Electron correlation in ion-atom collisions

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We study the role of electron correlation during a high-energy ion-atom collision (*dynamic correlation*). We show how to define a reference calculation in which correlation is not included during the collision whereas it is included in the initial and final states (*frozen-correlation approximation*). Correlation may be characterized by a typical time t_{corr}. The frozen-correlation approximation corresponds to the form of the transition amplitude when assuming that t_{corr} is much larger than the collision time. We apply our theory to double excitation and single ionization of helium and show that dynamic correlation may play a more important role in ionization than in double excitation. [S1050-2947(96)03010-7]

I. INTRODUCTION

Ion (atom)–atom collision processes involving excitation of more than one electron raise the question of the role of the electron-electron interaction. Following common usage in atomic collision processes, we shall name correlation the whole electron-electron interaction. This definition of correlation is at variance with the one commonly used in atomic structure theory. In a sense, the present contribution will give further justification for this convention.

The role of electron correlation is well established for the case of low-energy ion (atom)–atom collisions. In the low-energy regime, one makes use of the molecular theory of atomic collisions based on adiabatic (Born-Oppenheimer) molecular wave functions for the electronic states. The latter are determined for nuclei fixed at a given internuclear distance. There is (at least in principle) no problem in accounting for electron correlation in these molecular states. The dynamics arises, then, from the nuclear motion which induces transitions between adiabatic states. Therefore correlation is entirely embedded in the adiabatic molecular states. The role of correlation during the collision has been made explicit, e.g., by a change of representation in the basis of adiabatic states (*diabatic II* processes [1]) or by using a basis of molecular states not including correlation [2]. In sum, the problem of correlation in this energy range is more a practical problem than one of principle.

Another simple situation occurs when the first order of some perturbation series (Born or distorted wave) is valid. Then transition amplitudes can be expressed as the matrix element of an operator involving the projectile-target interaction between fully correlated initial and final states. Again,

the problem is basically a practical one: how well can we describe the correlated atomic states and how can we calculate the relevant matrix element?

A really intricate situation arises when neither approach can be used. For example, if one wishes to go beyond the first order of a perturbative series, one gets usually an evolution operator which depends explicitly on the electron-electron interaction. In this context the notion of *dynamic correlation* arises in relation with the fact that the exact evolution operator contains the electron-electron interaction explicitly.

A breakthrough in allowing for dynamic correlation was achieved in the work of Reading and Ford [3,4]. These authors have been able to carry out a converged calculation, using close-coupling techniques, for double ionization of helium by ions. This tour de force relies on various clever ingredients (like the solution of the so-called *interpretation problem* allowing separation of single and double ionization while using a basis of L^2 functions) out of which we single out two points connected with the present discussion. First, the algorithm used in [3,4] is based on the remark that during a small enough time the evolution of the system can be described in terms of an evolution operator not involving electron correlation. As we show later, this use of a time picture to characterize correlation is an essential point. Second, the results obtained in [3,4] for double ionization differ totally from those of a so-called independent-electron method (IEM). This has been considered ever since as the most convincing proof of the role of dynamic correlation since in the IEM each electron is assumed to evolve independently in the field of the projectile.

In the context of perturbation theory, important contributions were made by McGuire [5] and Stolterfoht [6]. McGuire [5] has discussed in detail the relation between electron correlation and the various orders of perturbation theory in describing multiple excitation processes. He has stressed the importance of using the intermediate picture to develop approximations of dynamic correlation. Stolterfoht

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[6] has insisted on the difference of time scale associated with correlation and the projectile-target interaction, respectively.

Our objective here is to provide an answer to the still pending question: what is the role of dynamic correlation? In fact, Reading and Ford [3,4] make a complete calculation fully including correlation. However, they do not define the reference calculation excluding dynamic correlation and *only* dynamical correlation. The independent-electron model used in [3,4] neglects correlation in the initial and final states as well as during the collision. Defining an approximation excluding dynamic correlation but including correlation in the initial and final states is not a straightforward problem in general. We consider throughout this work the particular case in which the correlated electrons are bound to the same atom (the target or the projectile) in both the initial and final state (a brief discussion of more general situations is given in the conclusion). This means that the electron-electron interaction cannot be treated as a perturbation since any perturbing potential should go to zero before and after the collision. We therefore show that an approximate treatment requires a particular condition on the time associated with correlation. Let t_{corr} be a typical time (to be defined later) associated with correlation and t_{coll} the collision time (associated with the projectile-target interaction). Then we show that the evolution without dynamic correlation corresponds to the limit $t_{corr}/t_{coll} \to \infty$. In other terms, by looking at the form of the evolution operator when letting t_{corr}/t_{coll} go to infinity, we obtain an approximate form which corresponds to neglecting dynamic correlation.

Our theory is used to study the role of dynamic correlation in double excitation and single ionization of helium. The case of double excitation is particularly striking as final-state correlation is essential to compare theory with experiment. We are thus in a position to explore the role of dynamic correlation in a multiple excitation process while accounting for correlation in both the initial and final state.

A brief account of our work has already been published [7]. Atomic units are used unless otherwise stated.

II. GENERAL THEORY

We treat the problem in the impact parameter method. It has been known for many years that the latter provides an accurate description of ion(atom)-atom collisions to first order in the electron to proton mass ratio. Any formalism developed in the impact parameter method has an equivalent in the full quantal theory. As we show below, the impact parameter method allows us to express our ideas in a more intuitive and transparent form. In the impact parameter method everything works as if one were solving a time dependent Schrödinger equation (TDSE) for a straight line trajectory of the projectile. The internuclear vector $\mathbf{R}$ is given by $\mathbf{R} = \boldsymbol{\rho} + \mathbf{v}t$ where $\boldsymbol{\rho}$ is the impact parameter and $\mathbf{v}$ the (constant) projectile velocity. For simplicity we consider the projectile to be a bare ion of charge Z_P. We call H_0 the Hamiltonian of the isolated target, $V(t)$ the interaction between the projectile and target electrons, and V_{ee} the whole electron-electron interaction. We consider that V_{ee} may be split into $W_1 + W$, where W_1 is a sum of one-electron operators and W is a nonseparable two-electron operator. Then

$$H_0 = h_0 + W. \tag{1}$$

We call $\widetilde{\psi}_n$ the eigenfunction of H_0 with eigenenergy E_n. For simplicity, we drop the internuclear potential from the equations and consider that the interaction with the projectile is short range. The correct treatment of Coulomb potentials involves well documented modifications that we leave aside here to avoid obscuring the main objective of the present development (which does not mean that it can be neglected in the treatment of a specific problem). Under these conditions, we have to solve the TDSE

$$\left[H_0 + V(t) - i\frac{d}{dt} \right] \Psi_i(t) = \left[H(t) - i\frac{d}{dt} \right] \Psi_i(t) = 0, \tag{2}$$

with initial condition

$$\lim_{t \to -\infty} \Psi_i(t) = \psi_i(t), \tag{3}$$

where $\psi_i(t) = \exp(-iE_it)\widetilde{\psi}_i$. The exact solution of Eq. (2) can be written in terms of the evolution operator $U(t,t')$ associated with $H(t)$:

$$\Psi_i(t) = U(t,t')\Psi_i(t') = \lim_{t' \to -\infty} U(t,t')\psi_i(t'). \tag{4}$$

All the above equations are written in the so-called Schrödinger picture. For reasons that are apparent later, it is advantageous to work in the intermediate picture (see also [5]). We label any quantity in the intermediate picture by a tilde. The wave function $\widetilde{\Psi}_i(t) = e^{iH_0t}\Psi_i(t)$ is now a solution of the TDSE:

$$\left(e^{iH_0t}V(t)e^{-iH_0t} - i\frac{d}{dt} \right) \widetilde{\Psi}_i(t) = 0, \tag{5}$$

with the initial condition $\lim_{t \to -\infty} \widetilde{\Psi}_i(t) = \widetilde{\psi}_i$.

