On the Galilean transformation of the few-electron wave functions.

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Abstract

The Galilean transformations of the few-electron atomic wave functions are considered. We discuss the few-electron wave functions constructed in the model of independent electrons as well as the truly correlated (or highly accurate) wave functions. Results of our analysis are applied to determine the probability of formation of the negatively charged tritium/protium ions during the nuclear \((n, ^{3}\text{He}; t, p)\)–reaction of the helium-3 atoms with thermal/slow neutrons.
The general formulas for the Galilean transformation of the non-relativistic, single-particle wave function $\Psi(\mathbf{r}, t)$ are well known since the middle of 1920’s [1]. A complete discussion of this problem can be found, e.g., in [2] and [3]. If $\Psi(\mathbf{r}, t)$ is such a wave function written in the reference frames which are at rest, then the corresponding wave function $\Psi'(\mathbf{r}', t)$ in the moving frames takes the form

$$\Psi'(\mathbf{r} - \mathbf{V}t, t) = \Psi(\mathbf{r}, t) \exp\left[\frac{im}{\hbar}(-\mathbf{V} \cdot \mathbf{r} + \frac{1}{2}V^2 t)\right]$$  \hspace{1cm} (1)$$

or

$$\Psi'(\mathbf{r}, t) = \Psi(\mathbf{r} + \mathbf{V}t, t) \exp\left[\frac{im}{\hbar}(-\mathbf{V} \cdot \mathbf{r} - \frac{1}{2}V^2 t)\right]$$  \hspace{1cm} (2)$$

From Eq.(2) one easily finds the following transformation formulas for the non-relativistic wave function of an arbitrary few-particle system. To avoid analysis of very general quantum systems in this study we restrict ourselves to the consideration of few-electron atomic systems only. By an ‘atomic system’ we mean the bound few-electron atom with one very heavy center which also has a positive electric charge $Qe$. The forces of electric attraction between nucleus and electrons bind this system together. The competing forces of electric repulsion between electrons decrease the final value of binding energy, but they are relatively small and cannot destroy the whole atom, or produce electron ionization in it.

The general formulas for the Galilean transformations of the actual few-electron (atomic) wave function follow from formulas, Eqs.(1) - (2). For such systems one finds a number of advantages to write all formulas in atomic units, where $\hbar = 1, e = 1, m_e = 1$. In this units for the $N$-electron atomic system we have

$$\Psi'(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) = \Psi(\mathbf{r}_1 + \mathbf{V}t, \ldots, \mathbf{r}_N + \mathbf{V}t, t) \exp\left[i(-\mathbf{V} \cdot \sum_{i=1}^{N} \mathbf{r}_i - N\frac{1}{2}V^2 t)\right]$$  \hspace{1cm} (3)$$

where all electrons are assumed to be independent, or non-correlated. By approximating the actual $N$-electron wave functions by the trial functions constructed in the model of independent electrons one can show that the formula, Eq.(3), is also correct in the general case, i.e. when all electron-electron correlations are included. Briefly, we can say that the Galilean transformation of the actual (i.e. truly correlated) wave function is represented by the same formula, Eq.(3), where the phase factor does not depend (and cannot depend) upon any of the electron-electron coordinates.

In reality, we need the formulas for the Galilean transformations of the $N$-electron wave functions in the limit $t \to 0$. This limit corresponds to the sudden approximation [4], [5].
for few-electron atomic systems. For instance, all processes, decays and reactions in atomic nuclei proceed significantly faster than usual electron transitions in atoms. Therefore, the sudden approximation can be applied to determine the probabilities of the electron-electron transitions during nuclear reactions in atoms. In many cases it is important to know the probabilities to form various ‘final atomic states’ after some fast nuclear process in the atomic nucleus. The ‘incident’ atomic state is usually known. In many cases the newly created nuclei (or ‘nuclear fragments’) are rapidly moving after the nuclear reaction and/or decay. In such cases one finds numerous advantages to determine the final state probabilities by using the moving frames with the origin located at the central atomic nucleus. In these frames if the nucleus begins to move, then all atomic electrons suddenly take the speed $-\mathbf{V}_n$, where the subscript $n$ means the nucleus. Now, the formula for the sudden (Galilean) transformation of the non-relativistic wave function of a $N$-electron atomic system takes the form

$$
\Psi'(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \exp(i\mathbf{V}_n \cdot \mathbf{r}_1 + i\mathbf{V}_n \cdot \mathbf{r}_2 + \ldots + i\mathbf{V}_n \cdot \mathbf{r}_N)\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad (4)
$$

