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Time ordering in atomic collisions

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Abstract. We present a general treatment for the effect of time ordering in the many-electron processes induced by charged-particle impact. We show that time ordering is essential in order to obtain odd power Z terms in the cross section which is necessary to get different values for positively and negatively charged projectiles. A second-order calculation is performed for the double ionization of helium. The electron–electron interaction is taken into account only by the shake-off term. The interference between the shake-off and second-order term is responsible only for a part of the dependence of the cross sections on the sign of the charge of the projectile.

1. Introduction

The fact that the cross sections for two-electron processes in high-velocity atomic collisions with charged particles (double ionization, ionization excitation, double excitation) vary with the sign of the charge was treated theoretically by several groups [1–6]. McGuire [1] has suggested that the interference between the first-order (shake) and the second-order (TS2) amplitudes gives rise to a Z^3 term in the cross section, and this is the cause of the difference. Becker [7], assuming that the collision is dipole dominated, has shown that, because the shake mechanism is monopole in character, the two amplitudes do not interfere.

Reading and Ford [2] have made the first elaborate calculations for a two-electron transition, the double ionization of helium, using the forced-impulse method. They have shown that, for the double ionization, even for relatively high energies, there are significant non-dipole contributions, and the Z^3 terms are important. They have obtained the observed difference in the cross sections for positively and negatively charged projectiles. In a recent, more complete work [8] they have reported very good quantitative agreement with experimental data for the double-ionization cross section of helium by charged particles. From their complicated calculations one cannot separate the contributions of different simple mechanisms.

One of the aims of the present paper is to investigate to what extent the interference between the shake and the TS2 amplitude is responsible for the Z^3 term.

In order to obtain the interference term we must go beyond the independent-electron approximation for the TS2 process, where the two-electron amplitude is considered a product of two one-electron amplitudes [9, 10]. In this approximation the shake-off and the TS2 amplitudes do not interfere, because they are 90° out of phase.

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If one treats the two-electron process within the time-dependent perturbation theory, the probability amplitude can be expressed in terms of the Dyson series [11, 12]. A higher-order term contains a succession of interactions with the projectile in different moments of time. Generally the operators describing the interactions occurring in different moments do not commute, one has to take into account the proper order of the interactions. It is usual to define a time-ordering operator, which takes care of the time ordering. McGuire and Straton [5] have shown that time ordering is essential in order to obtain the Z^3 term in the cross section for a two-electron process. They have applied the theory for the double excitation of helium [5, 13] using correlated two-electron wavefunctions. The difference in cross sections obtained for positive and negative projectiles has proved to be very small.

Stolterfoht [14] has given a simple method for evaluating the time-ordered second-order amplitude for relaxed orbitals. Furthermore, for the particular case of frozen orbitals, he has shown that, if in a two-electron process the effect of one electron on the other during the collision is neglected, the TS2 amplitude reduces to a product of one-electron amplitudes. So this is in fact the independent-electron approximation, and the time ordering is lost. In some special cases, when one of the intermediate states is forbidden by the Pauli exclusion principle, time ordering occurs even for frozen orbitals [15, 16]. In a recent paper Végh *et al* [17] have separated the time-ordering contribution to the second-order amplitude, taking into account the change in the screening potential during the collision. They have performed calculations for the double excitation of lithium, where the time-ordering effect has been proved to be significant.

In the present paper we present a general discussion on the time-ordering effect, and we link the different treatment of McGuire and Straton [5], Stolterfoht [14] and Végh *et al* [17]. We present calculations for the double ionization of helium, comparing our results with the cross sections obtained by Ford and Reading [8] and the experimental data. The importance of the considered two mechanisms (shake-off and TS2), and the effect of time ordering is discussed.

2. Time ordering in general

2.1. Evolution of the electronic system

The ionization and the excitation of atoms and molecules by charged particles with high energy can be described semiclassically, i.e. the projectile moves on a classical trajectory. In most of the cases the trajectory can be assumed to be linear, and the reaction of the target on the projectile can be neglected.

The probability amplitude for a given $i \to f$ transition of the target electrons is given by the matrix element

$$a(\boldsymbol{B}) = \langle f|U(-\infty, +\infty)|i\rangle, \tag{1}$$

where $\boldsymbol{B}$ is the impact parameter and U is the evolution operator of the electronic system. The evolution operator can be obtained by solving the time-dependent Schrödinger equation in the interaction picture

$$i\frac{\partial}{\partial t}U(t, t_0) = V_I(t)U(t, t_0) \tag{2}$$

with the condition $U(t_0, t_0) = 1$. Here

$$V_I(t) = \mathrm{e}^{\mathrm{i}H_0 t}V(t)\mathrm{e}^{-\mathrm{i}H_0 t}. \tag{3}$$

H_0 is the unperturbed Hamiltonian of the target electrons, and $V(t)$ is the interaction potential between the projectile and the target electrons in the Schrödinger picture. Integrating formally equation (3) we obtain the integral equation

$$U(t,t_0) = 1 - \mathrm{i}\int_{t_0}^{t} \mathrm{d}t'\, V_I(t')U(t',t_0) \tag{4}$$

which can be solved by successive iterations. The solution is an expansion in the powers of the perturbative interaction and it is equivalent to the Born series

$$\begin{aligned} U(t,t_0) &= 1 + \sum_{n=1}^{\infty}(-\mathrm{i})^n \int_{t_0}^{t} \mathrm{d}t_n\, V_I(t_n) \int_{t_0}^{t_n} \mathrm{d}t_{n-1}\, V_I(t_{n-1}) \ldots \int_{t_0}^{t_2} \mathrm{d}t_1\, V_I(t_1) \\ &= 1 + \sum_{n=1}^{\infty}(-\mathrm{i})^n \int_{t_0}^{t} \mathrm{d}t_n\, V_I(t_n) \int_{t_0}^{t} \mathrm{d}t_{n-1}\, \Theta(t_n - t_{n-1}) V_I(t_{n-1}) \ldots \\ &\quad \ldots \int_{t_0}^{t} \mathrm{d}t_1\, \Theta(t_2 - t_1) V_I(t_1). \end{aligned} \tag{5}$$

Here $\Theta(t_i - t_{i-1})$ is the Heavyside step function.

