Time correlation in two-electron transitions produced in fast collisions of atoms with matter and light

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Time connection between electrons in dynamic atomic systems is considered. We describe time correlation in terms of the Dyson time ordering operator T. In this paper we decompose T into an uncorrelated term T_{unc}, plus a correlated term $T_{cor}=T-T_{unc}$, which interconnects the time-dependent external interactions. We show that time correlation between electrons requires both T_{cor} *and* spatial electron-electron correlation. Two examples are analyzed. In transfer ionization the time correlation operator incoherently changes the shape of an electron-electron Thomas peak. In double excitation the influence of T_{cor} in amplitudes for coherently interfering pathways changes resonance intensities and profiles.

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Understanding time correlation between electrons requires connecting the concept of spatial correlation with time. Spatial correlation arises from the Coulomb interactions between electrons [1–3]. Without this correlation the electrons are independent in both space and time, i.e., they do not mix with one another in space and they evolve independently in time [3]. In this paper we address time correlation *between* electrons, namely, how electrons communicate about time. We show that both temporal correlation of external interactions and spatial correlation between electrons are required for time correlation between electrons.

Cross sections of multielectron atoms dynamically interacting with both matter and light have been widely studied for many years [4–6]. In the last decade studies of multiple electron transitions have lead to more detailed understanding of correlated dynamic reaction mechanisms [3,7–10]. Now, new experimental techniques [10–12] are providing data in unprecedented detail, which can be used to test in greater depth new descriptions of collision dynamics. Thus, both a conceptual and an observational basis is now available for more explicit studies of how time works in quantum multiparticle dynamics. In this paper we analyze two atomic processes in which time correlation between electrons affects reaction cross sections. The first case is a kinematic peak in a reaction in which electron transfer and ionization both occur. In this case time correlated and time uncorrelated amplitudes add incoherently. The second case is double electron excitation where coherent reaction pathways interfere. In the second case time correlation between electrons produces a large effect on both the shape and intensity of a double excitation resonance.

Time dependence is imposed on a quantum system [13–16] by an external time-dependent interaction $V_I(t)$. The general expression for the probability amplitude, $a_{fi}(t)=\langle f|U_I(t,t_i)|i\rangle$, for scattering of one or more electrons from $|i\rangle$ at time t_i to $|f\rangle$ at time t may be described most conveniently in the interaction representation [3,5] using the evolution operator $U_I(t,t')$, which satisfies

$$i\,\partial U_I(t,t')/\partial t = V_I(t)U_I(t,t'), \tag{1}$$

with the initial condition $\lim_{t\to-\infty}U_I(t,-\infty)=\hat{I}$. The formal solution for the evolution operator may be expressed as a time ordered exponential [4,5],

$$U_I(t,t_i)=T\exp\left\{-i\int_{t_i}^{t}V_I(t')dt'\right\} = \sum_{k=0}^{\infty}\frac{(-i)^k}{k!}\int_{t_i}^{t}\cdots\int_{t_i}^{t}T(V_I(t_1)\cdots V_I(t_k))dt_1\cdots dt_k, \tag{2}$$

where T is the Dyson time ordering operator,

$$T(V_I(t_1)V_I(t_2)\cdots V_I(t_k)) \equiv \sum_{P(1,2,\ldots,k)}\theta(t_1-t_2)\,\theta(t_2-t_3)\cdots\theta(t_{k-1}-t_k) \times V_I(t_1)V_I(t_2)\cdots V_I(t_k). \tag{3}$$

Here $\theta(t-t')$ is the Heaviside step function. The sum above is taken over all possible permutations P of the parameters $1,2,\ldots,k$. The Dyson time ordering operator T imposes ordering of the $V_I(t_j)$ interactions in time to enforce causality

in the time evolution of the system [5]. Here $V_I(t) = \Sigma_j^N V_{Ij}(t)$ is implicitly summed over electrons.

