

Spatial and temporal correlation in dynamic, multi-electron quantum systems

A L Godunov¹, J H McGuire¹, P B Ivanov², V A Shipakov², H Merabet³,
R Bruch³, J Hanni³ and Kh Kh Shakov¹

¹ Department of Physics, Tulane University, New Orleans, LA 70118-5698, USA

² Troitsk Institute for Innovation and Fusion Research, Troitsk, 142092, Russia

³ Department of Physics, University of Nevada Reno, Reno, NV 89557, USA

Received 14 August 2001, in final form 27 September 2001

Published 10 December 2001

Online at stacks.iop.org/JPhysB/34/5055

Abstract

Cross sections for ionization with excitation and for double excitation in helium are evaluated in a full second Born calculation. These full second Born calculations are compared to calculations in the independent electron approximation, where spatial correlation between the electrons is removed. Comparison is also made to calculations in the independent time approximation, where time correlation between the electrons is removed. The two-electron transitions considered here are caused by interactions with incident protons and electrons with velocities ranging between 2 and 10 au. Good agreement is found between our full calculations and experiment, except for the lowest velocities, where higher Born terms are expected to be significant. Spatial electron correlation, arising from internal electron–electron interactions, and time correlation, arising from time ordering of the external interactions, can both give rise to observable effects. Our method may be used for photon impact.

1. Introduction

Space and time provide a conceptual platform for describing material properties and how they change. Space and time are remarkably similar. In the classical wave equation x and vt are mathematically interchangeable. In relativity ict becomes the fourth space-time dimension. Much of our description involves locating objects or events in space and time, as in the case of particle trajectories. In quantum mechanics localization is tempered by uncertainty in both space and time. Often more useful than describing objects and events, however, is describing connections between objects and events themselves and how they change. This interconnectedness is often called correlation. Studies of correlation in space have provided useful understanding about the geometry of multi-particle systems and how energy is distributed in these systems. In this paper we compare and contrast correlation in space with correlation in time between electrons in a quantum system perturbed by an external time-dependent interaction $V(t)$, e.g. an interaction with a charged particle or a photon.

Spatial correlation in dynamic multi-electron systems has been a focus of study for the past decade or more (Diaz *et al* 2000, Kirchner *et al* 2000, McGuire 1997, Ford and Reading 1996, Stolterfoht 1993). Recently Godunov and McGuire (2001), McGuire *et al* (2001) have proposed a method for describing time correlation between electrons. In their development time correlation is conceptually analogous to spatial correlation. Both are described as a deviation from an uncorrelated limit represented mathematically as a simple product. However unlike spatial correlation, time correlation between electrons arises from time ordering of the external $V(t)$ interactions together with spatial correlation between electrons. Specifically the Dyson time ordering operator T has been separated into a time independent uncorrelated term, T_{unc} , plus a correlated term, $T_{\text{cor}} = T - T_{\text{unc}}$. In the uncorrelated independent time approximation (ITA), T_{cor} is neglected and causality between electrons is lost. The effect of T_{cor} is non-local in time. As we demonstrate later, the time correlation term, T_{cor} , corresponds to energy-non-conserving terms in the Green function, which are not present in the time propagation of classical systems. In previous papers (Godunov and McGuire 2001, McGuire *et al* 2001) it has been shown that in many cases time correlation between electrons is not important. In these cases the computer time required decreases by at least two orders of magnitude. Hence the ITA can be a relatively efficient method for dealing with complex, dynamic multi-electron systems, as can the independent electron approximation (IEA), where spatial correlation is removed. On the other hand, examples have been found (McGuire *et al* 2001) where the effect of time correlation between electrons is large, e.g. more than a factor of two. These examples may be of interest in developing an understanding of how information is transmitted quantum mechanically in multi-electron systems.

In this paper we compare the mathematical and conceptual description of correlation between electrons in space and in time. Both spatial and temporal correlation arise from non-commutivity in time of the many-body operators for the external interaction $V(t)$. The IEA, where spatial correlation between electrons is removed, and the ITA, where temporal correlation between electrons is removed, are compared. In our results section we present second Born calculations for excitation–ionization and double excitation in helium interacting with incident protons and electrons. By comparing full second Born calculations with calculations done in the IEA and the ITA, we are able to assess the influence of both spatial and temporal correlation. Our results are compared to experiment. Some applications are considered in our discussion.

2. Theory

2.1. Time evolution

Formally, a scattering experiment may be described by a scattering matrix S , which transforms initial states of a projectile–target system into the final states of the system, $\Psi_E(+\infty) = S\Psi_E(-\infty)$. This equation is essentially static, reflecting the stationarity of any spectral measurement. To account for the system’s dynamics, the S -matrix is assumed to be a limit of an evolution operator $U(t, t_0)$, such that

$$\Psi_E(t) = U(t, t_0)\Psi_E(t_0) \quad (1)$$

for any time values t, t_0 , with $S = \lim U(t \rightarrow +\infty, t_0 \rightarrow -\infty)$. Since time evolution described by the operator $U(t, t_0)$ cannot be directly observed, we speak of a virtual evolution.

In this paper the explicit time dependence of an external interaction $V(t)$ is separated from a time independent term, H_0 . That is, the total Hamiltonian is given by,

$$H = H_0 + V(t). \quad (2)$$

The evolution operator obeys the equation (Goldberger and Watson 1964)

$$i\hbar \frac{\partial U(t, t_0)}{\partial t} = V_I(t)U(t, t_0) \quad (3)$$

in the interaction representation, with

$$V_I(t) = e^{iH_0 t} V(t) e^{-iH_0 t} = \sum_j^N e^{iH_0 t} V_j(t) e^{-iH_0 t} = \sum_j^N V_{Ij}(t), \quad (4)$$

corresponding to the interaction of a system of N electrons interacting with an external, time dependent potential. For example, $V_j(t)$ would be $Z/|\vec{R}(t) - \vec{r}_j|$ for a particle of charge Z with a trajectory $\vec{R}(t)$, or $\vec{p}_j \cdot \vec{A}(t)$ for an external photon field characterized by a vector potential $\vec{A}(t)$. The formal solution for the evolution operator may be found from iteration, namely (Goldberger and Watson 1964):

$$\begin{aligned} U(t, t_0) &= \sum_{n=0}^{\infty} (-i)^n \int_{t_0}^t dt_n \dots \int_{t_0}^{t_3} dt_2 \int_{t_0}^{t_2} dt_1 V_I(t_n) \dots V_I(t_2) V_I(t_1) \\ &\equiv \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t dt_n \dots \int_{t_0}^{t_2} dt_2 \int_{t_0}^{t_1} dt_1 T V_I(t_n) \dots V_I(t_2) V_I(t_1) \\ &\equiv T \exp\left(-i \int_{t_0}^t V_I(t') dt'\right). \end{aligned} \quad (5)$$