2.2. Time ordering

In general the operators $V_I(t)$ do not commute for different values of time, and formula (5) expresses causality. Since $t_i > t_{i-1}$, the operator $V_I(t_i)$ has to be on the right side of the $V_I(t_{i+1})$. It is usual to write this formula in a form given by Dyson, extending formally the region of each integral to (t_0, t)

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} T \int_{t_0}^{t} \mathrm{d}t_n\, V_I(t_n) \int_{t_0}^{t} \mathrm{d}t_{n-1}\, V_I(t_{n-1}) \ldots \int_{t_0}^{t} \mathrm{d}t_1\, V_I(t_1). \tag{6}$$

The T time-ordering operator takes care of the arrangement of the n factors $V(t_i)$ in the order of increasing time from right to left, and the factor of $1/n!$ corrects for multiple counting of time regions [12]. Thus $U(t,t_0)$ is constrained by T to 'propagate' forward in time. Specifically, T imposes causality on $U(t,t_0)$ by enforcing $t_i > t_{i-1}$. This condition is the same classically and quantum mechanically. The operator T does not cause a finite spread over time, Δt of wavepackets.

If we approximate T by $T_{\mathrm{av}} = 1$, we neglect the time order in which the successive interactions occur and we have no time-ordering effect.

2.3. The effect of time ordering

If $T = T_{\mathrm{av}} = 1$ then there is no effect due to the time order of the interaction terms. Consequently, the effect of time ordering is carried by the operator

$$T - T_{\mathrm{av}} = n! \prod_{1}^{n} \Theta(t_i - t_{i-1}) - 1. \tag{7}$$

Referring to the cross sections calculated neglecting the time ordering we can state the following theorem, proposed earlier by McGuire and Straton [5] and Stolterfoht [14]. Now a general proof will be given.

Theorem 1. Transition probabilities and cross sections do not depend on the sign of the projectile (i.e. $Z \to -Z$) if the effects of time ordering are ignored.

Proof. If the effects of time ordering are ignored, then $T = T_{\rm av} = 1$ and,

$$U(\infty, -\infty) = \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{\infty} V_I(t_n)\mathrm{d}t_n \ \ldots \int_{-\infty}^{+\infty} V_I(t_1)\mathrm{d}t_1$$
$$= U_{\rm even} + \mathrm{i}U_{\rm odd} \tag{8}$$

where $U_{\rm even}$ and $U_{\rm odd}$ are even and odd in V (or Z). Each factor of $\int_{-\infty}^{+\infty} V_I(t)\,\mathrm{d}t$ can be regarded as causing the transition of the system from a state $|I'\rangle$ to a state $|I\rangle$, and yields a matrix element of $\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}(E_I - E_{I'})t}\langle I|V(t)|I'\rangle\,\mathrm{d}t$ which is purely real or purely imaginary depending on the parity of the states (real for $l + m - l' - m'$ even and imaginary, if this sum is odd). Because in the product of the integrals each intermediate state occurs twice, the phase of the product depends only on the parity of the initial and the final states. Thus, for a given transition, $U_{\rm even}$ and $U_{\rm odd}$ are purely real (or purely imaginary). Consequently,

$$|a|^2 = |\langle f|U(\infty, -\infty)|i\rangle|^2 = U_{\rm even}^2 + U_{\rm odd}^2 \tag{9}$$

which is an even function of Z, and thus invariant under $Z \to -Z$.

Dependence on the sign of the charge of the projectile is obtained only if one has odd terms in Z. This is possible only by the interference between $U_{\rm even}$ and $U_{\rm odd}$. Including time ordering each term may have real and imaginary parts, thus the interference occurs. □

3. Time ordering in second order

Expanding the evolution operator, U, in powers of the interaction potential, V, one has,

$$a = a^{(1)} + a^{(2)} + \cdots + a^{(N)} + \cdots. \tag{10}$$

Now we truncate the expansion past second order in V so that

$$a \simeq a^{(1)} + a^{(2)}. \tag{11}$$

A variety of cases for the interaction V are possible. If all electron–electron interactions are included in the H_0 Hamiltonian, than $V(t)$ is the sum of the individual projectile–electron interactions $\sum_{i=1}^{n} V_i(t)$, where n is the number of active electrons. Applying the many-body perturbation theory, $V(t)$ may contain electron–electron interactions, also.

3.1. One-electron transitions

Let us consider first the interaction with only a single electron, i.e. $V = V_1$. For the first-order term in V_1 one has

$$a^{(1)} = -\mathrm{i}\langle f| \int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}H_0 t} V_1(t) \mathrm{e}^{-\mathrm{i}H_0 t}|i\rangle$$
$$= -\mathrm{i} \int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}(E_f - E_i)t}\langle f|V_1(t)|i\rangle. \tag{12}$$

This term contains no time ordering. This amplitude is imaginary for even-parity transitions and real for odd-parity transitions.

The second order amplitude in V_1 is given by,

$$a^{(2)} = -\langle f| \int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}H_0 t} V_1(t) \mathrm{e}^{-\mathrm{i}H_0 t} \int_{-\infty}^{t} \mathrm{d}t'\ \mathrm{e}^{-\mathrm{i}H_0 t'} V_1(t') \mathrm{e}^{\mathrm{i}H_0 t'}|f\rangle$$
$$= -\sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}(E_f - E_k)t}\langle f|V_1(t)|k\rangle \int_{-\infty}^{t} \mathrm{d}t'\ \mathrm{e}^{\mathrm{i}(E_k - E_i)t'}\langle k|V_1(t')|i\rangle$$

$$= -\sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}E_f t}\langle f|V_1(t)|k\rangle \int_{-\infty}^{\infty} \mathrm{d}t'\, \Theta(t-t')\mathrm{e}^{\mathrm{i}E_k(t-t)'}\langle k|V_1(t')|i\rangle \mathrm{e}^{-\mathrm{i}E_i t'}. \tag{13}$$

There is an illustrative way for separating the term responsible for the time-ordering effect [5, 13]. We perform the following Fourier transformation

$$\begin{aligned}\Theta(t-t')\mathrm{e}^{\mathrm{i}E_k(t-t')} &= \int_{-\infty}^{+\infty} \mathrm{d}\Omega\, \mathrm{e}^{-\mathrm{i}\Omega(t-t')}\left[\delta(\Omega - E_k) + \frac{\mathrm{i}}{\pi} P \frac{1}{\Omega - E_k}\right] \\ &\equiv [\delta_{av} + \mathrm{i}P]\end{aligned} \tag{14}$$

where δ_{av} and $\mathrm{i}P$ denote operators.

