# Accurate evaluation of multiple-excitation cross sections from one-electron amplitudes

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We show that a theory that neglects dynamic correlation in ion-atom collisions (the *frozen correlation approximation*, FCA) is able to provide accurate multiple-excitation cross sections from one-electron amplitudes. Important requirements for the success of the FCA are (i) inclusion of correlation in both the initial and final states, and (ii) inclusion of screening effects during the collision. We find an excellent agreement between fully correlated and FCA results for double excitation of He by bare ions, thus showing that the FCA can be efficiently used in the evaluation of multiple-excitation cross sections when fully correlated calculations are not accessible. [S1050-2947(97)02103-3]

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## I. INTRODUCTION

The study of multiple-excitation processes in ion-atom collisions raises the question of how the electron-electron interaction $V_{ee}$ can be treated in dynamical problems. Fully correlated theories are very involved and have only been applied to two-electron problems. For example, the forced impulse method [1] and the discretized close-coupling method [2,3] have been used to study double ionization and double excitation of He by ion impact, and have provided cross sections in good agreement with the experimental ones. However, it is clear that, for more complex systems, electron correlation has to be approximated in some way to make calculations accessible. The simplest solution is given by the independent electron model (IEM) in which electron correlation is neglected in the description of the initial and final states as well as in the dynamics (according to the common Hartree-Fock language and at variance with our previous works we will call in this paper electron correlation the nonseparable part of $V_{ee}$). The simple picture provided by the IEM is inadequate when electron correlation cannot be neglected in the initial and/or final states, as for double excitation of the target [2]. Therefore, it is of practical and conceptual interest to go beyond the IEM and include the relevant part of the electron-electron interaction while preserving the simplification that arises when electron correlation plays a negligible role in the dynamics.

A first attempt to understand the role of electron correlation during the collision was made by McGuire [4], who called *scattering correlation* the nonseparable two-electron contributions to the evolution operator. In contrast, he called *static correlation* that part related exclusively to the initial and final states. Stolterfoht [5] suggested that dynamic correlation may be negligible when the collision time $t_{\mathrm{coll}}$ is much smaller than the correlation time $t_{\mathrm{corr}}$. All these concepts being based on physical intuition, it has not been until very recently that dynamic correlation has been quantitatively evaluated. In a recent work [6,7] we have introduced the frozen correlation approximation (FCA), which freezes electron correlation during the collision, thus allowing one to state the role of dynamical correlation by comparing with fully correlated results. In that work we have shown that, irrespective of how important correlation is to describe the initial and final states, $V_{ee}$ does not play a significant role in the dynamics when $t_{\mathrm{coll}} \ll t_{\mathrm{corr}}$. This is very attractive since, in the FCA, many-electron transition amplitudes are obtained from one-electron amplitudes and therefore multiple-excitation cross sections can be obtained when it is hard to use fully correlated theories.

Our previous calculations using the FCA were aimed at illustrating the role of $V_{ee}$ in the dynamics and therefore were performed by freezing the whole electron-electron interaction $V_{ee}$. However, we have indicated in [7] that a more general (but equally simple) FCA can be set up by freezing part of $V_{ee}$ only. For instance, one can account in the uncorrelated propagator for screening effects in the dynamics that would be neglected if the whole $V_{ee}$ was frozen. By doing so, the FCA may provide a much better description of the process while keeping its simplicity: the expression of many-electron amplitudes in terms of one-electron amplitudes. It contains the usual IEM as a particular case but goes beyond the latter because the former includes electron correlation in the initial and final states. Thus it can be applied to the study of multiple excitation and ionization where electron correlation cannot be neglected in the initial and/or final state. In the present paper we show how this generalization of the FCA is in fact a very efficient and simple way to obtain accurate cross sections for multiple-electron processes. In order to show its accuracy one has to compare with fully correlated calculations, which are only available for two-electron systems. Our generalization of the FCA is applied to double excitation of He for which fully correlated results are available [2,3]. In Sec. II we briefly summarize the FCA, paying particular attention to the extension proposed in [7]. In Sec.