A. The frozen-correlation approximation

The evolution of $\widetilde{\Psi}_i(t)$ in time is given by the evolution operator

$$\widetilde{U}(t,t') = e^{iH_0t}U(t,t')e^{-iH_0t'}. \tag{6}$$

The evolution operators U and $\widetilde{U}$ satisfy the equations

$$i\frac{d}{dt}U(t,t') = H(t)U(t,t'), \tag{7a}$$

$$i\frac{d}{dt}\widetilde{U}(t,t') = e^{iH_0t}V(t)e^{-iH_0t}\widetilde{U}(t,t'). \tag{7b}$$

Let us now introduce the evolution operator $u(t,t')$ associated with the TDSE when we drop W from the Hamiltonian. We define a corresponding intermediate picture in which the evolution operator is $\widetilde{u}(t,t') = e^{ih_0t}u(t,t')e^{-ih_0t'}$. Note that h_0 [the target Hamiltonian without the nonseparable part of the electron-electron interactions, see Eq. (1)] appears in this definition instead of H_0. The operators u and $\widetilde{u}$ satisfy

$$i\frac{d}{dt}u(t,t')=h(t)u(t,t'), \tag{8a}$$

$$i\frac{d}{dt}\widetilde{u}(t,t')=e^{ih_0t}V(t)e^{-ih_0t}\widetilde{u}(t,t'), \tag{8b}$$

where $h(t)=h_0+V(t)$. A very simple relation can be found between $\widetilde{U}$ and $\widetilde{u}$ when the collision time is vanishingly small. Following Messiah [8], we write

$$\widetilde{U}(t,t')=\widetilde{u}(t,t')\widetilde{U}'(t,t') \tag{9}$$

and the operator $\widetilde{U}'(t,t')$ satisfies the equation

$$i\frac{d}{dt}\widetilde{U}'(t,t')=H_I'(t)\widetilde{U}'(t,t'),$$

$$H_I'(t,t')=\widetilde{u}^\dagger(t,t')H'(t)\widetilde{u}(t,t'),$$

$$H'(t)=e^{iH_0t}V(t)e^{-iH_0t}-e^{ih_0t}V(t)e^{-ih_0t}. \tag{10}$$

The structure of the operator H' is simple. As we have noted above, the intermediate representation associated with H_0 is different from the one associated with h_0. The operator $H'(t)$ is the difference between the form of $\widetilde{V}(t)$, the projectile target interaction, in both representations. It differs from zero only during the collision time, i.e., when the projectile target interaction is active $[V(t)\neq 0]$. Since $H_0=h_0+W$, it can be immediately seen that $H'(t)$ describes the variation in the evolution due to the presence of W during the collision. From (9) we define the following approximation:

$$\widetilde{U}(t,t')\rightarrow\widetilde{u}(t,t'). \tag{11}$$

Since over a *small* time interval δ we have

$$\widetilde{U}'(t+\delta,t)=1-iH_I'(t)\delta+0(\delta^2). \tag{12}$$

Equation (11) corresponds to $\lim_{\delta\rightarrow 0}\widetilde{U}(t,t')=\widetilde{u}(t,t')$, i.e., to a sudden approximation. Now, the time dependence of $\widetilde{U}'$ is entirely due to the presence of $V(t)$ with which we may associate a characteristic time t_{coll}. Therefore Eq. (11) means that 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. We make this statement more quantitative later.

The operator $\widetilde{W}$ in the interaction picture satisfies the equation

$$i\frac{d}{dt}\widetilde{W}(t)=[\widetilde{W},H_0] \tag{13}$$

and is therefore constant if W commutes with h_0 (e.g., if W is a number). Under the latter condition, one has exactly $H'(t)=0$ and therefore $\widetilde{U}=\widetilde{u}$. For this reason we call approximation (11) the *frozen-correlation* approximation (FCA).

It should be stressed that the sudden approximation (11) takes the simple form we have obtained only by use of the intermediate picture. No such limit exists for the operator $U(t,t')$ in the Schrödinger picture. This can be immediately verified by looking at the form of U and u for a small time interval:

$$U(t+\delta,t)=1-iH(t)\delta+0(\delta^2), \tag{14a}$$

$$u(t+\delta,t)=1-ih(t)\delta+0(\delta^2). \tag{14b}$$

The difference between the generators of U and u is W and therefore it cannot be associated with t_{coll}. We shall discuss this in more detail later.

B. Alternative derivation of the FCA

It is of interest to follow an alternative derivation that will be helpful in the following discussion. We first introduce some extra notations. We call $\widetilde{\phi}_j$ the eigenfunctions of h_0 with eigenvalue ε_j and $\phi_j(t)=\exp(-i\varepsilon_j t)\widetilde{\phi}_j$. The eigenfunctions of H_0 can be expressed in terms of $\widetilde{\phi}_j$ as

$$\widetilde{\psi}_n=\sum_j a_j^{(n)}\widetilde{\phi}_j. \tag{15}$$

We define a dynamic basis $\{\widetilde{\Phi}_n\}$ in the following way:

$$\lim_{t\rightarrow-\infty}\widetilde{\Phi}_n(t)=\widetilde{\psi}_n \tag{16}$$

and $\widetilde{\Phi}_n$ satisfies the TDSE

$$\left[e^{ih_0t}V(t)e^{-ih_0t}-i\frac{d}{dt}\right]\widetilde{\Phi}_n(t)=0. \tag{17}$$

In other terms, the function $\widetilde{\Phi}_n(t)$ evolves under the influence of h_0 and $V(t)$ only. Some comments are in order on the signification of the function $\widetilde{\Phi}_n(t)$.

First, it is essential at this level to work in the intermediate picture so that the limit (16) exists. This is so because the asymptotic functions are time independent in the intermediate picture. Asymptotically, the function $\widetilde{\Phi}_n(t)$ is time independent as shown by Eq. (17) whenever $V(t)$ is zero. There is no way to impose a limit for t tending to infinity of $\Phi_n(t)$ in terms of $\psi_n(t)$ because of the energy factors in $\phi_j(t)$ and $\psi_n(t)$. No time independent correspondence between $\phi_n(t)$ and $\psi_n(t)$ similar to (15) exists.

Secondly, the *evolution* of $\widetilde{\Phi}_n(t)$ does not include any effect of W. The effect of W enters only through the initial condition (16). For this reason, we shall speak of an evolution with *frozen correlation*. What we mean through this expression can be understood intuitively in the following way. Consider the functions $\widetilde{\Phi}_j^0(t)$ satisfying the same equation (17) as $\widetilde{\Phi}_n(t)$ but with the initial condition $\widetilde{\Phi}_j^0(t)\rightarrow_{t\rightarrow-\infty}\widetilde{\phi}_j$. The functions $\widetilde{\Phi}_j^0(t)$ are the solution of a problem in which the two electrons never interact. The set of functions $\{\widetilde{\Phi}_j^0(t)\}$ is a complete orthonormal set (because of the completeness and orthogonality of the asymptotic functions $\widetilde{\phi}_j$). The functions $\widetilde{\Phi}_n(t)$ can be expressed *at any time* in terms of $\widetilde{\Phi}_j^0(t)$ through

$$\widetilde{\Phi}_n(t) = \sum_j a_j^{(n)} \widetilde{\Phi}_j^0(t), \qquad (18)$$

where the coefficients $a_j^{(n)}$ are *independent of time*. This property expresses what we mean by an evolution with frozen correlation: the role of W in $\widetilde{\Phi}_n(t)$ appears only through the time independent coefficients $a_j^{(n)}$. This does not mean that the average value of W is constant in the course of the collision when the evolution is given by (17). Let us define the average value of W at time t as

$$\overline{W}(t) = \langle \widetilde{\Phi}_n(t) | W | \widetilde{\Phi}_n(t) \rangle. \qquad (19)$$

This quantity depends on time because $\widetilde{\Phi}_j^0$ in (18) depends on time. This variation with time of $\overline{W}(t)$ is only due to the interaction with the projectile and not to any action of W in the course of the collision since W does not appear in the TDSE (17). In other terms, a variation of $\overline{W}(t)$ with time is not in contradiction with the idea expressed earlier that cor-

relation is frozen. In particular, the evolution given by Eq. (17) is compatible with a nonzero transition probability to a given final correlated state.

It is important to realize the latter point to understand that the difference between $\widetilde{\Psi}_n$ and $\widetilde{\Phi}_n$ can be characterized neither by the change in $\overline{W}(t)$ nor by its magnitude. As we show later, the difference between both functions is of higher order in W.

The set of $\widetilde{\Phi}_n(t)$ functions is complete and orthonormal. This comes out of the completeness and orthogonality of the asymptotic set $\widetilde{\psi}_n(t)$ as for the usual solutions of the time-dependent Schrödinger equation.