For the second-order amplitude we obtain

$$\begin{aligned}a^{(2)} = -\sum_k \frac{1}{2}\Bigg[&\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t}\langle f|V_1(t)|k\rangle \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'}\langle k|V_1(t')|i\rangle \\ &+ \frac{\mathrm{i}}{\pi}\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}E_f t}\langle f|V_1(t)|k\rangle \int_{-\infty}^{+\infty} \mathrm{d}t'\, P \\ &\times \int_{-\infty}^{+\infty} \mathrm{d}\Omega\, \mathrm{e}^{-\mathrm{i}\Omega(t-t')}\frac{1}{\Omega - E_k}\mathrm{e}^{-\mathrm{i}E_i t'}\langle k|V_1(t')|i\rangle\Bigg] \\ = a^{(2)}_{\text{no time ordering}} &+ \mathrm{i}a^{(2)}_{\text{time ordering}}.\end{aligned} \tag{15}$$

Here the first term can be identified as the time-averaged T_{av} term, obtained by taking $T = 1$. This is 90° out of phase with the first-order term and does not interfere. The second term is only responsible for the time-ordering effect and does interfere with the first-order term.

Any Z^3 effects such as polarization of the target electron cloud (including those in classical particle calculations such as CTMC) arise from the interference between the first-order amplitude and the $T - T_{\mathrm{av}}$ contribution of the second-order amplitude. These effects may always be associated with time-ordering effects.

3.2. Two-electron transitions

For systems with two electrons that interact with the projectile, we take $V = V_1 + V_2$. Now the H_0 Hamiltonian for the atom includes the $1/r_{ij}$ electron–electron interaction, which leads to electron correlation, namely

$$H^0 = \sum_i \left[-\frac{\nabla_i^2}{2} - \frac{Z_T}{r_i} + \sum_{j<i}\frac{1}{r_{ij}}\right]. \tag{16}$$

The first-order amplitude in V for the two-electron transition is similar to that for the one-electron transition.

$$\begin{aligned}a^{(1)} &= -\mathrm{i}\langle f|\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}H_0 t}[V_1(t) + V_2(t)]\mathrm{e}^{-\mathrm{i}H_0 t}|i\rangle \\ &= -\mathrm{i}\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_i)t}\langle f|[V_1(t) + V_2(t)]|i\rangle.\end{aligned} \tag{17}$$

Here $|i\rangle$ and $|f\rangle$ are two-electron wavefunctions.

If many-body perturbation theory is used, these wavefunctions are written as a product of one-electron wavefunctions. In the many-body perturbation picture the transition of the

second electron is caused by an electron–electron interaction. In this picture the lowest-order amplitude is of second order.

The second-order amplitude in the projectile–electron interaction, V, is given by

$$a^{(2)} = -\sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t} \langle f|[V_1(t) + V_2(t)]|k\rangle \times \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'} \langle k|[V_1(t') + V_2(t')]|i\rangle. \tag{18}$$

The terms in $(V_1)^2$ and $(V_2)^2$ do not alone cause two-electron transitions, only with additional electron–electron interaction. In the many-body perturbation theory the corresponding terms are at least third order. We assume that these terms can be neglected in a second-order theory. Then we obtain the expression of the second-order amplitude given also by Stolterfoht [14], namely

$$a^{(2)} = -\sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t} \langle f|V_1(t)|k\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'} \langle k|V_2(t')|i\rangle - \sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t} \langle f|V_2(t)|k\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'} \langle k|V_1(t')|i\rangle. \tag{19}$$

Similarly to (15), the non-time-ordered and the time-ordering term can be separated.

3.2.1. The use of CI wavefunctions. The two-electron wavefunctions $|i\rangle$, $|f\rangle$ and $|k\rangle$ cannot be calculated exactly. A good approximation can be reached by the use of configuration-interaction (CI) wavefunctions, which are written as a sum of products of one-electron orbitals

$$\begin{aligned} |i\rangle &= \sum_l c_l |i_1^l\rangle |i_2^l\rangle \\ |f\rangle &= \sum_j d_j |f_1^j\rangle |f_2^j\rangle \\ |k\rangle &= \sum_s b_s |k_1^s\rangle |k_2^s\rangle. \end{aligned} \tag{20}$$

Introducing the initial- and final-state CI wavefunctions in the first-order amplitude (17), one gets a sum of products of overlap integrals and one-electron transition amplitudes

$$a^{(1)} = -\mathrm{i}\sum_l \sum_j c_l d_j^* \langle f_2^j|i_2^l\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_i)t} \langle f_1^j|V_1(t)|i_1^l\rangle - \mathrm{i}\sum_l \sum_j c_l d_j^* \langle f_1^j|i_1^l\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_i)t} \langle f_2^j|V_2(t)|i_2^l\rangle. \tag{21}$$

These terms can be interpreted as follows. The term containing the basic configurations both from initial and the final states ($l = 1$ and $j = 1$, c_1 and d_1 being the largest coefficients), can be regarded as the shake term. If the one-electron orbitals from the initial and the final basic configurations have the same symmetry, the overlap integral $\langle f_i^1|i_i^1\rangle$ (for i equals 1 or 2) may be non-zero, and the shake process contributes to the transition of the second electron.

The terms with $j = 1$ and $l \neq 1$ are responsible for the initial-state correlation, while those with $j \neq 1$ and $l = 1$ express the final-state correlation. The terms with $j \neq 1$ and

$l \neq 1$ contain both initial- and final-state correlation, but usually are less important, because both coefficients c_l and d_j are small.