This formula is written in the form which can directly be used for an arbitrary $N$-electron atom with independent and/or quasi-independent electrons. In such cases the wave function depends upon the $N$ electron-nuclear $r_i = r_{in}$ coordinates (scalars) only. However, all actual, few-electron wave functions are truly correlated, i.e. they explicitly depend upon both the electron-nuclear $r_i = r_{in}$ and electron-electron $r_{ij}$ coordinates, which are also called the interparticle coordinates (or Hylleraas coordinates). Formulas for the Galilean transformations of the electron-electron coordinates $r_{ij}$ can be obtained from their definitions. Indeed, according to the definition of $r_{ij}$ we can write the following identities $r_{ij} = | \mathbf{r}_i - \mathbf{r}_j | = | \mathbf{r}_i - \mathbf{r}_n - (\mathbf{r}_j - \mathbf{r}_n) | = | \mathbf{r}_i - (\mathbf{r}_n - \mathbf{V}\delta t) - [\mathbf{r}_j - (\mathbf{r}_n - \mathbf{V}\delta t)] | = r_{ij}$, where $\delta t$ is infinitely small. This means that the electron-electron coordinates $r_{ij}$ does not depend upon $\mathbf{V}$, i.e. it does not change during the sudden motion of the nucleus. It follows from here that the sudden Galilean transformations of the truly correlated wave function are also described by the same formula, Eq. (4).

The formula, Eq. (4), can be applied to determine the probability of formation of the tritium $^3\text{H}^-$ ion during the reaction of the $^3\text{He}$ nuclei with slow/thermal neutrons

$$
^3\text{He} + n = ^3\text{H} + ^1\text{H} + 0.764 \text{ MeV} \quad (5)
$$

in the two-electron helium-3 atom. In the reaction Eq. (5) the notations $^3\text{H}$ and $^1\text{H}$ stand for the tritium nucleus (or $t$ nucleus) and protium (or $p$ nucleus). The reaction, Eq. (5), is
of great interest for the burning of the high-dense \( \rho \geq 100 \ g \cdot cm^{-3} \) deuterium plasmas [1, 8]. The reaction, Eq.(5), in the two-electron \(^3\)He atom and one-electron \(^3\)He\(^+\) ion was considered in our earlier studies [9], [10]. The cross-section \( \sigma \) of this nuclear reaction for thermal neutrons with \( E_n \approx 0 \) is very large \( \sigma_{\text{max}} \approx 5330 \cdot 10^{-24} \ cm^2 \) (or 5330 barn) [11]. The velocities of the two nuclear fragments formed in the reaction, Eq.(5), with thermal neutrons are \( v_t \approx 1.59632 \) a.u. and \( v_p \approx 4.78797 \) a.u. for the tritium and protium nuclei, respectively. In this study all particle velocities are given in atomic units, where \( \hbar = 1 \), \( m_e = 1 \), \( e = 1 \) and the unit of atomic velocity is \( v_e = \alpha c \approx 2.1882661 \cdot 10^8 \ cm \cdot sec^{-1} \). Here and everywhere below \( c \) is the speed of light in vacuum and \( \alpha = \frac{e^2}{\hbar c} \) is the dimensionless fine structure constant. This ‘atomic velocity’ \( v_e \) is the velocity of the 1s–electron in the hydrogen atom with the infinitely heavy nucleus \( ^\infty\text{H} \). It is clear that in atomic units \( v_e = 1 \).

Let us evaluate the probabilities of formation of the negatively charged tritium and protium ions. In other words, we want to determine the probabilities of formation of the two-electron \(^3\)H\(^-\) and \(^1\)H\(^-\) ions during the nuclear reaction, Eq.(5), in the two-electron \(^3\)He atom. According to the theory of sudden approximations and in respect with Eq.(3) such a probability of formation of the tritium ion (\(^3\)H\(^-\) or T\(^-\)) is written in the form

\[
P_{if} = |A_{if}|^2,
\]

where \( A_{if} \) is the probability amplitude which is written in the form

\[
A_{if} = \langle \Phi_{T^-}(r_1, r_2) | \Psi'_{He}(r_1, r_2) \rangle = \langle \Phi_{T^-}(r_1, r_2) | \exp(iV_t \cdot r_1 + iV_t \cdot r_2) \Psi_{He}(r_1, r_2) \rangle \tag{6}
\]

where \( V_t \) is the speed of the tritium nucleus after the reaction, Eq.(5). In other words, the probability amplitude is the overlap integral between the tritium ion and helium-3 wave functions, but the wave function of the helium-3 atom must be taken in the moving reference frames.