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III we compare our results with those obtained from fully correlated theories.

Atomic units are used throughout unless otherwise specified.

## II. THEORY

We work in the framework of the impact parameter method. We call $H_0$ the Hamiltonian of the isolated target and $V(t)$ the interaction between the projectile and target electrons. We call $\tilde{\psi}_n$ the eigenfunction of $H_0$ with eigenenergy $E_n$. For the sake of simplicity, we work in the intermediate picture and any quantity in this picture will be labeled with a tilde. We have to solve the time-dependent Schrödinger equation

$$\left( e^{iH_0 t} V(t) e^{-iH_0 t} - i \frac{d}{dt} \right) \tilde{\Psi}_i(t) = 0 \tag{1}$$

with the initial condition

$$\lim_{t \to -\infty} \tilde{\Psi}_i(t) = \tilde{\psi}_i . \tag{2}$$

The exact solution of Eq. (1) can be written as

$$\tilde{\Psi}_i(t) = \tilde{U}(t,t') \tilde{\Psi}_i(t') = \lim_{t' \to -\infty} \tilde{U}(t,t') \tilde{\psi}_i , \tag{3}$$

where the evolution operator $\tilde{U}(t,t')$ satisfies

$$i \frac{d}{dt} \tilde{U}(t,t') = e^{iH_0 t} V(t) e^{-iH_0 t} \tilde{U}(t,t') . \tag{4}$$

Now, we write the electron-electron interaction potential $V_{ee}$ as the sum of two terms:

$$V_{ee} = W_1 + W, \tag{5}$$

where $W_1$ is a sum of one-electron operators

$$W_1 = \sum_i v_i \tag{6}$$

and $W$ is a nonseparable operator. We can define $W_1$ as an averaged screening potential whereas the complement $W$ corresponds to what we call correlation. In this work we use for $v_i$ an analytical fit of the Hartree-Fock potential corresponding to the ground state of the target (see Sec. III). We define a new target Hamiltonian $h_0$ in which $W$ (the nonseparable part of the electron-electron interaction) is excluded:

$$h_0 = H_0 - W. \tag{7}$$

The corresponding evolution operator $\tilde{u}(t,t')$ satisfies

$$i \frac{d}{dt} \tilde{u}(t,t') = e^{ih_0 t} V(t) e^{-ih_0 t} \tilde{u}(t,t') . \tag{8}$$

The frozen correlation approximation consists in replacing the exact evolution operator $\tilde{U}$ defined in Eq. (4) by $\tilde{u}$:

$$\tilde{U}(t,t') \to \tilde{u}(t,t') . \tag{9}$$

We have shown that this approximation is valid when $t_{\mathrm{coll}}/t_{\mathrm{corr}} \ll 1$ [7] so that it will be a reasonable approximation when the typical time associated with the action of the projectile target interaction is much shorter than the time required for $W$ to produce an appreciable change in the evolution of the system during the collision. The approximate transition amplitude to a given final state $\tilde{\psi}_f$ is

$$t_{if} = \lim_{t_f \to \infty} \lim_{t_i \to -\infty} \langle \tilde{\psi}_f | \tilde{u}(t_f, t_i) | \tilde{\psi}_i \rangle . \tag{10}$$

Therefore electron correlation is fully included in the description of the initial and final states, but it does not appear in the evolution of the system. This is equivalent to freezing correlation during the collision as discussed in [7].

The operator $\tilde{u}(t_f, t_i)$ is the *exact* evolution operator for a problem in which $W$ is zero and thus verifies *all* properties of an exact evolution operator. In particular, the transition amplitude (10) is invariant under a change in time origin. The latter property is demonstrated in the Appendix.