Using the CI (20) wavefunctions for the second-order amplitude (19), one obtains

$$a^{(2)} = -\sum_k \sum_{j,l} \sum_{r,s} d_j * c_l b_r b_s^* \langle f_2^j | k_2^r \rangle \langle k_1^s | i_1^l \rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t} \langle f_1^j | V_1(t) | k_1^r \rangle \times \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'} \langle k_2^s | V_2(t') | i_2^l \rangle - \sum_k \sum_{j,l} \sum_{r,s} d_j * c_l b_r b_s^* \langle f_1^j | k_1^r \rangle \langle k_2^s | i_2^l \rangle \times \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_k)t} \langle f_2^j | V_2(t) | k_2^r \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t'} \langle k_1^s | V_1(t') | i_1^l \rangle. \tag{22}$$

The evaluation of the second-order amplitude in this form seems impossible, some simplifications are necessary. One of the possibilities is to apply the closure approximation by replacing the energy of each intermediate state, E_k, by the same average value E. In this case we can use the closure relation

$$\sum_k \sum_{r,s} b_r b_s^* |k_1^r\rangle |k_2^r\rangle \langle k_1^s| \langle k_2^s| = 1, \tag{23}$$

and for the second-order amplitude we obtain

$$a^{(2)} = -\sum_{j,l} d_j^* c_l \left[\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E)t} \langle f_1^j | V_1(t) | i_1^l \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E - E_i)t'} \langle f_2^j | V_2(t') | i_2^l \rangle + \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E)t} \langle f_2^j | V_2(t) | i_2^l \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(E - E_i)t'} \langle f_1^j | V_1(t') | i_1^l \rangle \right]. \tag{24}$$

The time-ordering part of this second-order amplitude is sensitive to the value of the average energy E. If this is taken to be the mean value of the initial-state and the final-state energies, then $E_f - E = E - E_i = \Delta E/2$. In these conditions the second-order amplitude reduces to a sum of products of one-electron amplitudes, as we show below. The restriction of the time ordering $t' < t$ is equivalent to $t > t'$, so we can write

$$\begin{aligned} a^{(2)} &= -\sum_{j,l} d_j^* c_l \left[\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t} \langle f_1^j | V_1(t) | i_1^l \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t'} \langle f_2^j | V_2(t') | i_2^l \rangle \right. \\ &\quad \left. + \int_{-\infty}^{+\infty} \mathrm{d}t' \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t'} \langle f_1^j | V_1(t') | i_1^l \rangle \int_{t'}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t} \langle f_2^j | V_2(t) | i_2^l \rangle \right] \\ &= -\sum_{j,l} d_j^* c_l \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t} \langle f_1^j | V_1(t) | i_1^l \rangle \\ &\quad \times \left[\int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t'} \langle f_2^j | V_2(t') | i_2^l \rangle + \int_{t}^{+\infty} \mathrm{d}t' \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t'} \langle f_2^j | V_2(t') | i_2^l \rangle \right] \\ &= -\sum_{j,l} d_j^* c_l \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t} \langle f_1^j | V_1(t) | i_1^l \rangle \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t'} \langle f_2^j | V_2(t') | i_2^l \rangle. \end{aligned} \tag{25}$$

In this case time ordering is lost, and the interference with the first-order term is zero. In order to maintain time ordering and the difference in cross sections for positive and negative projectiles, one must choose another value for the average energy of the intermediate states.

In the following, the approximations using single-configuration separable wavefunctions will be presented.

3.2.2. Independent electron approximation. Neglecting electronic correlation one may approximate the unperturbed Hamiltonian as a sum of one-electron Hamiltonians

$$H^0 \approx h_1 + h_2. \tag{26}$$

Here h_i may contain only the nuclear potential, or may be a Hartree–Fock Hamiltonian

$$h_i = -\frac{\nabla_i^2}{2} + V_{N-1}(\boldsymbol{r}_i) \tag{27}$$

where

$$V_{N-1}(\boldsymbol{r}_i) = -\frac{Z_T}{r_i} + \sum_{j\neq i} \int \mathrm{d}\boldsymbol{r}_j \, \frac{|\phi_j(\boldsymbol{r}_j)|^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{28}$$

is the screening potential.

Now we express the two-electron wavefunctions as a product of two one-electron wavefunctions. Theoretically the wavefunctions corresponding to the (26) Hamiltonian can be expressed with the Slater determinants, and two terms should be used for each state in order to obtain the proper symmetry regulated by the Pauli principle. However, if in the initial state the two electrons are described by the same spatial wavefunction (e.g the $1s^2$ state for He), the two electrons should be in singlet state; therefore, the spin wavefunction is antisymmetric, so the spatial wavefunction has to be symmetric. The initial-state wavefunction can be expressed by a symmetric product $|i_1\rangle|i_2\rangle$, and the wavefunction for the final state is symmetrized

$$f(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2^{-1/2}[f_A(\boldsymbol{r}_1) f_B(\boldsymbol{r}_2) + f_B(\boldsymbol{r}_1) f_A(\boldsymbol{r}_2)]. \tag{29}$$

The transition amplitude can be written as

$$\langle f|U|i\rangle = 2^{-1/2}[\langle f_A(\boldsymbol{r}_1) f_B(\boldsymbol{r}_2)|U|i(\boldsymbol{r}_1) i(\boldsymbol{r}_2)\rangle + \langle f_B(\boldsymbol{r}_1) f_A(\boldsymbol{r}_2)|U|i(\boldsymbol{r}_1) i(\boldsymbol{r}_2)\rangle], \tag{30}$$

but because by interchanging $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ the two terms are equivalent, it reduces to

$$\langle f|U|i\rangle = 2^{1/2}\langle f_A(\boldsymbol{r}_1) f_B(\boldsymbol{r}_2)|U|i(\boldsymbol{r}_1) i(\boldsymbol{r}_2)\rangle. \tag{31}$$

Thus, the use of product wavefunctions is not contradictory to the Pauli principle, and we will use $|i\rangle = |i_1\rangle|i_2\rangle$ and $|f\rangle = |f_1\rangle|f_2\rangle$.

The energies corresponding to a sum of one-electron Hamiltonians are sums of single electron energies: $E_f = \epsilon_{f_1} + \epsilon_{f_2}$, $E_i = \epsilon_{i_1} + \epsilon_{i_2}$.

The first-order amplitude for a two-electron process in the IEA is zero, because of the orthogonality of the initial and final one-electron states. As for the second-order amplitude, the sum over the intermediate states is much more simplified. That is, there are only two intermediate states possible: $\langle i_1 i_2| \to \langle f_1 i_2|$ corresponding to V_1 followed by V_2 or $\langle i_1 i_2| \to \langle i_1 f_2|$ corresponding to V_2 followed by V_1. The energies of these states are $\epsilon_{f_1} + \epsilon_{i_2}$ and $\epsilon_{i_1} + \epsilon_{f_2}$ respectively. Using $|k\rangle = |k_1 k_2\rangle$, we get $\langle k_1 k_2|V_1(t)|i_1 i_2\rangle = \delta_{k_2 i_2}\langle k_1|V_1(t)|i_1\rangle$ and $\langle f_1 f_2|V_1(t)|k_1 k_2\rangle = \delta_{f_2 k_2}\langle f_1|V_1(t)|k_1\rangle$. Introducing the product wavefunctions in (19), and trivially summing over the δs in the intermediate states, we have

$$\begin{aligned} a^{(2)} = &-\int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1} - \epsilon_{i_1})t} \langle f_1|V_1(t)|i_1\rangle \int_{-\infty}^{t} \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2} - \epsilon_{i_2})t'} \langle f_2|V_2(t')|i_2\rangle \\ &-\int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2} - \epsilon_{i_2})t} \langle f_2|V_2(t)|i_2\rangle \int_{-\infty}^{t} \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1} - \epsilon_{i_1})t'} \langle f_1|V_1(t')|i_1\rangle. \end{aligned} \tag{32}$$

Thus the sum over intermediate states, $|k\rangle$, collapses.