In the incident and final wave functions we can separate three internal variables \( r_{32}, r_{31}, r_{12} \) (or relative coordinates \( r_{ij} = |r_i - r_j| = |r_{ij}| \)) from other six \((3 + 3)\) variables which correspond to the translational and rotational degrees of freedom of the whole three-body system. Here and everywhere below the notations 1 and 2 mean the electrons, while the notation/index 3 stands for the central (heavy) nucleus. In atoms with one heavy nucleus the internal coordinates coincide with the interparticle, or relative coordinates. In general, the expression for the probability amplitude \( A_{if} \), Eq.(5), is reduced to the following form

\[
A_{if} = \int \int \int Y_{LM}^T(r_{31}, r_{32}) \Phi_{T^-}(r_{32}, r_{31}, r_{21}) \exp(iV_t \cdot r_{32} + iV_t \cdot r_{31}) \times Y_{LM}^{He}(r_{31}, r_{32}) \Psi_{He}(r_{32}, r_{31}, r_{21}) r_{32} r_{31} r_{21} dr_{32} dr_{31} dr_{21} \tag{7}
\]
for the tritium $^3\text{H}^-$ (or T$^-$) ion. The notations $\mathcal{Y}_{LM}^{-}(r_{31}, r_{32})$ and $\mathcal{Y}_{LM}^{\text{He}}(r_{31}, r_{32})$ used in this equation designate the corresponding bi-polar harmonics [12, 13]. They are taking care about non-zero angular momenta of the incident and final atomic species. It should be mentioned here that the negatively charged hydrogen ion H$^-$ has only one bound $1^1S(L = 0)$—state. Also, in this study we restrict ourselves to the case when the incident $^3\text{He}$ atom was in its ground $1^1S(L = 0)$—state. In this case all bipolar harmonics in Eq.(7) equal unity and the probability amplitude, Eq.(7), takes the form

$$A_{if} = \int \int \Phi_{T^-}(r_{32}, r_{31}, r_{21}) j_0(V_t \cdot r_{32})j_0(V_t \cdot r_{31})\Psi_{\text{He}}(r_{32}, r_{31}, r_{21})r_{32}r_{31}r_{21}dr_{32}dr_{31}dr_{21}$$

$$= \frac{1}{V_t^2} \int \int \Phi_{T^-}(r_{32}, r_{31}, r_{21})\sin(V_t \cdot r_{32})\sin(V_t \cdot r_{31})\Psi_{\text{He}}(r_{32}, r_{31}, r_{21})r_{12}dr_{32}dr_{31}dr_{21}$$

(8)

where $V_t$ is the speed of the tritium nucleus after the nuclear reaction in the $^3\text{He}$ atom.

The wave functions of the ground $1^1S(L = 0)$—states in the two-electron H$^-$ ion and He atom are usually approximated with the use of highly accurate variational expansion written in the relative/perimetric coordinates $r_{32}, r_{31}$ and $r_{21}$ or $u_1, u_2, u_3$ (more details can be found, e.g., [14]). The most advanced of such expansions is the exponential variational expansion in the relative coordinates. It takes the following form (for the bound $S(L = 0)$—states in the two-electron systems):

$$\psi(r_{32}, r_{31}, r_{21}) = \frac{1}{\sqrt{2}}[1 + (-1)\kappa]\hat{P}_{12} \sum_{i=1}^{N} C_i \exp(-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i r_{21})\chi(1, 2)$$

(9)

where $C_i$ are the linear variational coefficients, $\hat{P}_{12}$ is the permutation of the two identical particles (electrons 1 and 2) and $N$ is the total number of terms in the trial function $\psi(r_{32}, r_{31}, r_{21})$ which is an accurate approximation of the actual wave function $\Psi(r_{32}, r_{31}, r_{21})$. In Eq. (9) the notation $\chi(1, 2)$ stands for the two-electron spin function. For the singlet states one needs to chose $\chi(1, 2) = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$ and $\kappa = 0$ in Eq.(9). The total energies obtained for the ground $1^1S$—states of the H$^-$ ion and He atom with the use of Eq.(9) can be found in Table I. The wave functions, Eq.(9), are used in calculations of the probability to form the bound tritium ion $^3\text{H}^-$. If the $\Phi_{T^-}(r_{32}, r_{31}, r_{21})$ and $\Psi_{\text{He}}(r_{32}, r_{31}, r_{21})$ in Eq.(8) are represented in the form of Eq.(9), then the probability amplitude $A_{if}$ is written as the double sum of the following three-particle integrals

$$B_{0,1;0}^{(0)}(a, b, c; V_t) = \frac{1}{V_t^2} \int \int \exp(-ar_{32} - br_{31} - cr_{21})\sin(V_t \cdot r_{32}) \times \sin(V_t \cdot r_{31})r_{12}dr_{32}dr_{31}dr_{21}$$