Here T is the Dyson time ordering operator, which orders the $V_I(t)$ with increasing time:

$$T V_I(t_n) \dots V_I(t_2) V_I(t_1) \equiv \sum_{P(1,2,\dots,n)} \theta(t_n - t_{n-1}) \dots \theta(t_2 - t_1) V_I(t_n) \dots V_I(t_2) V_I(t_1). \quad (6)$$

Here $\theta(t_i - t_j)$ is the Heaviside step function. The sum above is taken over all possible permutations P of the parameters $1, 2, \dots, n$. It is worth noting that the *only* time dependence occurs in $T V_I(t_n) \dots V_I(t_2) V_I(t_1)$. And chronological ordering of T places a causal-like constraint on the order of interactions $V_I(t_n) \dots V_I(t_2) V_I(t_1)$.

The idea of time ordering is closely related to the commutativity of operators in the interaction representation. Since $H_0 = H_0(\vec{x}, \vec{p})$, and $V = V(\vec{x})$, the two operators do not commute: $[H_0, V(t)] \neq 0$. This is a consequence of the fundamental non-commutativity of the position and momentum operators for the same particle, inherent in quantum mechanics. However, this also means that $[V_I(t), V_I(t')] \neq 0$ for $t \neq t'$, even though $[V_I(t), V_I(t)] = 0$ (Sunakawa 1977). Hence, Dyson time ordering becomes a non-trivial operation in quantum time evolution. Indeed, as is shown later, both spatial and temporal correlation in time evolution occur when various $V_{Ij}(t)$ terms in equation (4) fail to commute.

2.2. The Hamiltonian

The total Hamiltonian of the collision system with both the projectile and target is given by

$$H = \sum_j H_{0j} + \sum_{k \neq j} v_{jk}^c + \sum_j V_j(t), \quad (7)$$

where H_{0j} are the one-electron Hamiltonians of the target electrons including the usual kinematic terms, interaction with the target nucleus, and possibly the terms describing the electron's interaction with some average electron correlation potential. The interactions between the electrons of the target are described with the time-independent terms v_{jk}^c , arising from the Coulomb interaction $1/r_{jk}$, with subtraction of the mean field accounted for in H_{0j} .

Here $V_j(t)$ describes the time dependent interaction of target electrons with the projectile. We assume that the eigenstates of

$$H_0 = \sum_j H_{0j} + \sum_{k \neq j} v_{jk}^c \quad (8)$$

can be determined and form a complete set of basis states, so that, at any time t , the state of the whole system can be represented by a superposition of eigenstates of H_0 .

In this paper, we omit antisymmetrization operators in all the expressions for conceptual simplicity. However, we fully include this electron exchange in our calculations. In fast collisions exchange effects are often small.

2.2.1. Correlation in space and the IEA. Obtaining the eigenstates of the H_0 given by equation (8) is often a non-trivial task in itself for a many-electron system. Coupling these multi-electron eigenstates to interactions with a time dependent external interaction is even more difficult. Therefore approximating the many electron term v_{jk}^c by an average effective one electron term simplifies the dynamic many-body problem considerably. Without correlation the Hamiltonian for the N -electron system reduces to a sum of N uncoupled Hamiltonians. This is the key step in the IEA. The single particle Hamiltonians then commute with each other; $[H_{0j}, H_{0k}] = 0$. As a result the target's electrons can be considered independently of one another. In the fully correlated system, however, the operators $V_{Ij}(t) = e^{iH_0 t} V_j(t) e^{-iH_0 t}$ are multi-electron operators due to the v_{jk}^c terms in H_0 , unlike the $V_j(t)$, which are single electron scalar functions. As a consequence it is only in the IEA that $[H_{0j}, V_k(t)] = \delta_{jk} [H_{0k}, V_k(t)]$ so that the $V_I(t)$ reduces to a sum of single particle operators,

$$V_I(t) = \sum_j e^{iH_0 t} V_j(t) e^{-iH_0 t} = \sum_j e^{iH_{0j} t} V_j(t) e^{-iH_{0j} t} = \sum_j V_{Ij}(t). \quad (9)$$

Only when spatial electron correlation is removed do the $V_{Ij}(t')$ commute, with the $V_{Ik}(t')$. When these various $V_{Ij}(t')$ terms commute the evolution operator reduces to a product of evolution operators for individual electrons,

$$\begin{aligned} U(t, t_0) &= T \exp\left(-i \int_{t_0}^t \left(\sum_j V_{Ij}(t')\right) dt'\right) = \prod_j T \exp\left(-i \int_{t_0}^t V_{Ij}(t') dt'\right) \\ &= \prod_j U_j(t, t_0) \equiv U_{IEA}(t, t_0). \end{aligned} \quad (10)$$

Now the electrons evolve independently during the collision. This problem may now be easily solved by the method of separation of variables so that the solution is a simple product of single electron terms. The transition probability is then also a product of independent-single electron probabilities (McGuire 1997).

It should be noted here that all phase information between electrons is lost in the IEA. There is now no time ordering between electrons, although time ordering for each individual electron remains.