Similarly to (25) it can be shown that, within the independent-electron approximation, the second-order amplitude reduces to a product of one-electron amplitudes.

$$\begin{aligned} a^{(2)} = &-\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon_{i_1})t}\langle f_1|V_1(t)|i_1\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon_{i_2})t'}\langle f_2|V_2(t')|i_2\rangle \\ &-\int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon_{i_1})t'}\langle f_1|V_1(t')|i_1\rangle \int_{t'}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon_{i_2})t}\langle f_2|V_2(t)|i_2\rangle \\ = &-\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon_{i_1})t}\langle f_1|V_1(t)|i_1\rangle \int_{-\infty}^{\infty} \mathrm{d}t' \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon_{i_2})t'}\langle f_2|V_2(t')|i_2\rangle \\ = &\, a_1^{(1)} a_2^{(1)}. \end{aligned} \tag{33}$$

This is an essential result of Stolterfoht [14] for two-electron transitions if the orbital energies do not change during collision, i.e. there is no correlation. Stolterfoht has called these states frozen energy orbitals. Now time ordering is lost. In the independent electron approximation time ordering enters in the higher-order single-electron amplitudes. Thus Z^3 effects may arise due to time ordering in the $V_1(V_2)^2$ or $(V_1)^2V_2$ terms. However, through second order, for two-electron transitions there is no time-ordering effect without correlation.

3.2.3. Independent orbitals with shifted energies. Now we relax the frozen-orbital restriction and allow the energies of the electron orbitals to change due to the effect of the electron–electron interaction. Our unperturbed Hamiltonian remains a sum of one-electron Hamiltonians. To keep the time-ordering effect, we must choose the H^0 Hamiltonian depending on the order of the interactions, in other words we have to take into account the change in the screening potential during the collision. For simplicity we keep track only of the two active electrons. We treat the case when the order of the interactions with the projectile is $V_2(t)V_1(t')$ with $t > t'$. The one-electron Hamiltonians can be written as

$$\begin{aligned} h_1 &= -\frac{\nabla_1^2}{2} + V_{N-1}(\boldsymbol{r}_1) \\ h_2 &= -\frac{\nabla_2^2}{2} + V'_{N-1}(\boldsymbol{r}_2). \end{aligned} \tag{34}$$

V'_{N-1} is calculated with the first electron in the final state. In case of the ionization, when the first electron leaves the atom, instead of $V'_{N-1}(\boldsymbol{r}_2)$ we can take $V_{N-2}(\boldsymbol{r}_2)$ (screening approximation). For the initial state the wavefunctions for both electrons are calculated in the V_{N-1} potential (Hartree–Fock wavefunctions), because both electrons are in the ground state. Thus the initial state of the electron 2 is not orthogonal to the final state, because the final state is calculated in the V'_{N-1}. In the following formulae the eigenstates of the Hamiltonian containing the initial screening potential will be unprimed, and the eigenstates of the Hamiltonian with V'_{N-1} or the V_{N-2} Hamiltonian will be labelled prime. The initial state $|i_1 i_2\rangle$ is not an eigenstate of the $H^0 = h_1 + h_2$ Hamiltonian, but because usually the overlap integral between $|i_2\rangle$ and the proper eigenstate of the h_2 ($|i'_2\rangle$) is large, we can approximately write

$$(h_1 + h_2)|i_1 i_2\rangle \approx (\epsilon_{01} + \epsilon'_{02})|i_1 i'_2\rangle \approx E_0|i_1 i_2\rangle, \tag{35}$$

where E_0 is the ground-state energy of the two electrons.

Let us express the transition amplitudes in this approximation. If the change in the screening during the two-electron transition is taken into account, because of the non-orthogonality of the initial and final states, the first-order amplitude is non-zero. Considering

both interactions we obtain

$$a^{(1)} = -\mathrm{i}\langle f_2'|i_2\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}+\epsilon_{f_2}-E_0)t}\langle f_1|V_1(t)|i_1\rangle$$
$$-\mathrm{i}\langle f_1'|i_2\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}+\epsilon_{f_2}-E_0)t}\langle f_2|V_2(t)|i_2\rangle. \tag{36}$$

This term is usually called the shake amplitude (shake-off or shake-up).

A problem arises at this step of our method. We obtain two different final states, namely $|f_1 f_2'\rangle$ and $|f_1' f_2\rangle$, depending on the order of the interactions. Obviously, this has no physical meaning because the final state is fully characterized by the energies and angular momenta of the two electrons. With both electrons in the continuum the screening can be only poorly approximated to be caused by a bound electron. Thus, in the final state we neglect the interaction of the two electrons, and the $|f_i\rangle$ screened wavefunction relaxes in the $|f_i'\rangle$ unscreened wavefunction. We multiply each term by an overlap of type $\langle f_i'|f_i\rangle$. Taking into account only the asymptotic region, where the two wavefunctions differ just in a constant phaseshift, the overlap integral (calculated for the partial waves) is simply

$$\langle f_i'|f_i\rangle_{l_i} = \cos\delta_{p_i l_i}\delta(p_i - p_i'), \tag{37}$$

where $\delta_{p_i l_i}$ is the phaseshift due to the short-range screening potential. The $|f_i\rangle$ states can be taken to be intermediate states, and we will have to perform an integration over these, making the δ function disappear. With these corrections the first-order amplitude has the form

$$a^{(1)} = -\mathrm{i}\langle f_2'|i_2\rangle\langle f_1'|f_1\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}+\epsilon_{f_2}-E_0)t}\langle f_1|V_1(t)|i_1\rangle$$
$$-\mathrm{i}\langle f_1'|i_2\rangle\langle f_2'|f_2\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}+\epsilon_{f_2}-E_0)t}\langle f_2|V_2(t)|i_2\rangle. \tag{38}$$

Applying the $H^0 = h_1 + h_2$ Hamiltonian for the second-order amplitude where h_1 and h_2 are given by (34), one obtains

$$a^{(2)} = -\sum_k \int_{-\infty}^{+\infty} \mathrm{d}t \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}+\epsilon_{f_2})t}\langle f_1 f_2'|V_2(t)|k_1 k_2'\rangle \mathrm{e}^{\mathrm{i}E_k(t'-t)}\langle k_1 k_2'|V_1(t')|i_1 i_2\rangle \mathrm{e}^{-\mathrm{i}E_0 t'}, \tag{39}$$

where for simplicity we have taken only one possible order of the interactions.