In the FCA, many-electron transition amplitudes can be written in terms of one-electron transition amplitudes. Indeed, the eigenstates of $h_0$ are products of one-electron orbitals $\varphi_j$, and the many-electron basis functions $\tilde{\psi}_n$ can be expressed in terms of these as

$$\tilde{\psi}_n = \sum_{jk \cdots s} \alpha^n_{jk \cdots s} \varphi_j \varphi_k \cdots \varphi_s . \tag{11}$$

Under the action of $\tilde{u}(t,t_i)$ the previous form is conserved during the collision because $\tilde{u}$ can be written as a product of one-electron operators. Therefore, the one-electron orbitals evolve in time (because of the interaction with the projectile) whereas the coefficients $\alpha^n_{jk \cdots s}$ are time independent (frozen correlation). From Eq. (10) it follows that the transition amplitude between initial and final correlated states can be written in terms of one-electron amplitudes $a_{jl}$:

$$t_{if} = \sum_{jk \cdots s, lm \cdots t} \alpha^i_{jk \cdots s} \alpha^f_{lm \cdots t} a_{jl} a_{km} \cdots a_{st} . \tag{12}$$

Then, in practice, one only needs to perform one-electron calculations to evaluate the many-electron amplitude.

The first order of perturbation theory for $\tilde{u}$ yields the Born-FCA approximation, which is obviously not equivalent to the exact Born approximation obtained from the first order of pertubation theory to $\tilde{U}$. This is not a shortcoming of the FCA theory. As we have clearly stated in our derivation [7], the FCA makes no assumption on the *strength* of $W$ but only on its characteristic time $t_{\mathrm{corr}}$ ($t_{\mathrm{coll}}/t_{\mathrm{corr}} \ll 1$). The Born approximation is only valid when $W$ is weak. Therefore, the Born FCA is valid if *both* $W$ is weak and $t_{\mathrm{coll}}/t_{\mathrm{corr}} \ll 1$. In other terms, the Born-FCA approximation is the form taken by the Born approximation when $t_{\mathrm{coll}}/t_{\mathrm{corr}} \ll 1$.

Reading *et al.* [8] have correctly remarked that when $W_1 = 0$ (i.e., $W = V_{ee}$) the Born-FCA approximation may give a transition probability decreasing at large impact parameters $\rho$ like $1/\rho^2$ (thus yielding a divergent total cross section) in strong disagreement with the exact result (including correlation in the dynamics). What this statement means is that, when $W = V_{ee}$, the condition $t_{\mathrm{coll}}/t_{\mathrm{corr}} \ll 1$ may break

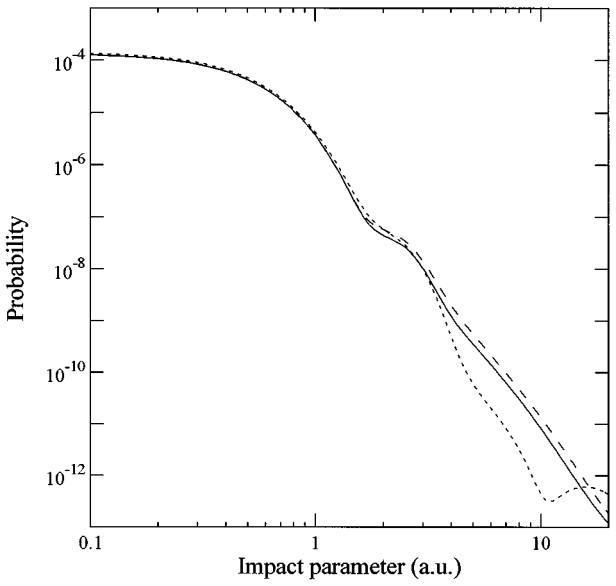


FIG. 1. Excitation probability of the $^1S^e(2s^2)$ doubly excited state of He by 2-MeV protons as a function of impact parameter. Full curve, calculations including dynamic correlation; dashed curve, frozen correlation approximation with $W=V_{ee}-W_1$; dotted curve, frozen correlation approximation with $W=V_{ee}$.

down at large impact parameters. It brings the interesting conclusion that $V_{ee}$ may not be neglected entirely in the dynamics at large impact parameters (and certainly not that the FCA suffers from any basic inconsistency). It does not invalidate either the FCA as a reference calculation when $W=V_{ee}$ since transitions in multiple processes take place usually over a limited range of impact parameters. For example, we give in Fig. 1 the excitation probability of the $2s^2\,^1S^e$ doubly excited state of He as a function of impact parameter. In our close-coupling FCA calculations, we work in a finite space such that the total cross section does not diverge even for $W=V_{ee}$. Still one can see that the relative error in the FCA is much larger at large impact parameters with no significant consequence on total cross sections since this large relative difference appears in a range of impact parameters that contributes negligibly to the total cross section (only the use of a logarithmic scale in Fig. 1 allows one to see such a discrepancy at large impact parameters). A similar result has been noted by Reading *et al.* [8] for the case of double ionization.

