
ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM

Invariant Exchange Perturbation Theory for Multicenter Systems: Time-Dependent Perturbations

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Abstract—A formalism of exchange perturbation theory (EPT) is developed for the case of interactions that explicitly depend on time. Corrections to the wave function obtained in any order of perturbation theory and represented in an invariant form include exchange contributions due to intercenter electron permutations in complex multicenter systems. For collisions of atomic systems with an arbitrary type of interaction, general expressions are obtained for the transfer (T) and scattering (S) matrices in which intercenter electron permutations between overlapping nonorthogonal states belonging to different centers (atoms) are consistently taken into account. The problem of collision of alpha particles with lithium atoms accompanied by the redistribution of electrons between centers is considered. The differential and total charge-exchange cross sections of lithium are calculated.

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1. INTRODUCTION

Time-dependent perturbation theory (TDPT) has been developed and is widely used in nonrelativistic quantum mechanics. This theory describes a wide class of phenomena such as collisions of composite particles, atoms, and molecules that result in a change in the composition of the particles. These processes are not adiabatic; however, a certain range of interatomic distances (distances between composite particles), which can be interpreted as intermediate distances, plays an important role even in these processes. This is a domain of interaction in which a permutation of composite particles associated with the redistribution of electrons occurs. Exchange forces, which are related to the permutation symmetry of the wave function of a system of particles, decay rather rapidly, exponentially, as the distance between the interacting atoms increases. Invariant perturbation theory and the diagram technique [1–4], in spite of the fact that they cover both nonrelativistic and relativistic scales, do not directly take into account the processes that are related to interatomic and intermolecular overlapping of electron shells of multicenter systems and occur at these intermediate distances. The problem of consistent description in terms of Feynman diagrams lies in the fact that the general formalism is based on the orthogonal basis of electron states, whereas electron states belonging to different atomic (molecular) centers are not orthogonal.

To describe processes involving nonorthogonal electron states with regard to their overlaps, one should apply special techniques in each specific case (see, for example, [5–9]). In [10], the authors consid-

ered a three-center problem with a single electron (when a molecular hydrogen ion collides with the nucleus of a helium atom), where the so-called “exchange” interaction is taken into account asymptotically when simulating the wave function. In this case, it would be correct to refer to the multicenter phenomena as interference phenomena, because one deals with a superposition of states of the same electron.

In [11], when considering molecular collisions with charge exchange, the authors used a quasiclassical method with a semiphenomenological technique to take into account exchange phenomena, which play a key role in the case of slow collisions. This fact stimulates the construction of a perturbation theory with time-dependent perturbations that takes into account the indistinguishability between identical particles in any order. This allows one to develop a unique algorithm for calculating transfer probabilities, including algorithms for the problems of multicenter collisions (an atom + a molecule).

There are two fundamental difficulties that arise when constructing a perturbation theory series with regard to intercenter electron exchange, which were discussed in detail in the monograph [12] and papers [13–20]. First, this is the problem of overfilling the basis of wave functions antisymmetrized with regard to intercenter permutations, as commonly believed, due to their nonorthogonality. Second, a zero approximation function antisymmetrized with respect to intercenter permutations is not an eigenfunction of the zero approximation Hamiltonian \hat{H}_0 , i.e., the Hamiltonian describing a multiatomic system without inter-

atomic interaction, due to the noninvariance of the latter with respect to electron permutations between atoms. It is important that, when constructing an exchange perturbation theory (EPT) series, one does not need the orthogonality of wave functions: as shown in [16, 18, 19], the basis antisymmetric functions, while remaining nonorthogonal, may constitute a complete set.

In the stationary case, the form of the unperturbed part of the Hamiltonian and the perturbation operator, invariant with respect to intercenter permutations, that allows one to successively determine corrections to the energy of an interacting system of atoms with the use of a properly symmetrized basis of wave functions was obtained in [13, 15–19]. The algorithm developed for obtaining corrections to the energy and the wave functions in any order of EPT does not require additional procedures of antisymmetrization and orthogonalization of antisymmetric functions.

An attempt to construct a formalism of time-dependent exchange perturbation theory (TDEPT) was made in [14, 20], where expressions were obtained for the transfer amplitudes in the first two orders with regard to intercenter permutation and the formalism itself was applied to the description of a spin-flip process under the collision of an alkali atom with a buffer atom of a noble gas. However, in these works, the projector that allows one to express the perturbation operator and the Hamiltonian of the unperturbed system was used as a logical projector, whose explicit form was obtained in [15, 16].

The present study is a continuation of [19], where we presented the formalism of EPT for the stationary case. In this paper, the EPT formalism is developed for the case of nonstationary perturbations for which a formula for the n th term of arbitrary time functions of perturbation is obtained in any order of perturbation theory, and the formalism is reduced to the standard form of invariant perturbation theory. General expressions are obtained for the scattering (S) matrix and the transfer (T) matrix for arbitrary types of interaction in which intercenter electron permutations between overlapping nonorthogonal states are consistently taken into account. The formalism obtained is applied to the description of the collision of a double-charged helium ion (the alpha particle) with a lithium atom followed by charge exchange.

2. EXCHANGE PERTURBATION THEORY FORMALISM FOR TIME-DEPENDENT PERTURBATIONS

When considering the processes occurring during collisions of composite particles (atoms or molecules), it is assumed that a part of electrons belongs to the first center (particle), another part belongs to the second, etc. Accordingly, in zero approximation, i.e., when the interaction between particles is neglected, the wave function of the system of particles is expressed as a

simple product of the wave functions of isolated atoms; in terms of the Dirac symbols, this is the vector $|\Phi^0\rangle$. The vector of state antisymmetrized with respect to intercenter permutations is expressed as

$$|\Psi^0\rangle = \hat{A}|\Phi^0\rangle,$$

where \hat{A} is the antisymmetrization operator; the normalization condition $\langle\Phi_n^0|\Psi_n^0\rangle = 1$ differs from the similar condition $\langle\Psi^0|\Psi^0\rangle = 1$ used in EPT by a factor \sqrt{P} , where P is the total number of electron permutations. When there is a time-dependent perturbation in a multicenter system, that is related, for example, to collisions accompanied by redistribution of particles or ion charge-exchange processes, one should solve the following Schrödinger equation for antisymmetrized states:

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}|\Psi\rangle = (\hat{H}_0 + \hat{V}(t))|\Psi\rangle. \quad (1)$$

The operators on the right-hand side of this equation were obtained in [15–19] in a form invariant with respect to intercenter permutations. The difference lies in the fact that now the invariant perturbation operator contains explicit time dependence:

$$\hat{V}(t) = \sum_{p=0}^P V^{(p)}(t)\Lambda^{(p)}, \quad \hat{H}_0 = \sum_{p=0}^P H^{0(p)}(t)\Lambda^{(p)},$$

where $V^{(p)}(t)$ is a perturbation operator corresponding to the p th intercenter electron permutation and the operator

$$\Lambda^{(p)} = \sum_n |\Phi_n^{0(p)}\rangle \frac{f_n}{P} \langle\Phi_n^{0(p)}|$$

is a projector onto the space of vectors of the p th permutation that acts on the antisymmetrized vector:

$$\begin{aligned} \Lambda^{(p)}|\Psi_i^{(0)}\rangle &= \sum_n |\Phi_n^{0(p)}\rangle \frac{f_n}{P} \langle\Phi_n^{0(p)}|\Psi_i^{(0)}\rangle \\ &= \sum_n |\Phi_n^{0(p)}\rangle \frac{f_n}{P} \langle\Phi_n^{0(0)}|\Psi_i^{(0)}\rangle (-1)^{g_p} \\ &= \sum_n |\Phi_n^{0(p)}\rangle \frac{f_n}{P} \delta_{ni} (-1)^{g_p} \frac{P}{f_i} = (-1)^{g_p} |\Phi_n^{0(p)}\rangle. \end{aligned} \quad (2)$$

The zero-approximation antisymmetric wave vector of the initial state is an eigenvector of the Hamiltonian of the unperturbed system,

$$\hat{H}_0|\Psi_i^0\rangle = E_i^0|\Psi_i^0\rangle$$

that is invariant with respect to intercenter permutations, while the energy eigenvalue E_i^0 remains real [15–19].

The set of eigenstates $\{|\Phi_n^{0(p)}\rangle\}$ of the unperturbed system for any of p permutations possesses the properties of orthogonality and completeness [16, 17]:

$$\begin{aligned} (\Phi_m^{0(p)}|\Phi_n^{0(p)}) &= \delta_{mn}, \\ \sum_n |\Phi_n^{0(p)}\rangle\langle\Phi_n^{0(p)}| &= \hat{1}, \\ |\Phi_m^{0(p)}\rangle\langle\Phi_n^{0(p)}| &\approx \delta_{mn}S_n^{(p-p')}, \end{aligned} \quad (3)$$

where $S_n^{(p-p')}$ is the overlap integral of the wave functions related to the relative number of intercenter permutations of electrons ($p - p'$). We use a “truncated” overlapping; i.e., we take into consideration the intercenter overlaps only for the states of the same name according to the hierarchy of inequalities

$$(\Phi_m^{0(p)}|\Phi_n^{0(p')}) \ll (\Phi_n^{0(p)}|\Phi_n^{0(p')}) \sim (\Phi_m^{0(p)}|\Phi_m^{0(p')}).$$

In [16, 18], we proved that the basis of antisymmetrized functions of the unperturbed system possesses the property of completeness:

$$\sum_n |\Psi_n^0\rangle\langle\Psi_n^0| = \hat{1}. \quad (4)$$

Just as in the standard perturbation theory, which does not take into account exchange terms, a solution is constructed by iterating with respect to the small parameter contained in the perturbation operator $\hat{V}(t)$. Retaining terms of order at most one in Eq. (1), we take a solution for the first correction $|\Psi^1(t)\rangle$ to the wave function in the form of an expansion,

$$|\Psi^1(t)\rangle = \sum_n C_n^{(1)}(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |\Psi_n^0\rangle, \quad (5)$$

where the expansion coefficients are to be determined. Following the algorithm described in detail in [14, 20], we introduce a projector onto the subspace of vectors parallel to the vector $|\Psi_i^0\rangle$,

$$\hat{P}_i = |\Psi_i^0\rangle\langle\Psi_i^0|,$$

where $\hat{P}_i|\Psi_i^0\rangle \equiv |\Psi_i^0\rangle$, and a projector onto the subspace of vectors orthogonal (complementary) to $|\Psi_i^0\rangle$,

$$\hat{O}_i = 1 - \hat{P}_i,$$

where $\hat{O}_i|\Psi_i^0\rangle \equiv 0$. Acting by the projector \hat{O}_i on both sides of the Schrödinger equation for the first correction to the function and using the property of completeness (4), we obtain the following expression for the expansion coefficients:

$$C_n^{(1)}(t) = \frac{f_0}{i\hbar P} \int_0^t \exp(i\omega_{ni}t') (\Phi_n^{0(0)}|\hat{O}_i\hat{V}|\Psi_i^0) dt'. \quad (6)$$

where $\omega_{in} = (E_i - E_n)/\hbar$ are the transfer frequencies.