Using the $\widetilde{\Phi}_n(t)$ functions as a basis, we may write

$$\widetilde{\Psi}_i(t) = \sum_n c_n(t) \widetilde{\Phi}_n(t), \qquad (20)$$

with $\lim_{t \to -\infty} c_n(t) = \delta_{ni}$. This gives the coupled equations

$$i \frac{d}{dt} c_n(t) = \sum_m c_m(t) \langle \widetilde{\Phi}_n(t) | e^{iH_0 t} V(t) e^{-iH_0 t} - i\,d/dt | \widetilde{\Phi}_m(t) \rangle = \sum_m c_m(t) \langle \widetilde{\Phi}_n(t) | e^{iH_0 t} V(t) e^{-iH_0 t} - e^{ih_0 t} V(t) e^{-ih_0 t} | \widetilde{\Phi}_m(t) \rangle. \qquad (21)$$

Until now everything is exact. Let us understand the signification of the above equations. The functions $\widetilde{\Phi}_n(t)$ correspond to the solution of the time dependent Schrödinger equation under the influence of h_0 and $V(t)$ alone. Through the coupled equations (21), we measure how much the exact solution $\widetilde{\Psi}_i(t)$ differs from $\widetilde{\Phi}_i(t)$. Note that the full (exact) dynamics due to $h_0 + V$ is contained in $\widetilde{\Phi}_n$. We may transform (21) into the integral equation

$$c_n(t) = \delta_{ni} - i \sum_m \int_{-\infty}^t dt'\, c_m(t') \langle \widetilde{\Phi}_n(t') | e^{iH_0 t'} V(t') e^{-iH_0 t'} - e^{ih_0 t'} V(t') e^{-ih_0 t'} | \widetilde{\Phi}_m(t') \rangle. \qquad (22)$$

The two important features of this expression are that (i) the coupling arises from the presence of W since, in general, $[H_0, W] \neq 0$, and (ii) the W interaction is effective only over the time interval when $V(t)$ is nonzero. Under the condition $t_{\mathrm{coll}} \to 0$, equivalent to saying that $V(t)$ is a δ function, one gets

$$c_n(t) = \delta_{ni}. \qquad (23)$$

In other terms, the prescription $\widetilde{\Psi}_i(t) \to \widetilde{\Phi}_i(t)$ gives the solution of the problem in the limit $t_{\mathrm{coll}} \to 0$. Note that the fact that $V(t)$ is set equal to a δ function in (22) is compatible with a nonzero transition probability for the reason explained earlier.

C. Validity of the frozen-correlation approximation

We closely follow Messiah [8] (Chap. XVII, Sec. II.8). For simplicity, we assume that the collision takes place over a finite time starting from $t = t_1$. From Eqs. (4) and (17) we may write

$$\widetilde{\Psi}_i(t) = \widetilde{U}(t, t_1) \widetilde{\psi}_i, \qquad (24a)$$

$$\widetilde{\Phi}_i(t) = \widetilde{u}(t, t_1) \widetilde{\psi}_i. \qquad (24b)$$

As we have noted above, the operator W appears only through H_I' and therefore the action of the operator W is limited to the time interval over which $V(t)$ is active, i.e., $H_I' = 0$ before and after the collision. Furthermore H_I' is zero when the operator W in the intermediate picture ($e^{iH_0 t} W e^{-iH_0 t}$ or $e^{ih_0 t} W e^{-ih_0 t}$) is independent of time, i.e., $\widetilde{W}$ commutes with h_0 [see Eq. (13)]. Then, any deviation from the frozen-correlated approximation must be accounted for by H_I' in the time interval $(t_1, t_1 + t_{\mathrm{coll}})$. Here we try to analyze the validity of this approximation by considering $\widetilde{U}'$ up to first order in t_{coll}. For a small collision time t_{coll} we can write from Eq. (10)

$$\widetilde{U}'(t_1 + t_{\mathrm{coll}}, t_1) \simeq 1 - i \int_{t_1}^{t_1 + t_{\mathrm{coll}}} H_I'(t') dt'. \qquad (25)$$

Notice that in the frozen-correlation approximation, $\widetilde{U}' = 1$, which is the zero order solution of the previous equation. Accordingly, small deviations from this approximation will be accounted for by the first-order term including H_I':

$$\widetilde{U}'(t_1+t_{\rm coll},t_1)\simeq 1-it_{\rm coll}\bar{H}'_I(t_1+t_{\rm coll},t_1), \qquad (26)$$

where

$$\bar{H}'_I(t_1+t_{\rm coll},t_1)=\frac{1}{t_{\rm coll}}\int_{t_1}^{t_1+t_{\rm coll}}H'_I(t')dt' \qquad (27)$$

is an average operator over the collision time. The best way to measure the validity of the sudden approximation (11) to $\widetilde{U}$ is to calculate the deviation between $\widetilde{\Phi}_i(t_1+t_{\rm coll})$ and $\widetilde{\Psi}_i(t_1+t_{\rm coll})$ through their overlap:

$$w=1-|\langle\widetilde{\Psi}_i(t_1+t_{\rm coll})|\widetilde{\Phi}_i(t_1+t_{\rm coll})\rangle|^2$$
$$=\langle\widetilde{\Psi}_i(t_1+t_{\rm coll})|\widetilde{Q}\widetilde{\Psi}_i(t_1+t_{\rm coll})\rangle, \qquad (28)$$

where

$$\widetilde{Q}=1-|\widetilde{\Phi}_i(t_1+t_{\rm coll})\rangle\langle\widetilde{\Phi}_i(t_1+t_{\rm coll})|. \qquad (29)$$

If the frozen-correlation approximation is exact, then $w=0$, because $\widetilde{\Psi}_i(t_1+t_{\rm coll})=\widetilde{\Phi}_i(t_1+t_{\rm coll})$. In the general case, using Eqs. (9) and (24), w can be written

$$w=\langle\widetilde{\psi}_i|\widetilde{U}'^{\dagger}(t_1+t_{\rm coll},t_1)\widetilde{u}^{\dagger}(t_1+t_{\rm coll},t_1)\widetilde{Q}\widetilde{u}(t_1+t_{\rm coll},t_1)\widetilde{U}'(t_1+t_{\rm coll},t_1)|\widetilde{\psi}_i\rangle. \qquad (30)$$

Substituting (26), we obtain

$$w=t_{\rm coll}^2\langle\widetilde{\psi}_i|\bar{H}_I'^{\dagger}(t_1+t_{\rm coll},t_1)\widetilde{u}^{\dagger}(t_1+t_{\rm coll},t_1)\widetilde{Q}\widetilde{u}(t_1+t_{\rm coll},t_1)\bar{H}'_I(t_1+t_{\rm coll},t_1)|\widetilde{\psi}_i\rangle$$
$$=t_{\rm coll}^2\{\langle\widetilde{\psi}_i||\bar{H}'_I(t_1+t_{\rm coll},t_1)|^2|\widetilde{\psi}_i\rangle-|\langle\widetilde{\psi}_i|\bar{H}'_I(t_1+t_{\rm coll},t_1)|\widetilde{\psi}_i\rangle|^2\}=t_{\rm coll}^2[\Delta\bar{H}'_I]^2. \qquad (31)$$

We may now introduce the definition

$$t_{\rm corr}=\frac{1}{\Delta\bar{H}'_I}. \qquad (32)$$

The term $\Delta\bar{H}'_I$ is the root mean square deviation from the mean value of $\bar{H}'_I(t)$. The latter is the average over time of the energy fluctuations caused by the operator W in the exact propagation with respect to the average when W is neglected in the evolution. Then, the characteristic time $1/\Delta\bar{H}'_I$ for these average energy fluctuations can be interpreted as the correlation time $t_{\rm corr}$. Notice that, as expected, we get the correct limit $t_{\rm corr}\rightarrow\infty$ when W is a constant in the intermediate picture (i.e., when $H'_I=0$).

From Eqs. (28), (31), and (32), $t_{\rm corr}/t_{\rm coll}$ may be calculated readily when the exact solution is known since

$$\frac{t_{\rm coll}}{t_{\rm corr}}=w^{1/2}=[1-|\langle\widetilde{\Psi}_i(t_1+t_{\rm coll})|\widetilde{\Phi}_i(t_1+t_{\rm coll})\rangle|^2]^{1/2}. \qquad (33)$$

In sum, we have defined a time $t_{\rm corr}$ characterizing the action of the operator W during the collision and *only* during the collision. This time is associated with the root mean square of the energy fluctuations, averaged over the collision time, caused by the operator W with respect to an evolution that neglects it. Coming back to our initial equations establishing the relation between $\widetilde{U}$ and $\widetilde{u}$, we see that the sudden approximation on $\widetilde{U}'$ has the desirable properties since the term neglected goes to zero when $t_{\rm coll}/t_{\rm corr}$ goes to zero. Therefore Eq. (11) is the form for the evolution operator in the absence of dynamic correlation.

D. Generality of the FCA

To conclude this section, we would like to note the generality of our formalism. The term W that we wish to treat approximately may be the whole electron-electron interaction V_{ee}. It is quite clear that nothing is changed formally if we split the Hamiltonian in a different way. A first possibility would be to approximate only part of V_{ee}. The potential V_{ee} would be split into say W_1+W and W_1 would be included in h_0 whereas W would be treated approximately along the line developed above. For example, one could think, in the spirit of the Hartree-Fock approximation, of defining W_1 as an averaged screening potential whereas the complement W would correspond to something that could be called correlation. It is not clear how one can perform such a division of V_{ee} as exemplified by the difficulties encountered in the time-dependent Hartree-Fock method. What we want to stress here is that an approximate treatment of W can always be done along the line developed above.