A sensible choice of $W_1$ will ensure that the FCA behaves correctly at large impact parameters. So, for the calculation of multiple processes, it is clearly advisable to use a nonzero $W_1$ not only to increase the accuracy in the transition probability at finite impact parameters but also to avoid any difficulty in the evaluation of total cross sections. In other terms, $W_1$ should be chosen so that the condition $t_{\rm coll}/t_{\rm corr}\ll 1$ be verified even at large impact parameters, $t_{\rm corr}$ being associated with the particular correlation potential $W$ resulting from a given choice of $W_1$. We will see in the following section that, in practice, results are not very sensitive to $W_1$ in the region of short impact parameters, so that the Hartree-Fock potential of the initial state may be the easiest choice.

## III. RESULTS

We apply the above formalism to double excitation of He. We concentrate here on the first singlet resonance $^1S^e(2s^2)$, located around an electron energy of 33 eV. The fully correlated close-coupling results used for comparison in this work have been reported previously [2] so that they will not be discussed in detail here. For the present study it is enough to recall that electron correlation was included in the initial and final states, as well as in all the intermediate states of the basis expansion. Also the exact correlated two-electron Hamiltonian was used to solve the time-dependent Schrödinger equation. Calculations in the FCA have been performed in the same subspace as the fully correlated ones in order to get a meaningful comparison (see [9]). The explicit analytical form of the one-electron screened potential used in the definition of $W_1$ in Eq. (6) is [10]

$$v_i=\frac{1}{r_i}-\frac{1}{r_i}(1+\alpha r_i)e^{-\beta r_i}, \tag{13}$$

where $\alpha=1.665$ and $\beta=3.36$. This potential is almost identical to the exact Hartree-Fock one and has the advantage that all matrix elements can be evaluated analytically.

We give in Fig. 1 the transition probability to the $^1S^e(2s^2)$ doubly excited state by impact of 2 MeV protons, obtained from the FCA with $W=V_{ee}-W_1$. Comparison with the fully correlated results and those obtained with $W=V_{ee}$ (i.e., when the whole electron-electron interaction $V_{ee}$ is frozen) shows a significant improvement in the region of large impact parameters. Similarly, we have found an improvement for the $^1P^o(2s2p)$ and $^1D^e(2p^2)$ resonances. As explained in Sec. II, our approximation consists in allowing for the effect of screening ($W_1$) in the dynamics but not for a modification of $W_1$ caused by the time evolution of the system. This is consistent with our choice of $W_1$ as the Hartree-Fock potential of the initial state. The excellent agreement between the FCA results obtained with $W=V_{ee}-W_1$ and the fully correlated ones confirms the validity of this choice. In the case of the $^1P^o(2s2p)$ and $^1D^e(2p^2)$ resonances, the agreement with the fully correlated results at large impact parameters is less remarkable than in the case of the $^1S^e(2s^2)$ resonance, indicating that the evolution in time of the screening plays a more important role. As mentioned above this is not important to obtain accurate cross sections because the contribution of large impact parameters is negligible. These results show not only that double excitation does not require dynamic correlation in the corresponding energy range, in agreement with our previous findings [6,7], but also that the FCA is a useful alternative to fully correlated calculations.