The validity of IEA to atomic reactions requires that the average field in which individual electrons move does not change in time (frozen orbitals). Diaz *et al* (2000) have successfully applied a method that uses mean field potentials which differ initially and finally, but remain frozen during the collision. This approach is conceptually similar to the more complete forced impulse method of Reading and Ford (1987), where correlation does not change between the external interactions, $V(t)$. Kirchner *et al* (2000) have recently introduced a formulation that allows the effective screening among the electrons to change during the collision.

2.2.2. *Correlation in time and the ITA.* The time evolution of different target electrons becomes interdependent (correlated) if the Hamiltonian H_0 cannot be split into a sum of single electron terms. The operators $V_{Ij}(t)$ and $V_{Ik}(t')$ do not commute, and the evolution operator is not separable. This means that the presence of spatial correlations results in correlated time evolution of the electron amplitudes. The interaction of the projectile with one of the electrons influences all the other electrons, and the target reacts as a whole.

One may associate with each external interaction a transition between virtual target states. In this picture, one may ask whether the result of interaction first with a state j and then a state k is different from interacting first with k , and then with j . If the two interactions cannot be commuted, the system is temporally aligned. Then the time evolution for each individual interaction time is no longer translationally invariant, and the associated energy is not conserved. Only on the macroscopic level is energy conservation restored.

In analogy with IEA, we can introduce the ITA assuming that time evolution of a target electron occurs independently on other electrons in some time averaged field (Godunov and McGuire 2001). Formally, we assume that, under certain conditions, one might rewrite equation (5) as

$$\begin{aligned} U(t, t_0) &= T \exp\left(-i \sum_j \int_{t_0}^t V_{Ij}(t') dt'\right) \approx T_{\text{av}} \exp\left(-i \sum_j \int_{t_0}^t V_{Ij}(t') dt'\right) \\ &= \prod_{j=1}^N T_{\text{av}} \exp\left(-i \int_{t_0}^t V_{Ij}(t') dt'\right) = \prod_{j=1}^N \bar{U}_j(t, t_0) = U_{ITA}(t, t_0). \end{aligned} \quad (11)$$

The operator T_{av} gives uncorrelated temporal propagation, yet includes a time averaged contribution from time ordering. Thus we take $T_{\text{unc}} \equiv T_{\text{av}}$. Temporal correlation is defined as the difference between an exact result and an uncorrelated limit, e.g. $T_{\text{cor}} = T - T_{\text{unc}}$. This also corresponds to the statistical notion of correlation as a fluctuation about some mean value (Balescu 1975)⁴. The correlated term, T_{cor} , regulates sequencing and gives time correlation or time entanglement of the interactions $V_I(t)$. In dynamic systems (McGuire *et al* 2001) time correlation is provided by enforcement of time ordering on the sequence of interactions, $V_I(t_n) \dots V_I(t_2)V_I(t_1)$, which causes the quantum system to change.

Thus, in the second order one has,

$$T V_I(t) V_I(t') \equiv \theta(t - t') V_I(t) V_I(t') + \theta(t' - t) V_I(t') V_I(t). \quad (12)$$

Godunov and McGuire (2001) have shown in this case that,

$$T_{\text{unc}} V_I(t) V_I(t') = \frac{1}{2} (V_I(t) V_I(t') + h V_I(t') V_I(t)), \quad (13)$$

$$T_{\text{cor}} V_I(t) V_I(t') = \frac{1}{2} \text{sign}(t - t') [V_I(t), V_I(t')]. \quad (14)$$

For the N -electron target $V_I(t) = \sum_{k=1}^N V_{Ik}(t)$, and the time ordering operator T can be rewritten as,

$$T = T_{\text{unc}}^{jj} + T_{\text{cor}}^{jj} + T_{\text{unc}}^{jk} + T_{\text{cor}}^{jk}. \quad (15)$$

Here T_{cor}^{jk} represents a time correlation between different electrons (cross correlation) while T_{cor}^{jj} corresponds to autocorrelation (Mandel and Wolf 1995) for a single electron, namely,

$$T_{\text{unc}}^{jj} V_I(t) V_I(t') = \frac{1}{2} \sum_{i=1}^N (V_{Ii}(t) V_{Ii}(t') + V_{Ii}(t') V_{Ii}(t)), \quad (16)$$

$$T_{\text{cor}}^{jj} V_I(t) V_I(t') = \frac{1}{2} \sum_{i=1}^N \text{sign}(t - t') [V_{Ii}(t), V_{Ii}(t')], \quad (17)$$

⁴ A simple product form is uncorrelated with this definition of correlation.

$$T_{\text{unc}}^{jk} V_I(t) V_I(t') = \frac{1}{2} \sum_{i \neq l}^N (V_{Ii}(t) V_{Il}(t') + V_{Il}(t') V_{Ii}(t)), \quad (18)$$

$$T_{\text{cor}}^{jk} V_I(t) V_I(t') = \frac{1}{2} \sum_{i \neq l}^N \text{sign}(t - t') [V_{Ii}(t), V_{Il}(t')]. \quad (19)$$

By definition (Godunov and McGuire 2001), the ITA corresponds to neglecting time correlation between different electrons, i.e. $T_{\text{cor}}^{jk} = 0$. With this definition the wave amplitudes for individual electrons still retain effects of time ordering. Of course it is possible to remove the sequencing effects in the single electron amplitudes as well by $T_{\text{cor}}^{jj} = 0$. When the uncorrelated limit is taken for a single electron, we call it the independent sequencing approximation, since all sequencing of the external interactions is uncorrelated in time. Even in this independent sequencing approximation, one may deal with a spatially correlated many-electron system.

Effects of time ordering in a one-electron system have been observed (Zhao *et al* 1997) using an external time varying magnetic field for $V(t)$ and measuring phase dependent fluctuations in resonance fluorescence spectra.

2.3. Time–energy transformations

The wave amplitude propagating in time has a conjugate representation in energy space, corresponding to the Fourier transformation from time to energy. This gives some insight into the nature of time correlation and time ordering.