For the study of the intermediate states let us take the matrix element

$$\langle f_1 f_2'|V_2(t)|k_1 k_2'\rangle = \delta_{f_1 k_1}\langle f_2'|V_2(t)|k_2'\rangle, \tag{40}$$

where $|f_1\rangle$ and $|k_1\rangle$ are both eigenstates of the h_1 Hamiltonian. In the case of the other matrix element

$$\langle k_1 k_2'|V_1(t')|i_1 i_2\rangle = \langle k_2'|i_2\rangle\langle k_1|V_1(t')|i_1\rangle \tag{41}$$

$|i_2\rangle$ is calculated in the V_{N-1} potential, while $|k_2'\rangle$ is the eigenstate of h_2. But the overlap integral of the $|i_2\rangle$ state is much larger with the ground state of the h_2, $|i_2'\rangle$, than with the excited and continuum states, and so $\langle k_2'|i_2\rangle \approx \delta_{k_2' i_2'}$. In these conditions we neglect the other possible intermediate states, and retain only one, in which one electron is in the final state, and the other in the modified ground state $|i_2'\rangle$. The unperturbed energy of this intermediate state is obtained by

$$H^0|f_1 i_2'\rangle = h_1|f_1\rangle|i_2'\rangle + |f_1\rangle h_2|i_2'\rangle = (\epsilon_{f_1} + \epsilon_{02}')|f_1 i_2'\rangle. \tag{42}$$

Considering only the above intermediate state with one electron in the final state and the other in the ground state, but taking into account both of the possible orders of the interactions, the second-order amplitude can be expressed as

$$a^{(2)} = -\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon'_{02})t}\langle f'_2|V_2(t)|i'_2\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon_{01})t'}\langle f_1|V_1(t')|i_1\rangle$$
$$-\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon'_{01})t}\langle f'_1|V_1(t)|i'_1\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon_{02})t'}\langle f_2|V_2(t')|i_2\rangle. \tag{43}$$

This term is commonly called the TS2 amplitude. Since $\epsilon_{0i} \neq \epsilon'_{0i}$, the transition energies depend on the order of the interactions.

One would obtain a similar result using the closure approximation as in equation (24) applied for single-configuration wavefunctions. The advantage of the present method is of giving the energy of the intermediate states.

In these conditions the second-order amplitude does not reduce to a product of one-electron amplitudes, as in (33) for IEA because the energy transfers and wavefunctions depend on the order of the interactions.

Applying the same argument as for the first-order amplitude, we multiply each term in (43) by an overlap integral of type (37), which expresses the relaxation of a screened continuum wavefunction into an unscreened one

$$a^{(2)} = -\langle f'_1|f_1\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon'_{02})t}\langle f'_2|V_2(t)|i'_2\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon_{01})t'}\langle f_1|V_1(t')|i_1\rangle$$
$$-\langle f'_2|f_2\rangle \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_1}-\epsilon'_{01})t}\langle f'_1|V_1(t)|i'_1\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\epsilon_{f_2}-\epsilon_{02})t'}\langle f_2|V_2(t')|i_2\rangle. \tag{44}$$

The effects of time ordering can be separated. Following Végh *et al* [17] we introduce an energy shift, Δ, so that an electron is less tightly bound by $-\Delta$ if another electron is present and more tightly bound by $+\Delta$ if the other electron has already made a transition. In our notations

$$\Delta = \frac{\epsilon_{01} + \epsilon_{02} - \epsilon'_{01} - \epsilon'_{02}}{2}. \tag{45}$$

Végh *et al* [17] have shown that $a^{(2)} = a_1^{(1)}a_2^{(1)} + C(\Delta) + S(\Delta)$ where $C(\Delta) \sim \cos\Delta(t-t') - 1$ and $S(\Delta) \sim \sin\Delta(t-t')$ so that both corrections are small for fast collisions. C has the same phase as the a_1a_2 term, but S is always 90° out of phase.

Now we show that the treatment of the time ordering by McGuire and Straton [5] and by Végh *et al* [17] are equivalent. Rewriting the formula (19) of the second-order amplitude with the energy-shift notation and keeping only two intermediate states, namely $|k\rangle$ and $|\bar{k}\rangle$, we get

$$a^{(2)} = -\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_1+\Delta)t}\langle f|V_1(t)|k\rangle \int_{-\infty}^{t} \mathrm{d}t' \mathrm{e}^{\mathrm{i}(\Delta E_2-\Delta)t'}\langle k|V_2(t')|i\rangle$$
$$-\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_2+\Delta)t}\langle f|V_2(t)|\bar{k}\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_1-\Delta)t'}\langle \bar{k}|V_1(t')|i\rangle. \tag{46}$$

If we separate the non-time ordered part of the amplitude as in equation (15) and we assume as in [17] that

$$\langle f|V_1(\tau)|k\rangle = \langle \bar{k}|V_1(\tau)|i\rangle = V_{bd}(\tau)$$
$$\langle f|V_2(\tau)|\bar{k}\rangle = \langle k|V_2(\tau)|i\rangle = V_{ac}(\tau), \tag{47}$$

we obtain

$$a^{(2)}_{\text{no time ordering}} = -\tfrac{1}{2}\Bigg[\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_1+\Delta)t} V_{bd}(t) \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_2-\Delta)t'} V_{ac}(t') + \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_2+\Delta)t} V_{ac}(t) \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_1-\Delta)t'} V_{bd}(t')\Bigg]$$
$$= \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_1)t} V_{bd}(t) \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_2)t'} V_{ac}(t') \cos\Delta(t-t')$$
$$= \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_1)t} V_{bd}(t) \int_{-\infty}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_2)t'} V_{ac}(t') + C(\Delta). \tag{48}$$

Thus C is an effect of the correlation that corresponds to a shift in binding energy in the intermediate state.