Experimentally, double excitation shows up as a resonance effect in the spectrum of electrons ejected from the target. The electron yield as a function of electron energy shows a characteristic structure above a smooth background that can be fitted for each resonance by

$$Y(\epsilon)=[A(\hat{\mathbf{k}})\epsilon+B(\hat{\mathbf{k}})]/(1+\epsilon^2), \tag{14}$$

where $\epsilon=2(E_{\rm el}-E_r)/\Gamma_r$, $E_r$ and $\Gamma_r$ are the resonance position and width, and $E_{\rm el}$ is the electron energy. The parameters $A$ and $B$ (Shore parameters) depend on the electron

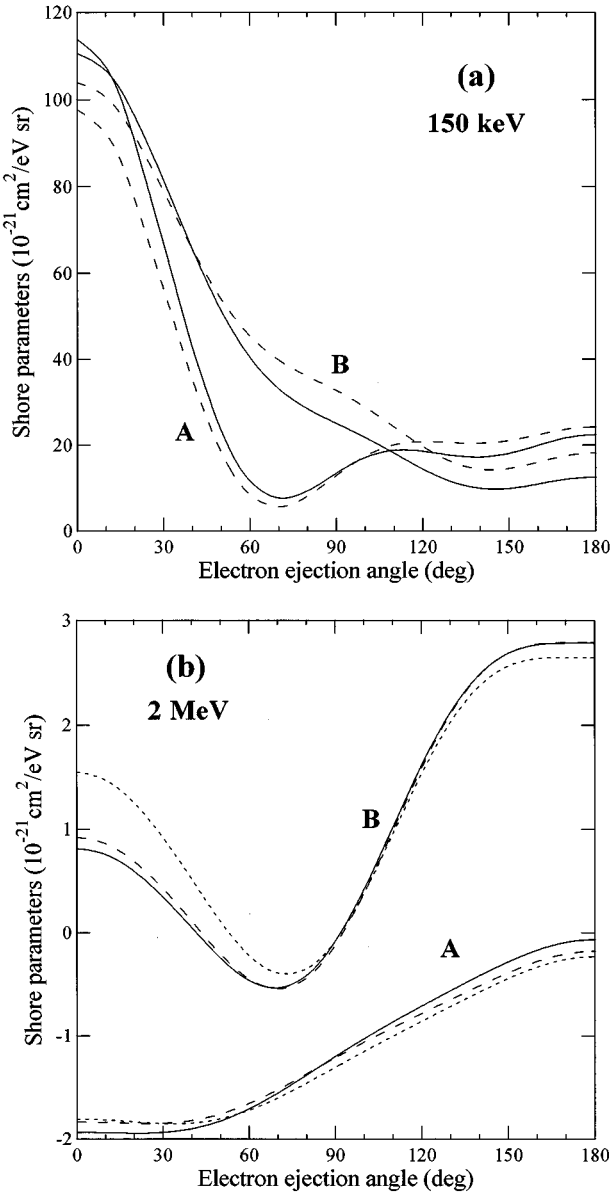


FIG. 2. Shore parameters for excitation of the $^1S^e(2s^2)$ resonance of He by (a) 150-keV and (b) 2-MeV protons as a function of electron ejection angle. Full curve, calculations including dynamic correlation; dashed curve, frozen correlation approximation with $W=V_{ee}-W_1$; dotted curve, frozen correlation approximation with $W=V_{ee}$.