2.3.1. Time correlation and energy non-conservation. Let us consider the product of two coated interactions,

$$V_I(t') V_I(t) = e^{iH_0 t'} V(t') e^{-iH_0 t'} e^{iH_0 t} V(t) e^{-iH_0 t}. \quad (20)$$

The operator $e^{-iH_0(t'-t)}$ propagates the full wave amplitude from time t to time t' undisturbed by V . Without time ordering t' may be either after or before t . Using the eigenstates of H_0 , we obtain the matrix elements of (20), namely

$$\begin{aligned} \sum_v \int dE_v e^{iEt'} \langle E | V(t') | E_v \rangle e^{-iE_v t'} e^{iE_v t} \langle E_v | V(t) | E \rangle e^{-iEt} \\ = \sum_v \int dE_v \langle E | V(t') | E_v \rangle e^{-i(E_v - E)(t' - t)} \langle E_v | V(t) | E \rangle \quad (\text{no time ordering}), \end{aligned} \quad (21)$$

where a sum and integration over all quantum numbers describing the virtual intermediate states v is assumed. Here the time propagation is associated with the factor $\exp(-i(E_v - E)(t' - t))$. When time ordering is included, the correct time ordered propagator becomes $\theta(t' - t) \exp[-i(E_v - E)(t' - t)]$.

Many atomic calculations, including those discussed in this paper, are performed in the limit of stationary scattering. Hence, it is instructive to consider the Fourier transform of the time ordered propagator itself (Goldberger and Watson 1964),

$$\int d(t' - t) \theta(t' - t) e^{-i(E_v - E)(t' - t)} = \frac{i}{E_v - E + i0} = \pi \delta(E_v - E) + i \frac{P_v}{E_v - E}. \quad (22)$$

Here P_v denotes the principal value. This transformation relates propagation of an atomic state in time to its connection with virtual states with various energies E_v . The first term on the left, which contains no time ordering, permits only $E_v = E$. The second term is non-zero only

when $E_v \neq E$, i.e. when the transient intermediate energy E_v differs from the total energy E of the system. This corresponds to quantum fluctuations of the intermediate energy about the total energy. The principal value term P_v violates conservation of energy for short times, constrained by the quantum uncertainty, $|E_v - E|\Delta t \geq \hbar$. It is this off-energy-shell, principal value term that is the Fourier transform of T_{cor} of equation (14) that produces time correlation. This term is called ‘off-energy-shell’ because the magnitude of the intermediate momentum \vec{k}_v differs from the magnitude of the total momentum \vec{k} and thus $k_v^2/2M \neq k^2/2M$, which defines a shell in k -space on which energy is conserved. We note that the $T_{\text{cor}} = T - T_{\text{unc}}$ terms are rotated by 90° in the complex time plane with respect to the often dominant T_{unc} operator. This 90° phase shift is useful in keeping track of terms that produce time correlation.

In the ITA there is no time ordering. Then operator T is replaced by a constant, C , and $\int d\tau e^{-iE_v\tau} C e^{iE\tau} = 2\pi C \delta(E_v - E)$. This term is on the energy shell. Thus without the principal value term in equation (22), there is no off-shell contribution. In this case only terms sequence-averaged over $V_I(t')V_I(t)$ contribute.

2.3.2. Sequencing and causality. In equation (22) the time ordering is carried by the $+i0$ term. This means that waves are coming into the intermediate states v of equation (20) and are later scattered. That is, $G_0 = 1/(E' - E + i0)$ is a plane wave Green function, with time propagating forward from $V_I(t)$ to $V_I(t')$. In energy space the full wavefunction, an eigenstate of the full Hamiltonian H , can be related to the eigenstates of H_0 (Goldberger and Watson 1964, Ivanov 1989), namely,

$$|E\rangle = GV|E(0)\rangle = \sum_{n=0}^{\infty} (G_0V)^n |E(0)\rangle = \sum_{n=0}^{\infty} \left(\frac{1}{E_v - E + i0} V \right)^n |E(0)\rangle. \quad (23)$$

Hence the time ordering in equation (5) corresponds to a product of plane wave Green functions, $G_0 = 1/(E_v - E + i0)$, which enforce causal-like time propagation, step by step from one V to the next. In this sense one may consider time ordering to be a generalization of causality from two points in time to many points in time.

3. Results

In this section we present calculations testing the influence of correlation in space and correlation in time between electrons. We consider two-electron transitions in helium interacting with incident protons and electrons. Our calculations are second order in the external interaction, $V(t)$.

In principle time correlation between electrons may be evaluated in either t -space by including T_{cor} in equation (15) or in E -space by the corresponding off-shell terms in equation (22). In either case calculations including time correlation between electrons are difficult and time consuming, even in second order. In the collision energy regime in which our calculations were done, it is clear that it is important to include at least one interaction of the projectile with each electron. Thus all $V_{I1}V_{I2}$ terms are included exactly, but third-order terms such as $V_{I1}^2V_{I2}$ and $V_{I1}V_{I2}^2$ are omitted. Hence time correlation between the two electrons is included. Our calculations were done in the E -space formulation, so the effects of time correlation between electrons is tested by running our computer codes with and without the off-shell term in equation (22). When the off-shell terms responsible for time correlation are omitted, we obtain the relatively simple ITA.

When spatial correlation is removed, the second-order calculation reduces to a product of two relatively simple uncoupled first-order terms, consistent with equation (10). This corresponds to the IEA, where there is no spatial correlation between electrons. We also

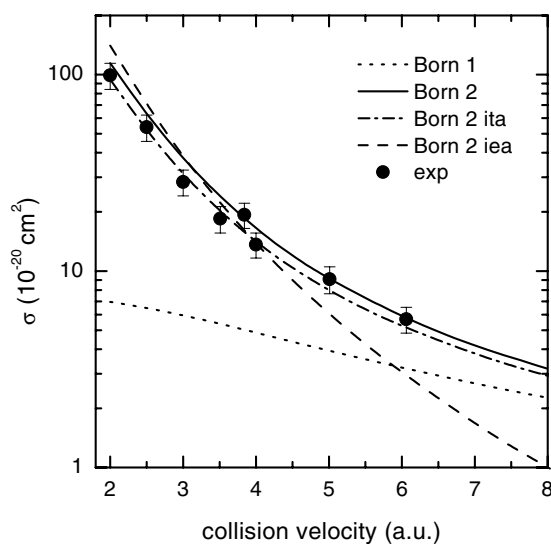


Figure 1. Cross section for the ionization–excitation of helium to $\text{He}^+(2p) \ ^1\text{P}$ state by proton impact. Present theoretical results: —, full second-order calculations; - - -, calculations in the ITA; - · - ·, IEA; · · · · ·, first Born approximation. Experimental results Merabet *et al* (2001b): ●.

consider calculations first order in $V(t)$, where one electron is excited by $V(t)$ and the second by correlation. These two approximations are discussed in detail elsewhere (McGuire 1997).