As for the time-ordering part of the second-order amplitude

$$a^{(2)}_{\text{time ordering}} = -\frac{\mathrm{i}}{2\pi} \sum_k \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}E_f t} \langle f|V_1(t)|k\rangle \times \int_{-\infty}^{+\infty} \mathrm{d}t'\, P \int_{-\infty}^{+\infty} \mathrm{d}\Omega\, \mathrm{e}^{-\mathrm{i}\Omega(t-t')} \frac{1}{\Omega - E_k} \mathrm{e}^{-\mathrm{i}E_i t'} \langle k|V_1(t')|i\rangle, \tag{49}$$

the principal-value integral over Ω can be performed analytically. Retaining only two intermediate states, with the notations of equations (46) and (47) the time-ordering contribution is written

$$a^{(2)}_{\text{time ordering}} = \tfrac{1}{2}\Bigg[\int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_1+\Delta)t} V_{bd}(t) \int_{t}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_2-\Delta)t'} V_{ac}(t') + \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Delta E_2+\Delta)t} V_{ac}(t) \int_{t}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}(\Delta E_1-\Delta)t'} V_{bd}(t')\Bigg]$$
$$= -\mathrm{i} \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\Delta E_1 t} V_{bd}(t) \Bigg[\int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}\Delta E_2 t'} - \int_{t}^{+\infty} \mathrm{d}t'\, \mathrm{e}^{\mathrm{i}\Delta E_2 t'}\Bigg] \sin\Delta(t'-t)$$
$$= S(\Delta). \tag{50}$$

So S becomes the time-ordering effect and is identical to the principal-value part from the treatment of McGuire and Straton [5].

Time ordering and electron correlation are different. However, as previously noted, time ordering may not occur without correlation in second order for a two-electron transition.

4. Application for double ionization of helium

The presented method was previously applied for the ionization–excitation [18] and double excitation [19] of helium. In the present work we present the results of our calculations performed for the double ionization of helium by protons and antiprotons.

Because of the complexity of the problem we restrict ourself to single-configuration wavefunctions. Thus, we neglect the initial- and final-state correlations. However, the shake term in the first-order amplitude and the time-ordering term in the second-order amplitude are present, because we have taken into account the change in the screening during the collision. Because the electron correlations might be important in the two-electron transitions, we do not expect to obtain accurate results. Our goal is to investigate to what extent the interference between the shake and the TS2 terms is responsible for the observed difference in cross sections for positive and negative projectiles.

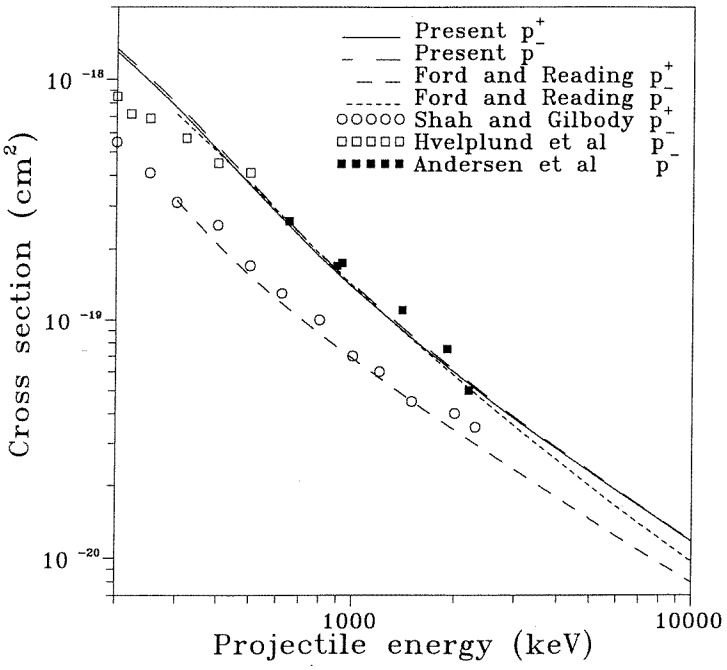

Figure 1. Cross sections for the double ionization of helium by proton and antiproton impact as a function of the projectile energy. Our results are compared with the theoretical cross sections of Ford and Reading [8], the experimental data of Shah and Gilbody [21] for protons and of Hvelplund *et al* [22] and Andersen *et al* [23, 24] for antiprotons.

For the ground state of helium we have used the Hartree–Fock wavefunctions of Clementi and Roetti [20]. The continuum wavefunctions for the second interacting electron, moving in the field of the bare nucleus, are Coulomb wavefunctions. For the first electron, which moves in a screened potential by the second electron, the wavefunction is obtained by numerical integration. Calculations were made by expansion into the partial waves, taking into account partial waves up to $l = 4$.

We have calculated separately the shake-off amplitude and the real and imaginary parts of the TS2 amplitude, and have let them interfere. The cross sections obtained considering these two mechanisms as a function of the projectile energy, are presented in figure 1. These are compared with the experimental data of Shah and Gilbody [21] for protons, of Hvelplund *et al* [22] and Andersen *et al* [23, 24] for antiprotons, and with the theoretical calculations of Ford and Reading [8].

We do obtain a difference in cross sections for protons and antiprotons, and the values for antiprotons are higher. However, instead of the factor-of-two difference between 0.3 and 2 MeV projectile energy, our calculated difference is only 5%. The results for antiprotons fit very well with the experimental data, but cross sections for protons are too high.

