

LETTER TO THE EDITOR

Independent time approximation for dynamically interacting multi-electron systems

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Abstract

We propose an independent time approximation (ITA), defined by simplifying the chronological operator, namely, $T \simeq T_{\text{unc}}$, where T_{unc} is the uncorrelated limit of the chronological operator T . The concept of the time correlation is analogous to spatial electron correlation. In both cases ‘correlation’ is the difference between an exact result and an uncorrelated limit. In the uncorrelated ITA the time correlation operator $T_{\text{cor}} = T - T_{\text{unc}}$ is neglected and causality between electrons is lost. In second-order calculations of a two-electron transition the ITA reduces computer time by over two orders of magnitude. Greater savings are expected when higher orders or more electrons are included.

There is a need to bridge from understanding of simple static atomic systems to more complex dynamic systems, especially in those that may be of practical value. The N -body problem is, however, difficult. Kohn (1999) estimated that the minimum number of parameters needed in a computer calculation to characterize the N -body problem varies as e^{3N} for large N . Fortunately computer capacity is doubling approximately every 1.5 years. Combining these two exponential rates one finds that it takes about 7 years to develop computer capacity to increase N by one. Thus to extend our understanding, for example, from a strong field interacting with helium to a strong field interacting with carbon, which has four more interacting electrons, requires about 28 years. To complete the periodic table at this level would take about 700 years, and DNA would require a thousand times the age of the universe. Thus it makes sense to consider faster, but approximate methods for dealing with complex, dynamic N -body systems.

The notion of correlation has been a powerful tool in bridging from simple to complex N -body systems and has been applied in a productive variety of ways (Fetter and Walecka 1971, Balescu 1975, Blaizot and Ripka 1986, Dreizler and Gross 1990, Froese Fischer 1996, Stanley *et al* 1996). Most correlation work in atomic systems has been based on spatial electron correlation. Most of this work has dealt with evaluation of wavefunctions and energies in a wide variety of static materials. In recent years methods for dealing with dynamics of electron correlation in atomic collisions have been developed (Gross *et al* 1996, Martin and Salin 1997, Marchalant *et al* 1997a, b, 1999a, b, 2000, Bronk *et al* 1998, Bent *et al* 1998, Pfeiffer *et al* 1999, Kheifets *et al* 1999, Kheifets and Bray 2000, Kirchner *et al* 2000c, Whelan 2000).

In particular the independent electron approximation (IEA), in its various guises (McGuire 1997, Kirchner *et al* 1997, 1998, 2000a, b, c), has provided a simple way to treat dynamic multi-electron systems. It is now possible to handle systems of up to 16 electrons with such methods (Luedde and Dreizler 1985, 1999, Kuerpick *et al* 1995). However, the notion of time correlation has not yet been developed. Recently we introduced a method to treat time correlation and entanglement between electrons (McGuire *et al* 2001, 1999). In this letter we propose an independent time approximation (ITA) in which time correlations between different electrons are neglected. We illustrate our method with calculations second order in an external $V(t)$, but with electron correlation included to all orders. In our second-order calculations the saving in computer time is more than two orders of magnitude. Based on Kohn's estimate, one may expect the saving to increase exponentially as the number of electrons in the system increases.

In this letter we focus on the time-dependent evolution in multi-electron systems. The evolution operator is conveniently expressed in the interaction representation as a time-ordered exponential (Goldberger and Watson 1964, Fetter and Walecka 1971, Bogoliubov and Shirkov 1983), namely,

$$\begin{aligned} U_I(t, t_i) &= T \exp \left\{ -i \int_{t_i}^t V_I(t') dt' \right\} \\ &= \sum_{k=0}^{\infty} \frac{(-i)^k}{k!} \int_{t_i}^t \cdots \int_{t_i}^t T V_I(t_1) \cdots V_I(t_k) dt_1 \cdots dt_k. \end{aligned} \quad (1)$$

