

Electron Correlation in Multiple Excitation of Atoms by High-Energy Ions

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We derive a general expression for the transition amplitude when assuming that the correlation time is much larger than the collision time. This *frozen-correlation* approximation provides a reference calculation without *dynamic* correlation, which allows, for the first time, a quantitative evaluation of the role of electron correlation *during* the collision in a multiple excitation process. In a close-coupling formalism, the procedure is equivalent to fixing configuration mixing during the collision while allowing one-electron orbitals to evolve in time. The variation under a change of the projectile charge sign of double excitation of He by high-energy ion impact can be explained by the weak role of dynamic correlation.

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It is striking that the role of electron correlation in ion-atom collisions is still controversial, whereas in atomic structure theory the concept is well documented and can be unambiguously defined (e.g., as the difference between exact and Hartree-Fock calculations). In ion-atom collisions, it is the role of the *whole* electron-electron interaction V_{ee} which is still under scrutiny and, following most authors in the field, we shall use here *correlation* as an equivalent to V_{ee} . With the aim of elucidating the specific role of V_{ee} in the dynamics, attention has been naturally directed toward multiple processes, i.e., processes in which more than one electron is excited [1,2]. Fully correlated theories are available for double ionization [3] and double excitation (see, e.g., [4,5]) of helium. Double ionization is generally considered as the most striking evidence of the major role played by electron correlation in a multiple excitation process [3]. However, this conclusion is based on a comparison with an independent electron model (IEM) in which one considers not only that each electron is excited independently of the other but also that the initial and final states include no contribution from V_{ee} . The latter assumption is unrealistic (which explains why the IEM is often modified in an *ad hoc* manner). Hence we are in the paradoxical situation that our inability to state the role of electron correlation *during* the collision lies in the absence of a meaningful reference calculation in which it is neglected.

We propose a general formulation allowing one to sort out the role of electron correlation *during* (and *only during*) the collision (dynamic correlation [1]). Our main point is that the key feature of dynamic correlation is not its *strength* but its *rate of change* with time. The implementation of our theory in a close-coupling framework allows one to get for the first time unambiguous information on dynamic correlation in a multiple excitation process.

One might be tempted to start from perturbation theory, i.e., consider V_{ee} as weak in comparison with the interaction between the projectile and target electrons. However, for the case of target excitation, V_{ee} does not vanish (as it should in perturbation theory) when the projectile and target separate. This means that no calculation can be done by just dropping V_{ee} from the evolution operator. On the other hand, it has been shown [2,3] that many processes can be understood by assuming that the correlation time t_{corr} is much larger than the collision time t_{coll} . We show that the condition $t_{\text{corr}} \gg t_{\text{coll}}$ is the basis on which one may build a consistent theory neglecting correlation during the collision.

We use the impact parameter method in which we solve the time dependent Schrödinger equation (TDSE) for a straight line trajectory of the projectile (here a bare ion of charge Z_p and velocity \mathbf{v}):

$$\left(H_0 + V(t) - i \frac{d}{dt} \right) \Psi(t) = 0, \quad (1)$$

where H_0 is the helium Hamiltonian and $V(t)$ is the interaction with the projectile. Let $\psi_n(t)$ be the solution of (1) when $V(t) = 0$ and $\tilde{\psi}_n$ the time independent function in the interaction picture: $\tilde{\psi}_n = \exp(iH_0 t) \psi_n$. The transition amplitude for a collision process in which the target goes from the initial state I to the final state F is

$$T_{IF} = \lim_{t_f \rightarrow \infty} \lim_{t_i \rightarrow -\infty} \langle \tilde{\psi}_F | \tilde{U}(t_f, t_i) | \tilde{\psi}_I \rangle, \quad (2)$$

where

$$\tilde{U}(t_f, t_i) = \exp(iH_0 t_f) U(t_f, t_i) \exp(-iH_0 t_i) \quad (3)$$

and $U(t_f, t_i)$ is the evolution operator associated with the TDSE (1). The limit of (3) for $t_{\text{coll}}/t_{\text{corr}} \rightarrow 0$ can