Taking into account the fact that

$$\hat{O}_i|\Psi_i^0\rangle \approx |\Psi_i^0\rangle,$$

$$(\Phi_n^{0(0)}|\hat{O}_i = (\Phi_n^{0(0)}| - (\Phi_n^{0(0)}|\Psi_i^0\rangle\langle\Psi_i^0|)(\Phi_n^{0(0)}| \approx (\Phi_n^{0(0)}|, \quad (7)$$

$$(\Phi_i^{0(0)}|\hat{O}_i = (\Phi_i^{0(0)}| - (\Phi_i^{0(0)}|\Psi_i^0\rangle\langle\Psi_i^0|) \equiv 0,$$

we rewrite expression (6) for the expansion coefficients, which are the transfer amplitudes between states i and n , as

$$C_n^{(1)}(t) = \frac{f_n}{i\hbar P} \int_0^t \exp(i\omega_{ni}t') (\Phi_n^{0(0)}|\hat{V}|\Psi_i^0) dt'. \quad (8)$$

The matrix elements, appearing in (8), of the invariant perturbation operator that has a complicated form and contains Λ projectors (2) can be transformed to a simpler expression containing a simple perturbation operator corresponding to the zero (original) permutation of electrons:

$$\begin{aligned} (\Phi_n^{0(0)}|\hat{V}|\Psi_i^0) &= (\Phi_n^{0(0)}| \sum_{p=0}^P V_p \sum_n \frac{1}{f_n} \Lambda_n^p |\Psi_i^0\rangle \\ &= (\Phi_n^{0(0)}|\hat{V} \sum_{p=0}^P V_p \frac{(-1)^{g_p}}{f_i} |\Phi_i^{0(p)}\rangle). \end{aligned} \quad (9)$$

Now, we permute electrons in each p th integral so that a ket vector turns into a vector of zero permutation, while a bra vector becomes p -permuted; in this case, the perturbation operator of the p th permutation turns into the original operator; i.e., it will correspond to the zero permutation:

$$\begin{aligned} &(\Phi_n^{0(0)}| \sum_{p=0}^P V_p \frac{(-1)^{g_p}}{f_i} |\Phi_i^{0(p)}\rangle \\ &= \frac{f_n}{f_i^P} \sum_{p=0}^P \frac{(-1)^{g_p}}{f_n} (\Phi_n^{0(p)}| V_{p=0} |\Phi_i^{0(p=0)}\rangle = \frac{f_n}{f_i} \langle\Psi_n^0| V_0 |\Phi_i^{0(0)}\rangle). \end{aligned} \quad (10)$$

Passing, on the basis of (10), to matrix elements with nonsymmetrized interaction operators in expression (8), we obtain a final expression for the amplitude:

$$C_{n_1}^{(1)}(t) = \frac{f_{n_1}^2}{i\hbar P} \int_0^t \exp(i\omega_{n_1 i} t') \langle\Psi_{n_1}^0| V_{p=0} |\Phi_i^{0(0)}\rangle dt', \quad (11)$$

which, under neglect of exchange, reduces to an ordinary formula of the standard perturbation theory in the case of a discrete spectrum of states. The main difference lies in the fact that, even in the first correction, the new formula contains, in addition to the “direct” contribution, exchange contributions associated with electron permutations between atoms (centers). In this sense, the perturbation theory series is a two-parameter one, because it contains an independent small term related to the overlap degree of wave functions centered at different atoms. Superexchange contributions [17] may arise even in the first correction if

we consider collisions between molecules or between an atom and a molecule.

Similarly, retaining terms of up to the second order in expression (1) and taking into account property (4), we obtain an equation for the second correction, the solution of which we also represent as

$$|\Psi_i^2\rangle = \sum'_b C_b^{(2)}(t) \exp\left(-\frac{i}{\hbar} E_b t\right) |\Psi_b^0\rangle, \quad (12)$$

where the prime at the sum indicates the absence of terms with $b = i$ and the expansion coefficients for the second correction to the wave vector have a form similar to that obtained in [20] but expressed in different notations:

$$C_b^{(2)}(t) = \frac{f_b^2}{i\hbar P} \int_0^t dt' \exp\left(\frac{i E_b t'}{\hbar}\right) (\Phi_b^{0(0)} | \hat{O}_i \hat{V} | \Psi_i^1(t')). \quad (13)$$

Let us write out a full expression for the second correction: in this expression, the expansion coefficients are transformed to the form corresponding to the formalism of perturbation theory with a symmetry-adapted Hamiltonian with regard to expressions (7) and (10):

$$\begin{aligned} |\Psi_i^2\rangle &= \sum'_{n_2} \exp\left(-\frac{i}{\hbar} E_{n_2} t\right) |\Psi_{n_2}^0\rangle \left(\frac{f_0^2}{i\hbar P}\right)^2 \\ &\times \sum'_{n_1} \int_0^t dt' \exp(i\omega_{n_2 n_1} t') \langle \Psi_{n_2}^0 | V^{p=0} | \Psi_{n_1}^{0(0)} \rangle \\ &\times \int_0^{t'} dt'' \langle \Psi_{n_1}^0 | V^{p=0} | \Psi_i^{0(0)} \rangle \exp(i\omega_{n_1} t''). \end{aligned} \quad (14)$$

The general structure of this expression is largely the same as in perturbation theory with orthogonal basis; however, the matrix elements are contained in the overlap integrals, which take into account exchange and superexchange contributions. Then, in the n th approximation we have

$$\begin{aligned} |\Psi_i^n\rangle &= \sum'_{n_n} \sum'_{n_{n-1}} \dots \sum'_{n_1} \left(\frac{f_0^2}{i\hbar P}\right)^n |\Psi_{n_n}^0\rangle \exp\left(-\frac{i}{\hbar} E_{n_n} t\right) \\ &\times \int_0^t dt_1 \langle \Psi_{n_n}^0 | V_{p=0}(t_1) | \Phi_{n_{n-1}}^{0(0)} \rangle \exp(i\omega_{n_n n_{n-1}} t_1) \\ &\times \int_0^{t_1} dt_2 \langle \Psi_{n_{n-1}}^0 | V_{p=0}(t_2) | \Phi_{n_{n-2}}^{0(0)} \rangle \exp(i\omega_{n_{n-1} n_{n-2}} t_2) \dots \\ &\times \int_0^{t_{n-1}} dt_n \langle \Psi_{n_1}^0 | V_{p=0}(t_n) | \Phi_i^{0(0)} \rangle \exp(i\omega_{n_1} t_n). \end{aligned} \quad (15)$$

Series (15) is characterized by that the transfer matrix elements, taken at later instants of time, are on the left

of the operators taken at earlier instants of time, because always

$$t > t_1 > t_2 > \dots > t_n > 0.$$

Expression (15) can be made more symmetric by introducing the time ordering operator $\hat{\tau}$:

$$\begin{aligned} |\Psi_i^n\rangle &= \frac{1}{n!} \left(\frac{f_0^2}{i\hbar P}\right)^n \sum'_{n_n} \sum'_{n_{n-1}} \dots \sum'_{n_1} |\Psi_{n_n}^0\rangle \exp\left(-\frac{i}{\hbar} E_{n_n} t\right) \\ &\times \int_0^t \dots \int_0^{\hat{\tau}} [\langle \Psi_{n_n}^0 | V_{p=0}(t_1) | \Phi_{n_{n-1}}^{0(0)} \rangle \exp(i\omega_{n_n n_{n-1}} t_1) \dots \\ &\times \langle \Psi_{n_1}^0 | V_{p=0}(t_n) | \Phi_i^{0(0)} \rangle \exp(i\omega_{n_1} t_n)] dt_1 \dots dt_n. \end{aligned} \quad (16)$$

Thus, in the case of perturbations that explicitly depend on time, we have obtained a correction to the wave function of a multicenter system with regard to exchange phenomena due to intercenter electron permutations in any order of perturbation theory. This expression admits a limit passage to the state of the system when intercenter overlaps become insignificant and the whole expression turns into an ordinary relation of TDPT for an orthogonal basis.

The general expression for the expansion coefficients that determines a perturbation-induced transfer from the initial state $|i\rangle$ to the final state $|f\rangle$ can be expressed in an invariant form:

$$C_f(t) = \langle \Psi_f^0 | \hat{T} \exp\left[-\frac{if_0^2}{\hbar P} \int_0^t \hat{W}(t') dt'\right] | \Phi_i^{0(0)} \rangle, \quad (17)$$

where

$$\hat{W}(t) = \exp\left(\frac{i}{\hbar} H_0^{p=0} t\right) V^{p=0}(t) \exp\left(-\frac{i}{\hbar} H_0^{p=0} t\right) \quad (18)$$

is a perturbation operator taken in the interaction representation. Then the probability of transfer to the final state at time t is $w_{fi} = |C_f|^2$ if the transfer occurs to a state of the discrete spectrum and $dw_{fi} = |C_f|^2 dv_f$ if the transfer occurs into an interval dv_f of states of the continuous spectrum. Thus, we have obtained expressions for the probability of transfers from the initial state of the system to any final state with regard to exchange phenomena due to the intercenter overlap of wave functions.

3. PROBABILITY OF QUANTUM TRANSFERS AND THE S MATRIX OF MULTICENTER SYSTEMS

Let the states $|i\rangle$ and $|f\rangle$ and their energies E_i and E_f be eigenstates and eigenvalues of the Hamiltonian operator of two noninteracting subsystems corresponding to the equation

$$\hat{H}_0 |\Psi_i^0\rangle = E_i |\Psi_i^0\rangle.$$

The perturbation operator

$$\hat{V} = \sum_{p=0}^P V^{(p)} \Lambda^{(p)},$$

which induces transfers between these states, does not depend on time in the Schrödinger representation.