The time dependence is imposed (Briggs and Rost 2000, McGuire and Weaver 1986) by an external interaction, $V_I(t)$. $V_I(t) = \sum_j^N V_{Ij}(t)$ is summed over electrons and $V_{Ij}(t) = e^{-iH_0 t} V_j(t) e^{iH_0 t}$ is a many electron operator if the unperturbed Hamiltonian, H_0 , contains correlation (McGuire 1997). Here T is the Dyson time ordering operator defined by,

$$\begin{aligned} T V_I(t_1) V_I(t_2) \cdots V_I(t_k) \\ \equiv \sum_{P(1,2,\dots,k)} \theta(t_1 - t_2) \theta(t_2 - t_3) \cdots \theta(t_{k-1} - t_k) V_I(t_1) V_I(t_2) \cdots V_I(t_k). \end{aligned} \quad (2)$$

$\theta(t - t')$ is the Heaviside step function. The sum above is taken over all possible permutations, P , of the parameters $1, 2, \dots, k$ imposing ordering of the $V_I(t_j)$ interactions in time to enforce causality in the time evolution of the system (Messiah 1961, Goldberger and Watson 1964).

Time correlation of physical observables is provided by both the many-electron $V_{Ij}(t)$ operators and the time-ordering operator, T , which imposes time sequencing on the overall $V_I(t)$. We require that the definition of correlation in time be independent of the mathematical form of $V_I(t)$. Hence, 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 equation (2). Thus, 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 *single product* of $V_I(t_j)$ and is uncorrelated in time. This defines the uncorrelated time limit. In this limit there is no time correlation in U_I . Accordingly, we now separate the T operator into two terms,

$$T = T_{\text{unc}} + (T - T_{\text{unc}}) \equiv T_{\text{unc}} + T_{\text{cor}} \quad (3)$$

where T_{unc} is the uncorrelated part of T , and $T_{\text{cor}} \equiv T - T_{\text{unc}}$, acting on $V_I(t_1) \cdots V_I(t_k)$, is the time correlation operator (McGuire *et al* 2001).

In first order in V_I there is no time correlation. In second order one has,

$$T V_I(t) V_I(t') = \theta(t - t') V_I(t) V_I(t') + \theta(t' - t) V_I(t') V_I(t) \quad (4)$$

where

$$T_{\text{unc}} V_I(t) V_I(t') = \frac{1}{2} V_I(t) V_I(t') + V_I(t') V_I(t), \quad (5)$$

whence it is easily shown that,

$$T_{\text{cor}} V_I(t) V_I(t') = \frac{1}{2} \text{sign}(t - t') [V_I(t), V_I(t')]. \quad (6)$$

Calculations using $T \simeq T_{\text{unc}}$ correspond to an ITA where the $V_I(t_j)$ interactions are not correlated in time. In this uncorrelated limit a second order two-step process is reduced to two independent one-step processes (Satchler 1983, Bibdak and Koshel 1972). Since entanglement is conceptually and mathematically similar to electron correlation (Grobe *et al* 1994, McGuire 1997), our time correlation operator, T_{cor} , may also be regarded as a time entanglement operator. From equation (6) it is clear that this operator is non-local in time. Observable effects due to T_{cor} occur in both single- (Zhao *et al* 1997, Mandel and Wolf 1995) and multiple-electron transitions (McGuire 1997, Nagy *et al* 1997, Stolterfoht 1993). However, we are primarily interested in the importance of time correlation between different electrons.

In multiple electron transitions correlation in time between electrons generally requires spatial electron–electron correlation in addition to time ordering (Nagy *et al* 1996, McGuire 1997, McGuire *et al* 2001). Physically this is obvious. In the uncorrelated IEA without exchange, the probability is represented as a product of single electron probabilities, namely,

$$\begin{aligned} P(t) &= |a_{fi}(t)|^2 = \Pi_j |\langle f_j | U_{Ij}(t, t_i) | i_j \rangle|^2 \\ &= \Pi_j |a_j(t)|^2 = \Pi_j P_j(t) \text{ (IEA)}. \end{aligned} \quad (7)$$

Here a_{fi} is the probability amplitude for the multi-electron system from an initial state $|i\rangle$ to a final state $|f\rangle$, and $a_j(t)$ is the probability amplitude for a single electron. In this spatially uncorrelated limit there is no mechanism for sequencing or time correlation between transitions of different electrons. Without spatial electron correlation phase information between electron wave amplitudes is lost. Only when spatial electron correlation is included can T_{cor} cause time correlation between different electron transition amplitudes.