Another class of approximations could be built by adding part of $V(t)$ to W and freezing the combination of both. We just mention this option in passing as a full discussion is not the objective of our present work.

III. APPLICATIONS

A. Relation with the independent-electron model

In the independent-electron model the electron-electron interaction V_{ee} is approximated by a sum of one-electron potentials for the definition of the initial state as well as for the time evolution of the system:

$$W_1=\sum_n W_n^i. \qquad (34)$$

Here the index n means that the corresponding operator acts only on functions of the electron n. The evolution operator in

the IEM includes the effect of W_1 and because of (34) it can be written as a product of one-electron operators:

$$\widetilde{U}^{\text{IEM}}(t,t') = \prod_n \widetilde{U}_n^{\text{IEM}}(t,t'), \tag{35}$$

where $\widetilde{U}_n^{\text{IEM}}(t,t')$ is acting only on functions of electron n. The same property applies in the FCA:

$$\widetilde{u}(t,t') = \prod_n \widetilde{u}_n(t,t'). \tag{36}$$

In the IEM the initial and final states are described by a single Slater determinant. In contrast, the initial and final states used in the FCA fully include electron correlation and therefore they are written as linear combinations of Slater determinants [see Eq. (15)].

To be more specific, we consider the case of two electrons with different spins when spin dependent forces are neglected. In the IEM, the initial and final states take the form

$$\widetilde{\psi}_{I,F}^{\text{IEM}} = \varphi_i^{I,F}(1)\varphi_j^{I,F}(2) \tag{37}$$

so that

$$t_{IF}^{\text{IEM}} = \lim_{t\to\infty} \lim_{t'\to-\infty} \langle \varphi_k^F(1)|\widetilde{U}_1^{\text{IEM}}(t,t')|\varphi_i^I(1)\rangle$$

$$\times \langle \varphi_l^F(2)|\widetilde{U}_2^{\text{IEM}}(t,t')|\varphi_j^I(2)\rangle \tag{38}$$

whereas in the FCA

$$\widetilde{\psi}_{I,F} = \sum_{ij} \alpha_{ij}^{I,F} \varphi_i^{I,F}(1)\varphi_j^{I,F}(2) \tag{39}$$

and

$$t_{IF} = \lim_{t\to\infty} \lim_{t'\to-\infty} \sum_{ijkl} \alpha_{ij}^I \alpha_{kl}^F \langle \varphi_k^F(1)|\widetilde{u}_1(t,t')|\varphi_i^I(1)\rangle$$

$$\times \langle \varphi_l^F(2)|\widetilde{u}_2(t,t')|\varphi_j^I(2)\rangle. \tag{40}$$

The potential neglected in the IEM (in both the initial state and the evolution operator) is

$$W = V_{ee} - W_1. \tag{41}$$

Now, as discussed at the end of Sec. II, the FCA can also include the effect of W_1 in the evolution of the system through h_0 (hence freezing only W instead of V_{ee}). In this case, $\widetilde{u}_n(t,t') = \widetilde{U}_n^{\text{IEM}}(t,t')$, and therefore the IEM can be obtained from the FCA by restricting the sum in Eq. (39) to a single term. It is important to note that correlation may be neglected in the dynamics while being fully included in the initial and final states (as in the FCA) but that the converse is not true. If the channel Hamiltonians do not include correlation, then it makes no sense to include correlation in the collision since otherwise the interaction potential would not go to zero at infinity. Any approximation on the definition of the asymptotic states must be consistent with the Hamiltonian describing the time evolution.

In spite of the similarity between the IEM and the FCA, the physical content of the two approximations is different. In one case (the IEM) W is neglected throughout, i.e., one assumes that the neglected part is *weak*. In the other case (the FCA) we assume nothing on the *strength* of W but that $\widetilde{W}$ evolves slowly in time. From the previous analysis, it is clear that the IEM is the particular form taken by the FCA when an independent-electron approximation is valid for both the initial and final states.

B. Perturbation theory and multiple excitation processes

A lot of work has been devoted to the interpretation of multiple-electron processes at high energies using the perturbative approach and the IEM picture because the latter gives simple interpretations of the mechanisms involved in multielectron processes. Consider again for simplicity the case of two electrons with different spins. If we neglect completely the interaction of, say, electron 1 with the projectile, then

$$t_{IF}^{\text{IEM}} = \lim_{t\to\infty} \lim_{t'\to-\infty} \langle \varphi_k^F(1)|\varphi_i^I(1)\rangle\langle \varphi_l^F(2)|\widetilde{U}_2^{\text{IEM}}(t,t')|\varphi_j^I(2)\rangle. \tag{42}$$

The excitation of electron 1 arises only from the overlap between the initial and final orbitals, which is usually called *shakeoff* [9]. This result is independent of any approximation made on $\widetilde{U}_2^{\text{IEM}}$. In particular, the first order of perturbation theory gives

$$t_{IF}^1[\text{IEM}] = t_{IF}^1(ij;kl) = -i\left\{ \langle \varphi_k^F(1)|\varphi_i^I(1)\rangle \int_{-\infty}^{+\infty} dt\langle \varphi_l^F(2)|\widetilde{V}_2(t)|\varphi_j^I(2)\rangle + \langle \varphi_l^F(2)|\varphi_j^I(2)\rangle \int_{-\infty}^{+\infty} dt\langle \varphi_k^F(1)|\widetilde{V}_1(t)|\varphi_i^I(1)\rangle \right\}, \tag{43}$$

which shows, as is well known, that shakeoff is necessary to produce a many-electron excitation to first order of perturbation theory.

To excite N electrons by ''independent'' interactions with the projectile, one needs to evaluate the Nth order of perturbation theory of the full N-electron problem. Thus the latter

processes decay faster with energy as N increases. To second order we get

$$t_{IF}^2[\text{IEM}] = t_a^2(ij;kl) + t_b^2(ij;kl), \tag{44}$$

where

$$t_a^2(ij;kl) = -\left\{\langle\varphi_k^F(1)|\varphi_i^I(1)\rangle\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt'\langle\varphi_l^F(2)|\widetilde{V}_2(t)\widetilde{V}_2(t')|\varphi_j^I(2)\rangle\right.$$

$$\left.+\langle\varphi_l^F(2)|\varphi_j^I(2)\rangle\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt'\langle\varphi_k^F(1)|\widetilde{V}_1(t)\widetilde{V}_1(t')|\varphi_i^I(1)\rangle\right\},$$

$$t_b^2(ij;kl) = -\left\{\int_{-\infty}^{+\infty}dt\langle\varphi_k^F(1)|\widetilde{V}_1(t)|\varphi_i^I(1)\rangle\int_{-\infty}^{+\infty}dt'\langle\varphi_l^F(2)|\widetilde{V}_2(t')|\varphi_j^I(2)\rangle\right\}. \quad (45)$$

The term t_a corresponds to a second order transition for one electron associated with a shake-off for the other, i.e., only one-electron interacts with the projectile. The term t_b corresponds to a product of one-electron amplitudes in first order of perturbation theory. Their relative importance, and their variation with energy in particular, depends on all parameters of the transition considered.

We turn now to the FCA approximation. The main result of Sec. II is that W and $V(t)$ *cannot* be treated on an equal footing: it is not possible to carry out a multiple scattering picture based on a perturbation expansion in both W and $V(t)$. Our theory shows that there is a *hierarchy* in approximating W and $V(t)$ since an approximate treatment of W requires $t_{corr} \gg t_{coll}$ and therefore it is only *within* the time interval t_{coll} that an approximation to $V(t)$ can be introduced. If we neglect completely the interaction of electron 1 with the projectile, then

$$t_{IF}^{FCA} = \lim_{t\to\infty}\lim_{t'\to-\infty}\sum_{ijkl}\alpha_{ij}^I\alpha_{kl}^F\langle\varphi_k^F(1)|\varphi_i^I(1)\rangle$$

$$\times\langle\varphi_l^F(2)|\widetilde{u}_2(t,t')|\varphi_j^I(2)\rangle. \quad (46)$$

The approximation on the dynamics is exactly the same as in the shakeoff case derived earlier in the IEM: electron 2 gets excited as a result of the role of W in the initial and/or final state. We do not see any reason not to call the corresponding process a shakeoff process. The fact that we describe the states of electron 1 in a Hartree-Fock or fully correlated manner is not relevant to the approximation made on the dynamics.