The second-order amplitude for ionization–excitation of helium was calculated by a direct summation over the discrete intermediate states of the type $(1snl) \ ^1\text{L}$ and integration over electron continuum states $(n\epsilon l) \ ^1\text{L}$ ($n = 1, 2$). Discrete states with $n \leq 3$ and $l \leq 2$ provide the main contribution to the amplitude. The inclusion of single-electron excitation configurations with n up to 5 and l up to 4 as well as low-lying autoionizing states does not change the results of calculations significantly (i.e. less than 5%). However, inclusion of the single electron continuum $(n\epsilon l) \ ^1\text{L}$ ($n = 1, 2$) in the intermediate states was important, and improved the agreement with experimental data. The continuum partial waves with l up to 7 were included in the calculations. Spatial correlation in the bound states is included within the multi-configuration Hartree–Fock (MCHF) method (Froese Fisher 1996). The continuum wavefunctions of an electron in the field of the recoil He^+ ion were calculated in the frozen-core Hartree–Fock approximation (Cowan 1981). The symmetrical orthogonalization procedure has been applied to ensure the orthogonality of the wavefunctions used. The details of our calculation for two-electron excitation of autoionizing states of helium has been previously described (Godunov *et al* 1997).

Our first examples, shown in figures 1–3, are for ionization of one electron with excitation of the second electron in helium. In figure 1 we present total cross sections for ionization–excitation by proton impact as a function of the velocity of the projectile. It is clear in this figure that the first Born calculation is not accurate at the lower projectile velocities shown, but does converge to the full second Born calculation (which includes first Born contributions) at the higher velocities as expected. At high velocities the IEA fails. The failure is due to the absence of first Born contributions, which arise due to spatial correlation between electrons. In figure 1 the effect of time correlation results in increasing the total cross section. In the regime shown here, the ratio of ITA to full second Born cross sections falls from about 1.2 to 1.1 between $v = 2$ and 9 au.

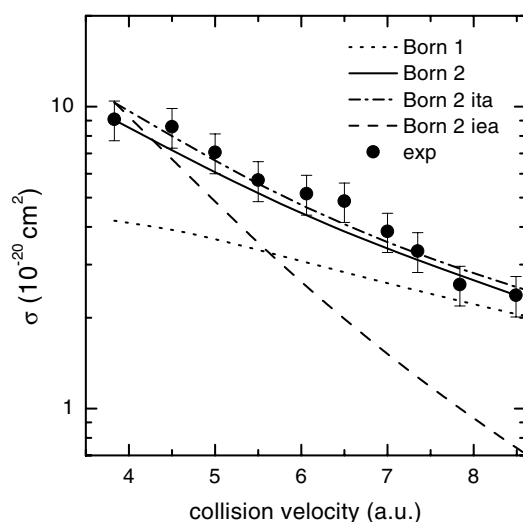


Figure 2. Cross section for the ionization–excitation of helium to $\text{He}^+(2p)^1\text{P}$ state by electron impact. Present theoretical results: —, full second-order calculations; — · —, calculations in the ITA; ---, IEA; ·····, first Born approximation. Present experimental results: ●.

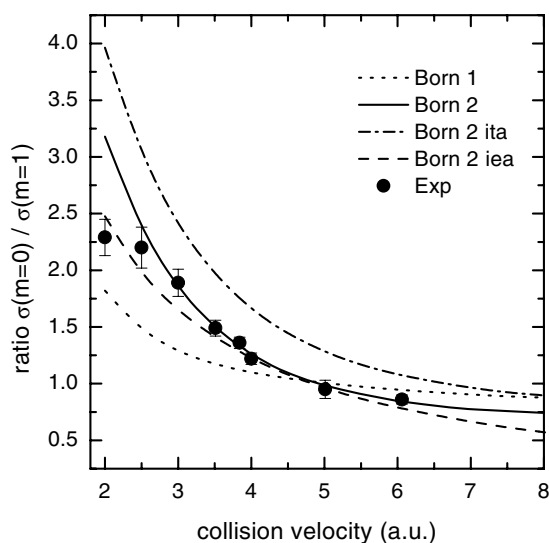


Figure 3. Ratio of cross sections of ionization–excitation into $m_\ell = 0$ or ± 1 by proton impact. Present theoretical results: —, full second-order calculations; — · —, calculations in the ITA; ---, IEA; ·····, first Born approximation. Experimental results Merabet *et al* (2001b): ●.

Figure 2 is the same as figure 1 except that the incident projectile is an electron instead of a proton. It can be seen that ionization–excitation by electron impact is similar to the case for proton impact, except that the effect of time correlation reduces the total cross section. We note that the experimental cross sections have been normalized to our full second Born calculation at high velocity (Merabet *et al* 2001b).

