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International Journal of Mass Spectrometry 192 (1999) 65–73



Time ordering in fast double ionization

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Received 4 January 1999; accepted 18 March 1999

Abstract

We consider the role of time ordering in the production of multiply charged ions by examining the role of time ordering in two-electron transitions such as double ionization of atoms in fast ion–atom and photon–atom collisions. If two or more electrons are uncorrelated in space, then transitions of these electrons evolve independently in time. If the electrons are correlated, then the transition of one electron can affect the time evolution of the other electron. In the interaction picture correlation in time is carried by the part of the time-ordering operator T which is antisymmetric in time. It is this part of T that gives nonequal weight to the time ordering of the interactions causing the electron transitions. The antisymmetric part of T is nonzero only if electron correlation is present. Thus, correlation in time between transitions of different electrons is connected to spatial electron correlation due to the electron–electron interaction. We also note an invariance in the product of the time and charge symmetry of the projectile in fast ion–atom collisions. Consequently, effects of the antisymmetric part of T may be found in regions where there are substantial contributions antisymmetric in the projectile charge, Z (e.g. Z^3 contributions) to transition probabilities and cross sections, as evident in double ionization of atoms and molecules. (Int J Mass Spectrom 192 (1999) 65–73) © 1999 Elsevier Science B.V.

Keywords: Time ordering; Electron correlation; Few-electron transitions

1. Introduction

In interactions of atoms and ions with other atoms and ions as well as with photons, it is possible for more than one electron to make a transition. Indeed this is one way in which multiply charged ions may be produced, namely multiple ionization in a single collision. One of the simplest cases is that of fast

double ionization which is relatively easy to observe. In ion–atom collisions the high velocity limit of double ionization is dominated by dynamics of electron correlation [1–3], and at moderately high velocities there is an interplay between electron–electron and electron–projectile mechanisms—a so-called Z^3 regime since the cross sections include effects of the third power of the projectile ion charge Z [2,4]. The Z^3 terms are nonzero only if electron correlation is included.

In these fast collisions the transitions are often thought to occur simultaneously. Here the transit time of the projectile is small compared to the orbit time of

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the target electrons. In contrast, in very slow ion–atom collisions two transitions may be sufficiently separated in time that they are incoherent and one may think about two separate events occurring in a well-ordered time sequence. The main point of this article is to explore the gap between simultaneous and sequential transitions and to relate effects of coherent time ordering of moderately fast two-electron transitions to electron correlation.

In this article we shall focus on velocities several times faster than the orbit time of the target electrons. It is in this regime that Z^3 effects are relatively large. It has been previously noted that effects of time ordering between the transitions are required for nonzero Z^3 effects [5–9]. We shall elaborate upon this point and detail the connections between time ordering of different electron transitions and electron correlation. In other words we shall explore the interconnection between correlation in space and time in transitions of two electrons. In addition we note an invariance of observable transition probabilities and cross sections with regard to the product of the sign of the projectile charge and the time symmetry of the projectile interaction. This projectile charge time symmetry will be compared to the more general charge conjugation and time reversal symmetries (\mathcal{C} and \mathcal{T}) which independently hold for the purely electromagnetic interactions considered here.

2. Formulation

In general, the probability amplitude for one or more transitions in a many-electron system may be written as the projection of the full time-dependent many-electron wave function $\Psi_i(t)$ onto a specified final state,

$$\begin{aligned} a_{fi} &= \langle f | \Psi_i(t \rightarrow +\infty) \rangle \\ &= \langle f | U_I(t_f \rightarrow +\infty, t_i \rightarrow -\infty) | i \rangle \end{aligned} \quad (1)$$

