_\nu\rangle = [1+\exp(-\lambda-\lambda'\epsilon_\nu)]^{-1}$. The interpretation of Eq. (5) as entropy defines a temperature T and a chemical potential μ such that $\lambda = \partial S_{\max}/\partial\langle n\rangle = \mu(kT)^{-1}$ and $\lambda' = \partial S_{\max}/\partial\langle E\rangle = -(kT)^{-1}$.

If the capture occurs preferably to a given state of the projectile A, E_n is independent of n, Eq. (7) reduces to Eq. (2), and $\lambda' \cong 0$. In order to test Eq. (8) in this form against the large body of experimental charge-state fractions $P_{\text{expt}}(k,n)$ of the recoil ion B,[5] we plot the "surprisals"[11] $\ln[P_{\text{expt}}(k,n)/P_k^0(n_0,n)]$ as functions of n, where $P_k^0(n_0,n)$ is given by Eq. (4). Since $\ln[P_k(n_0,n)/P_k^0(n_0,n)] = \lambda n$ according to Eq. (8) any nonlinear behavior of the surprisals indicates either inappropriate constraint selection or recoil-ion production by a dominating mechanism.

For A^{q+}-Ar,Xe collisions the surprisals disclose a very definite pattern as demonstrated for Xe in Fig. 1. Grouping of the $P_{\text{expt}}(k,n)$ values for different projectiles closest in $\Delta E(q,k)$ results in projectile-independent surprisal plots. This shows that $\Delta E(q,k)$ is the decisive energy parameter. In $P_k^0(n_0,n)$, n_0 ($\leq N=6$) has been obtained from Eq. (3) by use of the Dirac-Fock method and the results agree with the experimental n_0 values. As shown in Fig. 1 the $k=1$ surprisals are linear functions of n with negative slopes indicating agreement with Eq. (8) for $\lambda'=0$. For $k=2$ and 3 this linearity is absent in a nonstatistical transition region from negative to positive slopes. The change in the sign of λ occurs at $q \gtrsim 6$ for which the simultaneous capture of an inner-shell electron (Xe: $4d$, Ar: $2p$) with an additional np (Xe: $n=5$, Ar: $n=3$) electron becomes possible according to our Dirac-Fock

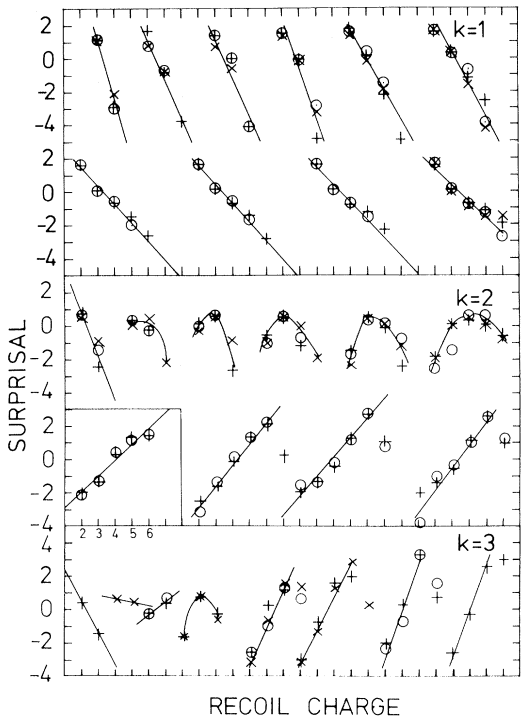

FIG. 1. Recoil charge-state surprisals for single ($k=1$), double ($k=2$), and triple ($k=3$) capture in A^{q+}-Xe collisions [A: Ar (crosses), Kr (plusses), Xe (circles)] as a function of the recoil charge n. Each surprisal plot corresponds to a λ value and to a specific average energy access ΔE. The ΔE values can be read from Fig. 2 since it shows the one-to-one correspondence between λ and ΔE. The surprisals start at the left with recoil charge $n=k$ (an example for $k=2$ is given in the lower left corner) except the two last $k=3$ surprisals which start with $n=4$.

calculations. This process, dominant at the threshold, is followed by Auger transitions producing a maximum of the charge-state distribution at $n = k + 1$. As illustrated by Fig. 1 this nonstatistical behavior gradually disappears at sufficiently large $\Delta E(q,k)$ where the distinction between inner- and outer-shell vacancy production becomes irrelevant. The nonlinearity cannot be caused by omission of Eq. (7) since the projectiles are essentially unexcited after the collision[2] making $E_n \simeq \Delta E(q,k)$ independent of n. Note that since Müller, Groh, and Salzborn[2] express their distributions in terms of a reduced energy variable, these features are obscured in their work. The points corresponding to $n = 7$ $(k = 2, 3)$ are below the linear surprisals in Fig. 1 since they represent the removal of a $5s$ electron for which the prior probability (4) with $N = 6$ is inappropriate.

In Fig. 2 the parameter λ is shown for Xe for each k as a function of the average energy access ΔE associated with each surprisal. It can be parametrized by $\lambda = a(k)\Delta E + b(k)$, where a and b are somewhat different for Ar and Xe.[12] The analogy to the Fermi-Dirac distribution suggests the identification of ΔE as the "heat bath" of the statistically distributed multiple electron loss processes.