When the initial time is $-\infty$ and the final time is $t = \infty$, the matrix elements $C_{ij}(\infty) \equiv C_f(17)$ are elements of the S matrix [2]:

$$C_{ij}(\infty) = \langle \Psi_f^0 | S | \Phi_i^{0(0)} \rangle.$$

Hence,

$$\begin{aligned} C_{ij}(\infty) &= \langle \Psi_f^0 | S | \Phi_i \rangle \\ &= \langle \Psi_f^0 | \hat{\tau} \exp \left(-\frac{i f_0^2}{\hbar P} \int_{-\infty}^{\infty} \hat{W}(t) dt \right) | \Phi_i^{0(0)} \rangle \\ &\equiv \langle \Psi_f^0 | \left[1 + \frac{1}{i\hbar P} \int_{-\infty}^{\infty} \hat{W}(t) dt + \frac{1}{(i\hbar)^2} \left(\frac{f_0^2}{P} \right)^2 \right. \\ &\quad \times \left. \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \hat{W}(t_1) \hat{W}(t_2) + \dots \right] | \Phi_i^{0(0)} \rangle \\ &= \sum_{\alpha} \langle \Psi_f^0 | S^{(\alpha)} | \Phi_i^{0(0)} \rangle. \end{aligned} \quad (19)$$

Taking into account expressions (17) and (19), we can transform the matrix elements of the first and second order to the form [2]

$$\begin{aligned} \langle \Psi_f^0 | S^{(1)} | \Phi_i \rangle &= -\frac{i f_0^2}{\hbar P} \langle \Psi_f^0 | V_0 | \Phi_i^{0(0)} \rangle \int_{-\infty}^{\infty} \exp \left[i(E_f - E_i) \frac{t}{\hbar} \right] dt \\ &= -2\pi i \delta(E_f - E_i) \frac{f_0^2}{P} \langle \Psi_f^0 | V_0 | \Phi_i^{0(0)} \rangle, \\ \langle \Psi_f^0 | S^{(2)} | \Phi_i^{0(0)} \rangle &= -2\pi i \delta(E_i - E_f) \left(\frac{f_0^2}{P} \right)^2 \\ &\quad \times \sum_n \frac{\langle \Psi_f^0 | V_0 | \Phi_i^{0(0)} \rangle \langle \Psi_n^0 | V_0 | \Phi_i^{0(0)} \rangle}{E_i - E_n + i\eta}. \end{aligned} \quad (20)$$

The matrix elements of higher orders are transformed analogously.

We consider transfers, under a stationary perturbation associated with the interaction of electron centers (atoms, ions, etc.) with each other, to states different from the initial one, i.e., $\langle \Psi_f^0 | \Phi_i^{0(0)} \rangle \approx 0$. Then we can express the matrix elements of the S matrix (19) as

$$\langle \Psi_f^0 | S | \Phi_i^{0(0)} \rangle = -2\pi i \delta(E_f - E_i) \langle \Psi_f^0 | T | \Phi_i^{0(0)} \rangle, \quad (21)$$

where the matrix element of transfer on the energy surface is given by

$$\begin{aligned} \langle \Psi_f^0 | T | \Phi_i^{0(0)} \rangle &= \frac{f_0^2}{P} \langle \Psi_f^0 | V_0 | \Phi_i^{0(0)} \rangle + \left(\frac{f_0^2}{P} \right)^2 \sum_n \frac{\langle \Psi_f^0 | V_0 | \Phi_n^{0(0)} \rangle \langle \Psi_n^0 | V_0 | \Phi_i^{0(0)} \rangle}{E_i - E_n + i\eta} + \dots + \left(\frac{f_0^2}{P} \right)^v \\ &\quad \times \sum_{n, n_1, \dots, n_{v-2}} \frac{\langle \Psi_f^0 | V_0 | \Phi_n^{0(0)} \rangle \dots \langle \Psi_{n_{v-2}}^0 | V_0 | \Phi_i^{0(0)} \rangle}{(E_i - E_n + i\eta)(E_i - E_{n_1} + i\eta) \dots (E_i - E_{n_{v-2}} + i\eta)} \dots \end{aligned} \quad (22)$$

Since the functions $\Phi_n^{0(0)}$ are the eigenfunctions of the nonsymmetrized Hamiltonian $H_{p=0}^0$, it follows that, for example, the second term in (22) admits the following transformation:

$$\begin{aligned} &\left(\frac{f_0^2}{P} \right)^2 \sum_n \frac{\langle \Psi_f^0 | V_0 | \Phi_n^{0(0)} \rangle \langle \Psi_n^0 | V_0 | \Phi_i^{0(0)} \rangle}{E_i - E_n + i\eta} \\ &- \sum_n \langle \Psi_f^0 | \frac{f_0^2}{P} V_0 | \Phi_n^{0(0)} \rangle \langle \Psi_n^0 | \left(\frac{f_0^2}{P} \right)^{-1} (E_i - H_{p=0}^0 + i\eta)^{-1} | \Phi_n^{0(0)} \rangle \\ &\quad \times \langle \Psi_n^0 | \left(\frac{f_0^2}{P} \right)^2 V_0 | \Phi_i^{0(0)} \rangle. \end{aligned} \quad (23)$$

Introducing a renormalized perturbation operator $V_0^{\mathbb{N}} = (f_0^2/P)V_0$, we can rewrite the transfer operator T as

$$\begin{aligned} T &= V_0^{\mathbb{N}} + V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} \right)^{-1} (E_i - H_{p=0}^0 + i\eta)^{-1} V_0^{\mathbb{N}} \\ &\quad + V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} (E_i - H_{p=0}^0 + i\eta) \right)^{-1} \\ &\quad \times V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} (E_i - H_{p=0}^0 + i\eta) \right)^{-1} V_0^{\mathbb{N}} + \dots \end{aligned} \quad (24)$$

Equality (24) can be considered as a solution to the following operator equation by the method of successive approximations:

$$T = V_0^{\mathbb{N}} + V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} \right)^{-1} (E_i - H_{p=0}^0 + i\eta)^{-1} T. \quad (25)$$

Then the transfer probability per unit time is expressed as

$$w_{if} = \frac{|\langle \Psi_f^0 | S | \Phi_i^0 \rangle|^2}{r} = \frac{2\pi}{\hbar} \delta(E_f - E_i) |\langle \Psi_f^0 | T | \Phi_i^0 \rangle|^2. \quad (26)$$

$$\lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt$$

4. COLLISIONS, SCATTERING, AND REACTIONS WITH REGARD TO INTERCENTER EXCHANGE

The S matrix can be used as a scattering matrix to describe the scattering of composite particles with regard to intercenter exchange of identical particles that constitute the colliding particles. To calculate the effective cross section and reaction, we divide expression (26) by j_i , the flux density of incident particles:

$$\sigma_{if} = \frac{2\pi\mu_i}{\hbar^2 k_i} \delta(E_f - E_i) |\langle \Psi_f^0 | T | \Phi_i^0 \rangle|^2,$$

where μ_i is the reduced mass of colliding particles and k_i is the wave vector of the relative motion, and we use the T operator on the energy surface introduced in (21) and (24). Since the final states lie in the continuous spectrum, the explicit expression for the density $\rho(E_f)$ of final states per volume per energy interval should be substituted into (26) and integrated over the energy of the final states. When describing a collision with redistribution of particles, we take the operator consisting of the sum of the kinetic energy of relative motion (with reduced mass) and the operator of the internal state of the colliding atoms (molecules),

$$H_0^{p=0} = -\frac{\hbar^2}{2\mu_i} \nabla_i^2 + H_i^{p=0}(r_1, r_2, \dots)_i \quad (27)$$

as the initial Hamiltonian (for the initial distribution of electrons between centers, which corresponds to the permutation $p=0$). The eigenvalue of energy and the eigenvector with regard to the spin state are given by

$$E_i = \frac{\hbar^2}{2\mu_f} k_i^2 + \varepsilon_{n_i},$$

$$|\Phi_i\rangle = \Phi_i(\mathbf{R}_i - \mathbf{r}_1, \mathbf{R}_i - \mathbf{r}_2, \mathbf{R}_i - \mathbf{r}_3, \dots) \times \chi(\xi_1, \xi_2, \xi_3, \dots) \exp(i\mathbf{k}_i \cdot \mathbf{R}_i). \quad (28)$$

respectively, where ε_{n_i} is the internal energy of electron states at the colliding centers, \mathbf{R} and \mathbf{r} are the radius vectors of the positions of nuclei and electrons, respectively, χ is the spin part of the wave function, and χ_i are spin variables.

The Hamiltonian describing the final state, without regard to the interaction between the reaction products, is expressed in the following symmetric form:

$$\hat{H}_{0f} = \sum_{p=0}^p H_f^{0(p)} \Lambda_f^{(p)}, \quad (29)$$

$$H_f^{0(0)} = -\frac{\hbar^2}{2\mu_f} \nabla_p^2 + H_i^p(r_1, r_2, \dots)_f$$

The energy eigenvalues of this Hamiltonian and the antisymmetric eigenvector of the final state are given by

$$E_f = -\frac{\hbar^2}{2\mu_f} k_f^2 + \varepsilon_{n_f}, \quad (30)$$

$$|\Psi_f\rangle = \hat{A} \Phi_f(\mathbf{R}_f - \mathbf{r}_1, \mathbf{R}_f - \mathbf{r}_2, \mathbf{R}_f - \mathbf{r}_3, \dots) \times \chi(\xi_1, \xi_2, \xi_3, \dots) \exp(i\mathbf{k}_f \cdot \mathbf{R}_f).$$

The number of final states per energy interval for scattering along the unit vector \mathbf{n}_f into a solid angle element $d\Omega$ is given by

$$d\rho(E_f) = \frac{\mu_f k_f}{(2\pi)^3 \hbar^2} d\Omega;$$

then

$$d\sigma_{fi} = j^{-1} dw_{fi} = \frac{\mu_i \mu_f k_f}{(2\pi \hbar^2)^2 k_i} |\langle \Psi_f^0 | T | \Phi_i^0 \rangle|^2 d\Omega. \quad (31)$$

In the general case, the T matrix satisfies the operator equation (25); for scattering processes, this equation can be transformed into (see the Appendix)

$$V_0^{\mathbb{N}} \left(\frac{f_0}{P} \right)^{-1} (E_i - \hat{H} + i\eta)^{-1} V_0^{\mathbb{N}} + V_0^{\mathbb{N}} = T. \quad (32)$$

Here \hat{H} is the total Hamiltonian,

$$\hat{H} = H_0^{p=0} + V^{p=0} = -\frac{\hbar^2}{2\mu_i} \nabla_i^2 + H_i^{p=0}(r_1, r_2, \dots)_i + V^{p=0}.$$