Here $U_I(t_i, t_f)$ is the evolution operator that describes the time development of the system from t_i to t_f due to an explicitly time-dependent interaction $V_I(t)$. The subscript I indicates that we will use the interaction

representation where the correlated eigenstates $|s\rangle$ of an atomic Hamiltonian H_0 are considered as known and U_I provides the time-dependent change in the total wave function $\Psi(t)$ due to a known interaction $V_I(t)$. In the interaction representation $V_I(t) = e^{-iH_0 t} V(t) e^{iH_0 t}$ where $V(t)$ is an interaction external to the many-electron target. U_I satisfies the following equation (we take $\hbar = 1$).

$$\partial U_I / \partial t = i V_I(t) U_I \quad (2)$$

This can be integrated to give

$$\begin{aligned} U_I(t_f, t_i) &= T \exp \left[i \int_{t_i}^{t_f} V_I(t) dt \right] \\ &= 1 + i \int_{t_i}^{t_f} V_I(t') dt' \\ &\quad + \frac{(i)^2}{2!} \int_{t_i}^{t_f} T V_I(t'') V_I(t') dt'' dt' + \dots \end{aligned} \quad (3)$$

where T is the time-ordering operator which insures that $V_I(t'')$ occurs after $V_I(t')$ for $t'' > t'$, as described in the following. In a perturbation expansion the effects of time ordering first appear in the second-order term.

Time ordering: The interaction $V(t)$ may change the energy E . Causality is imposed on the time order (or sequencing) of the interactions by requiring that $V(t'')$ occur after $V(t')$. The time ordering comes from integration of Eq. (2) and arises directly from the time-dependent Schrödinger's equation. This time ordering may be expressed by a Heavyside function $\Theta(t'' - t') = 1$ (or 0), if $t'' > t'$ (or if $t' > t''$). Thus in the matrix elements in Eq. (1), time propagation is expressed as, $T = 2\Theta(t'' - t')$.

Time ordering has been recently observed in interactions of photons with atoms [25]. These effects arise in observable phase dependence of resonance fluorescence spectra. In interactions with charged particles time ordering of two transitions has been considered by various authors [3,5–7].

$$\sum_s V_{fs}(t^n) e^{iE_s(t^n-t')} V_{si}(t') \quad (\text{without time ordering}) \tag{4}$$

$$\sum_s V_{fs}(t^n) \Theta(t^n - t') e^{iE_s(t^n-t')} V_{si}(t') \quad (\text{with time ordering})$$

The sum over intermediate states s is consistent with the Uncertainty Principle, where the uncertainty in time may be often estimated by the collision time.

3. Multiple-electron transitions

Let us consider a two-electron transition for simplicity. The more general N -electron case follows the same general pattern. For two electrons, the interaction is assumed to be a linear sum of terms, namely,

$$V_I(t) = V_{I1}(t) + V_{I2}(t) \tag{5}$$

The subscripts 1 and 2 refer to the two electrons. We emphasize that the $V_{Ij}(t)$ operators are not single electron operators in the interaction representation. Specifically, $V_{Ij}(t) = e^{-iH_0 t} V_{Ij}(t) e^{iH_0 t}$ where $V_{Ij}(t)$ is a one electron operator, and H_0 is the Hamiltonian of the atom including correlation. That is, $H_0 = \sum_j H_{0j} + \sum_{j,k} v_{jk}$, where v_{jk} is a correlation interaction (such as $1/r_{jk}$) that couples electrons. Because H_0 includes correlation $V_{Ij}(t)$ is a many-electron operator and it affects all electrons. The main point of this article is that this spatial correlation leads to a time correlation of the multiple-electron time-dependent transition amplitudes and transition probabilities.

At this point we neglect exchange. Neglect of exchange is plausible in fast collisions [3]. Neglecting exchange allows one to regard the electrons as distinguishable. This is conceptually helpful. When exchange is not small, the mathematical development is expected to be similar, but the simplifying conceptual picture will be lost.