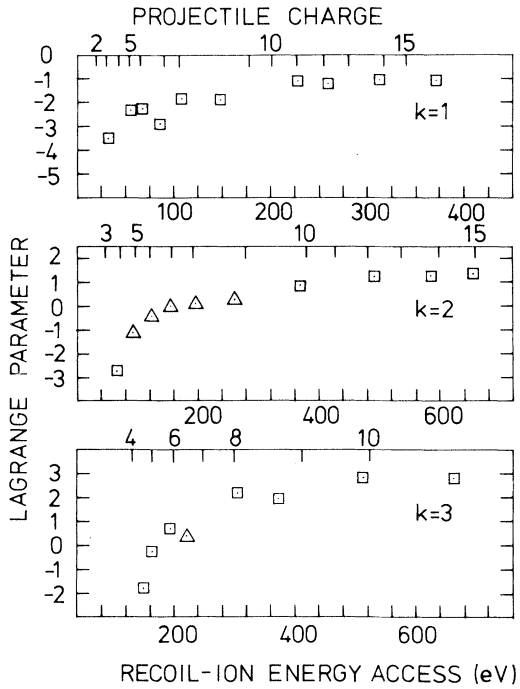

FIG. 2. The Lagrange parameter λ for single $(k = 1)$, double $(k = 2)$, and triple $(k = 3)$ capture in A^{q+}-Xe collisions (A: Ar, Kr, Xe) as a function of ΔE. The squares correspond to linear surprisals. The triangles representing the transition regime were obtained by calculations from the constraints (2) and (6). For illustration the upper nonlinear scale gives the corresponding q value for Xe^{q+}-Xe collisions.

Since single-electron capture occurs preferably into a given Rydberg state[13] Eq. (7) again becomes redundant. Simple estimates based on energy resonance conditions[13] indicate that the fraction of ΔE accessible for multiple excitation is given by $\Delta E' = I_1[1 + (q-1)^{1/2}/(2q-1)^{1/2}]$, where I_1 is the ionization potential of the target atom. This average reduction in the energy excess ΔE makes vacancy creation followed by Auger processes unlikely but autoionization in the outermost shell is still possible. The $\Delta E'$ value at which λ becomes approximately constant ($\lambda \simeq -1.8$ for Ar and -1.2 for Xe) is the one required for direct double ionization. Above this limit the increase of $\Delta E'$ only leads to higher kinetic energies in direct ionization without the appearance of new processes. Therefore there are no nonstatistical features in the $k = 1$ surprisals.

Multiple ionization also occurs in multiphoton absorption as first observed by L'Huillier *et al.*[8,14] using a 50-psec laser pulse at 0.53 and 1.064 μm and in the 10^{12} to 10^{14} W cm^{-2} intensity range. The large number of alternative routes leading to ionization suggests a similar test of randomness as above. As for single-electron capture we plot in Fig. 3 $\ln[P_{\text{expt}}/P_1^0(n_0,n)]$ as a function of n, where P_{expt} is now the observed multiphoton charge-state fraction,[14] P_1^0 is given by Eq. (4), and n_0 is the maximum measured charge. We obtain linear surprisals with negative slopes indicating no significant inner-shell vacancy production as in single-electron capture. The situation may differ in multi-

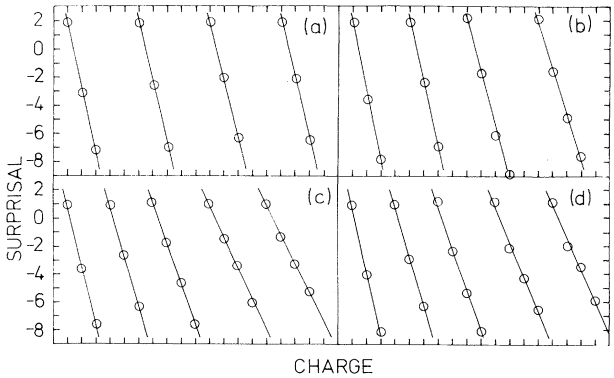

FIG. 3. Surprisals for multiple ionization in multiphoton absorption for different targets and wavelengths: (a) Ar, 1.06 μm; (b) Kr, 1.06 μm; (c) Xe, 1.06 μm; (d) Xe, 0.53 μm. The surprisal for each laser intensity starts at the left with charge $n = 1$.

ple ionization by ultraviolet multiphoton absorption[15] similarly to double- and triple-electron capture. The λ values range from -5 to -2, increasing linearly as a function of the laser intensity[12] except for the highest Xe cases. They would correspond to $2 \lesssim q \lesssim 6$ in one-electron capture as Fig. 2 demonstrates for Xe^{q+}-Xe collisions. As can easily be estimated from the experimental parameters[5] these q values create a transient electric field of the order of 10^{10} V m^{-1} lasting for a few picoseconds at the site of the target atom. A similar field is created by the laser pulse in the multiphoton experiments.[8,14] From a microscopic point of view this prompts the identification of the electric field as the common stochastic process underlying both modes of multiple electron loss.

In conclusion, the usefulness of a MEP analysis for testing the degree of statistical behavior in collisions between slow multiply charged ions and atoms has been demonstrated. It shows that the stochastic behavior of transfer ionization is related to the intensive transient electric field at the target atom.

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