As an example, we derive an expression for the charge-exchange cross section of ions during the collision of a proton with an alkali atom with two electrons in the outer shell. The original permutation ($p=0$) of electrons is as follows: an impinging proton (center I) and an atom (center II) with numbered outer electrons 1 and 2. The relative motion of the proton and atom is described by the operator of kinetic energy $(\hbar^2/2\mu)/\nabla_p^2$, where μ is the reduced mass of the colliding particles. The outer electrons in the alkali atom (center II) are described by the Hamiltonian

$$H(1, 2) = -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{Ze^2}{r_{111}} - \frac{Ze^2}{r_{112}} + \frac{e^2}{r_{12}},$$

and the set of eigenfunctions $\{\varphi_i(\mathbf{r}_{111})\varphi_i(\mathbf{r}_{112})\chi(\xi_1, \xi_2)\}$ corresponds to the energy eigenvalues (for the outer shell) ε_i . The interaction between the proton and atom is described by the perturbation operator

$$V_{p=0} = \frac{Ze^2}{R_{1,II}} - \frac{e^2}{r_{11}} - \frac{e^2}{r_{12}}.$$

Thus, the Hamiltonian of the unperturbed system with the original electron permutation is

$$H_0^{p=0} = H(1, 2) - \frac{\hbar^2}{2\mu} \nabla_p^2.$$

The initial state $|i\rangle$ corresponds to the incident wave,

$$|\Phi_i(1, 2)\rangle = (\varphi_i(\mathbf{r}_{I1})\varphi_i(\mathbf{r}_{I2})) \times \chi_a(\xi_1, \xi_2) \exp(i\mathbf{k}_i \cdot \mathbf{R}_{I,II}), \quad (33)$$

$$\chi_a(\xi_1, \xi_2) = (\alpha_1\beta_2 - \beta_1\alpha_2)/\sqrt{2},$$

where α_i and β_i are the spinors of the first and the second electron, respectively. The final state $|f\rangle$, which corresponds to a hydrogen atom and a singly charged ion of an alkali metal, is described by an antisymmetric function (for an open channel) and corresponds to energy

$$\frac{\hbar^2 k_f^2}{2\mu} = \varepsilon_i - \varepsilon_f + \frac{\hbar^2 k_i^2}{2\mu} \geq 0.$$

The antisymmetric vector of the final state is expressed as

$$\begin{aligned} |\Psi_f(1, 2)\rangle &= \exp(i\mathbf{k}_f \cdot \mathbf{R}_{I,II}) \frac{1}{f_f} (\psi_{f1}(\mathbf{r}_{I1})\varphi_{f2}(\mathbf{r}_{II2}) \\ &\pm \psi_{f1}(\mathbf{r}_{I2})\varphi_{f2}(\mathbf{r}_{II1})) \chi_{a/s}(\xi_1, \xi_2), \\ \langle \Psi_f(1, 2) | \Phi_f(1, 2) \rangle &= 1, \\ f_f^{a/s} &= \langle (\psi_{f1}(\mathbf{r}_{I1})\varphi_{f2}(\mathbf{r}_{II2})) \\ &\times \chi_{a/s}(\xi_1, \xi_2) | \psi_{f1}(\mathbf{r}_{I1})\varphi_{f2}(\mathbf{r}_{II2})\chi_2(\xi_2)\chi_1(\xi_1) \\ &\pm \langle (\psi_{f1}(\mathbf{r}_{I2})\varphi_{f2}(\mathbf{r}_{II1}))\chi_{a/s}(\xi_1, \xi_2) \\ &\times | \psi_{f1}(\mathbf{r}_{I1})\varphi_{f2}(\mathbf{r}_{II2})\chi_2(\xi_2)\chi_1(\xi_1). \end{aligned} \quad (34)$$

The scattering cross section for the singlet state is

$$\begin{aligned} \frac{d\sigma_{fi}^{\text{singl}}}{d\Omega} &= \frac{\mu_i \mu_f k_f}{(2\pi\hbar^2)^2 k_i |f_f^a|^2} \left| \frac{1}{f_f} \right|^2 \left| \langle \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{I,II}] \right. \\ &\times (\psi_n(\mathbf{r}_{I1})\varphi_i(\mathbf{r}_{II2}) + \psi_n(\mathbf{r}_{I2})\varphi_i(\mathbf{r}_{II1})) \chi_a(\xi_1, \xi_2) \Big| \hat{T} \Big| \\ &\times \left. \left| \varphi_n(\mathbf{r}_{II1})\varphi_n(\mathbf{r}_{II2})\chi_a(\xi_1, \xi_2) \right|^2. \end{aligned} \quad (35)$$

The triplet state is not realized during the scattering of the atom because of the orthogonality of the spin parts of the wave functions of the initial and final states.

In the first Born approximation, expression (35) with regard to (33) and (34) is rewritten as

$$\begin{aligned} d\sigma_{fi}^{\text{singl}} &= \frac{\mu_i \mu_f k_f}{(2\pi\hbar^2)^2 k_i |f_f^a|^2} \left| \frac{1}{f_f} \right|^2 \left| \langle \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{I,II}] \right. \\ &\times (\psi_n(\mathbf{r}_{I1})\varphi_i(\mathbf{r}_{II2}) + \psi_n(\mathbf{r}_{I2})\varphi_i(\mathbf{r}_{II1})) \chi_a(\xi_1, \xi_2) \Big| V_0 \Big| \\ &\times \left. \left| \varphi_n(\mathbf{r}_{II1})\varphi_n(\mathbf{r}_{II2})\chi_a(\xi_1, \xi_2) \right|^2 d\Omega. \end{aligned} \quad (36)$$

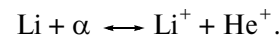
This expression coincides with the expression for the differential cross section of a collision with electron exchange, which was obtained by the Born–Oppenheimer method [2, §117; 21] and in the coordinate part of the asymptotic solution of which the principle of indistinguishability of electrons was taken into account post factum by choosing this solution as a superposition of two possible final states that differ from each other by the permutation of the numbers of electrons with the rule of signs corresponding to the singlet and triplet states.

When applying the general relations obtained for the differential cross section (31), the indistinguishability of electrons is taken into account automatically, without involving the additional procedure of antisymmetrization. In book [21], the authors considered the problem of collision of electrons with composite atoms (§3, Ch. 15) for finding the scattering amplitude of an electron by a two-electron atom in the Born–Oppenheimer approximation, in which they attempted to take into account the spin parts and electron permutations in the asymptotic solution.

However, the form of this solution is neither symmetric nor antisymmetric but represents a certain superposition of functions of states that differ by the permutation of the numbers of electrons. Thus, the rule of signs from the integral contributions to the scattering amplitude is not exactly and uniquely defined; this, as a consequence, requires the application of the variational method to optimize the solution.

5. COLLISION OF AN α PARTICLE WITH A LITHIUM ATOM WITH CHARGE EXCHANGE

Consider a three-electron system by an example of the reaction



The original wave vector is chosen as

$$\begin{aligned} |\Phi_i\rangle &= \Phi_{\text{Li}}(\mathbf{R}_i - \mathbf{r}_1, \mathbf{R}_i - \mathbf{r}_2, \mathbf{R}_i - \mathbf{r}_3) \\ &\times \chi(\xi_1, \xi_2, \xi_3) \exp(i\mathbf{k}_i \cdot \mathbf{R}_i), \end{aligned} \quad (37)$$

where the radius vector is measured from the α particle.

To obtain an antisymmetric function of the system of helium and lithium ions, we apply a normalized Young operator [22] to the nonsymmetrized function of the final state

$$\begin{aligned} |\Phi_f\rangle &= \Phi_{\text{Li}^+}(\mathbf{R}_f - \mathbf{r}_1, \mathbf{R}_f - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3) \\ &\times \chi(\xi_1, \xi_2, \xi_3) \exp(i\mathbf{k}_f \cdot \mathbf{R}_f). \end{aligned} \quad (38)$$

For a three-electron system, there exists only two standard Young diagrams (Fig. 1); here one should take into account that electrons 1 and 2 belonging to the $1s^2$ orbitals of the lithium ion in the ground state

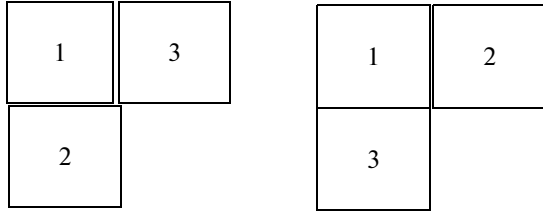


Fig. 1.

should always be in the singlet state. Thus, there exists only one standard Young diagram describing a three-electron two-center system that simultaneously satisfies the above condition.

The coordinate part of the antisymmetric function of the $\text{Li}^+ - \text{He}^+$ electron system has the form

$$\begin{aligned} \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \omega^{11} \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3) \\ &= \frac{1}{\sqrt{12}} (2 + 2P_{12} - P_{23} - P_{13} - P_{123} - P_{132}) \\ &\quad \times \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3), \end{aligned} \quad (39)$$

$$\begin{aligned} \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \omega^{21} \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3) \\ &= (P_{23} - P_{13} - P_{123} + P_{132}) \\ &\quad \times \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3), \end{aligned}$$

where ω^{11} and ω^{21} are the Young operators corresponding to the Young diagrams (see Fig. 1). Acting by the permutation operators P_{ij} , we obtain the following expression for the coordinate part of the wave function:

$$\begin{aligned} \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \frac{1}{\sqrt{12}} \{ 2\Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3) \\ &\quad + 2\Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_1) \Phi_{\text{He}^+}(\mathbf{r}_3) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_3) \Phi_{\text{He}^+}(\mathbf{r}_2) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{\text{He}^+}(\mathbf{r}_2) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_3) \Phi_{\text{He}^+}(\mathbf{r}_1) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{\text{He}^+}(\mathbf{r}_2) \}, \end{aligned} \quad (40)$$

$$\begin{aligned} \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \{ \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_3) \Phi_{\text{He}^+}(\mathbf{r}_2) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_1) \\ &\quad - \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_3) \Phi_{\text{He}^+}(\mathbf{r}_1) \\ &\quad + \Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{\text{He}^+}(\mathbf{r}_2) \}. \end{aligned}$$

Here are expressions for the corresponding spin parts:

$$\begin{aligned} \Xi_1 &= \tilde{\omega}^{11} \chi(123) = \frac{1}{\sqrt{12}} \{ 2\chi_{\text{Li}^+}(12)\chi_{\text{He}^+}(3) \\ &\quad + \chi_{\text{Li}^+}(13)\chi_{\text{He}^+}(2) - 2\chi_{\text{Li}^+}(21)\chi_{\text{He}^+}(3) \\ &\quad + \chi_{\text{He}^+}(32)\chi_{\text{He}^+}(1) - \chi_{\text{Li}^+}(23)\chi_{\text{He}^+}(1) \\ &\quad - \chi_{\text{Li}^+}(31)\chi_{\text{He}^+}(2) \}, \end{aligned} \quad (41)$$

$$\begin{aligned} \Xi_2 &= \tilde{\omega}^{21} \chi(123) = \frac{1}{2} \{ -\chi_{\text{Li}^+}(13)\chi_{\text{He}^+}(2) \\ &\quad + \chi_{\text{Li}^+}(32)\chi_{\text{He}^+}(1) - \chi_{\text{Li}^+}(23)\chi_{\text{He}^+}(1) \\ &\quad + \chi_{\text{Li}^+}(31)\chi_{\text{He}^+}(2) \}, \end{aligned}$$

where $\tilde{\omega}$ are adjoint Young operators taken from the tables presented in [22]. Now, instead of (38), we have an antisymmetrized vector of the final state:

$$|\Psi_f\rangle = \frac{1}{f_0} [\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_1(1, 2, 3) \quad (42)$$

$$+ \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_2(1, 2, 3)] \exp(i\mathbf{k}_f \cdot \mathbf{R}),$$

where f_0 is a normalization coefficient,

$$\begin{aligned} f_0 &= \langle \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_1(1, 2, 3) \\ &\quad + \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_2(1, 2, 3) \end{aligned} \quad (43)$$

$$\times |\Phi_{\text{Li}^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{\text{He}^+}(\mathbf{r}_3) \chi(\xi_1, \xi_2, \xi_3)\rangle.$$