The first Born approximation is in the FCA:

$$t_{IF}^1[FCA] = \sum_{ijkl}\alpha_{ij}^I\alpha_{kl}^F t_{IF}^1(ij;kl). \quad (47)$$

For higher orders of the perturbation series the FCA leads to a great simplification with respect to the fully correlated calculation. A straightforward generalization of (45) shows that the evaluation of the second Born approximation reduces to the calculation of one-electron amplitudes:

$$t_{IF}^2[FCA] = \sum_{ij}\sum_{kl}\alpha_{ij}^I\alpha_{kl}^F\{t_a^2(ij;kl)+t_b^2(ij;kl)\}. \quad (48)$$

The same holds for higher orders of the perturbation expansion. In particular, this way of writing the Born series allows a simple interpretation of the cross sections in terms of the value and the sign of the projectile charge. A very good

example, concerning projectile charge sign effects on proton-helium and antiproton(electron)-helium collisions, has been reported recently [7].

The conclusion of this section is that, in order to study the order in the interaction $V(t)$, one *does not* need to work with the IEM or, in other words, one does not have to assume that electron correlation is weak, but that $t_{corr} \gg t_{coll}$. Therefore the validity of this kind of analysis is not restricted to the case of small W. Whereas the FCA represents a further step with respect to the IEM, it still allows us to use the terminology developed for the IEM (shakeoff, number of electron-projectile interactions, etc). In other terms, this terminology makes sense whenever the FCA is valid, i.e., whenever dynamic correlation is not important, independently of the approximation used for the initial and final states.

C. Close coupling

In the FCA, multielectron transition amplitudes can be written in terms of single-electron transition amplitudes and, as a consequence, FCA close-coupling calculations are much easier than the fully correlated ones. To illustrate this point, we consider a two-electron system. The eigenstates of h_0 are products of one-electron orbitals φ_j. The two-electron basis functions $\widetilde{\psi}_n$ can be expressed in terms of these as

$$\widetilde{\psi}_n = \sum_{jk}\alpha_{jk}^n\varphi_j\varphi_k. \quad (49)$$

Under the action of $\widetilde{u}(t,t_i)$ the previous form is conserved during the collision because $\widetilde{u}$ can be written as a product of one-electron operators [see Eq. (36)]. Therefore 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

$$\lim_{t_f\to\infty}\lim_{t_i\to-\infty}\widetilde{u}(t_f,t_i)\widetilde{\psi}_I = \sum_{j,k,l,m}\alpha_{jk}^I a_{jl}a_{km}\varphi_l\varphi_m, \quad (50)$$

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 us to produce a final correlated state $\widetilde{\psi}_F$ having a configuration mixing that may differ significantly from that of the initial state $\widetilde{\psi}_I$. From (50) it follows that the transition amplitude between initial and final correlated states can be written in terms of the one-electron amplitudes a_{jl}:

$$t_{IF} = \sum_{j,k,l,m} \alpha_{jk}^I \alpha_{lm}^F A_{jk}^{lm} = \sum_{j,k,l,m} \alpha_{jk}^I \alpha_{lm}^F a_{jl} a_{km}. \qquad (51)$$

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

As discussed in Sec. II, the FCA is also useful because it provides the reference calculation in which dynamic correlation is neglected. Then, the importance of dynamic correlation could be assessed by simply comparing with the corresponding fully correlated calculation. As the fully correlated problem cannot be exactly solved in practice, one has to restrict this comparison to a finite configuration space. The close-coupling formalism allows us to perform such a comparison in a meaningful way.

Let us call P the projection operator onto the basis set used to solve the close-coupling equations in the fully correlated case. Then, the close-coupling method consists in replacing Eq. (2) by

$$P\left(H_0 + V(t) - i\frac{d}{dt}\right)P\Psi^P(t) = 0, \qquad (52)$$

which can be solved exactly. Now, as we have already pointed out in a previous work [10], all formal expressions written above in Sec. II can be extended to the solution of (52) 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 (2) by the operator U^P (or u^P) associated with (52). In other terms, we are able to calculate exactly the operators $\widetilde{U}^P$ and $\widetilde{u}^P$ by restricting our problem to the P space. The same P space is used in both cases so the only difference between calculations with $\widetilde{U}^P$ or $\widetilde{u}^P$ is that W is frozen in the latter.

D. Relation with the forced impulse method

It is of interest to contrast our frozen-correlation approximation with the forced impulse method (FIM) of Reading and Ford [3,4]. There is some connection between both methods in the sense that they both make use of an evolution operator that does not include W. We will show, however, that there are important differences.

Let us call $U^{\text{FIM}}(t,t_1)$ the approximate operator (in the Schrödinger picture) used in the FIM method in the time interval $[t_1,t]$. From Eq. (8) of [4], it can be defined, in our notations, through the differential equation

$$i\frac{d}{dt}\widetilde{U}^{\text{FIM}}(t,t_1) = e^{iH_0 t}V(t)e^{-ih_0 t}\widetilde{u}(t,t_1)e^{ih_0 t}e^{-iH_0 t}. \qquad (53)$$

Comparing with Eq. (7), we see that FIM replaces the operator U in the right-hand side of (7) by

$$\widetilde{U}^F(t,t_1) = e^{iH_0 t}e^{-ih_0 t}\widetilde{u}(t,t_1)e^{ih_0 t}e^{-iH_0 t}. \qquad (54)$$

In the Schrödinger picture, one gets

$$U^F(t,t_1) = u(t,t_1)e^{[ih_0(t-t_1)]}e^{[-iH_0(t-t_1)]} \qquad (55)$$

and

$$i\frac{d}{dt}U^{\text{FIM}}(t,t_1) = H(t)U^F(t,t_1). \qquad (56)$$

We look at Eq. (55) over the small interval $[t_1,t_1+\delta]$

$$U^F(t_1+\delta,t_1) = [1 - ih(t)\delta + 0(\delta^2)][1 + ih_0\delta + 0(\delta^2)]$$
$$\times[1 - iH_0\delta + 0(\delta^2)]$$
$$= 1 - iH(t)\delta + 0(\delta^2) = U(t_1+\delta,t_1) + 0(\delta^2).$$
$$(57)$$

Comparing with (56)

$$U(t_1+\delta,t_1) = U^{\text{FIM}}(t_1+\delta,t_1) + 0(\delta^2). \qquad (58)$$

So the FIM operator is correct up to first order in δ which should be contrasted with approximation (11) which is only correct to zero order. So the FIM method provides an algorithm for the calculation of the *exact* evolution operator: by cutting the collision time in small enough intervals, the exact operator can be calculated to any prescribed accuracy. The big advantage is that, in each interval, the time evolution due to the projectile interaction enters only through the operator u which is much simpler to evaluate. This most remarkable property has been named by Reading and MacKeller [11] the *response theorem*. So the FIM method provides an algorithm in which the evolution under the action of $V(t)$ and W is completely separated over the interval δ. The use of this clever scheme is not restricted to the particular problem considered here [separation of $V(t)$ and W]. It can be generalized to any truncation of the full Hamiltonian $H(t)$. Of course the constraint on the value of δ will depend on how this splitting of $H(t)$ is done.

We can see immediately the basic difference between the FIM approach and the frozen-correlation method. In the latter we do not get an algorithm for the calculation of the exact evolution operator. This must be expected since W does not appear at all in our approximate evolution operator [whereas it appears explicitly through H_0 in the FIM, see Eq. (53)]. In fact, it can be easily verified that the results are unchanged when chopping the collision in small time intervals. The frozen correlation is an approximation to the exact evolution operator which can only be accurate when $t_{\text{corr}} \gg t_{\text{coll}}$. It is useful in two different circumstances.

(i) It provides a reference on what is the result of an evolution without dynamic correlation. This is of interest particularly when it is not valid since dynamic correlation will be precisely the difference between the exact result and the one given by the frozen-correlation calculation. To make our point clear, let us make an analogy with the Born approximation. It is often very useful to compare the exact results with those obtained in the first Born approximation since it allows us to sort out the contribution of higher orders of the Born series. So a Born calculation may be of great value for comparison purposes when it is not accurate. The frozen-correlation calculation plays the role of such a reference as far as dynamic correlation is concerned.