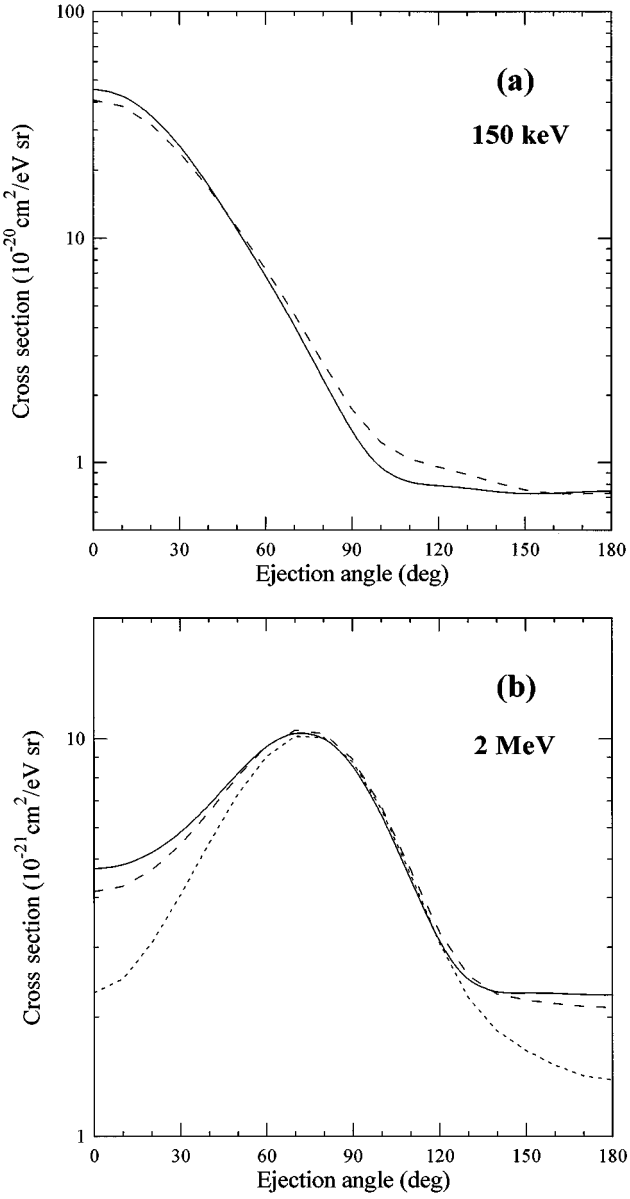


FIG. 3. Ionization cross section for the ejection of a 33-eV electron from He by (a) 150-keV and (b) 2-MeV protons as a function of electron ejection angle. Full curve: calculations including dynamic correlation; dashed curve: frozen correlation approximation with $W=V_{ee}-W_1$; dotted curve: frozen correlation approximation with $W=V_{ee}$.

ejection direction $\hat{\mathbf{k}}$ and characterize the shape of the resonance (in particular, the asymmetry is determined by the ratio $A/B$). The resonance shape (14) corresponds to an interference pattern involving the effect of electron correlation over a time much larger than $t_{\rm coll}$. In Fig. 2 we show the Shore parameters $A$ and $B$ corresponding to the $^1S^e(2s^2)$ resonance of He excited by 150-keV and 2-MeV protons, obtained with the FCA and fully correlated calculations. It can be observed that the agreement at 2 MeV is excellent and remains very good down to 150-keV impact energy. For comparison, the figure also includes our previous FCA results obtained with $W=V_{ee}$ at 2 MeV [6,7]. Notice that agreement between the latter and the fully correlated results was already very good and that the small discrepancies in the forward and the backward directions for the $B$ parameter have practically disappeared in the new FCA results. Calculations for 2-MeV projectile ions with charge up to $Z_P=9$ show the same kind of agreement.

The same conclusions hold for the ionization cross sections shown in Fig. 3. The agreement between our new FCA results and the fully correlated ones is excellent above 150-keV impact energies. In particular, the new results agree very well with the fully correlated ones in the forward and backward directions. As shown in Fig. 3(b), this is not the case of the FCA results obtained by freezing the whole electron-electron interaction $V_{ee}$. In Ref. [7] the difference between the latter FCA results and the fully correlated ones in the forward and backward directions was attributed to a poor

representation of dynamical screening effects when the whole $V_{ee}$ is frozen, i.e., when both $W$ and $W_1$ are frozen. The present results confirm this interpretation, since screening effects contained in $W_1$ are not frozen in the new FCA calculations.