The methods we use are straightforward in second-order calculations. After a Fourier transform of the evolution operator over time one obtains the standard second-order T -matrix, which includes the unperturbed Green function (McGuire *et al* 1999). This Green function in turn contains the Fourier images of T_{unc} and T_{cor} . The Fourier image of T_{unc} is an even function of energy, and is ‘on-shell’ as it is energy conserving. The second term, the Fourier image of T_{cor} , is ‘off-shell’. It is an odd function of energy. The contributions of T_{unc} and T_{cor} to the scattering amplitude are a factor of i out of phase, which enables one to trace the effects of these operators. Thus our identification of sequencing terms is not restricted to the intermediate representation. Operators for sequencing and correlation are the same in second order. In higher order calculations correlation in time corresponds to the difference between T and T_{unc} , while sequencing is associated with off-shell terms.

In the example shown in figure 1 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 . Calculations of cross sections are done with and without the T_{cor} time correlation terms. Our example shown is double-electron excitation of autoionizing states in helium by proton impact. Such autoionizing resonances have been studied experimentally using high-resolution spectroscopy for both electron (Lower and Weigold 1990) and ion (Bordenave-Montesquieu *et al* 1995, Godunov *et al* 1997) impact. In figure 1 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 the impact of 100 keV protons. The difference between the correlated and uncorrelated results is small for all three

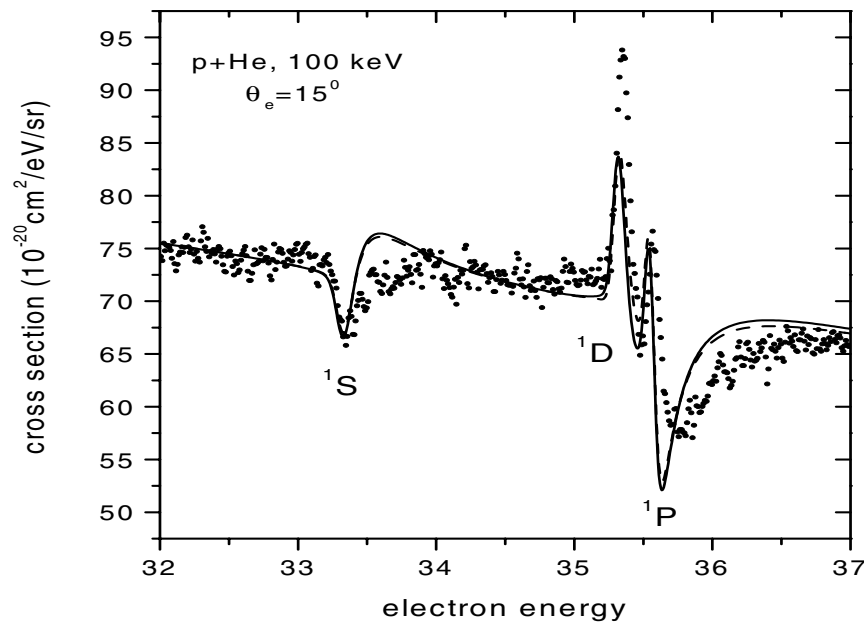


Figure 1. The effect of time-ordering on the autoionizing $2s^2(^1S)$, $2p^2(^1D)$ and $2s2p(^1P)$ resonances of helium in electron emission spectrum excited by 100 keV proton impact. The electron emission angle is 15° and averaged over all projectile scattering angles. The full curve represents our full second-order calculation including the T_{cor} term of equation (6); the broken curve gives the ITA with $T_{\text{cor}} = 0$. The calculation performed in the ITA is more than two orders of magnitude faster than the full second-order calculation, which includes time correlation between the two electrons. The data are from the group of Bordenave-Montesquieu (Godunov *et al* 1997).

resonances. 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). We expect that similar calculations with strong time-dependent electric and magnetic fields will also be largely unaffected by time correlation, except in special cases described below.

As is known from double ionization (Nagy *et al* 1997, McGuire 1997), differences between the correlated and uncorrelated calculations are due to coherence between the T_{cor} contribution and the first Born amplitude. This may be regarded as interference between reaction pathways. In figure 1 ionization may occur directly via the Coulomb interaction $V(t)$ with the proton or via a double excitation resonance. In special cases the effect of time correlation can be amplified, e.g. when the relative phase between competing pathways is close to $(2n + 1)\pi$. Such a case was considered in an earlier paper (McGuire *et al* 2000) to demonstrate that under certain conditions there can be strong effects due to time correlation. Such cases do not often occur, however. In most cases we have studied in high-velocity interactions the effect of time correlation is small and the ITA is accurate.