(ii) It is useful in its own stand to allow calculations without dynamic correlation when the exact calculation is not possible. It provides a well defined approximation in which correlation in the initial and final states can be fully included.
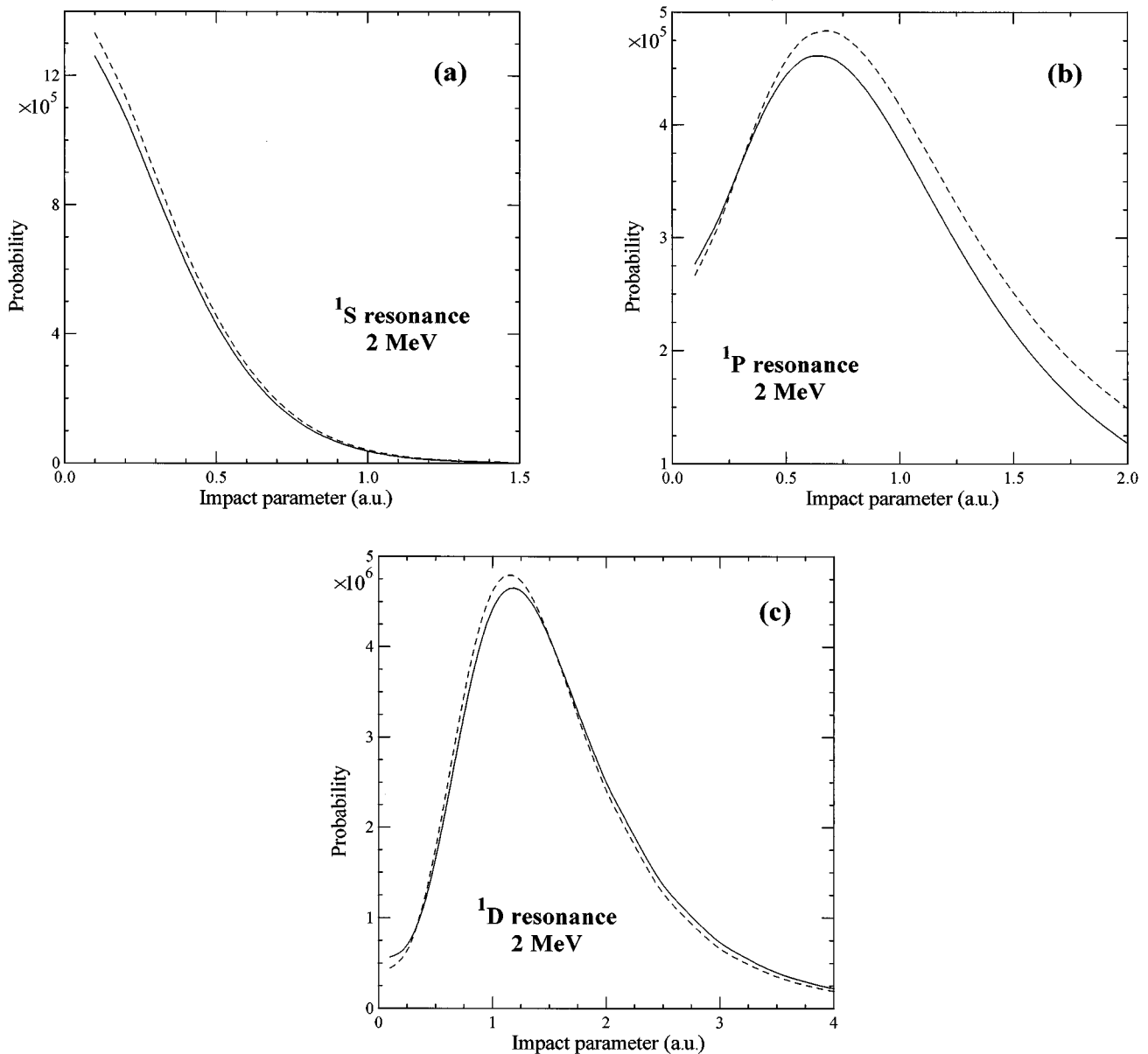
FIG. 1. Excitation probability of the first (a) $^1S^e$, (b) $^1P^o$, and (c) $^1D^e$ doubly excited state of He by 2-MeV protons as a function of impact parameter. The full curves correspond to calculations including dynamic correlation and the dashed curves to the frozen-correlation approximation.

It is particularly suited to cases when correlation cannot be neglected in the final state, e.g., when the latter is a multiply excited state, as we show later.

IV. RESULTS FOR DOUBLE EXCITATION

We apply the above formalism to double excitation of He with $W = V_{ee}$ in our FCA calculations. 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. We have used a close-coupling method to solve the TDSE 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 [10,13] for details). The description of the resonant states makes use of the Feschbach formalism in which one splits

the whole Hilbert space into two subspaces with corresponding projection operators P and Q. The doubly excited states correspond to bound eigenstates of QH_0Q and the continuum states to eigenstates of PH_0P. Electron correlation is included in both Q and P states. They are coupled by the nondiagonal PH_0Q operator. From our calculations, we may obtain the probability of exciting the doubly excited Q states as a function of impact parameter. Results are given in Fig. 1 for 2 MeV proton impact in both the fully correlated and frozen-correlated calculations. The difference between both calculations is very small. Similar results were obtained down to 0.5 MeV. These results show that double excitation does not require dynamic correlation in the corresponding energy range.

However, double excitation cannot be observed as such: it shows up as a resonance effect in the spectrum of electrons
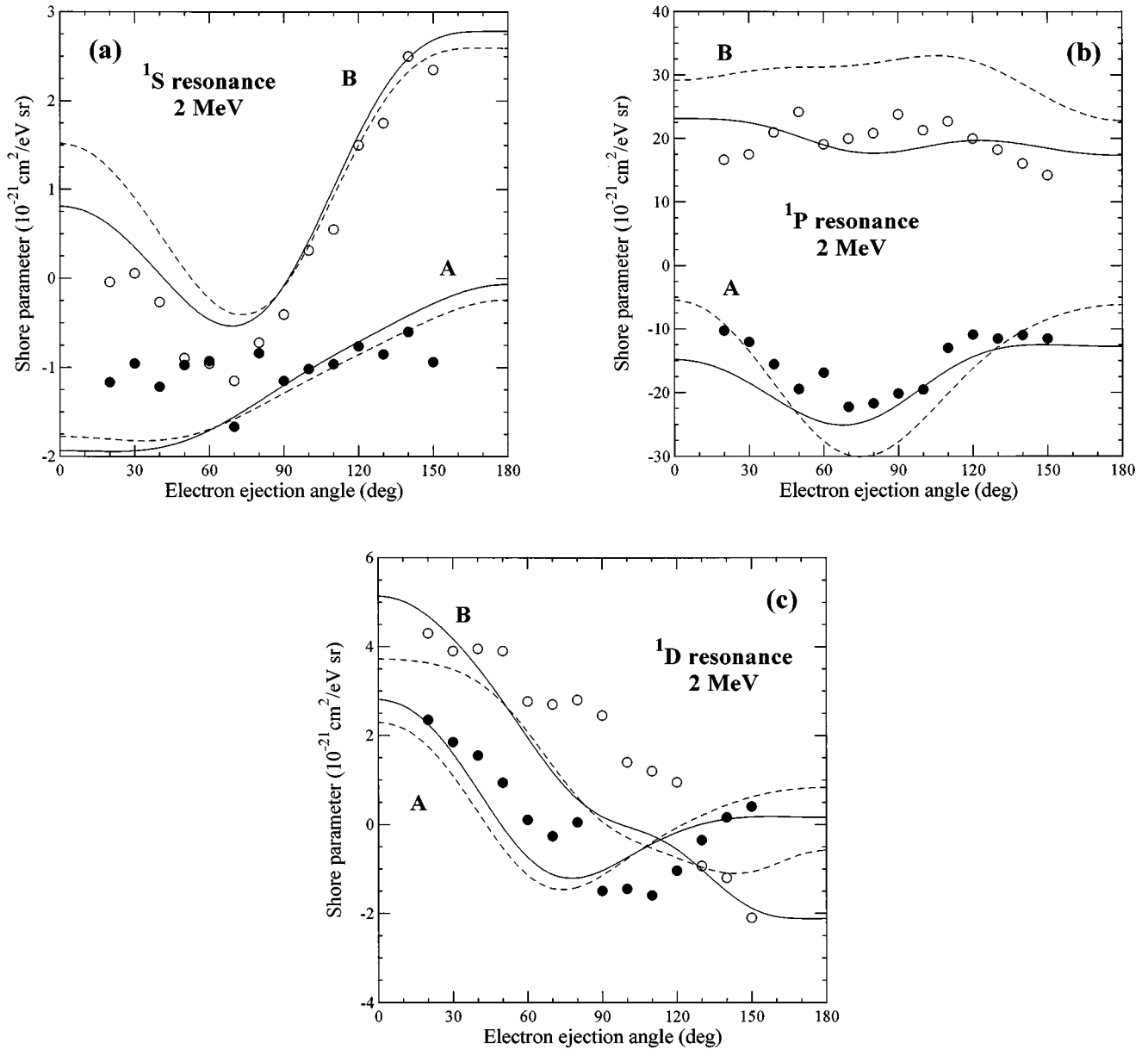
FIG. 2. Shore parameters for excitation of the first (a) $^1S^e$, (b) $^1P^o$, and (c) $^1D^e$ resonance of He by 2-MeV protons as a function of electron ejection angle. Circles: experiments of [12] for the A parameter (closed circles) and B parameter (opened circles). The full curves correspond to calculations including dynamic correlation and the dashed curves to the frozen-correlation approximation.