be easily obtained by assuming that V_{ee} is a constant (i.e., a number). Indeed, for V_{ee} constant, $U(t_f, t_i) = \exp(-iV_{ee}t_f)u(t_f, t_i)\exp(iV_{ee}t_i)$, where u is associated with the TDSE (1) in which H_0 is replaced by $h_0 = H_0 - V_{ee}$. Hence from (3), $\tilde{U}(t_f, t_i) = \tilde{u}(t_f, t_i)$, where [6]

$$\tilde{u}(t_f, t_i) = \exp(ih_0t_f)u(t_f, t_i)\exp(-ih_0t_i). \quad (4)$$

A more rigorous derivation for nonconstant V_{ee} gives [7]

$$\tilde{U}(t + t_{\text{coll}}, t) = \tilde{u}(t + t_{\text{coll}}, t) + O(t_{\text{coll}}/t_{\text{corr}}), \quad (5)$$

which proves that $\tilde{U} = \tilde{u}$ in the limit $t_{\text{coll}}/t_{\text{corr}} \rightarrow 0$ [8]. The substitution of \tilde{U} by \tilde{u} defines the *frozen correlation* approximation. The result (5) allows one to interpret the difference with respect to an exact calculation as dynamic correlation [9]. Note that in both calculations the initial and final states $\tilde{\psi}_n$ do include correlation. The actual value of $t_{\text{coll}}/t_{\text{corr}}$ can be estimated from the overlap S between the exact wave function and the approximate one at the end of the collision, following a procedure described by Messiah [10] and further developed in [7]:

$$t_{\text{coll}}/t_{\text{corr}} = (1 - S)^{1/2}. \quad (6)$$

In our recent work on the excitation of helium [4,5], we have used a close-coupling method to solve the TDSE (1) with a basis of 104 correlated two-electron states. The initial and final states, as well as the most relevant intermediate states included in our basis, are accurately described (see [4,11] for details). If we call P the projection operator onto this basis set, the close-coupling method consists in replacing Eq. (1) by

$$P\left(H_0 + V(t) - i\frac{d}{dt}\right)P\Psi^P(t) = 0, \quad (7)$$

which can be solved exactly in terms of a set of coupled differential equations. Now, as we have already pointed out [11], all formal expressions written above can be extended to the solution of (7) if we replace H_0 (or h_0) by $H_0^P = PH_0P$ (or $h_0^P = Ph_0P$) and the evolution operator U (or u) associated with (1) by the operator U^P (or u^P) associated with (7). In other terms, we are able to calculate exactly the operators \tilde{U}^P and \tilde{u}^P by restricting our problem to the P space. The same P space is used in both cases, so the only difference between calculations with \tilde{U}^P or \tilde{u}^P is that V_{ee} is frozen in the latter.

The eigenstates of h_0 in the P space are products of one-electron orbitals ϕ_j . The two-electron basis functions $\tilde{\psi}_n$ can be expressed in terms of these as

$$\tilde{\psi}_n = \sum_{jk} \alpha_{jk}^n \phi_j \phi_k. \quad (8)$$

Under the action of $\tilde{u}(t, t_i)$ the form (8) is conserved during the collision: The one electron orbitals evolve

in time (because of the interaction with the projectile), whereas the coefficients α_{jk}^n are time independent (frozen correlation). In particular, at the end of the collision, the initial function has evolved into

$$\lim_{t_f \rightarrow \infty} \lim_{t_i \rightarrow -\infty} \tilde{u}(t_f, t_i) \tilde{\psi}_I = \sum_{jklm} \alpha_{jk}^I a_{jl} a_{km} \phi_l \phi_m, \quad (9)$$

where the one-electron amplitudes a_{jl} describe transitions between one-electron orbitals ϕ_j and ϕ_l under the action of the projectile. It is this mixing between the one-electron orbitals by the projectile field which allows one to produce a final correlated state $\tilde{\psi}_F$ having a configuration mixing that may differ significantly from that of the initial state $\tilde{\psi}_I$. From (9) it follows that the transition amplitude between initial and final correlated states can be written in terms of the one-electron amplitudes a_{jl} :

$$t_{IF} = \sum_{jklm} \alpha_{jk}^I \alpha_{lm}^F A_{jk}^{lm} = \sum_{jklm} \alpha_{jk}^I \alpha_{lm}^F a_{jl} a_{km}. \quad (10)$$