As an instructive example, let us now consider the second-order term in the evolution operator of Eq. (3) in a two-electron system without exchange. Specifically, consider

$$\begin{aligned} U_I^{(2)}(t_f, t_i) &= \frac{(i)^2}{2!} \int_{t_i}^{t_f} \int_{t_i}^{t_f} T V_I(t'') V_I(t') dt'' dt' \\ &= \frac{(i)^2}{2!} \int_{t_i}^{t_f} \int_{t_i}^{t_f} T [V_{I1}(t'') + V_{I2}(t'')] \\ &\quad \times [V_{I1}(t') + V_{I2}(t')] dt'' dt' \\ &= \frac{(i)^2}{2!} \int_{t_i}^{t_f} \int_{t_i}^{t_f} T [V_{I1}(t'') V_{I1}(t') \\ &\quad + V_{I2}(t'') V_{I2}(t')] dt'' dt' \\ &\quad + \frac{(i)^2}{2!} \int_{t_i}^{t_f} \int_{t_i}^{t_f} T [V_{I1}(t'') V_{I2}(t') \\ &\quad + V_{I2}(t'') V_{I1}(t')] dt'' dt' \end{aligned} \tag{6}$$

The first two terms contain no cross terms in the 1, 2 electron indices. No time correlation between different electrons may arise from these terms since only one electron is affected by the T operator. Two-electron transitions arise from these terms only if electron–electron interactions cause one of the transitions. Furthermore, through second-order in $V(t)$ it is only the cross terms where time evolution of one electron can affect a transition of another electron.

3.1. Uncorrelated limit

The independent-electron approximation is reached in the limit that electron correlation is negligibly small, i.e. the uncorrelated limit where $v_{jk} \rightarrow 0$. Again, here we neglect electron exchange which will allow us to consider distinguishable electrons. Electron exchange usually vanishes rapidly as the energy of the projectile increases [3]. In this uncorrelated limit without exchange it is physically obvious that transitions of two (or more) electrons are independent. There is no connection in space and the transitions occur independently in time.

In the uncorrelated limit, the $V_{Ij}(t)$ operators reduce to single electron operators. This occurs because the unperturbed Hamiltonian H_0 contains no electron

correlation so that now $H_0 = \sum_j H_{0j}$ is a simple sum of independent terms. Then, $e^{iH_0t} = e^{i\sum_j H_{0j}t} = \prod_j e^{iH_{0j}t}$ so that all the $e^{iH_{0j}t}$ terms in $V_j(t)$ commute with $V_j(t)$ except the terms with $k = j$ in the definition of $V_j(t)$ below Eq. (5). Now $V_{lj}(t)$ and $V_{lk}(t)$ are single electron operators that commute with each other. In the second-order terms of Eq. (6), in the absence of any electron–electron interaction only the cross terms of Eq. (6) contribute to two-electron transitions since all other terms involve one electron operators which give no contribution to a two-electron transition. Although $T \neq 1$ may influence the transition of one electron, there is no coupling between electrons and so the time-ordering operators in cross terms in $V_{lj}(t'')V_{lk}(t')$ have no influence and one may replace T by $T = T_{av} = 1$ in second-order cross terms. All matrix elements are independent one-electron matrix elements. Time evolution over t' is decoupled from evolution over t'' in the absence of correlation.

More generally, it is easily shown [3] in the interaction picture that in the absence of electron correlation, the quantum probability amplitude for a multiple electron system $A(1, 2, 3, \dots, N)$ may be expressed as a product of independent single electron probability amplitudes $\Pi_j a_j$, i.e.,

$$\begin{aligned} A(1, 2, 3, \dots, N; t) &= \langle \Pi_j f_j | \Pi_j U_{lj} | \Pi_j i_j \rangle \\ &= \Pi_j \langle f_j | U_{lj} | i_j \rangle \\ &= \Pi_j a_j(t) \quad (\text{IEA}) \quad (7) \end{aligned}$$

This defines the independent-electron approximation (IEA) (without exchange). Energy is independently transferred by the projectile to each of the electrons. There is no time correlation between the various transitions between the states of the N -independent electrons. The clocks of the transitions are all set by the collision and are independent of one another.

