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Hylleraas- and Kinoshita-type wave functions with correct cusp conditions

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Finite terms Hylleraas- and Kinoshita-type variational wave functions are considered for three-body systems. In Coulombic case local properties of wave functions are restricted by the Kato's cusp conditions. It is showed that Kato's cusp conditions restrict the possible terms in variational calculations. Constraints for the linear expansion coefficients are also derived and a recursion type solution is given. Two trial functions with correct cusp conditions are determined for the ground state of the He atom. Local and global properties of these wave function are studied through calculations of mean values, local energy and quantities related to double photo-ionization.

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I. INTRODUCTION

For Coulombic systems the eigenfunctions exhibit peculiar properties. These strange local behaviours occur at those points in the configuration space where two or more charged particles come together and so the potential between them is infinite. Kato showed that at two particle coalescences the derivatives of the wave function with respect to some well defined specific coordinates are not continuous [1]. This phenomena is characterized by the Kato's cusp conditions.

The importance of the fulfilment of the Kato's cusp conditions have been demonstrated for double photo-ionization [2–4]. The simplest description of the double photo-ionization is the shake off mechanism. In dipole approximation at high photon energies the double photo-ionization cross section are expressed by the mean value [5, 6] $\langle\psi|\delta(\mathbf{r_1})|\psi\rangle$. In this paper we consider two-electron atoms and we denote the electron coordinates by $\mathbf{r_1}$, $\mathbf{r_2}$ and the ground state wave function of the atom by $\psi(\mathbf{r_1},\mathbf{r_2})$. The calculation of the double photo-ionization cross section can check the quality of the local properties of the wave function just at the electron-nucleus coalescence.

At higher photon energies the quasi-free mechanism dominates. The cross section now is determined not only by the region of the electron-nucleus coalescence but that part of the coordinate region where $|\mathbf{r_1}-\mathbf{r_2}|=0$ since the cross section expression contains the term $\langle\psi|\delta(\mathbf{r_{12}})|\psi\rangle$ and the function $\psi(\mathbf{r_1},\mathbf{0})$ [7, 8]. The behaviours of the wave function in these regions are described by the Kato's cusp conditions.

The ground state wave functions of three-body systems are mainly determined by variational methods. In highly accurate calculations, around twenty decimal digits accuracy for the ground state energy of the He atom, the basis size is roughly a thousand or more [9–13]. It is clear that even nowadays in scattering calculations it is computationally prohibitive to use such functions for the ground state. If we use smaller basis size the cusp conditions are severely violated and this may have effect on physical quantities. For example in the derivation of the double photo-ionization cross section it was assumed that the cusp conditions are satisfied [2].

In earlier papers describing the photo-ionization process few terms Hylleraas-type [14] wave functions are used for the initial state [2, 3, 7] and there were no attempts to use trial functions with correct cusp conditions. Ten and thirty-nine terms Kinoshita-type [15] wave functions, trial functions with logarithmic terms are also used to describe the photo-ionization [2, 7, 16] but without exact cusp conditions. The Hylleraas-type trial function is a power series expansion in terms of the Hylleraas variables s, t and u. A more general expansion was introduced by Kinoshita [15] where negative powers of the s and u variables can appear. It is known that the Hylleraas series cannot satisfy the Schrodinger equation in formal sense [17] and the main purpose of the use of negative powers is to overcome this difficulty [15].

In recent papers such a variational calculations are carried out, where interparticle coordinates are used, and the exact fulfilment of the cusp conditions are taken into account from the very beginning [18–20]. In this paper we follow this line of research but we use Hylleraas- and Kinoshita-type functions. The Kinoshita trial function has very few applications. However the power of the method is clearly demonstrated in [21, 22]. We do not know any calculation where Kinoshita-type function was used with correct cusp conditions.

The Kato's cusp conditions are studied mainly using the interparticle coordinates. Here we give the differential cusp equations in Hylleraas coordinates. For finite terms trial wave functions we study consequences of the cusp equations. It turns out that the fulfilment of the Kato's cusp condition restrict which type of Kinoshita terms can enter into a trial function. Furthermore we give the correct cusp equations in terms of the linear expansion coefficients and determine a recursive solution of

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the cusp equations. In the case of He atom we construct a Hylleraas- and a Kinoshita-type wave functions with correct cusp conditions and study the local and global properties of them through calculations of mean values, local energy and double photo-ionization.