We take the wave function of the initial state (37) as a three-electron function of the lithium atom with regard to the relative motion of the alpha particle and the atom:

$$\begin{aligned} \Phi_{\text{Li}}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_3) \chi(\xi_1, \xi_2, \xi_3) \exp(i\mathbf{k}_i \cdot \mathbf{R}) \\ = \frac{1}{f_{\text{Li}}} [\Psi_{\text{Li}1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_{\text{Li}1}(1, 2, 3) \quad (44) \\ + \Psi_{\text{Li}2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Xi_{\text{Li}2}(1, 2, 3)] \exp(i\mathbf{k}_i \cdot \mathbf{R}). \end{aligned}$$

Here the coordinate part has the form

$$\begin{aligned} \Psi_{\text{Li}1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ = \omega^{11} \phi_{1s}(\mathbf{R} - \mathbf{r}_1) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \phi_{2s}(\mathbf{R} - \mathbf{r}_3) \\ = \frac{1}{\sqrt{12}} (2 + 2P_{12} - P_{23} - P_{123} - P_{132}) \\ \times \phi_{1s}(\mathbf{R} - \mathbf{r}_1) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \phi_{2s}(\mathbf{R} - \mathbf{r}_3) \\ = \frac{2}{\sqrt{3}} [\phi_{1s}(\mathbf{R} - \mathbf{r}_1) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \phi_{2s}(\mathbf{R} - \mathbf{r}_3) \quad (45) \\ - \phi_{1s}(\mathbf{R} - \mathbf{r}_3) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \phi_{2s}(\mathbf{R} - \mathbf{r}_1)], \end{aligned}$$

$$\begin{aligned} \Psi_{\text{Li}2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \omega^{21} \phi_{1s}(\mathbf{R} - \mathbf{r}_1) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \\ &\quad \times \phi_{2s}(\mathbf{R} - \mathbf{r}_3) = (P_{23} - P_{13} - P_{123} + P_{132}) \\ &\quad \times \phi_{1s}(\mathbf{R} - \mathbf{r}_1) \phi_{1s}(\mathbf{R} - \mathbf{r}_2) \phi_{2s}(\mathbf{R} - \mathbf{r}_3) = 0, \end{aligned}$$

Comparison of parameters for the charge-exchange cross section

v , 10^6 cm/s	E , eV	k , au	σ , 10^{-15} cm 2 (61), (63)	σ , 10^{-15} cm 2 [25]	σ , 10^{-16} cm 2 [21, 23, 24]
0.25	0.01	5	500	—	—
0.50	0.04	10	130	—	—
0.75	0.09	15	57.8	26	—
1.0	0.16	20	32.5	—	—
1.25	0.25	25	26.4	—	—
2.5	1	50	17	22	—
5.0	4	100	10	—	—
7.5	9	150	8.75	18	—
10	16	200	8	—	—
25	25	500	5.6	—	—
50	400	1000	5.32	—	—
100	1600	2000	5.24	—	5
150	—	3000	5.22	—	3.5
200	—	4000	5.21	—	2.7
250	2500	5000	5.21	—	2
300	—	6000	5.20	—	1

where ϕ is the initial one-electron state of the Li atom. For the spin part of the wave function, we have

$$\begin{aligned}\Xi_{Li1} &= \tilde{\omega}^{11} \chi(123) = \tilde{\omega}^{11} |\alpha_1 \beta_2 \alpha_3\rangle \\ &= \frac{1}{\sqrt{12}} \{ 2|\alpha_1 \beta_2 \alpha_3\rangle + |\alpha_1 \alpha_2 \alpha_3\rangle + |\alpha_1 \beta_2 \alpha_3\rangle \\ &\quad - 2|\beta_1 \alpha_2 \alpha_3\rangle - |\alpha_1 \alpha_2 \beta_3\rangle - |\beta_1 \alpha_2 \alpha_3\rangle \} \\ &= \frac{\sqrt{3}}{2} \{ |\alpha_1 \beta_2 \alpha_3\rangle - |\beta_1 \alpha_2 \alpha_3\rangle \},\end{aligned}\quad (46)$$

$$\begin{aligned}\Xi_{Li2} &= \tilde{\omega}^{21} \chi(123) = \tilde{\omega}^{21} |\alpha_1 \beta_2 \alpha_3\rangle \\ &= \frac{1}{2} \{ -|\alpha_1 \alpha_2 \beta_3\rangle + |\alpha_1 \beta_2 \alpha_3\rangle - |\alpha_1 \alpha_2 \beta_3\rangle + |\beta_1 \alpha_2 \alpha_3\rangle \} \\ &= \frac{1}{2} \{ -2|\alpha_1 \alpha_2 \beta_3\rangle + |\alpha_1 \beta_2 \alpha_3\rangle + |\beta_1 \alpha_2 \alpha_3\rangle \}.\end{aligned}$$

Taking into account the orthogonality of the spin functions, we reduce the normalization coefficient to

$$\begin{aligned}f_0 &= \left\{ \langle \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \Psi_{Li^+}(\mathbf{r}_1, \mathbf{r}_2) \Psi_{He^+}(\mathbf{r}_3) \frac{\sqrt{3}}{2} \right. \\ &\quad \left. + \langle \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \Psi_{Li^+}(\mathbf{r}_1, \mathbf{r}_2) \Psi_{He^+}(\mathbf{r}_3) \frac{1}{2} \right\}, \\ f_{Li}^2 &= \{ \langle \Psi_{Li1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \Psi_{Li1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle \langle \Xi_{Li1} | \Xi_{Li1} \rangle \\ &\quad + \langle \Psi_{Li2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \Psi_{Li2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle \langle \Xi_{Li2} | \Xi_{Li2} \rangle \} = 4,\end{aligned}$$

where the normalization $f_{Li} = 2$ is determined from relations (44). Thus, the normalization coefficient f_0 reduces to

$$\begin{aligned}f_0 &= \int d^3 R \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] \\ &\times \left\{ \langle 2\Phi_{Li^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{He^+}(\mathbf{r}_3) \right. \\ &\quad + 2\Phi_{Li^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_1) \Phi_{He^+}(\mathbf{r}_3) \\ &\quad - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_3) \Phi_{He^+}(\mathbf{r}_2) \\ &\quad - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{He^+}(\mathbf{r}_2) \\ &\quad - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_3) \Phi_{He^+}(\mathbf{r}_1) \\ &\quad \left. - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{He^+}(\mathbf{r}_2) \right. \\ &\quad \times |\Phi_{Li^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{He^+}(\mathbf{r}_3) \rangle \frac{\sqrt{3}}{2} \\ &\quad + \langle 2\Phi_{Li^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_3) \Phi_{He^+}(\mathbf{r}_2) \\ &\quad - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_2) \Phi_{He^+}(\mathbf{r}_1) \\ &\quad - \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_2, \mathbf{R} - \mathbf{r}_3) \Phi_{He^+}(\mathbf{r}_1) \\ &\quad \left. + \Phi_{Li^+}(\mathbf{R} - \mathbf{r}_3, \mathbf{R} - \mathbf{r}_1) \Phi_{He^+}(\mathbf{r}_2) \right. \\ &\quad \left. \times |\Phi_{Li^+}(\mathbf{R} - \mathbf{r}_1, \mathbf{R} - \mathbf{r}_2) \Phi_{He^+}(\mathbf{r}_3) \rangle \frac{1}{2} \right\}.\end{aligned}\quad (47)$$

The initial one-electron states of the lithium atom are

$$\begin{aligned}\phi_{1s}(\mathbf{R}-\mathbf{r}_i) &= \sqrt{\alpha^3/\pi} \exp(-\alpha|\mathbf{R}-\mathbf{r}_i|), \\ \phi_{2s^1}(\mathbf{R}-\mathbf{r}_3) &= \sqrt{\alpha^3/8\pi} \exp(1-0.5\alpha|\mathbf{R}-\mathbf{r}_3|) \\ &\times \exp(-0.5\alpha|\mathbf{R}-\mathbf{r}_3|), \quad \alpha = 0.795.\end{aligned}\quad (48)$$

The one-electron coordinate wave functions of the final state of a helium-like lithium ion are given by

$$\begin{aligned}\phi^*(\mathbf{R}-\mathbf{r}_i) &= \sqrt{\alpha^{*3}/\pi} \exp(-\alpha^*|\mathbf{R}-\mathbf{r}_i|), \\ \alpha^* &= 1.192.\end{aligned}\quad (49)$$

For the final state of a hydrogen-like helium ion, we take the wave function in the form

$$\begin{aligned}\Psi_{\text{He}^+}(r_{\text{He}^+}) &= \frac{\beta^3}{\pi} \exp(-\beta r_{\text{He}^+}), \\ \beta &= 3.38.\end{aligned}\quad (50)$$

Thus, for the coordinate part of the function of the final state, we obtain

$$\begin{aligned}\Phi_{\text{Li}}(\mathbf{R}-\mathbf{r}_1, \mathbf{R}-\mathbf{r}_2, \mathbf{R}-\mathbf{r}_3) \\ &= \phi_{1s}(\mathbf{R}-\mathbf{r}_1)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s^1}(\mathbf{R}-\mathbf{r}_3) \\ &= \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha|\mathbf{R}-\mathbf{r}_1|) \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha|\mathbf{R}-\mathbf{r}_2|) \\ &\times \sqrt{\frac{\alpha^3}{8\pi}} (1-0.5\alpha|\mathbf{R}-\mathbf{r}_3|) \exp(-0.5\alpha|\mathbf{R}-\mathbf{r}_3|).\end{aligned}\quad (51)$$

The coordinate part of the nonsymmetrized function of the final state appearing in (38) has the form

$$\begin{aligned}\Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_1, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_3) \\ &= \phi^*(\mathbf{R}-\mathbf{r}_1)\phi^*(\mathbf{R}-\mathbf{r}_2)\Psi_{\text{He}^+}(r_{\text{He}^+}) \\ &= \sqrt{\frac{\beta^3}{\pi}} \exp(-\beta r_{\text{He}^+}) \sqrt{\frac{\alpha^{*3}}{\pi}} \exp(-\alpha^*|\mathbf{R}-\mathbf{r}_1|) \\ &\times \sqrt{\frac{\alpha^{*3}}{\pi}} \exp(-\alpha^*|\mathbf{R}-\mathbf{r}_2|).\end{aligned}\quad (52)$$