Note that the individual electron transitions may contain effects of time ordering. Except for the first order term, the $(T - T_{av})$ terms can and often do contribute to each order in perturbation theory. Thus, for example, in single electron transitions time ordering may play a role in higher order terms. This also

applies to each of the independent electron terms in an uncorrelated limit for multiple transitions where one has a product of independent single electron terms. However, in multiple electron transitions there is no time ordering between transitions without spatial electron correlation. This null result for cross terms in multiple electron transitions holds to each order in a perturbation expansion.

If electron exchange is included, then an exchange effect in time may arise which would be included in the uncorrelated independent electron limit (according to most present conventions). Here this complication is avoided by considering only fast collisions where electron exchange is small.

Conceptually the time clocks of the transitions are interdependent only if the electrons are interdependent, i.e. correlated. When correlation is included then effects of time ordering arise [3]. These effects cause the factor of two difference in total ionization cross sections by impact of particles and antiparticles via the Z^3 effect [2]. Transitions can be sequential only if there is electron correlation. Without electron correlation all transitions may be regarded as simultaneous. There is no sequencing or time ordering. The lack of simultaneity in multiple electron transitions has not been well explored experimentally in atomic reactions.

3.2. Correlated systems

If correlation is nonzero, then $H_0 = \sum_j H_{0j} + \sum_{j,k} v_{jk}$, where v_{jk} the correlation interaction is nonzero. The matrix elements of $V_j(t)$ in Eq. (6) are now two-electron matrix elements, e.g. $V_{lj}(t'')$ depends on both electrons and it is generally not possible to commute $V_{lj}(t'')$ with $V_{lk}(t')$ since $[v_{jk}, \nabla^2] \neq 0$. Now the ordering of the $V_{lj}(t'')_{lk}(t')$ terms can make a difference. With correlation time ordering contributes in the cross term of Eq. (6). Consequently the evolution over t'' is coupled to the evolution over t' .

Physical energy may be exchanged between the two electrons via the correlation interaction v_{jk} . Correlation energy influences the propagation in the intermediate states and $\langle f | TV_{lj}(t'')V_{lk}(t') | i \rangle$ may dif-

fer from $\langle f|TV_{I_k}(t'')V_{I_j}(t')|i\rangle$ in Eq. (6). For example one transition corresponding to $V_{I_j}(t')$ may depend differently on t' than another corresponding to $V_{I_k}(t')$. Then the correlation interaction has more time to rearrange the energy between the electrons in one sequence than in another. Different sequences contribute differently to the final overall transition amplitude. The individual transition amplitudes generally vary with energy and consequently the fast–slow order may have a different amplitude than the slow–fast order of the transition. In other words the probability amplitudes for different sequences of transitions may differ if electron correlation is nonzero.

3.2.1. Symmetric and antisymmetric time propagation

It is instructive to consider the Fourier transform of the time-ordered propagation in Eq. (3) above, namely,

$$\int dt e^{-iE't'}\Theta(t)e^{iEt} = \frac{i}{E' - E + i\eta}$$

$$= \pi\delta(E' - E) + iP_v \frac{1}{E' - E}$$

(8)

Here P_v denoted the principle value. Eq. (8) describes propagation in E space (conjugate to time space). In Eq. (8) the energy propagator is separated into terms symmetric and antisymmetric in energy E , which in turn corresponds to separation of the time propagation into corresponding terms symmetric and antisymmetric in time. The time ordering is carried by the $+i\eta$ term which eliminates terms that increase exponentially in time. It means that there are incoming plane waves propagating from some initial state which are later scattered. If there is no time ordering, then $T = 2\Theta(t'' - t')$ in Eq. (8) is replaced by a constant namely, $T = T_{av} = 2\Theta_{av}(t'' - t') = 1$ (and not 2 to avoid double counting), which is symmetric in time. Now one has the obvious result that $\int dt e^{-iE't'}e^{iEt} = \pi\delta(E' - E)$. We note that the $(T - T_{av})$ terms are rotated by 90° in the complex time plane with respect to the (usually dominant) T_{av} operator.