We apply now the above formalism to double excitation of He. Double excitation shows up as a resonance effect in the spectrum of electrons ejected from the target. We concentrate here on the first three singlet resonances $1S^e(2s^2)$, $1P^o(2s2p)$, and $1D^e(2p^2)$ located around an electron energy of 33 eV. 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

$$Y(\epsilon) = [A(\hat{\mathbf{k}})\epsilon + B(\hat{\mathbf{k}})]/(1 + \epsilon^2), \quad (11)$$

where $\epsilon = 2(E_{e1} - E_r)/\Gamma_r$, E_r , and Γ_r are the resonance position and width, and E_{e1} is the electron energy. The parameters A and B (Shore parameters) depend on the electron 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 (11) corresponds to an interference pattern due to the simultaneous excitation of a doubly excited state and its nearby continuum. This interference is caused by the effect of electron correlation over a time much larger than t_{coll} . Consequently, as the very definition of the Shore parameters involves electron correlation, no observable quantity can be determined without incorporating electron correlation in the final state.

In Fig. 1 we show the Shore parameters A and B describing double excitation to the $1S^e$ resonance of He by 2 MeV protons in both the frozen-correlated and the fully correlated calculations. These results are compared with the experimental ones of Bordenave-Montesquieu *et al.* [5]. We have already shown [4,5] that our fully correlated couple state calculations describe well the experimental findings under impact of protons with energies 0.1–3 MeV. One can observe, in addition, a good agreement between the frozen-correlated and fully correlated

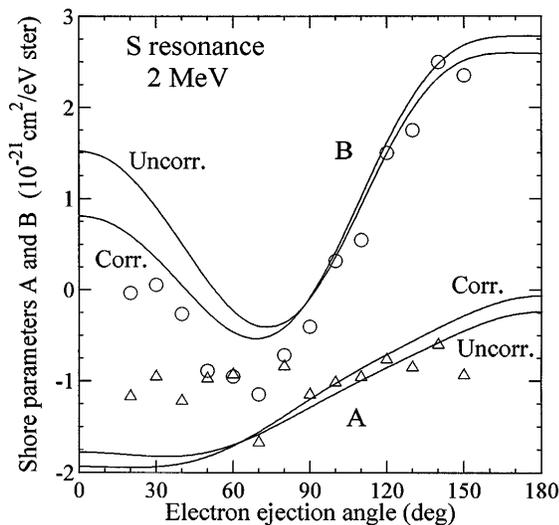


FIG. 1. Shore parameters A and B versus electron ejection angle describing the shape of the $1S^e$ resonance in ionization of helium by 2 MeV protons. Lines labeled “Corr.” correspond to fully correlated calculations and “Uncorr.” to calculations with correlation frozen during the collision. Symbols: experiments [5] (triangles: A , circles: B).

results. In Fig. 2 we compare transition probabilities for double excitation versus impact parameter ρ . Agreement between the full and frozen-correlated calculation is excellent (and similar agreement is obtained for the $1D^e$ resonance). This implies that, although electron correlation is very important for $t \gg t_{\text{coll}}$ in describing the interference between double excitation and ionization, it does not play a significant role *during* the collision. This is further confirmed by the value $t_{\text{coll}}/t_{\text{corr}} \approx 0.02$ resulting