## IV. CONCLUSION

The frozen correlation approximation (FCA) was first introduced in [6,7] to provide a reference calculation in which dynamic correlation is neglected and accordingly the whole electron-electron interaction $V_{ee}$ was neglected during the collision. This led us to the interesting conclusion that dynamic correlation does not play a significant role in multiple-excitation processes at high impact energies. In this paper we have gone a step further by incorporating screening effects during the collision. Since screening effects are usually reproduced by a separable average potential $W_1$, this means that only the nonseparable potential $W=V_{ee}-W_1$ is associated to correlation effects. This definition of correlation, which is in accordance with the usual one of the Hartree-Fock language, leads to a much better description of the collision process in the region of large impact parameters. Our results for double excitation and ionization of He by ion impact are excellent illustrations of this: transition probabilities and cross sections obtained by freezing $W$ instead of $V_{ee}$ are very close to the fully correlated ones. As in the original FCA [6,7], the many-electron transition amplitudes obtained in this way can be written as linear combinations of products of one-electron amplitudes. This result is completely general, i.e., it is independent on the particular form of the screening potential, provided the latter is written as a sum of one-electron potentials. This is interesting in view of future applications to more complicated systems that are not accessible by current fully correlated theories. The only information required to apply the FCA is (i) the configuration-mixing coefficients for both the initial and final states, and (ii) the one-electron transition amplitudes between the corresponding orbitals [see Eq. (12)].

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## APPENDIX

Here we show that the FCA transition amplitudes are invariant under a change of time origin. Let us define an operator $T$ that shifts the origin of time by $\delta$:

$$T\chi(t)=\chi(t+\delta). \tag{A1}$$

Then we write

$$\langle\tilde{\psi}_f|\tilde{u}(t_f,t_i)|\tilde{\psi}_i\rangle=\langle\tilde{\psi}_f|T^\dagger T\tilde{u}(t_f,t_i)T^\dagger T|\tilde{\psi}_i\rangle \tag{A2}$$

$$=\langle\tilde{\psi}_f|T\tilde{u}(t_f,t_i)T^\dagger|\tilde{\psi}_i\rangle, \tag{A3}$$

where we have used $TT^\dagger=1$ and the fact that $\tilde{\psi}_{i,f}$ do not depend on time, i.e., $T\tilde{\psi}_{i,f}\equiv\tilde{\psi}_{i,f}$. Now

$$T\tilde{u}(t_f,t_i)T^\dagger\equiv\tilde{u}(t_f+\delta,t_i+\delta) \tag{A4}$$

is the evolution operator corresponding to the new time origin. Consequently, Eq. (A3) proves the invariance of the transition amplitude defined in Eq. (10). Note that the proof is straightforward in the intermediate representation because time evolution associated to $H_0$ is not included in the asymptotic states [see Eqs. (1) and (2)]. Of course, a similar (but longer) proof can be obtained in the Schrödinger representation.

Reading *et al.* [8] have incorrectly stated that the FCA is not invariant under such a transformation. In fact, they find a spurious phase factor for any exact evolution operator because, when they shift the time origin, they use asymptotic states referred to the unshifted time origin [see Eqs. (13) and (15) of [8]]. As a consequence, the initial conditions they use for two different frames do not correspond to the same problem.

[1] J. F. Reading and A. L. Ford, Phys. Rev. Lett. **58**, 543 (1987); J. Phys. B **20**, 3747 (1987).
[2] F. Martín and A. Salin, J. Phys. B **28**, 639 (1995).
[3] A. Bordenave-Montesquieu *et al.*, J. Phys. B **28**, 653 (1995); F. Martín and A. Salin, J. Phys. B **27**, 2159 (1995).
[4] J. H. McGuire, Phys. Rev. A **36**, 1114 (1987); Adv. At. Mol. Opt. Phys. **29**, 217 (1992).
[5] N. Stolterfoht, Phys. Rev. A **48**, 2980 (1993); Phys. Scr. **42**, 192 (1990); **T46**, 22 (1993).
[6] F. Martín and A. Salin, Phys. Rev. Lett. **76**, 1437 (1996).
[7] F. Martín and A. Salin, Phys. Rev. A **54**, 3990 (1996).
[8] J.F. Reading, T. Bronk, and A.L. Ford, J. Phys. B **29**, 6075 (1996).
[9] F. Martín and A. Salin, J. Phys. B **28**, 671 (1995).
[10] L. Opradolce, P. Valiron, and R. McCarroll, J. Phys. B **16**, 2017 (1983).