The time-ordering operator $T = \Theta(t'' - t')$ is now separated into two terms, $T = (T_{av}) + (T - T_{av})$ and is used in the cross term of Eq. (6), namely,

$$U_{i,12}^{(2)}(t_f, t_i) \equiv \frac{(i)^2}{2!} \int_{t_i}^{t_f} T [V_{I_1}(t'')V_{I_2}(t') + V_{I_1}(t')V_{I_2}(t'')] dt'' dt'$$

$$= \frac{(i)^2}{2!} \int_{t_i}^{t_f} T_{av}[V_{I_1}(t'')V_{I_2}(t') + V_{I_1}(t')V_{I_2}(t'')] dt'' dt'$$

$$+ \frac{(i)^2}{2!} \int_{t_i}^{t_f} (T - T_{av})[V_{I_1}(t'')V_{I_2}(t') + V_{I_1}(t')V_{I_2}(t'')] dt'' dt'$$

(9)

The first term with T_{av} is symmetric in time and carries no time ordering. This term may be written using $T_{av} = 2\langle\Theta\rangle_{av} = 1$. The second term with $(T - T_{av})$ is antisymmetric in $(t'' - t')$, corresponding to the antisymmetry of $iP_v 1/(E' - E)$ in Eq. (8). This term insures causality and gives a direction to time in the evolution of the system. The $T - T_{av}$ contribution goes to zero if there is no correlation since then $T - T_{av}$ is antisymmetric in $(t'' - t')$ and the rest of the integrand is symmetric since the V_I terms commute.

When correlation is included both the time symmetric T_{av} and the antisymmetric $T - T_{av}$ terms may be affected [3,7]. The antisymmetric $T - T_{av}$ term is necessary for observable time-ordering effects since the T_{av} term does not contribute to sequencing. Thus, with electron correlation from the spatial v_{jk} correlation interaction, sequential transitions may occur via $T - T_{av}$. Then the transitions are correlated in both space and time. As noted at the end of Sec. 2 there is no time ordering without spatial electron correlation. So time ordering in a two-electron transition occurs only if there is spatial electron correlation. Electron correlation in space causes time correlation (i.e. sequencing) in fast two-electron transitions.

3.2.2. An example

As an illustrative example, let us consider a two-electron transition between initial and final states, $|i\rangle$ and $|f\rangle$. The probability amplitude for such a transition may be expressed as

$$\begin{aligned}
 a_{fi} &= \langle f | U_f(t_f, t_i) | i \rangle \\
 &\approx \langle f | 1 + i \int_{t_i}^{t_f} [V_{I1}(t') + V_{I2}(t')] dt' \\
 &\quad + \langle f | \frac{(i)^2}{2!} \int_{t_i}^{t_f} T [V_{I1}(t'') V_{I1}(t') \\
 &\quad + V_{I2}(t'') V_{I2}(t')] dt'' dt' \\
 &\quad + \frac{(i)^2}{2!} \int_{t_i}^{t_f} T_{av} [V_{I1}(t'') V_{I2}(t') \\
 &\quad + V_{I1}(t') V_{I2}(t'')] dt'' dt' \\
 &\quad + \frac{(i)^2}{2!} \int_{t_i}^{t_f} (T - T_{av}) [V_{I1}(t'') V_{I2}(t') \\
 &\quad + V_{I1}(t') V_{I2}(t'')] dt'' dt' | i \rangle \\
 &\approx i(Z/v)c_1 - (Z/v)^2(c_2 - ic'_2) \quad (10)
 \end{aligned}$$