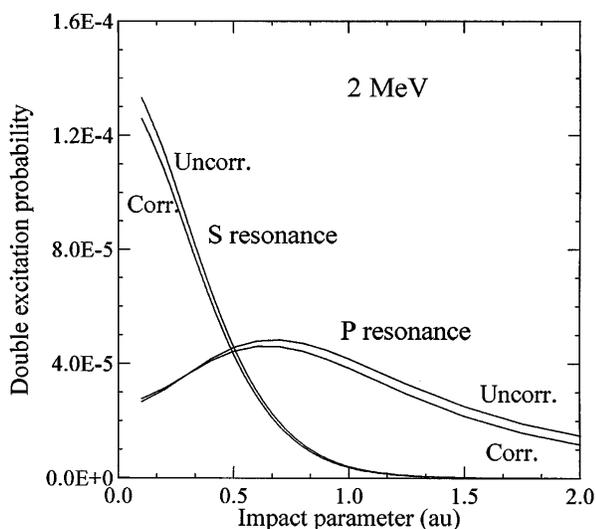


FIG. 2. Transition probabilities to the $1S^e$ and $1P^o$ doubly excited states versus impact parameter. Lines labeled “Corr.” correspond to fully correlated calculations and “Uncorr.” to calculations with correlation frozen during the collision.

from Eq. (6) for $\rho = 0.1-1.0$ a.u. Similar conclusions have been obtained for excitation of the $1D^e$ and $1P^o$ resonances. In the latter case, the agreement between the two calculations is slightly worse because the long-range dipole interaction between the initial ($1S^e$) and final ($1P^o$) states makes t_{coll} larger than for the other resonances (in fact, our calculations show that $t_{\text{coll}}/t_{\text{corr}}$ increases slowly with ρ).

We have also obtained a good agreement for 0.5 and 10 MeV. In principle, one could expect that the differences between the fully correlated and the frozen-correlated results should increase when the collision energy decreases because t_{coll} increases. This is indeed the case, but our results show that the differences are still relatively small at 0.5 MeV. In fact, the collision time does not vary significantly at high impact energies because the effective range of impact parameters where double excitation takes place is $\approx v/\Delta E$ (where ΔE is the excitation energy).

We have also studied the validity of the frozen-correlation approximation when increasing Z_P , at a fixed impact velocity. It has been often considered that the role of correlation should decrease with increasing projectile charge. In fact, we claim that the opposite should be true: t_{coll} increases with projectile charge because of contributions from an increasing range of internuclear distances [4,11]. Our results for 1.5 MeV/amu F^{9+} impact (Fig. 3) confirm this expectation since $t_{\text{coll}}/t_{\text{corr}} \approx 0.1$ and the agreement between both calculations is worse (although still reasonable).

The variation of multiple excitation processes with projectile charge sign has been considered as the main clue to the role of electron correlation [1-3]. The

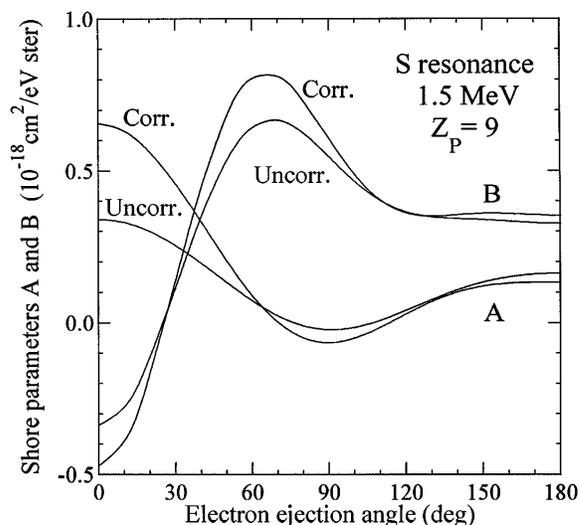


FIG. 3. Shore parameters A and B versus electron ejection angle describing the shape of the $1S^e$ resonance in ionization of helium by 1.5 MeV/amu F^{9+} ions. Lines labeled “Corr.” correspond to fully correlated calculations and “Uncorr.” to calculations with correlation frozen during the collision.