The cross sections due to the first- and second-order terms are represented in figure 2. We show separately the contribution of the independent-electron approximation (IEA). Adding to the IEA amplitude only the $C(\Delta)$ correction term resulting from the energy shift of the intermediate states, but neglecting the time ordering (the second-order amplitude remains, in fact, a product amplitude with shifted energies), the cross section is diminished by about 30%. The curve representing this approximation is labelled IEA-SH. Taking into account

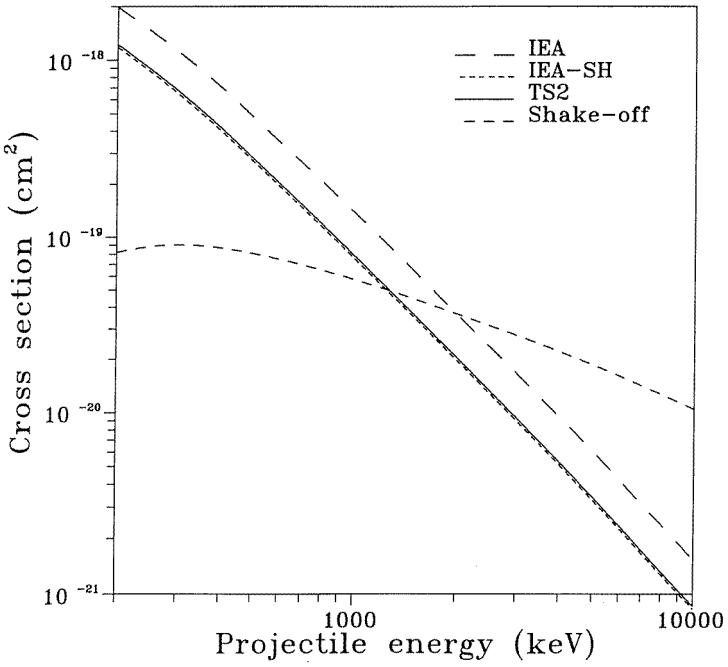

Figure 2. The contributions of the first- and second-order amplitudes to the double-ionization cross sections of helium. These contributions are independent of the sign of the charge of the projectile. IEA is the independent-electron, frozen-orbital approximation, IEA-SH is obtained by the non-time-ordered amplitude with shifted energies of the intermediate states. TS2 is the time-ordered second-order cross section, and the shake-off is the first-order term.

the time ordering, the second-order amplitude cannot be written any more as a product, and it has real and imaginary parts. The curve labelled TS2 represents the time-ordered second-order cross section. The time-ordering contribution to the cross section is about 5%.

The effect of time ordering is diminishing applying higher projectile energies, as it was shown by Végh *et al* [17], but this decrease is rather slow.

For projectile energies below 1 MeV the TS2 contribution dominates over the shake-off cross section. At 1.5 MeV the two contributions are equal, above this energy the shake-off becomes dominant. The shake-off amplitude interferes only with the time-ordering (S) part of the monopole term of the TS2 amplitude, and this is the reason why this interference, and the difference between cross sections for positive and negative projectiles, are obtained small.

Figure 3 represents the ratio of double- to single-ionization cross section as a function of the projectile energy. Experimentally the high-energy limit for this ratio is 0.27% (measured at 80 GeV amu^{-1} [25]). Our calculated ratio is higher. At projectile energies above 10 MeV only the shake-off contribution is important. Our ratio tends to a constant value of 0.36%. This is lower than the so-called shake-off limit, which is simply the square of the overlap integral $\langle f_2'|i_2\rangle$, with our wavefunctions 0.51%. This difference occurs because of the larger energy transfer in the shake-off amplitude than in the single-ionization amplitude.

We do not obtain the experimental ratio, because the initial- and final-state electronic correlations are ignored. The initial-state correlation can be handled by using CI wavefunctions for the initial state. Probably, in the case of the double ionization (in contrast

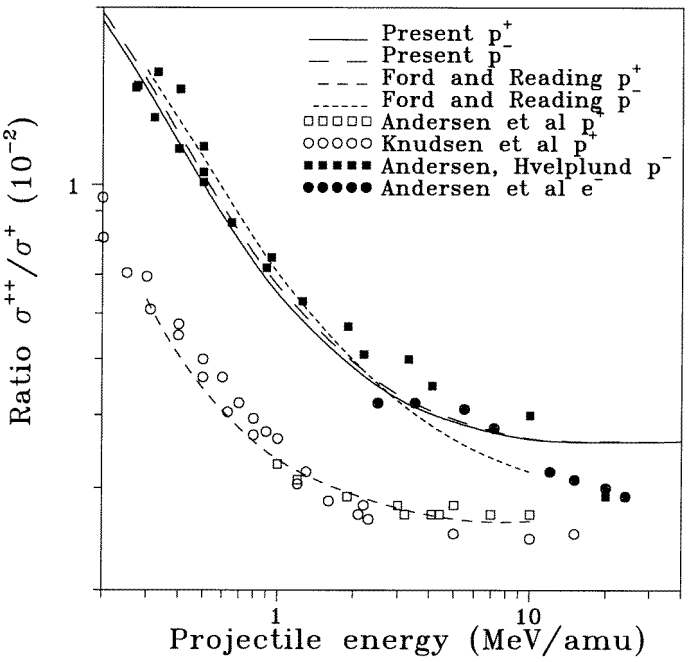

Figure 3. The ratio between double- and single-ionization cross sections for p^+, p^- and e^- colliding with helium atoms as a function of the projectile energy. Our results are compared with the theoretical ratios of Ford and Reading [8]. The experimental data are of Andersen *et al* [26] (open squares), Knudsen *et al* [27], Shah and Gilbody [21] and Puckett and Martin [28] (open circles) for protons, of Andersen *et al* [26, 23] and Hvelplund *et al* [22] for antiprotons (full squares) and of Andersen *et al* [26] for electrons (full circles).

to the ionization–excitation [18]) the initial-state correlations are not so important, because a CI wavefunction for the ground state usually does not contain configurations from the continuum. Although the overlap of the orbitals from different configurations with the continuum may be non-zero, the small coefficients will cause these contributions to be less important than the shake term caused by the overlap of the orbital from the basic configuration with the continuum.

But the final-state electron–electron interactions could be decisive. The production of correlated double-continuum wavefunctions is difficult, and at the moment it seems simpler to use the many-body perturbation theory. The TS1 term from the MBPT, meaning a projectile–electron interaction followed by an electron–electron interaction, contains time ordering, and could contribute to a larger difference between the cross sections obtained for positively and negatively charged projectiles.

5. Conclusions

We have presented a general treatment on the effect of time ordering in atomic collisions. We have proved in general, that time ordering is essential in order to reproduce the dependence of the cross sections on the sign of the charge of the projectile. We have discussed in more detail the two-electron processes up to second order. We have applied our model for the double ionization of the helium. The electron–electron interaction was taken into account

only by including the shake terms. The interference between the shake-off and second-order amplitudes explains only a part of the observed difference in cross sections for positively and negatively charged projectiles.

Our method can be improved by including the initial-state and final-state correlations of the two electrons. The initial-state correlation could be handled by using an accurate configuration-interaction wavefunction for the initial state. The final-state correlation could be treated within the many-body perturbation theory, taking into account the electron–electron interaction in the final state at least in first order (the TS1 term).

Acknowledgments

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