If the initial and final states are of well defined parity, then the matrix elements are all real or imaginary depending on the parity of the transition being even or odd. The first term in the perturbation expansion is zero since we assume that $\langle f | i \rangle = 0$. The first order terms are linear in the ratio of the projectile charge, Z to the collision velocity v giving a coefficient c_1 which is purely real (or imaginary). This term is nonzero only if there is some electron–electron interaction between the two electrons, either initial state correlation, final state correlation or shake. The terms quadratic in either V_{I1} or V_{I2} may contain time-ordering independent of electron–electron interactions. When Z/v and electron–electron effects are both small, say order ϵ , then these terms are of order ϵ^3 and the other terms are of order ϵ^2 . Thus the

quadratic terms V_{I1}^2 or V_{I2}^2 may be small compared to the cross terms in V_{I1} and V_{I2} which are retained in the last line. The T_{av} contribution is a factor of i out of phase with the $T - T_{av}$ contribution as discussed above. Again for transitions of well-defined parity c_2 and c'_2 are purely real (or imaginary).

As discussed previously [7], the Z^3 term in the transition probabilities and cross sections for the two-electron transition arise from interference between the first-order term, $i(Z/v)c_1$, and the $(T - T_{av})$ contribution containing time ordering from the second-order cross term, $-i(Z/v)^2c'_2$. Thus the Z^3 term requires nonzero contribution from $(T - T_{av})$, which is the part of T that causes sequencing of the two transitions. This is a correlation in time in that it gives a relation between the times of the two transitions and also in that it represents a deviation from a mean value [3]. This $(T - T_{av})$ contribution requires electron correlation to be nonzero. The Z^3 term also requires c_1 to be nonzero which in turn requires nonzero electron–electron interactions from the first-order term which is dominant in the high velocity limit.

3.2.3. Invariance of time-charge symmetry

A convenient way to isolate the influence of the $T - T_{av}$ propagation is to use the symmetry of time and charge. Note from Eq. (2) that the product of the charge and time symmetries of $V(t)$ is invariant if $V(t)$ is symmetric in time, which is often the case. Thus, whenever the sign of Z is odd, the time propagation is antisymmetric. This invariance applies to transition probabilities and cross sections as well as amplitudes in fast ion–atom collisions [7]. This is an invariance of charge conjugation and time reversal for the external interaction. This differs from usual \mathcal{CT} (charge conjugation and time reversal) invariance which applies to all particles in the system. Furthermore, for electromagnetic interactions considered here for atomic systems, both \mathcal{C} and \mathcal{T} are invariant. This is due to a phase convention introduced by Wigner [10] where $i \rightarrow -i$ under both \mathcal{C} and \mathcal{T} . \mathcal{T} invariance, for example, is satisfied by T_{av} and also by

$T - T_{av}$ since from Eq. (8) it follows that T_{av} and $(T - T_{av})$ are a factor of i out of phase.

By restricting attention to the time and charge symmetry of the interaction potential $V(t)$ only, one may probe in more detail time structures in dynamics of many-electron systems. We suggest looking for observable differences in transition probabilities when the sign of $V(t)$ is reversed. These differences occur only when time ordering arising from $T - T_{av}$ is present. This corresponds to differences in the sequence in which transitions occur.

4. Discussion

In this article we have considered time ordering in a general way and have shown that one may expect effects of time ordering in two-electron transitions at moderately high velocities in ion–atom collisions if there is interference between the time antisymmetric part of the time-ordering operator $(T - T_{av})$. This is the term that causes the two transitions to be not simultaneous, i.e. it causes sequencing. This sequencing occurs because the electrons interact with each other. Whenever such effects occur, there are asymmetries in the dependence of the probability and cross section on the charge of the projectile, Z . The development is limited here to the validity constraints of second-order perturbation expansions in Z/ν and correlation which is also small. It would be useful to have detailed calculations of specific reactions which predict effects of time ordering that are experimentally testable.