In excitation–ionization the electron excited into the excited level $\text{He}^+(2p)^1\text{P}$ may be excited into magnetic sublevels $m_\ell = 0$ or ± 1 . The ratio of the cross sections into $m_\ell = 0$

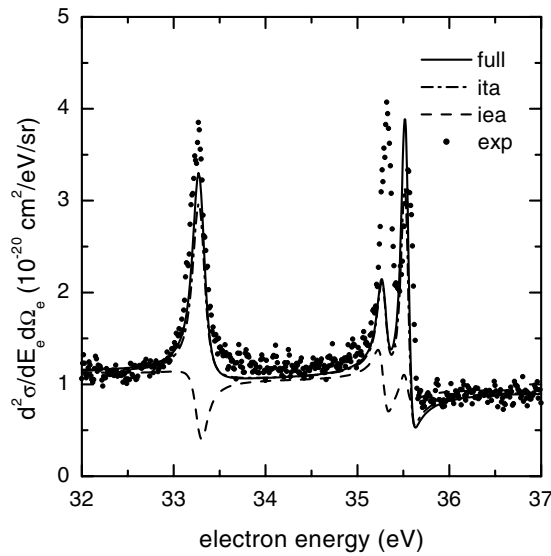


Figure 4. Effect of time-correlation on the autoionizing $2s^2(^1S)$, $2p^2(^1D)$ and $2s2p(^1P)$ resonances of helium in electron emission spectrum excited by 100 keV proton impact. The electron angle of emission is 110° and averaged over all projectile scattering angles. Present theoretical results: —, full calculations; — · —, calculations in the ITA; - - -, IEA; experimental data are from the group of Bordenave-Montesquieu (Godunov *et al* 1997).

or ± 1 has been observed (Merabet *et al* 2001b). The experiment was done at the University of Nevada-Reno using a 2 MV Van de Graaf machine to accelerate H^+ ions. An optically characterized Mo/Si multi-layer mirror (MLM) polarimeter (Merabet *et al* 1999) was used to measure the degree of linear polarization of the $He^+(2p)$ Lyman-alpha decay in the extreme ultraviolet region following proton impact on neutral helium gas (Bailey *et al* 1999, Merabet *et al* 2001a, b). The degree of linear polarization of the emitted light is related to ionization plus excitation magnetic substate cross sections for population from the helium ground state to the $He^+(2p)$ $m_\ell = 0$ and 1 magnetic sublevels, namely (Persival and Seaton 1958),

$$P(^2P^0) = \frac{3(\sigma(0) - \sigma(1))}{7\sigma(0) + 11\sigma(1)}. \quad (24)$$

The differential cross section is given by $\sigma = \sigma(0) + 2\sigma(1)$, where $\sigma(-1) = \sigma(+1)$ for our cylindrical collision symmetry.

We have calculated the ratio of cross sections into $m_\ell = 0$ or ± 1 . In figure 3 we present the ratio of these cross sections as a function of the velocity of the incident proton. The first Born calculation does not agree well with observation, even at the higher velocities shown. Calculations done in the IEA, which do not agree well with our full second Born calculations for absolute cross sections (e.g. figure 1), are surprisingly close to the data for the ratio in figure 3, except at the higher velocities where we expect the IEA to break down. The ITA lies above the data. Our full second Born calculation, including both spatial and temporal correlation is in good agreement with the observed ratio, except at the lowest velocities, where higher Born terms are expected to be significant.

The next case we consider is double electron excitation of autoionizing states in helium by proton impact. Such autoionizing resonances have been studied experimentally using high-resolution spectroscopy (Bordenave-Montesquieu *et al* 1995, Godunov *et al* 1997). In figure 4 we present calculations of the electron emission spectrum in the region of three resonances

in helium, namely $2s^2(^1S)$, $2p^2(^1D)$ and $2s2p(^1P)$ excited by impact of 100 keV protons. The difference between the time correlated and time uncorrelated results is so small that it is difficult to see for all three resonances shown in figure 3. Both the shapes and the intensities of all three resonances are well represented by the ITA. In these cases time correlation is not important. This is typical of most of the cases we have calculated, including double excitation by electrons as well as protons, excitation–ionization by protons and electrons, and a Thomas resonance in electron capture by a proton (McGuire *et al* 2001). Calculations in the IEA are very different from the experimental data both on the resonance shape and intensity.

As is well known (Fano 1961), the effect of interference between the direct and resonant ionization (via a double excitation) for excitation of the helium autoionizing resonances can be significant. In special cases the effect of time correlation can be amplified, e.g. when the relative phase between competing pathways is close to $(2n + 1)\pi$. An example with double excitation by electron impact was considered in an earlier paper (McGuire *et al* 2001). Such cases do not often occur, however. In most cases we have studied in high velocity interactions the effect of time correlation between electrons is small and the ITA is accurate.

4. Discussion

In this paper we compare the effects of correlation in space and correlation in time between electrons. In some respects these two types of correlation are similar. Generally correlated quantities are interconnected. In both cases correlation may be defined as a deviation from an uncorrelated limit, which may be written as a product of single electron terms (McGuire 1997, Godunov and McGuire 2001). There are also differences. In the time evolution operator $U(t, t_0)$, correlation in space between electrons occurs when $[V_{Ij}(t), V_{Ik}(t)] \neq 0$, while correlation in time between electrons occurs when $[V_{Ij}(t), V_{Ik}(t')] \neq 0$. Spatial correlation is caused by the internal $1/r_{ij}$ Coulomb interactions between electrons. We call the spatially uncorrelated limit the IEA. Others use similar phrases, such as the independent particle model (Ford and Reading 1996). In such models the particles are decoupled in both space and time, as discussed in section 2.2. In general time connections are caused by sequencing of external interactions. This requires both time dependent external interactions and time ordering. This general idea seems to hold classically, as well as quantum mechanically, although the specific effects we consider in this paper are quantum mechanical. Time correlation between electrons requires both a stepwise causal driving interaction and electron correlation. We call the limit in which time correlation between electrons disappears the ITA. In this limit time connections between external interactions may still be present in the single electron wave amplitudes. We call the limit in which time sequencing is removed in individual electron wave amplitudes the independent sequencing approximation. The manifestation of spatial and temporal correlation is generally different, as illustrated in our results in the previous section.

We have considered alternative approaches to the formulation of time correlation. One alternative was to formulate the problem in terms of sequencing of the actual transitions of electrons, e.g. ionization and then excitation. We found no convenient way to do this mathematically. In addition ‘transition’ implies transition to a well defined state. In multi-electron systems such states are not easy to define. In contrast, external interactions, $V(t)$, such as Coulomb interactions of electrons with charged projectiles or interactions of electrons with photons, are well defined. In any case the only possible source of time correlation is $T V_I(t_n) \dots V_I(t_2) V_I(t_1)$ since all time dependence is contained in this term, as noted below equation (5). In addition Briggs and Rost (2000) note that the time in $V(t)$ is classical and that ‘the TDSE (time dependent Schrödinger equation) is in fact a mixed quantum–classical equation’.