We seek correlation in time between the $V_I(t_j)$'s, which provide [3] the time dependence to the quantum wave amplitudes $a_{fi}(t)$ via Eq. (2). Requiring that correlation in time be independent of the mathematical form of $V_I(t)$, we use the *only* time dependent term available other than V_I, namely, the time ordering operator T. All time dependence in T arises from the $\theta(t_i - t_j)$ terms in Eq. (3). This implies that time correlation may be removed by replacing all $\theta(t_i - t_j)$ by a constant. Then $T(V_I(t_1)V_I(t_2)\cdots V_I(t_k))$ is a simple product of $V_I(t_j)$ and is therefore uncorrelated in time. Consequently, there is no time correlation in U_I without this contribution to time ordering. Therefore, we now separate the T operator into two terms,

$$T = T_{unc} + (T - T_{unc}) \equiv T_{unc} + T_{cor}, \tag{4}$$

where T_{unc} is the uncorrelated part of T and $T_{cor} \equiv T - T_{unc}$ acting on $V_I(t_1)\cdots V_I(t_k)$, is our time correlation operator. In first order in V_I there is no time correlation. In second order one has

$$T(V_I(t)V_I(t')) = \theta(t-t')V_I(t)V_I(t') + \theta(t'-t)V_I(t')V_I(t), \tag{5}$$

where

$$T_{unc}(V_I(t)V_I(t')) = \frac{1}{2}[V_I(t)V_I(t') + V_I(t')V_I(t)], \tag{6}$$

whence it is easily shown that

$$T_{cor}(V_I(t)V_I(t')) = \frac{1}{2}\mathrm{sgn}(t-t')[V_I(t), V_I(t')]. \tag{7}$$

Calculations using $T \simeq T_{unc}$ correspond to an independent time approximation [17], where the $V_I(t_j)$ interactions are disconnected in time. In second order a two step process is reduced to two independent one-step processes [18,19]. The time correlation term, T_{cor}, connects the $V_I(t)$ at different times as is evident in Eq. (7). This term can produce time-dependent effects in quantum wave amplitudes reminiscent, for example, of light passing through a Young's double slit where a time difference can influence interference patterns, as illustrated in our second calculation below. We note that the general concept of time correlation has been used in nonequilibrium statistical quantum mechanics [2] where it is similar to spatial correlation [2,3].

The simplest examples of time ordering occur in one-electron systems [4–6]. The group of Thomas has experimentally isolated effects of time ordering in a one electron transition in a Yb atom interacting with a time varying external magnetic field [20]. However, in this paper we focus on correlations in time between different electrons. In a system with N electrons, $V_I(t) = \Sigma_j^N V_{Ij}(t)$ with $V_{Ij}(t) = e^{iH_0 t}V_j(t)e^{-iH_0 t}$. Here, for example, $V_j(t)$ may be given by $Z/|\vec{R}(t) - \vec{r}_j|$ for a particle of charge Z, $\vec{d}_j \cdot \vec{E}_0 \cos\omega_0 t$ for a photon field, or $\vec{\mu}_j \cdot \vec{B}(t)$ for an external magnetic field. If the correlation interactions between electrons are included, the $V_{Ij}(t)$ are multielectron operators that do not commute with each other [3]. The nth-order term in Eq. (2) contains both single-electron terms proportional to $(V_{Ij})^n$ and cross terms containing interactions with different electrons, namely, $V_{Ik}V_{Ij}$ with $k \neq j$. The cross terms connect the time evolution of different electrons. For two electrons in second order, $V_I(t) = V_{I1}(t) + V_{I2}(t)$ and $V_I(t)V_I(t') = V_{I1}(t)V_{I1}(t') + V_{I1}(t)V_{I2}(t') + V_{I2}(t)V_{I1}(t') + V_{I2}(t)V_{I2}(t')$. In this paper we consider only the effects from cross terms. That is, we consider processes in which the effects of $V_{Ik}V_{Ij}$ terms for $k \neq j$ dominate or can be separated from those effects from $k = j$. In these interelectron cases, time correlation is caused by

$$T_{cor}(V_{Ik}(t)V_{Ij}(t')) = \frac{1}{2}\mathrm{sgn}(t-t')[V_{Ik}(t), V_{Ij}(t')], \quad k \neq j. \tag{8}$$

This term causes time correlation between electrons.

In multiple-electron transitions correlation in time between different electrons generally requires spatial electron-electron correlation in addition to time ordering [3,7,8], as we have indicated above mathematically. Physically this is obvious. In the uncorrelated independent electron approximation without exchange, the scattering probability is represented as a product of single electron probabilities, namely, $P(t) = |a_{fi}(t)|^2 = \Pi_j |\langle f_j | U_{Ij}(t,t_i) | i_j \rangle|^2 = \Pi_j P_j(t)$. In this limit there is no mechanism for time correlation between transitions of different electrons. Without spatial electron correlation, phase information between electrons is lost, for example. This also follows from Eq. (8). If the correlation interaction $1/|\vec{r}_i - \vec{r}_j|$ is approximated by a mean field potential, then $[V_{Ik}(t), V_{Ij}(t')] = 0$, since the many-electron operator $V_I(t) = \Sigma_j^N V_{Ij}(t)$ then reduces to a sum of commuting single electron operators [3]. Only when spatial electron correlation is included can T_{cor} cause time correlation between different electron transition amplitudes.