In the case shown in figure 1, our calculations ran more than 100 times faster when the ITA was applied. Such saving in computer time is typical in all of the second Born calculations we have done. We expect the savings to be larger when more electrons are considered and when more channels are included. Our experience is roughly consistent with Kohn's estimate

Table 1. Comparison of correlation in space and time.

	Spatial correlation	Temporal correlation
Cause	$v_{ij} = 1/r_{ij}$ internal Coulomb interactions	T and $V_I(t)$ time ordering of external interactions
Origin	$H_0 = \sum_j H_{0j} + v_{ij}$	$\dot{U}_I = -iV_I(t)U_I$
Uncorrelated limit	IEA	ITA
Product form	$\psi(x_1, x_2) = \prod_j \psi_j(x_j)$	$\psi(t_1, t_2) = \prod_j \psi_j(t_j)$
No fluctuations	$v_{\text{cor}} = v_{ij} - v_{\text{av}} = 0$	$T_{\text{cor}} = T - T_{\text{av}} = 0$
Average value	$v_{\text{av}} = v_{\text{mean field}}$	$T_{\text{av}} = T_{\text{unc}}$

of e^{3N} , although it takes a while to gain computational efficiency in adding another particle to the N -body system. Fortunately, increasing the number of coupled channels for each particle is easier in our experience.

There are similarities between the temporal ITA and the spatial IEA, as seen in table 1. Both time and space correlation can be defined as a deviation from an uncorrelated limit. The uncorrelated limit may be defined by a product form. Electron identity, which has been ignored for conceptual simplicity, may be restored by antisymmetrizing the uncorrelated single-electron wavefunctions. The uncorrelated limit may also be described by an average of the appropriate correlation operator, given in table 1. Then correlation may be defined in terms of the fluctuation from the average term, as performed in statistical mechanics (Balescu 1975). In both the spatial and temporal cases the average term can form the basis for useful approximate calculations.

There are also notable differences between temporal and spatial correlation, detailed in table 1. While correlation in space arises in the asymptotic target Hamiltonian, H_0 , and affects both the asymptotic wavefunction, $|i\rangle$, and the evolution operator, U_I , correlation in time occurs only in the time evolution operator $U_I(t, t_0)$. Correlation in space comes from $1/r_{ij}$ inter-electron interactions within the target. In the IEA phase coherence and time correlation between electrons are both lost, as is evident from equation (7). Time correlation arises from the time ordering of the external $V_I(t)$. When $T_{\text{cor}} = 0$, then T is replaced by a constant average value of T , namely T_{unc} . In this uncorrelated limit all time sequences of the $V_I(t)$ are equally weighted, leading to a single time averaging over each $V_I(t)$ in equation (1). Removing some or all of the sequencing terms is straightforward in practice since the T_{cor} terms are easily identified (McGuire *et al* 1999). The spatial correlation interaction, $1/r_{ij}$, is symmetric in \vec{r}_i and \vec{r}_j , while the time correlation operator, T_{cor} , is antisymmetric in t_i and t_j .

Time ordering itself is included in the time-dependent Schrödinger equation, e.g. $\dot{U}_I = -iV_I(t)U_I$ imposes causality (Goldberger and Watson 1964). This differs from classical mechanics, where cause and effect is normally imposed after the solution of the classical wave equation (Jackson 1975).

In summary, we have proposed an ITA for dynamically interacting multi-electron systems. If the electrons are initially uncorrelated in time (described by different times), then in the ITA these electrons evolve independently in time. In the stronger IEA all electronic wave amplitudes remain uncorrelated in space and time for all times. The ITA significantly reduces the computer time required to perform a calculation. In the case considered here of double electron excitation described in second order in the perturbing interaction, the saving is more than two orders of magnitude in computer time. Our approach applies to impact of ions, electrons and photons (including multi-photon effects) on atomic materials. Extension beyond second order and also to more complex (e.g. nanoscale) systems both appear feasible.

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