We wish to point out that there are two ways in which different electrons may be coupled in time. The first is direct (or spatially correlated), where the time coupling from $V(t)$ is shared among electrons via internal spatial interactions between the electrons. In this case the time propagation of the electrons is coupled. This is what we have called time correlation between electrons. The second case is indirect coupling via a strong external $V(t)$. If there is no electron–electron correlation, then the electrons may still couple independently with the external $V(t)$. For example, one or more electrons may become entangled with a strong laser field. In this case the electrons are independently coupled to the external field. This indirect independent coupling of different electrons with an external field is not what we mean by time correlation between electrons. An example may be instructive. In most cases the electrons in the initial state of a multi-electron system are correlated and may be treated coherently. However, the wave amplitudes for these electrons could be randomly excited by random external interactions. In the IEA with a strong interaction, $V(t)$, the wave amplitudes for each electron could evolve randomly, i.e. incoherently. Then, there would be no time correlation between these electrons. From our perspective they are not directly connected. In the presence of internal spatial correlation, time evolution of these electrons would become coordinated, i.e. internally coupled. Then different electrons would become correlated in time. Photons work much the same as electrons, except that there is no correlation interaction between photons in the non-relativistic limit.

Correlation between electrons may be useful in characterizing quantum transmission of information and sequencing in complex electronic systems. In applications from molecular dynamics (Levine and Bernstein 1974) to quantum computing (Bennet 1999), connections between electrons increase the number of possible reaction pathways. Electronic mixing can redistribute energy and facilitate transitions that would otherwise be forbidden. Both the external and internal interactions can be used to shape and dynamically control nanostructures (Macucci *et al* 2001). In these applications it would be of interest to be able to estimate where effects of space and time are significant. Spatial correlation will be strong when the action of the correlation interaction, $\int v dt$, is not small compared with \hbar . It is not yet clear to us where correlation in time is large in general.

In the introduction we noted the similarity of space and time. Space and time also differ. Space has no preferred direction. However, both causality and entropy give time a preferred direction. For example, in the expression for T_{cor} in equation (14), $\text{sign}(t-t') = (t-t')/|t-t'|$ may be regarded as a unit vector in the direction of increasing time. Entropy, on the other hand, is usually defined in terms of a temperature, which requires statistical equilibrium. In nuclear physics (Goodman and Jin 1996) the entropy of a many-body system (say 30 or so nucleons) may be identified after a collision when the system has reached thermal equilibrium. This equilibrium is characterized by a Maxwellian distribution of velocities of the nucleons. Particles that come out of the interaction quickly do not have such a distribution and are not in thermal equilibrium. Slower particles, which have interacted with one another, are thermalized. This can be tested experimentally. One may also calculate how long it takes for the system to reach equilibrium. For many electron systems, we propose that the equilibrium time may be the correlation time required for a correlated system to adjust. Such calculations may be compared to experiments that observe whether or not the electrons have reached thermal equilibrium. This line of analysis also suggests that time ordering (i.e. causality) may be more fundamental in defining the arrow of time than entropy.

Calculating how long it takes for correlation to take effect has been an unsolved problem for a number of years (Ford and Reading 1996). We point out that this correlation time may now be calculated, as in quantum optics (Mandel and Wolf 1995), by integrating over the normalized cross correlation function. Calculation or estimation of correlation times may be

generally useful in understanding how long transient effects last in quantum transmission of information. This could be useful, for example, in estimating the speed of quantum computing, or in determining the recovery time of nanostructures in which electrons have been excited by an external interaction, $V(t)$.

We noted before in section 2.2.2 that the various $V_I(t)$ are connected pairwise by T_{cor} . This is similar to spatial correlation where electrons couple pairwise via their mutual two body interactions. This pairwise coupling is the basis for the BBGKY hierarchy (Balescu 1975), where higher-order correlation functions can be generated from lower-order correlation functions in a systematic way. It may be possible to develop a BBGKY-like hierarchy for correlation in time.

We have used the intermediate representation to formulate time correlation between electrons since this representation is well suited to problems where the time dependence of $V(t)$ is explicit. This representation also has the advantage that knowledge of the eigenstates of H_0 can be used. In energy space it is convenient to use the Schrödinger representation, especially when the scattering is stationary (or approximately stationary). In quantum optics calculations are often done (Huang and Eberly 1993) in the intermediate representation. In collisions with charged particles the algebra is usually simpler in the Schrödinger representation. Also it is relatively easy to keep track of off-energy-shell terms in the Schrödinger representation. In principle, calculations could also be done in the Heisenberg representation. This tends to be awkward, however, since it is usually necessary to evaluate exponentials of commutators (McGuire 1987). In any case, observable effects corresponding to time correlation should be independent of the representation used.

In many cases the effect of time correlation between electrons is small (Godunov and McGuire 2001). This is fortunate in that the off-shell, time-entangled terms require more than one hundred times more computer time to evaluate than the simpler on-shell terms, even in our relatively simple second-order calculations. Many-body calculations are difficult because the number of parameters required is exponential in the number of bodies in the system (Kohn 1999). It has been estimated that at present rates it takes about seven years for computer capacity to expand enough to add one more particle to a computer calculation (Godunov and McGuire 2001). In calculations of dynamically correlated systems of particles, an independent time (or on-shell or wide band) approximation is widely used (Fang and Bartschat 2001, Madison 2000, Lucey *et al* 1999, Marchalant *et al* 1998, Nagy *et al* 1995, Straton 1995) to save computational time and effort. It has also been noted that off-shell effects disappear in the closure approximation if the average energy of propagation used for closure is taken to be one-half of the transition energy (Straton 1995). When this relatively easy ITA is valid, calculations of relatively complex systems are feasible. On the other hand, there are cases when temporal and spatial correlation is significant. Understanding these cases may be useful in developing new methods for quantum transmission of information.