In calculations presented in this paper electron exchange is included. Nevertheless, we note that it is conceptually convenient to neglect exchange. This simplifies the meaning of ''an electron'' and ''an electron transition'' and also it allows one to regard electrons as distinguishable. Inclusion of exchange is mathematically straightforward, but adds complexity both conceptually and technically. In fast atomic collisions the effects of exchange are often small.

In two examples below we have evaluated the effects of the T_{cor} operator in calculations through second order in $V_I(t)$ by separating the second order term in U_I into parts corresponding to the T_{unc} and T_{cor} parts of T. In second-order, this corresponds to separating the second-order contribution itself into on-shell and off-shell contributions as explained elsewhere [21]. Calculations of cross sections with both first- and second-order terms are then easily done with and without the T_{cor} time correlation terms. In both of our examples the second-order term contains interactions with

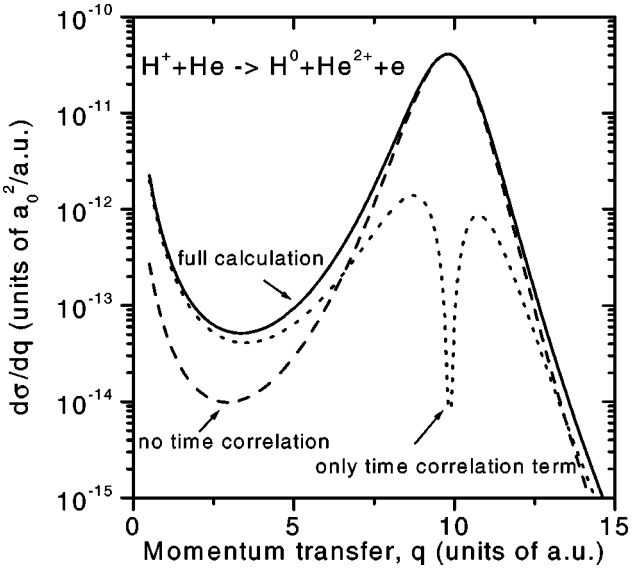

FIG. 1. Cross section for transfer ionization as a function of the momentum transfer q in 2.5 MeV proton-helium collisions in the vicinity of the electron-electron Thomas peak showing the effects of time correlation. Full curve, full second-order calculation including both T_{cor} and T_{unc} terms of Eq. (4); long dash, approximate calculation using only the uncorrelated time term T_{unc}; short dash, approximate calculation using only the correlated time term T_{cor}. In this case the effects of T_{cor} and T_{unc} add incoherently as explained in the text.

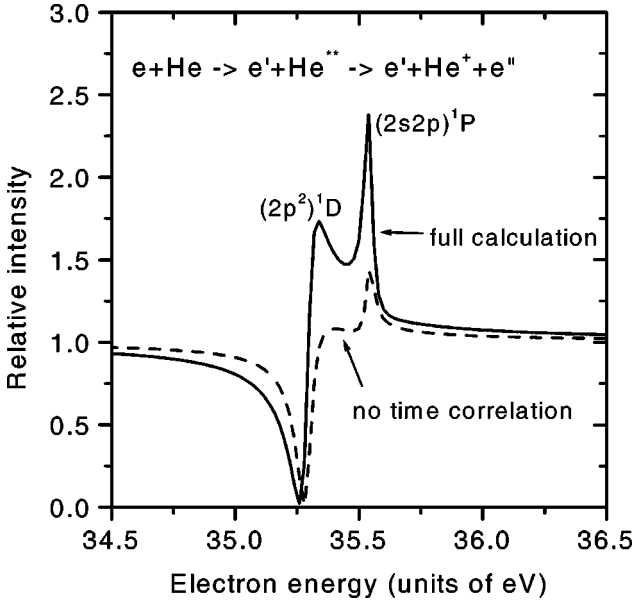

FIG. 2. Effect of time ordering on the autoionizing $(2p^2)^1D$ and $(2s2p)^1P$ resonances of helium in electron emission spectrum excited by 200 eV electron impact. The electron angle of emission is 60° and the projectile scattering angle is 30°. Full curve, full second-order calculation including the T_{cor} term of Eq. (4); broken curve, approximate calculation using only the uncorrelated time term T_{unc}. In this case the effects of T_{cor} and T_{unc} are partially coherent. The cross section is normalized to the background of direct ionization.

different electrons and higher order effects of time ordering from the same $V_I(t)$ are small. In the first example, contribution from the first Born term is negligible and the effect of T_{cor} adds incoherently to that of T_{unc}. In the second example there is a significant first Born contribution, which is coherent with the T_{cor} contribution and a relatively strong interference effect is found.