The nonsymmetrized perturbation operator for the original arrangement of electrons on the centers is taken as (in atomic units)

$$V_0 \equiv V(1, 2, 3) = -\frac{2}{r_{\alpha 1}} - \frac{2}{r_{\alpha 2}} - \frac{2}{r_{\alpha 3}} + \frac{6}{R}.\quad (53)$$

In view of the orthogonality of the spin factors, the matrix element of the interaction operator appearing in (31) has the form

$$\begin{aligned}\langle \Psi_f^0 | V_0^{\text{N}} | \Phi_i \rangle &= \frac{1}{f_0 f_{\text{Li}}} (\sqrt{3} \langle \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \\ &\times V_0^{\text{N}} \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] | \Psi_{\text{Li}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle \\ &+ \frac{3}{2} \langle \Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | V_0^{\text{N}} \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times | \Psi_{\text{Li}2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle) = \frac{1}{f_0 f_{\text{Li}}} \frac{f_0^2}{P} (\langle \Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times |(\phi_{1s}(\mathbf{R}-\mathbf{r}_1)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_3) \\ &- \phi_{1s}(\mathbf{R}-\mathbf{r}_3)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_1)) \rangle) \\ &= \frac{4}{\sqrt{3}} \frac{1}{P f_{\text{Li}}} \{ (\langle \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_1, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_3) \\ &- \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_3, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_1) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times |(\phi_{1s}(\mathbf{R}-\mathbf{r}_1)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_3) \\ &- \phi_{1s}(\mathbf{R}-\mathbf{r}_3)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_1)) \rangle) \\ &= \frac{4}{\sqrt{3}} \frac{1}{P f_{\text{Li}}} \{ (\langle \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_1, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_3) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times |(\phi_{1s}(\mathbf{R}-\mathbf{r}_1)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_3) \\ &- \langle \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_1, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_3) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times | \phi_{1s}(\mathbf{R}-\mathbf{r}_3)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_1) \rangle) \\ &- \langle \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_3, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_1) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times |(\phi_{1s}(\mathbf{R}-\mathbf{r}_1)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_3) \rangle) \\ &+ \langle \Phi_{\text{Li}^+}(\mathbf{R}-\mathbf{r}_3, \mathbf{R}-\mathbf{r}_2)\Phi_{\text{He}^+}(\mathbf{r}_1) | \\ &\times V_0 \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}_{\text{Li, II}}] \\ &\times |(\phi_{1s}(\mathbf{R}-\mathbf{r}_3)\phi_{1s}(\mathbf{R}-\mathbf{r}_2)\phi_{2s}(\mathbf{R}-\mathbf{r}_1) \rangle) \}.\end{aligned}\quad (54)$$

Here we should note the characteristic feature of application of the EPT method. Expression (54) for the matrix element of transfer from the initial state to the final state contains contributions due to inter-center electron permutations. These are integral contributions of the second, third, and fourth terms, which could not in principle appear in the case of the algorithm of conventional invariant perturbation theory, because, in view of the orthogonality of the basis and, as a consequence, the commutation rules of the creation–annihilation operators, these contributions would vanish due to the coefficient corresponding to the “third” electron when the interaction of the first

two electrons is taken into account. One should also pay attention to the rule of signs in the expression obtained, which is exact and uniquely defined by the Young diagrams for the group of permutations in accordance with the given value of the total spin of the interacting system.

To calculate the matrix elements appearing in (54), we should pass to a new, elliptic, system of coordinates, which is more convenient for the two-center problem,

$$\mu = \frac{r_{\text{He}^+} + r_{\text{Li}}}{R}, \quad \nu = \frac{r_{\text{He}^+} - r_{\text{Li}}}{R}, \quad \varphi,$$

where φ is the angle of rotation around the straight line connecting the two nuclei. In these coordinates, the volume element is

$$d\tau = \frac{R^3}{8}(\mu^2 - \nu^2)d\mu d\nu d\varphi.$$

Integration should be performed within the limits

$$1 \leq \mu \leq \infty, \quad -1 \leq \nu \leq 1, \quad 0 \leq \varphi \leq 2\pi.$$

In these elliptic coordinates, expression (54) for the transfer matrix element has the form

$$\begin{aligned} \langle \Psi_f^0 | V_0 | \Phi_i \rangle &= \frac{4}{\sqrt{3}} \frac{2f_0}{Pf_{\text{Li}}} \int d^3 R \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] \\ &\times \left\{ \Delta_{1s^*1s} \left[\left(\frac{6}{R} \Delta_{1s^*1s} S_{1s'2s} - 2A_{1s'2s} \Delta_{1s^*1s} \right. \right. \right. \\ &- 4K_{1s^*1s} S_{1s'2s} \left. \left. \left. - \left(S_{1s'1s} \left(\frac{3}{R} \Delta_{1s^*1s} - K_{1s^*1s} \right. \right. \right. \right. \right. \\ &- K_{1s^*2s} \left. \left. \left. - A_{1s'1s} \Delta_{1s^*2s} \right) \right] \right. \\ &- \Delta_{1s^*1s} \Delta_{1s^*2s} \left(\frac{3S_{1s'1s}}{R} - A_{1s'1s} \right) \\ &\left. \left. \left. + S_{1s'1s} (K_{1s^*1s} \Delta_{1s^*2s} + K_{1s^*2s} \Delta_{1s^*1s}) \right\}, \end{aligned} \quad (55)$$

where the following notation is used for the integral contributions:

$$\begin{aligned} \Delta_{1s^*1s} &= \langle \phi^* | \phi_{1s^*1} \rangle, \quad \Delta_{1s^*2s} = \langle \phi^* | \phi_{2s^*1} \rangle, \\ S_{1s'1s} &= \langle \Psi_{\text{He}^*}(\mathbf{r}) | \phi_{1s}(\mathbf{R} - \mathbf{r}) \rangle, \\ S_{1s'2s} &= \langle \Psi_{\text{He}^*}(\mathbf{r}) | \phi_{2s}(\mathbf{R} - \mathbf{r}) \rangle, \\ K_{1s^*1s} &= \left\langle \phi^* \left| \frac{1}{r} \right| \phi_{1s^*1} \right\rangle, \quad K_{1s^*2s} = \left\langle \phi^* \left| \frac{1}{r} \right| \phi_{2s^*1} \right\rangle, \quad (56) \\ A_{1s'1s} &= \left\langle \Psi_{\text{He}^*}(\mathbf{r}) \left| \frac{1}{r} \right| \phi_{1s}(\mathbf{R} - \mathbf{r}) \right\rangle, \\ A_{1s'2s} &= A_{1s'1s} = \left\langle \Psi_{\text{He}^*}(\mathbf{r}) \left| \frac{1}{r} \right| \phi_{2s}(\mathbf{R} - \mathbf{r}) \right\rangle. \end{aligned}$$

Analytical expressions for the above contributions are given in the Appendix. Here we should stress once again that the rule of signs in expressions (54) and (55) is determined by the type of the Young diagrams that are used for describing this particular system, which is in certain initial and final states, while the wave vector of the final state, which is determined only to a first approximation, preserves its antisymmetry. When there is a need to find a correction to the scattering amplitude to higher orders of approximation, the correction to the vector of state always preserves the antisymmetric form and, hence, defines a correct rule of signs in the integral contributions to the scattering amplitude.

The normalization coefficient has the form

$$\begin{aligned} f_0 &= \frac{4}{3} \langle 4\phi^*(\mathbf{R} - \mathbf{r}_1)\phi^*(\mathbf{R} - \mathbf{r}_2)\Psi_{\text{He}^+}(r_3) \\ &- 3\phi^*(\mathbf{R} - \mathbf{r}_1)\phi^*(\mathbf{R} - \mathbf{r}_3)\Psi_{\text{He}^+}(r_2) \\ &\times \phi^*(\mathbf{R} - \mathbf{r}_3)\phi^*(\mathbf{R} - \mathbf{r}_2)\Psi_{\text{He}^+}(r_1) \rangle \\ &\times \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] [\phi_{1s}(\mathbf{R} - \mathbf{r}_1)\phi_{1s}(\mathbf{R} - \mathbf{r}_2) \\ &\times \varphi_{2s}(\mathbf{R} - \mathbf{r}_3) - \phi_{1s}(\mathbf{R} - \mathbf{r}_3)\phi_{1s}(\mathbf{R} - \mathbf{r}_2)\varphi_{2s}(\mathbf{R} - \mathbf{r}_1)] \rangle \\ &= \frac{20}{3} \int d^3 R \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] \\ &\times (\Delta_{1s^*1s}\Delta_{1s^*1s}S_{1s'1s} - \Delta_{1s^*1s}\Delta_{1s^*2s}S_{1s'1s}). \end{aligned} \quad (57)$$

With regard to the normalization coefficients, expression (55) is rewritten as

$$\begin{aligned} \langle \Psi_f^0 | V_0 | \Phi_i \rangle &= 10 \frac{2^5}{3^{5/2}} \int d^3 R \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] \\ &\times (\Delta_{1s^*1s}\Delta_{1s^*1s}S_{1s'1s} - \Delta_{1s^*1s}\Delta_{1s^*2s}S_{1s'1s}) \\ &\times \int d^3 R \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}] \\ &\times \left\{ \Delta_{1s^*1s} \left[\left(\frac{6}{R} \Delta_{1s^*1s} S_{1s'2s} - 2A_{1s'2s} \Delta_{1s^*1s} \right. \right. \right. \\ &- 4K_{1s^*1s} S_{1s'2s} \left. \left. \left. - \left(S_{1s'1s} \left(\frac{3}{R} \Delta_{1s^*1s} - K_{1s^*1s} \right. \right. \right. \right. \right. \\ &- K_{1s^*2s} \left. \left. \left. - A_{1s'1s} \Delta_{1s^*2s} \right) \right] \right. \\ &- \Delta_{1s^*1s} \Delta_{1s^*2s} \left(\frac{3S_{1s'1s}}{R} - A_{1s'1s} \right) \\ &\left. \left. \left. + S_{1s'1s} (K_{1s^*1s} \Delta_{1s^*2s} + K_{1s^*2s} \Delta_{1s^*1s}) \right\}. \end{aligned} \quad (58)$$

From relations (57) and (58), we obtain the differential cross section of the charge-exchange process to a first approximation:

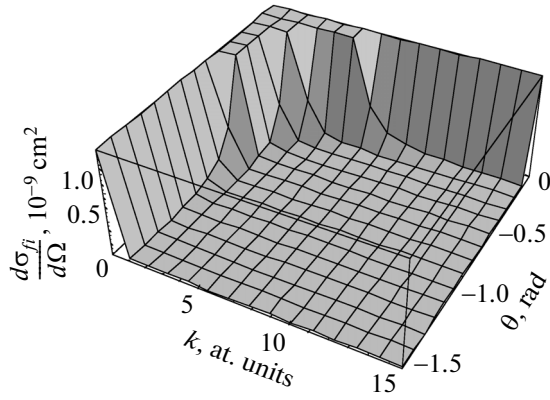


Fig. 2. Differential cross section (59) calculated in square centimeters for a collision energy of $E < 1$ eV.