5. Summary

In summary we have considered the effects of both spatial and temporal correlation between electrons in two-electron transitions in atomic targets caused by the impact of charged particles and photons. Our formulation is complete through second order in the external interaction $V(t)$ and all orders in the internal correlation interaction between the electrons. Spatial correlation arises from the internal interactions between the electrons. In the IEA, where correlation in space is removed, the electrons evolve independent in both space and time. Time correlation between electrons requires both time ordering of the external interactions, corresponding to causal propagation in time, and internal electron correlation. We have evaluated the effects

of spatial and temporal correlation between electrons in excitation–ionization and in double excitation resulting from collisions of helium with moderately fast protons and electrons. In the velocity range of 3–10 au our full second Born calculations are in good agreement with observation. In excitation–ionization with excitation into $m_\ell = 0$ or ± 1 magnetic sublevels in the (2p) state, the effect of both spatial and temporal correlation is larger than the errors in the observations presented here. Thus we have been able to present evidence for the presence of both correlation in space and correlation in time between electrons in some atomic reactions.

Acknowledgments

We thank B Shore and A Goodman for stimulating discussions. This work was supported by the Division of Chemical Sciences, Office of Science, US Department of Energy and, in part, by the Nevada Business and Science Foundation and ACSPECT Corporation, Reno, Nevada.

References

- Balescu R 1975 *Equilibrium and Non-Equilibrium Statistical Mechanics* (New York: Wiley) ch 21, section 1
- Bailey M, Merabet H and Bruch R 1999 *Appl. Opt.* **38** 4125
- Bennett C H 1999 *Quantum Information Science* (Report of the NSF Workshop in Arlington, VA, Oct. 28–29)
- Bogoliubov N N and Shirkov D V 1980 *Introduction to the Theory of Quantized Fields* (New York: Wiley)
- Bordenave-Montesquieu A, Moretto-Capelle P, Gleizes A, Andriamonje S, Martín F and Salin A 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 653
- Briggs J and Rost J M 2000 *Eur. Phys. J. D* **10** 311
- Also see McGuire J H and Weaver O L 1986 *Phys. Rev. A* **34** 2473 as well as the end of chapter 3 of McGuire 1997
- Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley: University of California Press)
- Diaz C, Salin A and Martin F 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** L403
- Fang Y and Bartschat K 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** L19
- Fano U 1961 *Phys. Rev.* **124** 1866
- Ford A L and Reading J F 1996 *Atomic, Molecular and Optical Physics Reference Book* ed G W F Drake (New York: AIP) ch 48
- Froese Fischer C 1996 *Atomic, Molecular and Optical Physics Reference Book* ed G W F Drake (New York: AIP) ch 21
- Godunov A L and McGuire J H 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** L223
- Godunov A L, Schipakov V A, Moretto-Capelle P, Bordenave-Montesquieu D, Benhenni M and Bordenave-Montesquieu A 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5451
- Goldberger M L and Watson K M 1964 *Collision Theory* (New York: Wiley)
- Goodman A L and Jin T 1996 *Phys. Rev. C* **54** 1165
- Huang H and Eberly J H 1993 *J. Mod. Spectrosc.* **40** 915
- Ivanov P B 1989 *PhD Thesis* Institute of Spectroscopy, Academy of Science, USSR
- Kirchner T, Horbatsch M, Ludde H J and Dreizler R M 2000 *Phys. Rev. A* **62** 042704
- Kohn W 1999 *Rev. Mod. Phys.* **71** 1253
- Levine R D and Bernstein R B 1974 *Molecular Reaction Dynamics* (New York: Oxford University Press)
- Lucey S P, Rasch J and Whelan C W 1999 *Proc. R. Soc. A* **455** 349
- Macucci M, Iannaccone G, Greer J, Martorell J, Sprung D W L, Schenk A, Yakimenko I I, Berggren K-F, Stokbro K and Gippus N 2001 *Nanotechnology* **12** 136
- Madison D H 2000 Private communication
- Mandel L and Wolf E 1995 *Optical Coherence and Quantum Optics* (Cambridge: Cambridge University Press) sections 4.3.1, 4.6.3 and 8.2
- Marchalant P J, Whelan C T and Walters H R J 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 1141
- Martin F and Salin A 1997 *Phys. Rev.* **55** 2004
- McGuire J H 1987 *Phys. Rev. A* **36** 1114
- McGuire J H 1997 *Electron Correlation Dynamics in Atomic Collisions* (Cambridge: Cambridge University Press)
- McGuire J H, Godunov A L, Tolmanov S G, Shakov Kh Kh, Schmidt-Böcking H, Dörner R and Dreizler R M 2001 *Phys. Rev. A* **65** 052706
- Merabet H, Bailey M, Bruch R, Fursa D V, Bray I, McConkey J W and Hammond P 1999 *Phys. Rev. A* **60** 1187

- Merabet H, Bruch R, Bailey M, Hanni J, Godunov A, McGuire J H and Schipakov V S 2001a *Proc. 22nd Int. Conf. on Photonic, Electronic and Atomic Collisions (Santa Fe, USA)* p 147
- Merabet H, Bruch R, Godunov A, McGuire J H and Hanni J 2001b *Phys. Rev. Lett.* submitted
- Messiah A 1970 *Quantum Mechanics* (New York: Wiley)
- Nagy L, Wang J, Straton J C and McGuire J H 1995 *Phys. Rev. A* **52** R902
- Persival and Seaton 1958 *Phil. Trans. R. Soc. A* **251** 113
- Reading J F and Ford A L 1987 *J. Phys. B: At. Mol. Phys.* **20** 3747
- Reading J F and Ford A L 1987 *Phys. Rev. Lett.* **58** 543
- Stolterfoht N 1993 *Phys. Rev. A* **48** 2980
- Stratton J C 1995 Private communication
- Sunakawa S 1977 *Quantum Scattering Theory* (Tokyo, Japan: Iwanami Shoten) ch 4
- Zhao H Z, Lu Z H and Thomas J E 1997 *Phys. Rev. Lett.* **79** 613