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

$$Y(\epsilon) = [A(\hat{\mathbf{k}})\epsilon + B(\hat{\mathbf{k}})]/(1+\epsilon^2), \qquad (59)$$

where $\epsilon = 2(E_{el} - E_r)/\Gamma_r$, E_r and Γ_r are the resonance position and width, and E_{el} 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 (59) corresponds to an interference pattern due to PH_0Q involving the effect of electron correlation over a time much larger than t_{coll}. Consequently, as the very definition of the Shore parameters involves elec-

tron correlation, no observable quantity can be determined without incorporating electron correlation in the final state.

In Fig. 2 we show the Shore parameters A and B corresponding to the lowest singlet resonances of He excited by 2-MeV protons obtained with the FCA and fully correlated calculations. A detailed comparison with the experiments of Bordenave-Montesquieu *et al.* [12] has been performed earlier and we have already shown [12,13] that our fully correlated coupled-state calculations describe well the experimental findings under impact of protons with energies 0.1–3 MeV. In the case of the $^1S^e$ and $^1D^e$ resonances, one can observe good agreement between the frozen-correlated and fully correlated results. This implies that, although electron correlation is very important for $t \gg t_{coll}$ in describing the interference between double excitation and ionization, it does not play a significant role *during* the collision. This is
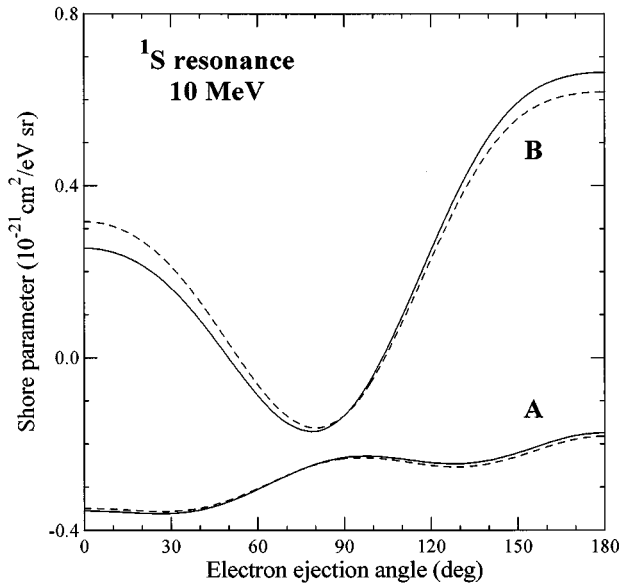
FIG. 3. Shore parameters A and B for excitation of the first $^1S^e$ resonance of He by 10-MeV protons as a function of electron ejection angle. The full curves correspond to calculations including dynamical correlation and the dashed curves to the frozen-correlation approximation.

further confirmed by the value $t_{coll}/t_{corr} \simeq 0.02$ resulting from Eq. (33) for $\rho = 0.1 - 1.0$ au. For the $^1P^o$ resonance, the agreement between the two calculations is slightly worse (see also Fig. 1) 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_{coll}/t_{corr} increases slowly with ρ). The fact that the agreement between the two calculations is worse in Fig. 2 than in Fig. 1 is due to two related factors. First, the interference patterns described by the Shore parameters are very sensitive to any detail in the calculation. Second, the ionization amplitude is sensitive to dynamic correlation particularly in the forward and backward directions as discussed in the next section.

One expects the difference between the fully correlated and frozen-correlated results to decrease with increasing collision energy because t_{coll} decreases. This is indeed the case as proved by our results for 10 MeV given in Fig. 3. The difference is still relatively small at 0.5 MeV (Fig. 4). 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 $\simeq v/\Delta E$ (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. Our results for 1.5 MeV/amu F^{9+} impact (Fig. 5) show that the frozen-correlation approximation is less accurate than for proton impact. The reason is that t_{coll} increases with Z_P because of contributions from an increasing range of internuclear distances (we get $t_{coll}/t_{corr} \simeq 0.1$). Therefore our results confirm that the relevant parameter is not the correlation strength (which should be relatively smaller with increasing Z_P) but the correlation time. This observation together with our earlier discussion on the dependence of the Shore parameters on the projectile charge sign [7] calls for a
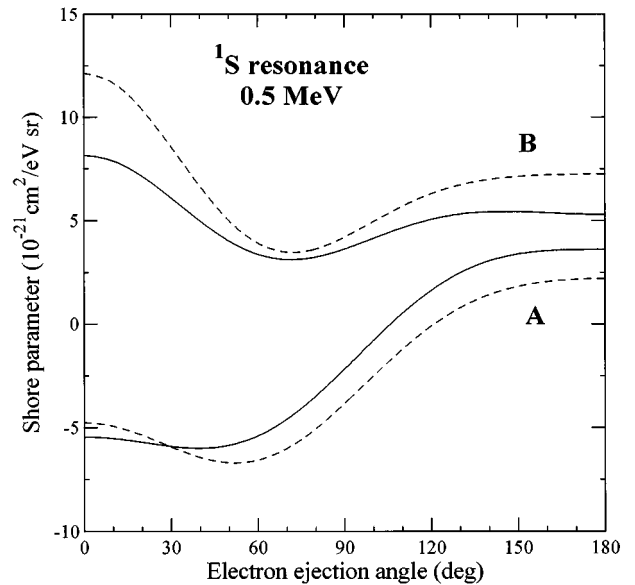

FIG. 4. Same as Fig. 3 for 0.5-MeV protons.

reassessment of the role of dynamic correlation in explaining the Z_P behavior of multiple-electron excitation.

V. IONIZATION

The results given in the preceding section have shown that the effect of dynamic correlation is much stronger on the resonance shape that on the resonance yield and that the resonance shape is more sensitive to correlation in the forward and backward directions than around 90°. This can be understood by looking at ionization. Our discrete representation of the continuum allows us to evaluate accurately the ionization cross section as a function of electron angle. Results have been given for an ejected electron energy in the resonance region [13,14] or for the ejection of low-energy electrons [15]. We have also proved that our calculations account for the *two-center effect* due to the fact that the ejected electron moves in the field of two Coulomb centers: that of the ionized target and that of the projectile [13–15]. The two-center effect enhances the emission of electrons in the forward direction and decreases it in the backward direction [16].