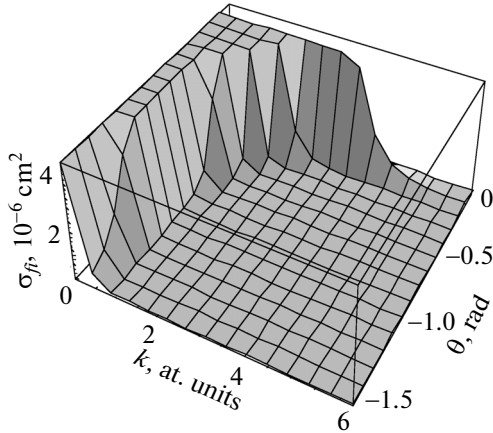


Fig. 3. Cross section $\sigma_{fi}(\theta, k) = 2\pi\sin(\theta)d\sigma_{fi}/d\Omega$ as a function of the scattering angle θ for $E < 0.1$ eV.

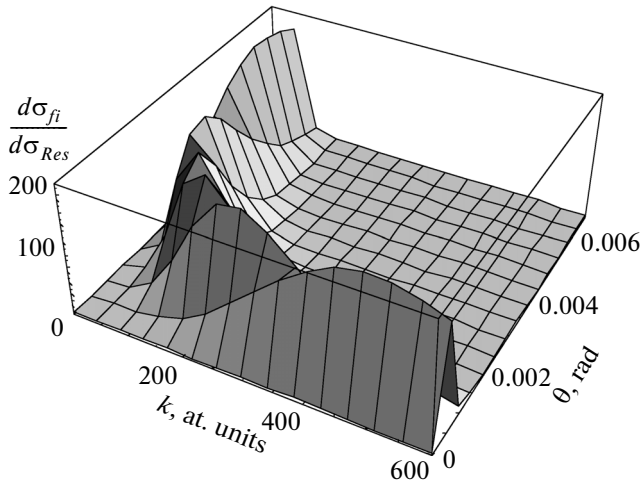


Fig. 4. Relative differential cross section in the full range of collision energies for small scattering angles θ .

$$\frac{d\sigma_{fi}}{d\Omega} = \frac{\mu_i\mu_f k_f}{(2\pi\hbar^2)^2 k_i} \langle \Psi_f^0 | V_0 | \Phi_i^0 \rangle^2, \quad (59)$$

where

$$\mu_i = \frac{M_{\text{Li}}M_{\alpha}}{M_{\text{Li}} + M_{\alpha}}, \quad \mu_f = \frac{M_{\text{Li}^+}M_{\text{He}^+}}{M_{\text{Li}^+} + M_{\text{He}^+}}$$

are the reduced masses of the colliding lithium atom and the alpha particle at the beginning of the process and the lithium ion and the helium ion at the end of the process, and k_i and k_f are the wave vectors of the relative motion.

6. RESULTS AND DISCUSSIONS

The analytical expression for the differential ion charge-exchange cross section is obtained by the Mathematica 8 software package. The main contribution to the cross section is made by small scattering angles $\theta \sim 1/ka_B$ (a_B is the Bohr radius) corresponding to the quantum limit [1, 2], which is clearly seen from the analysis of Figs. 2–4. A graphical representation of the differential cross section in a wide range of angles $0 < \theta < \pi/2$ is shown in Fig. 2 for energy of $E < 1$ eV, $0 < k < 5$. One can see that the most efficient process of charge exchange occurs in the quantum limit of scattering angles $\theta \leq 1/ka_B$. The differential cross section as a function of collision energy in the scattering cone is demonstrated in Fig. 3.

For comparison, we present the angular and energy dependence of the differential scattering cross section and the effective Rutherford differential cross section $d\sigma_{Res}$ for the collision of particles of the same mass and charge as the reaction products. Figure 4 shows the angular dependence of the ratio of the differential charge-exchange cross section to the Rutherford cross section for $E \approx 0.1$ eV. For other values of energy, up to 1 keV, the pattern is completely repeated. Here it is noteworthy that there exists a characteristic angle $\theta^* = 1/2ka_B$ for which the charge-exchange cross section is greater than the Rutherford cross section precisely by a factor of 200 throughout the collision energy range from 0.1 eV to 1 keV: a so-called charge-exchange ridge is formed.

Expression (59) in this quantum limit of small angles $\theta < 1/ka_B$ can be transformed into

$$\begin{aligned} \frac{d\sigma_{fi}}{d\Omega} &= 18.4 \times 10^3 \frac{(k\theta)^2}{[2.4 + (k\theta)^2]^2} \\ &\times \left\{ 2.4^2 + \frac{4.8(k\theta)^4}{[0.16 + (k\theta)^2]^2} + \frac{(k\theta)^8}{[0.16 + (k\theta)^2]^4} \right. \\ &\left. + (k\theta)^2 \left[1 + \frac{8(k\theta)^2}{[0.16 + (k\theta)^2]^2} + \frac{16(k\theta)^4}{[0.16 + (k\theta)^2]^4} \right] \right\}. \quad (60) \end{aligned}$$

The total cross section in this small-angle approximation (in the atomic system of units) has the form

$$\sigma = \pi \frac{1.84 \times 10^4}{k^2} \left\{ x + \frac{2.4}{x + 2.4} (12.8 \cdot 3) - \frac{3 \cdot 12.8}{2} \left(\frac{2.4}{x + 2.4} \right)^2 + \frac{12.8}{3} \left(\frac{2.4}{x + 2.4} \right)^3 + 10.4 \ln(x + 2.4) \right\}, \quad (61)$$

where $x = (k\theta^*)^2$.

In the low-energy limit $ka_B \sim 1$, the expression for the cross section is rewritten as

$$\sigma_{\text{low}} [\text{cm}^2] = \frac{414\pi}{k^2} 10^{-14}, \quad (62)$$

where the wave vector is taken in units of inverse Bohr radius. In the high-energy limit, we have

$$\sigma_{\text{high}} [\text{cm}^2] = \frac{46\pi}{k^2} 10^{-14} \times \left\{ (0.06k)^2 + 10.4 \ln \left[\frac{(0.06k)^2}{2.4} + 1 \right] \right\}, \quad (63)$$

where the solutions are matched at the point $k = 10$.

The results obtained for the charge-exchange cross section of lithium for the collision with a double-charged helium ion are in agreement with the results of the experiment carried out in [23] for fast collisions of double-charged helium ions (alpha particles) with helium atoms and of helium atoms with a proton throughout the collision energy range presented in the table. We take into account the fact that the ionization potential of a helium atom is five times greater than the ionization potential of a lithium atom [26]. The cross section of trapping to the ground state during the collision with a double-charged helium ion was calculated in [24], where the authors used the relations obtained for fast collisions of electrons with atoms, renormalized with regard to the mass and charge of the ion. These data show a satisfactory agreement with the experiment of [21] for high energies greater than 39 keV [23]. For low energies, this method gives too large values of charge-exchange cross sections. In the low-energy range, the results were compared with the theory of collisions of atomic particles outlined in book [25] (see the table). In this theory, the exchange phenomena are taken into account approximately, by singling out the Hamiltonian of an electron that performs a transfer, from the total Hamiltonian of the sys-

tem of electrons and neglecting the permutations of two or more electrons. In this case, the potential of the exchange interaction of a multielectron system is expressed in terms of the one-electron potential.

7. CONCLUSIONS

We have constructed an EPT formalism that is developed for all possible cases of perturbations, stationary and time-dependent ones, defined in the non-relativistic limit with regard to the possible degeneracy of the original state of a system in the absence of interaction. Taking into account the presence of exchange degeneracy, which, as pointed out in [16, 18, 19], is degeneracy with respect to the total electron spin of the system, we should emphasize that it is the functions antisymmetrized by the Young diagrams according to the value of the total spin of the system that represent correct wave functions.

A characteristic feature of the method developed is the consistent consideration of the principle of indistinguishability of electrons in composite multicenter (multiatomic) systems by finding a correct antisymmetric wave function by the method of successive approximations in any order of perturbation theory. The method of determining corrections to the wave function and energy (in the stationary case) does not require additional procedure of antisymmetrization and orthogonalization of the basis. This method consistently takes into account both paired exchange and three-center superexchange (in molecular systems) contributions for a uniquely defined rule of signs with which each matrix element appears in the final expression. As a consequence, the EPT method developed does not require the application of the variational procedure to optimize a solution. For the problems of scattering of composite (atomic and molecular) particles, we have consistently introduced the scattering (S) matrix and the transfer (T) matrix, which naturally include exchange and superexchange contributions that arise when one takes into account intercenter electron permutations in the colliding particles.

Since the EPT and TDEPT series are two-parameter ones, the hierarchy of contributions in each order of perturbation theory, determined by the intercenter overlapping parameter, is obvious: direct, exchange, and superexchange. Characteristic features of application of the EPT method developed have been demonstrated by an example given in Section 5 for the charge-exchange problem of a three-electron atom during a collision with a double-charged helium ion (alpha particle). Expression (58) for the matrix element of transfer from the initial state to the final state contains contributions attributed precisely to intercenter electron permutations. These are integral contributions of the second, third, and fourth terms that appear with signs related to the parity of electron per-

mutations with regard to intercenter permutations and that in principle could not appear when the algorithm and the diagram technique were applied within the conventional invariant perturbation theory.

Even if all possible electron permutations were taken into account by second quantization operators, the diagram technique would automatically make these contributions vanish due to the commutation relations of the creation–annihilation operators, which were derived only for an orthogonal basis. For a multicenter problem, one should introduce other operators of second quantization that take into account the nonorthogonality of one-electron states at different centers in the commutation conditions. There were attempts in the literature (see, for example, [27, 28]) to introduce such an apparatus of second quantization and “correct” the commutation relations of the creation–annihilation operators with regard to electron permutations between nonorthogonal states belonging to different centers. However, this resulted in complicated unitary transformations and transformations of these operators to some additional representation, which actually restricted the application of the diagram technique to two-electron systems [28]. Therefore, to date, the above contributions in expression (57) cannot be assigned standard types of Feynman diagrams. Here the diagrams phenomenologically represented in [17–19] to describe a stationary multicenter system are more relevant. However, the formalism of second quantization was not introduced consistently from the first principles for these diagrams.