(10)
where $a = \alpha_i(T^-) + \alpha_j(\text{He})$, $b = \beta_i(T^-) + \beta_j(\text{He})$ and $c = \gamma_i(T^-) + \gamma_j(\text{He})$. Theory of these integrals was developed in [15]. In particular, it was shown in [15] that such an integral is reduced to the following double sum (here we apply the Cauchy formula)

$$B_{0;0;1}^{(00)}(a, b, c; V) = \sum_{\kappa=0}^{\infty} \frac{(-1)^\kappa V^{2\kappa}}{(2\kappa + 2)!} \sum_{\mu=0}^{\kappa} C_{2\kappa+1}^{2\mu+1} \Gamma_{2\mu+1;2\kappa-2\mu+1;1}(a, b, c)$$  \hspace{1cm}(11)$$

where $C_{n}^{k}$ is the binomial coefficient, i.e. the number of combinations from $n$ by $k$ ($n \geq k$), and $\Gamma_{k,l,n}(a, b, c)$ is the basic three-particle integral defined in [15]. This formula allows one to determine the probability to form the bound $T^-$ (or $^3\text{H}^-$) and $^1\text{H}^-$ ions during the nuclear reaction, Eq.(5), in the two-electron $^3\text{He}$ atom. For instance, by using the approximate one-term wave functions for the ground state in the helium atom and hydrogen ion given in Table II of Ref.[9] we have found that the probability to form the bound $T^-$ (or $^3\text{H}^-$) ion in the reaction Eq.(5) is $\approx 0.77048798 \%$ (probability amplitude is $\approx 0.87777445 \cdot 10^{-1}$). Such a large probability of the $T^-$ ion formation means that these ions formed in the reaction, Eq.(5), can be detected in modern experiments. Analogous probability for the negatively charged protium ion is only $\approx 2.391074 \cdot 10^{-5} \%$ (probability amplitude is $\approx 0.48898613 \cdot 10^{-3}$), i.e. it is significantly smaller. This illustrates a very strong dependence of the final state probabilities upon the velocity $V$ of the final atomic fragment, if $V \geq 1$ [4], [9].

It is interesting to note that we can also use the formula, Eq.(11), in the case when $V = 0$. This case corresponds to the $\beta^-$ decay of the $^3\text{H}^-$ ion into the two-electron $^3\text{He}$ atom. The corresponding probability obtained with our one-term wave functions is $\approx 23.893045 \%$ (probability amplitude is $\approx 0.488052483$). These amplitude and final probability are very close to our earlier prediction made in 1998 [16]. Analogous calculations with the use of five-term variational wave functions (with the carefully optimized non-linear parameters) for the $\text{H}^-$ ion and He atom gives the following probabilities: $21.075287 \%$ ($\beta^-$ decay), $0.581089 \%$ ($^3\text{H}^-$ ion formation) and $1.842681 \cdot 10^{-5} \%$ ($^1\text{H}^-$ ion formation). The corresponding variational three-term energies for the $\infty\text{H}^-$ ion and $\infty\text{He}$ atom are -0.5277402583285 a.u. and $-2.903691563543$ a.u., respectively (compare with the ‘exact’ energies from Table I).