dependence of the Shore parameters on the projectile charge sign is a particularly striking result. It was shown in [12] that this charge sign effect disappears after integration over ejected electron angles. We have proved that this observation can be explained by a lack of interference between the first Born and second Born contributions to the transition amplitude [4]. The origin of this lack of interference has not been understood until now. It can be explained as a result of the frozen-correlation approximation. We know from our earlier calculations that the second Born approximation describes fairly well double excitation by protons and antiprotons at 2 MeV. This means that a calculation of the amplitude T_{IF} up to second order in Z_P is adequate. For the a_{jl} amplitudes a first order is enough because they correspond to single excitation of a one-electron system. Then

$$a_{jl} \approx \delta_{jl} + Z_P b_{jl}, \quad (12)$$

where b_{jl} is a Born I amplitude for a one-electron target, and, therefore,

$$t_{IF} \approx \sum_{jlm} \alpha_{jk}^I \alpha_{lm}^F \{Z_P [\delta_{km} b_{jl} + \delta_{jl} b_{km}] + Z_P^2 b_{jl} b_{km}\}.$$

The ϕ_j orbitals that enter a given configuration in (8) have their lm quantum numbers constrained by the parity of the state and the $3-j$ symbols implicit in the coefficients α_{jk} . The first order amplitudes b_{jl} are purely real or imaginary depending on the values of the quantum numbers lm in the initial and final one-electron orbitals ϕ_j (see, e.g., [2]). Then one can show in a straightforward way that if the linear term in Z_P is purely imaginary, the quadratic one is purely real and the converse. This proves the noninterference between first and second order amplitudes. Now this result does not correspond to an approximation on the initial and final helium functions: If a complete set of ϕ_j orbitals was used, the representation (8) would be exact and the conclusion would be the same. Therefore the noninterference proved here is exact whenever correlation is frozen during the collision. In particular, it is not restricted to a Hartree-Fock approximation for the initial and final states.

To conclude, we have derived a general expression for the transition amplitude assuming that the correlation time is much larger than the collision time. By doing calculations in a fixed subspace we have obtained a meaningful quantitative measure of the role of electron correlation during the collision in the case of double excitation of He by ions. In contrast with previous attempts, our method requires neither the use of perturba-

tion theory nor the Hartree-Fock approximation. The latter is never valid in practice for doubly excited states and leads, in general, to nonorthogonal initial and final states. Moreover, we have shown that the frozen-correlation approximation is useful over a wide range of impact energies ($E > 0.5$ MeV) and for projectile charges as large as $Z_P = 9$. Finally, it is the weak role of correlation during the collision which is responsible for the behavior observed when the sign of projectile charge is changed. The frozen-correlation concept can be used in a similar way to assess the role of electron correlation in a large variety of collision processes. It is useful in its own stand when a fully correlated calculation can hardly be achieved as providing a consistent way to evaluate the transition amplitude without dynamic correlation.

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- [1] J.H. McGuire, Phys. Rev. A **36**, 1114 (1987); Adv. At. Mol. Opt. Phys. **29**, 217 (1992).
- [2] N. Stolterfoht, Phys. Rev. A **48**, 2980 (1993); Phys. Scr. **42**, 192 (1990); **T46**, 22 (1993).
- [3] J.F. Reading and A.L. Ford, Phys. Rev. Lett. **58**, 543 (1987); J. Phys. B **20**, 3747 (1987).
- [4] F. Martín and A. Salin, J. Phys. B **27**, L715 (1994); **28**, 639 (1995); **28**, 671 (1995).
- [5] A. Bordenave-Montesquieu *et al.*, J. Phys. B **28**, 653 (1995).
- [6] Note that the approximation $V_{ee} = \text{const}$ is equivalent to replacing H_0 by h_0 in both $U(t_f, t_i)$ and the exponential factors of (3).
- [7] F. Martín and A. Salin (to be published).
- [8] In contrast, it is not possible to find a similar relation between U and u , so that $U = u$ is not a valid approximation even when $t_{\text{coll}} \ll t_{\text{corr}}$.
- [9] Previous methods [3,4,12] account for electron correlation but do not provide a reference calculation in which dynamic correlation is neglected. In particular, though the forced-impulse method [3] expresses the evolution operator over a small time interval in terms of u , it does account for dynamic correlation.
- [10] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961), p. 740.
- [11] F. Martín and A. Salin, J. Phys. B **28**, 671 (1995).
- [12] T. Morishita, K. Hino, S. Watanabe, and M. Matsuzawa, J. Phys. B **27**, L287 (1994).