As a first example we consider a resonant reaction in which both electron transfer and ionization occurs, namely, the purely second-order electron-electron Thomas peak in ionization-transfer [22]. In this two-step example, a positively charged particle first interacts with an electron in an atomic target. Then the target electron rescatters from a second target electron such that it travels out of the collision with the projectile. The first step precedes and causes the second step. Because of the electron-electron interaction in the second step, this ionization-transfer process is correlated. The time ordering of the two sequential interactions is carried by the T_{cor} term in U_I. In this particular example the effects of T_{cor} and of T_{cor} add incoherently since [21] the corresponding matrix elements differ by a factor of i. The cross section for this peak is shown in Fig. 1. This peak has been studied in detail experimentally [11,24,25]. The node in the contribution from time correlation at the center of the resonance in Fig. 1 is typical of anomalous dispersion, which is known to occur in two-step Thomas processes for electron transfer [23]. In such a case a dispersion relation connects the correlated contribution to the uncorrelated contribution and forces the correlated contribution to zero at the center of the resonance. Thus the effect of time correlation in this case is small even though the projectile-electron interaction fully precedes the electron-electron interaction.

The influence of time correlation between electrons is much stronger in our second example of double-electron excitation [10]. In Fig. 2 we present calculations of the electron emission spectrum in the region of the $(2p^2)^1D$ and $(2s2p)^1P$ resonances of helium excited by 200-eV electron impact. Unlike the previous example, there is interference between reaction pathways, namely, direct single ionization and single ionization proceeding through the double-excitation resonance. The effect of time correlation is amplified when the relative phase between competing pathways is close to $(2n+1)\pi$. In Fig. 2 one sees a strong effect from the time correlation term on both the shape and the intensity of $(2p^2)^1D$ and $(2s2p)^1P$ resonance spectrum. In the $(2p^2)^1D$ resonance time correlation changes the resonance shape from a windowtype to a nearly asymmetric resonance profile. At the same time the intensity of the $(2s2p)^1P$ resonance increases by a factor of three. The effect of time correlation varies with scattering angle θ_f emission angle θ_e, and other collision parameters. The example shown in Fig. 2 was chosen to illustrate a case where the effect of time correlation between electrons is unusually strong. Calculations for double electron excitation by fast-ion impact also show effects of various strength due to time correlation. Such resonances have been studied experimentally using high-resolution spectroscopy for both electron [26] and ion [10] impact.

Spatial correlation and time correlation between electrons

are conceptually and mathematically similar in some respects. Correlated quantities are interconnected. In both cases correlation may be mathematically defined as the difference between an exact and an uncorrelated limit where the uncorrelated limit may be written as a product of single-electron terms [17]. However, there are some differences. Spatial electron correlation is caused solely by interactions between electrons, i.e., $1/r_{ij}$ Coulomb interactions, sometimes modified by mean field potentials. Time correlation between electrons requires *both* time-ordered external time-dependent interactions *and* electron-electron interactions. Time ordering imposes causality. Thus time connections between electrons depend not only on electrons interacting with one another but also on a time dependent driving force with causality. In this sense time correlation between electrons is more complex than static spatial correlation.

In summary, we have considered time correlation between electrons in fast two-electron transitions. Time dependence enters via an external $V_I(t)$, e.g., an interaction with the field of a charged particle or laser. Time correlation among the $V_I(t_j)$'s in the time evolution of the system is imposed by the Dyson time ordering operator T. This operator may be decomposed into an uncorrelated term T_{unc} that does not interconnect the external interactions plus a time correlation term $T_{cor}=T-T_{unc}$, which does. When T_{cor} is combined with spatial correlation, electrons are connected in time as well as in space. This gives time correlation between electrons, which in turn can give time sequencing in multielectron quantum systems. Two examples were given, one with and one without interfering pathways to a final state. Our approach applies to impact of ions, atoms, electrons, and photons (including multiphoton effects) on systems of atoms. Extension past second order in V_I and also to more complex (e.g., nanoscale) systems, both appear feasible.

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