To perform quantum-chemical calculations, as well as to describe the collisions of composite particles with regard to quantum transfers, it is long past time to develop a method of second quantization and a diagram technique [29, 30]. The TDEPT formalism presented in this work allows one to consistently take into account and analytically calculate exchange contributions when describing the collisions of atomic particles. For instance, the transfer matrix element (58) is represented analytically by means of the Mathematic 10 software package and the diagrams used in [19]. Here one should take into account that there is no theoretically substantiated and analytically verified apparatus of second quantization for such a multicenter system. In [27, 29], the authors point out that “... the application of second quantization facilitates both the calculations themselves and the comparison of chemically similar systems. At the same time, the overlapping of the orbitals centered on different atoms is of primary chemical importance; therefore, it should be retained in the formalism in the explicit form. The wave functions of such systems are defined in different Hilbert spaces; therefore, it is hardly possible to compare them within first quantization. There are many things that can be made fast and elegantly applying second quantization, while they are hardly solvable without it”

Property of Completeness of a Nonorthogonal Set

To demonstrate the property of completeness, we act by operator (2) on an arbitrary antisymmetric vector $|\Psi\rangle$. Then we can write

$$\begin{aligned} \sum_n |\Psi_n^0\rangle \frac{f_n^p}{P} (\Phi_n^{0(0)}|\Psi\rangle) &= \sum_n \sum_{p=0}^P \frac{(-1)^{g_p}}{P} |\Phi_n^p\rangle (\Phi_n^{0(0)}|\Psi\rangle) \\ &= \sum_n \sum_{p=0}^P \frac{(-1)^{g_p}}{P} |\Phi_n^p\rangle (\Phi_n^p|\Psi\rangle) (-1)^{g_p} = \frac{1}{P} \sum_{p=0}^P |\Psi\rangle = |\Psi\rangle. \end{aligned} \quad (\text{A.1})$$

Operator Equation for the T Matrix

The operator equation (25) is transformed into one of the following equations:

$$\begin{aligned} V_0^{\mathbb{N}} &= \left[\hat{1} - V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} \right)^{-1} (E_i - H_{p=0}^0 + i\eta)^{-1} \right] T, \\ V_0^{\mathbb{N}} &= \left[(E_i - H_{p=0}^0 + i\eta) \left(\frac{f_0^2}{P} \right) - V_0^{\mathbb{N}} \right] \\ &\quad \times \left(\frac{f_0^2}{P} \right)^{-1} (E_i - H_{p=0}^0 + i\eta)^{-1} T, \\ V_0^{\mathbb{N}} &= (E_i - H + i\eta) \left(\frac{f_0^2}{P} \right) \left(\frac{f_0^2}{P} \right)^{-1} \\ &\quad \times (E_i - H_{p=0}^0 + i\eta)^{-1} T. \end{aligned} \quad (\text{B.1})$$

The total Hamiltonian

$$\hat{H} = H_{p=0}^0 + V^{p=0} = H_p^0 + V_p$$

remains invariant with respect to electron permutations. Multiplying the operator equality (B.1) on the left by

$$\left(\frac{f_0^2}{P} \right) (E_i - H_{p=0}^0 + i\eta) \left(\frac{f_0^2}{P} \right)^{-1} (E_i - \hat{H} + i\eta)^{-1},$$

we obtain

$$V_0^{\mathbb{N}} \left(\frac{f_0^2}{P} \right)^{-1} (E_i - \hat{H} + i\eta)^{-1} V_0^{\mathbb{N}} + V_0^{\mathbb{N}} = T. \quad (\text{B.2})$$

Here \hat{H} is the total Hamiltonian,

$$\begin{aligned} \hat{H} &= H_0^{p=0} + V^{p=0} \\ &= -\frac{\hbar^2}{2\mu_i} \nabla_i^2 + H_i^{p=0}(r_1, r_2, \dots)_i + V^{p=0}. \end{aligned}$$

APPENDIX C

Integral Contributions to the Charge-Exchange Cross Section of a Lithium Atom

Let us present exact analytical expressions for the integral contributions (56), which appear in the final expressions (59) and (60) for the scattering cross section:

$$\begin{aligned}
\Delta_{1s^*1s} &= \langle \phi^* | \phi_{1s^*} \rangle = \frac{8(\alpha\alpha^*)^{3/2}}{(\alpha + \alpha^*)^3}, \\
\Delta_{1s^*2s} &= \langle \phi^* | \phi_{2s^*} \rangle = \frac{8(\alpha\alpha^*/2)^{3/2}}{(\alpha/2 + \alpha^*)^3} \left(1 - \frac{3\alpha}{\alpha + 2\alpha^*}\right), \\
S_{1s^*1s} &= \langle \psi_{\text{He}^+}(\mathbf{r}) | \phi_{1s}(\mathbf{R} - \mathbf{r}) \rangle \quad (\text{C.1}) \\
&= \frac{8(\alpha\beta)^{3/2}}{\beta^2 - \alpha^2} \sinh\left[\frac{R}{2}(\alpha - \beta)\right] \exp\left[-\frac{R}{2}(\alpha + \beta)\right] \\
&\times \left(\frac{1}{\alpha + \beta} + \frac{\coth[R(\alpha - \beta)]/2}{\alpha - \beta} - \frac{8\alpha\beta}{R(\alpha^2 - \beta^2)^2}\right), \\
S_{1s^*2s} &= \langle \psi_{\text{He}^+}(\mathbf{r}) | \phi_{2s}(\mathbf{R} - \mathbf{r}) \rangle = \frac{(\alpha\beta)^{3/2}}{\sqrt{2}} \\
&\times \frac{R \sinh\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right] \exp\left[-\frac{R}{2}\left(\frac{\alpha}{2} + \beta\right)\right]}{\beta^2 - (\alpha/2)^2} \\
&\times \left\{ \frac{4}{R(\alpha/2 + \beta)} - \frac{8\alpha\beta}{R^2((\alpha/2)^2 - \beta^2)^2} \right\} \\
&+ \frac{4 \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]}{R(\alpha/2 - \beta)} - \frac{\alpha \left\{1 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\}}{R(\alpha/2 + \beta)} \quad (\text{C.2}) \\
&- \frac{2\alpha \left\{3 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\}}{R(\alpha/2 + \beta)^2} - \frac{12\alpha}{R^2(\alpha/2 + \beta)^3} \\
&+ \frac{12\alpha}{R^2(\alpha/2 - \beta)^3} + \frac{\alpha \left\{1 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\}}{R(\alpha/2 - \beta)} \\
&- \frac{2\alpha \left\{1 + \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\}}{R[(\alpha/2)^2 - \beta^2]}
\end{aligned}$$

$$\left. \begin{aligned}
&2\alpha \left\{1 - 3 \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\} \\
&+ \frac{\left\{1 - 3 \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} - \beta\right)\right]\right\}}{R(\alpha/2 - \beta)^2}
\end{aligned} \right\},$$

$$\begin{aligned}
K_{1s^*1s} &= \left\langle \phi^* \left| \frac{1}{|s|} \right| \phi_{1s^*} \right\rangle \\
&= \frac{4(\alpha\alpha^*)^{3/2}}{(\alpha + \alpha^*)^2} \sinh\left[\frac{R}{2}(\alpha + \alpha^*)\right] \exp\left[-\frac{R}{2}(\alpha + \alpha^*)\right] \quad (\text{C.3}) \\
&\times \left\{1 + \frac{4}{R(\alpha + \alpha^*)} - \coth\left[\frac{R}{2}(\alpha + \alpha^*)\right]\right\},
\end{aligned}$$

$$\begin{aligned}
A_{1s^*1s} &= \left\langle \psi_{\text{He}^+}(\mathbf{r}) \left| \frac{1}{r} \right| \phi_{1s}(\mathbf{R} - \mathbf{r}) \right\rangle \\
&= \frac{4(\alpha\beta^*)^{3/2}}{\alpha^2 - \alpha'^2} \sinh\left[\frac{R}{2}(\alpha - \beta)\right] \exp\left[-\frac{R}{2}(\alpha + \beta)\right] \quad (\text{C.4}) \\
&\times \left\{1 + \frac{4\alpha}{R(\alpha^2 - \beta^2)} - \coth\left[\frac{R}{2}(\alpha - \beta)\right]\right\},
\end{aligned}$$

$$\begin{aligned}
K_{1s^*2s} &= \left\langle \phi^* \left| \frac{1}{|s|} \right| \phi_{1s^*} \right\rangle = \frac{\sqrt{2}(\alpha\alpha^*)^{3/2}}{(\alpha/2 + \alpha^*)^2} \\
&\times \sinh\left[\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right] \exp\left[-\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right] \\
&\times \left\{1 + \frac{4}{R(\alpha/2 + \alpha^*)} - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right]\right\} \quad (\text{C.5}) \\
&- \frac{R\alpha}{2} \left\{1 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right]\right\}
\end{aligned}$$

$$\begin{aligned}
&\left. \begin{aligned}
&2\alpha \left\{1 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right]\right\} \\
&- \frac{\left\{1 - \coth\left[\frac{R}{2}\left(\frac{\alpha}{2} + \alpha^*\right)\right]\right\}}{\alpha/2 + \alpha^*} - \frac{6\alpha}{R(\alpha/2 + \alpha^*)^2}
\end{aligned} \right\}, \\
A_{1s^*2s} &= A_{1s^*1s} = \left\langle \psi_{\text{He}^*} \left| \frac{1}{r} \right| \phi_{2s}(\mathbf{R} - \mathbf{r}) \right\rangle = \frac{\sqrt{2}(\alpha\beta)^{3/2}}{(\alpha/\beta)^2 - \beta^2} \\
&\times \sinh\left[\frac{R}{2}\left(\frac{\alpha}{2} + \beta\right)\right] \exp\left[-\frac{R}{2}\left(\frac{\alpha}{2} + \beta\right)\right]
\end{aligned}$$

$$\begin{aligned}
& \times \left\{ 1 - \coth \left[\frac{R}{2} \left(\frac{\alpha}{2} - \beta \right) \right] \right\} \\
& - \frac{R\alpha}{2} \left\{ 1 - \coth \left[\frac{R}{2} \left(\frac{\alpha}{2} - \beta \right) \right] \right\} \\
& - \frac{\alpha \left\{ 1 - \coth \left[\frac{R}{2} \left(\frac{\alpha}{2} - \beta \right) \right] \right\}}{\alpha/2 + \beta} \\
& - \frac{\alpha \left\{ 1 - \coth \left[\frac{R}{2} \left(\frac{\alpha}{2} - \beta \right) \right] \right\}}{\alpha/2 - \beta} \\
& - \left. \frac{2\alpha}{R(\alpha/2 + \beta)^2} - \frac{2\alpha}{R(\alpha/2 - \beta)^2} \right\}. \tag{C.6}
\end{aligned}$$

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