An example of a reaction where such effects are expected to occur is double excitation and double ionization of atoms and molecules by incident ions. We note that such a large Z^3 effect is surprisingly large since it is restricted by quasiselection rules [11]. In double electron excitation of helium such effects are remarkable both in cross section of excitation and resonance yield of autoionizing electrons [12] not to mention effects in the line profiles of the Auger transitions from the doubly excited states [13,12]. However, if the autoionizing nature of the double excited states of helium is not taken into account then

Z^3 effects in the double electron excitation are not large [12]. In double ionization of helium this Z^3 effect [14] can be a factor of 2 for $Z/\nu \approx 10$ a.u. in total cross sections. Some results [15,16] are also available for H_2 and H^- . With the advent of the COLTRIMS method for observing differential cross sections [17], it may be possible to probe this effect in more detail and look for regions where the effect may be even greater than a factor of 2 [3,4].

Another intriguing possibility is to look in differential spectra for transfer ionization. Here relatively little has been done to look for such effects although excellent COLTRIMS data [17,18] has recently become available in helium for proton energies ranging from $\nu = 2$ to $\nu = 10$ a.u. In this data evidence has been found for both independent capture and ionization by the projectile and also for a second-order effect where one electron knocks out a second electron during a two-step capture process. Theory for both is available [19–22] as is theory for both shakeoff and shakeover [3]. In differential cross sections one may vary the scattering angle (or momentum transfer) as well as the charge of the projectile to change the relative importance of various scattering amplitudes. This case would be interesting since one could explore the question, which is more likely to occur first: transfer or ionization? and why?

Some of the approximations used here include use of perturbation theory, neglect of electron exchange, and use of the interaction picture. Although no detailed work has been done to explicitly show whether or not any of these approximations introduce constraints fundamental to the physics in other regimes, it may be possible that some of the basic results including the need for spatial correlation to produce sequencing between transitions and the invariance of the sign of charge and time symmetries of the projectile could be independent of these approximations as is suggested by the general nature of our discussion in Secs. 3.1 and 3.2.3. Of course at moderate to low collision velocities the many-electron problem becomes generally more difficult [23,24]. We have also written the formulation in such a way that one may apply the results to impacts of photons. Time ordering has been observed in interactions of photons with

atoms [25]. These effects arise in observable phase dependence of resonance fluorescence spectra. It is well known that ion–atom and photon–atom collisions are related within the constraints of first order perturbation theory [3,26]. And some interrelation has been suggested as well in the case of strong fields [27].

All transition sequences are identical if there is no electron correlation. If, however, correlation is non-zero, then electronic energies in the atomic system rearrange and one transition sequence may be more likely than another. In principle, the change in the probability distribution arising from nonsymmetric time evolution may be associated with a change in entropy occurring in the dynamics many-electron atomic transitions. The spatial electron correlation also provides mechanisms for electrons to communicate about time, i.e. to generate time correlations among multiple-electron transitions.

5. Summary

In summary, if two or more electrons are uncorrelated in space (i.e. the correlation potential $v_{jk} = 0$), then transitions of these electrons occur independently. In this uncorrelated limit, the electrons evolve independently in time. On the other hand, if the electrons are correlated (i.e. $v_{jk} \neq 0$), then the transition of one electron can affect the time evolution of the other electron(s). In the interaction picture correlation in time is carried by the part $T - T_{av}$ of the time-ordering operator T which is antisymmetric in time. It is this part of T that gives unequal weight to the time ordering of the interactions causing the electron transitions. Thus, correlation in time between transitions of different electrons carried by $T - T_{av}$ is connected to spatial electron correlation due to the electron–electron interaction v_{jk} . Also the product of the time ordering and charge symmetries of the projectile is invariant. Thus one may be able to examine the role of time sequencing in the production of multiply charged ions by studying cross sections and transitions where observable Z^3 effects are present.

Acknowledgements

The authors gratefully acknowledge useful discussion with H.J. Lüdde, H.J. Ast, and S. Keller. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. Two of the authors (J.H.M. and B.W.S.) thank the Alexander von Humboldt Foundation for Research Awards. The work of one of the authors (B.W.S.) is supported in part under the auspices of the U.S. Department of Energy at Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

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