We give in Fig. 6 our results for the ionization cross section as a function of electron ejection angle for both the frozen- (with $W = V_{ee}$) and fully-correlated calculations. The ejected electron energy is 33 eV, i.e., that corresponding to the first resonances. It is immediately seen that the largest difference between the two calculations appears in the forward and backward directions. These are precisely the regions for which the two-center effect is stronger [16]. That there is a strong relation between dynamic correlation and the two-center effect can be easily understood. The two-center effect is related to a long-range interaction with the projectiles which introduces, in a close-coupling calculation, a coupling between the various angular momenta in the final channel. The screening of the target nuclear charge by the bound electron felt by the ejected electron differs appreciably from the screening in the initial bound state. The absence of dynamic correlation does not allow a variation of this screen-
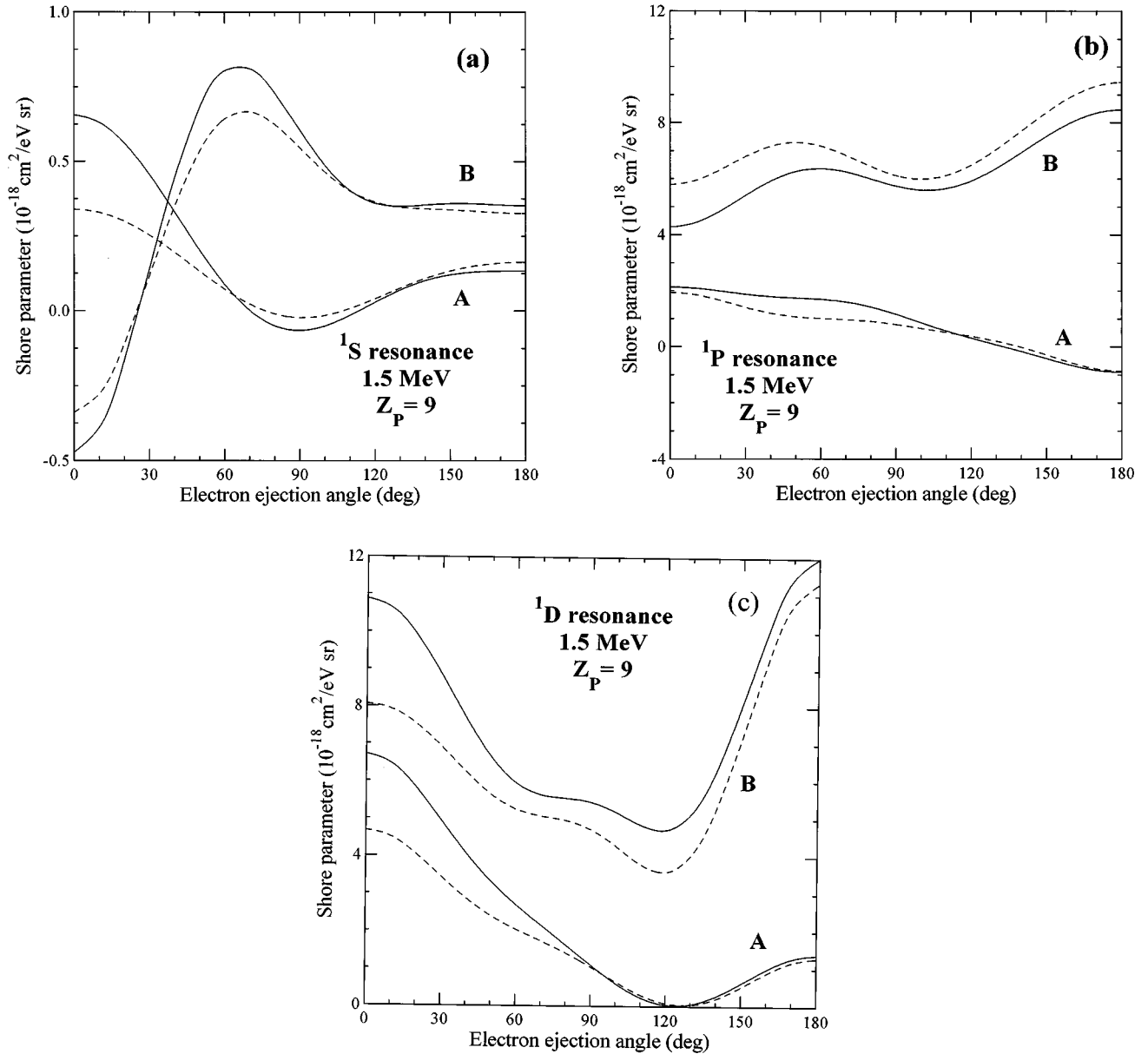
FIG. 5. Shore parameters for excitation of the first (a) $^1S^e$, (b) $^1P^o$, and (c) $^1D^e$ resonance of He by 1.5-MeV/amu F^{9+} ions as a function of electron ejection angle. The full curves correspond to calculations including dynamic correlation and the dashed curves to the frozen-correlation approximation.

ing during the collision as in fully correlated calculation. It is therefore not surprising that the two-center effect be reduced by comparison with the fully correlated calculation. Our analysis can be confirmed by looking at the ratio between the frozen and correlated calculations as a function of Z_P as shown in Fig. 7. For $30 < \theta < 120$, both calculations yield similar results. Forward scattering is dominated by the two-center effects and it can be seen that the difference between the two calculations decreases when the projectile charge increases, as expected. The situation is slightly more complex in the backward direction: the decrease of the cross section in the backward direction is due to a destructive interference between the amplitudes for the various angular momenta, which make the results sensitive to any approximation. However, it can be checked that the cross-section

ratio (Fig. 7) increases when Z_P increases and becomes larger than one for $Z_P = 6$ and 9. In the latter case, the two-center effect is strong and therefore the decrease in the target nucleus screening induces an increase in the electron yield (an effect opposite to the one seen in the forward direction).

To summarize, we can say that the two-center effect amplifies the role of dynamic correlation. This is totally consistent with the theory developed in the previous sections: the long-range interaction between the projectile and target electron is associated with a much longer collision time.

VI. CONCLUSION

We have shown that the theory not including dynamic correlation corresponds to the limit $t_{\mathrm{corr}}/t_{\mathrm{coll}} \to \infty$. It does not
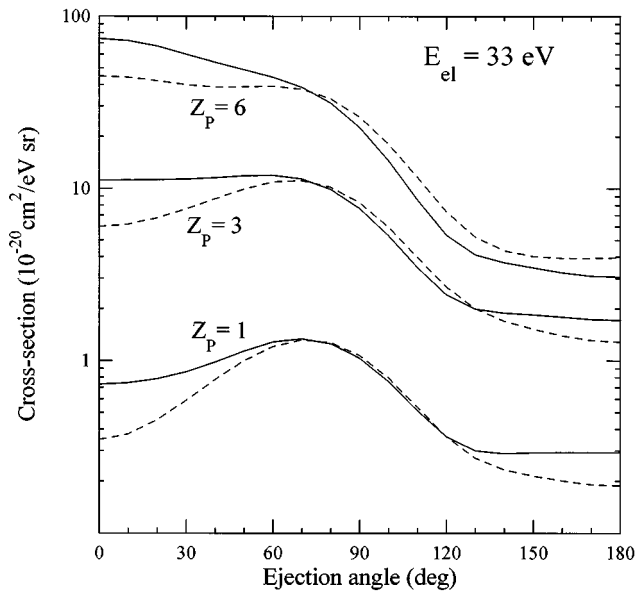
FIG. 6. Ionization cross section for the ejection of a 33-eV electron from He by bare ions of charge $Z_P = 1$, 3, 6 and energy 1.5 MeV/amu as a function of electron ejection angle. The full curves correspond to calculations including dynamic correlation and the dashed curves to frozen correlation.
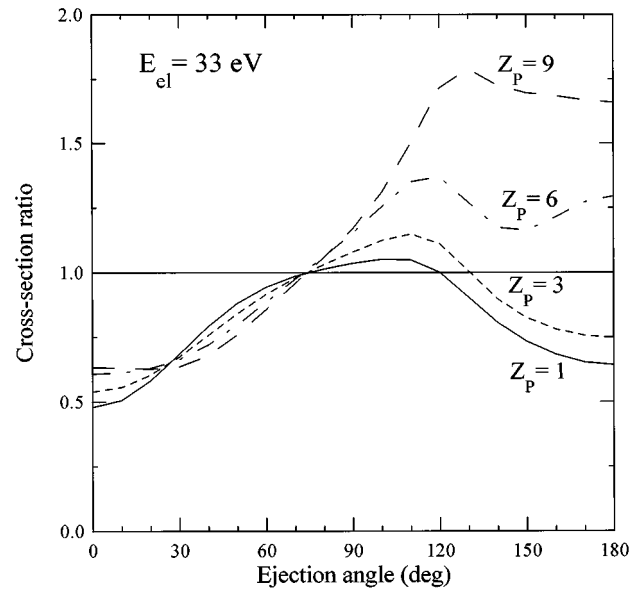

FIG. 7. Ratio of the He ionization cross section in the frozen-correlation approximation to the fully correlated result as a function of electron ejection angle. The ejected electron energy is 33 eV and the projectiles are bare ions of charge $Z_P = 1$, 3, 6, 9 and energy 1.5 MeV/amu.

correspond to any assumption on the strength of correlation but only to its time evolution. The FCA provides the reference calculation in which dynamic correlation is neglected. We have carried out calculations for double excitation and single ionization of helium with and without dynamic correlation. We have thus obtained a rigorous evaluation of the specific role of dynamic correlation in these collisions. We have shown in particular that the role of dynamical correlation is more important for single ionization of helium in the forward and backward direction than for double excitation.

The frozen-correlation approximation provides a convenient generalization of the independent-electron model since the former includes correlation in the initial and final states. The structure of the FCA is quite close to that of the IEM and it cannot be excluded that it may be the explanation for the success of the IEM in various cases. The FCA improves over the IEM while still allowing us to use the terminology of many-electron ion(atom)-atom collisions originally set up in the context of the IEM (shake off, number of interactions with the projectile, etc.). Finally the frozen-correlation approximation allows us to do calculations in a simple way for processes like double capture for which the inclusion of dynamic correlation is extremely difficult.

We have considered specifically cases in which the correlated particles are on the same atom (target or projectile) before and after the collision, like double excitation of helium or double capture from helium. In these cases, a perturbative approach of correlation is not appropriate because correlation does not go to zero asymptotically. The situation is different in a case like

$$H(1s) + H(1s) \rightarrow H(1s) + H(2p). \tag{60}$$
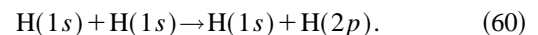
Obviously correlation goes to zero asymptotically so perturbation theory, if valid, may be applied without contradiction [17].

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