Note that our variational few-term wave functions constructed for the $\text{H}^-$ ion and He atom by using with carefully optimized non-linear parameters are the best functions in their class. Nevertheless, it is very interesting to check our predictions by applying variational wave functions for the $\text{H}^-$ ion and He atom with significantly larger number of terms, e.g., the trial wave functions from Table I. However, right now such calculations cannot be performed,
since there is an additional problem here related with the use of the non-orthogonal basis sets in calculations of the overlap integrals which include the two different wave functions. This problem was never discovered in earlier studies where different expectation values were always computed for the same systems. In such cases the bound state wave functions are exactly the same (i.e. identical) for the ‘incident’ and ‘final’ state. For instance, by using our trial wave functions written in the non-orthogonal basis we can determine the probabilities of ‘non-excitation’ during the two following processes

\[ ^3\text{He}(1^1S; V = 0) + n = ^3\text{He}(1^1S; V) + n' \]  
\[ ^3\text{H}^-(1^1S; V = 0) + n = ^3\text{H}^-(1^1S; V) + n' \]

Briefly, the atomic nuclei of the \(^3\text{He}\) atom and \(^3\text{H}^-\) ion are suddenly accelerated to the final speed \(V\) by fast neutrons. Such processes were studied in detail in [17]. The question is to evaluate the probabilities of the incident atoms to stay in the same \(^1\text{S}\)-states (ground states) and keep two bound electrons. Such probabilities have been determined with the method described above and variational wave functions which contain up to 400 terms. The results for the \(^3\text{He}\) atom and \(^3\text{H}^-\) ions can be found in Table II for \(V = 0.0, 1.0, 1.59632, 2.0, 3.5\) and 4.78797 (all these velocities are expressed in atomic units (\(a.u.\))). The computed probabilities are numerically stable and they converge when the total number of basis functions \(N\) in Eq.(9) increases. Note again that in these cases the incident and final wave functions are identical to each other.

This situation changes drastically, if we consider the overlap integrals of two different wave functions written in the non-orthogonal basis sets. We do not know the correct order of non-orthogonal basis vectors in both wave functions and this leads to some serious problems in calculations. For instance, let us change the order of basis vectors in the He-wave function, Eq.(9). It does not change the norm of this wave function, but numerical value of the overlap integral with the tritium ion wave function will be changed substantially, since the transformation which connects these two non-orthogonal basis sets is not unitary (or orthogonal). Briefly, this means that we cannot predict the correct order of basis functions in the two approximate wave functions. But only such an order is appropriate for correct calculations of the final state probabilities. Some simple method recommended for solution of this problem, e.g., the use of natural expansions of the wave functions and/or addition orthogonalization of these functions, either lead to a substantial loss of overall numerical
accuracy, or to other problems. At this moment we are trying to solve this interesting problem and develop the new, reliable method for accurate computations of the final state probabilities.

For the first time we have developed the closed and transparent procedure which allows one to calculate the probabilities of formation of few-electron atomic species during nuclear reactions in the incident atom(s). To evaluate such probabilities in earlier studies we have to apply approximate procedures with model (one-electron) wave functions. By using the results of this study we evaluated the probability of formation of the tritium ($^3$H$^-$) ion in the nuclear reaction, Eq. (5), $\approx 0.8 - 1\%$ (not 8% as it was predicted earlier). The approach developed here can be applied to more complicated cases, e.g., to the reaction of the $^{10}$B nuclei with slow neutrons in the five-electron boron atom (this reaction is used in the boron neutron capture therapy to treat cancer).

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TABLE I: The total energies $E$ of the ground $1^1S(L = 0)$–states in the negatively charged hydrogen ion $^\infty\text{H}^-$ and $^\infty\text{He}$ atom (in atomic units). $K$ is the total number of basis functions used.

| $K$ | $E(^\infty\text{H}^-)$ | $E(^\infty\text{He})$ |
|-----|-------------------------|-------------------------|
| 3500| -0.527751 016544 377196 590213 | -2.903724 377034 119598 030965 |
| 3700| -0.527751 016544 377196 590333 | -2.903724 377034 119598 030983 |
| 3840| -0.527751 016544 377196 590389 | -2.903724 377034 119598 030995 |
| 4000| -0.527751 016544 377196 590446 | -2.903724 377034 119598 031033 |

TABLE II: The probabilities of non-excitation $p_f$ (in %) for the processes, Eq.(12) and Eq.(13), with the $^3\text{He}$ atom and $^3\text{H}^-$ ion. $V$ is the final velocity (in a.u.) of the central atomic nucleus.

| $V$ | 0.0 | 1.0 | 1.59632 | 2.0 | 3.5 | 4.78797 |
|-----|-----|-----|--------|-----|-----|---------|
| $^3\text{He}$ | 100.0 | 46.90946 | 16.53096 | 6.95123 | 0.17532 | 7.48683·10$^{-3}$ |
| $^3\text{H}^-$ | 100.0 | 1.217223 | 2.27539·10$^{-2}$ | 2.61097·10$^{-3}$ | 4.2066·10$^{-6}$ | 6.0222·10$^{-9}$ |