Our work is organized as follows: the Hamiltonian and the trial wave functions are discussed in chapter II, the cusp equations are given in section III. The proof of the cusp equations are given in the Appendix. In section IV we outline how to correct a ten and a twenty terms wave functions in order to satisfy the cusp conditions. The results of the numerical calculations are presented also in this chapter. Finally conclusions are given.

II. HAMILTONIAN AND WAVE FUNCTION

For the description of S states of two-electron atoms it is enough to use three scalar variables. The Hylleraas variables are $s = r_1 + r_2 = |\mathbf{r_1}| + |\mathbf{r_2}|$, $t = r_1 - r_2 = |\mathbf{r_1}| - |\mathbf{r_2}|$ and $u = r_{12} = |\mathbf{r_{12}}| = |\mathbf{r_1} - \mathbf{r_2}|$. The variables r_1, r_2 and r_{12} are called interparticle coordinates.

The action of the Hamilton operator on a wave function $\phi(s,t,u)$ can be decomposed in the form

$$H\phi = H_{en}\phi + H_{ee}\phi + K\phi. \tag{1}$$

The electron-nucleus (e-n) interactions and the electron-electron (e-e) potential are contained in the operators H_{en} and H_{ee}, respectively. The explicit forms in Hylleraas coordinates are [13]

$$H_{en}\phi = -\phi_{ss} - \phi_{tt} - 2\frac{\phi_s + \phi_t + Z\phi}{(s+t)} - 2\frac{\phi_s - \phi_t + Z\phi}{(s-t)} \tag{2}$$

$$H_{ee}\phi = -\phi_{uu} + \frac{-2\phi_u + \phi}{u}, \tag{3}$$

where the standard shorthand mathematical notation is used for the partial derivatives. The full Hamiltonian contains one more term, K is a part of the kinetic energy operator. The other parts of the kinetic energy are included in the operators H_{en} and H_{ee}. We have

$$K\phi = -\frac{(u^2+st)(\phi_{s,u}+\phi_{t,u})}{(s+t)u} - \frac{(u^2-st)(\phi_{s,u}-\phi_{t,u})}{(s-t)u}. \tag{4}$$

For the wave function of a two electron atom Hylleraas suggested [14] an expansion of the form

$$\phi(s,t,u) = \exp(-\alpha s)\sum_{l,m,n} h_{l,m,n} s^l u^m t^n, \tag{5}$$

where α is a positive real number, l, m and n are non-negative integers, furthermore n is even for wave functions with singlet spin part. Since its introduction this form of variational trial function has huge number of successful applications. There are several generalizations of the Hylleraas expansion. A recent comparison of the convergence rate of the binding energy is given in [12] using the most important expansion forms.

An alternative expansion to the Hylleraas one is due to Kinoshita [15]. It was suggested to use such an expansion where negative powers in s and u are allowed. The explicit form reads

$$\phi(s,t,u) = \exp(-\alpha s)\sum_{l,m,n} k_{l,m,n} s^l \left(\frac{u}{s}\right)^m \left(\frac{t}{u}\right)^n. \tag{6}$$

The terms in a Kinoshita wave function are characterized by a triplet of non-negative integers. We will use the notation $[l,m,n]$ for such a triplet. When we talk about an $[l,m,n]$ term it means the function $w_{l,m,n}(s,t,u) = \exp(-\alpha s) s^l \left(\frac{u}{s}\right)^m \left(\frac{t}{u}\right)^n$.

Kinoshita showed [15] that the recursion relation satisfied by the coefficients $k_{l,m,n}$ does not lead to contradictions. This is not true for the original Hylleraas expansion [12, 17]. The result of the work [15] means that (6) can be considered as a formal solution, but of course this does not mean anything about the convergence of (6). If we use the restriction $l \geq m \geq n$ then we get back Hylleraas-type function so the Kinoshita ansatz is more general than the Hylleraas one so sometimes we use only the Kinoshita attribute.

III. CUSP CONDITIONS FOR KINOSHITA-TYPE WAVE FUNCTIONS

Equation (2) have two singularities the first one is at $s = -t$ and the second one is at $s = t$ they correspond to the e-n coalescences. The $u = 0$ singularity in (3) is due to the e-e interaction. We will use the following notation: a triplet of numbers in parentheses corresponds to the s,t and u values. Later we will use a relation among the s, t, u variables namely $s \geq u \geq |t| \geq 0$. A general point satisfying this restriction will be denoted by $\underline{P} = (s,t,u)$.

The singularities for the e-n coalescences occur at the points $(s,-s,s)$ and (s,s,s) (these correspond to the cases when $r_1 = 0$ and $r_2 = 0$). The e-e coalescences are at the points $(s,0,0)$ (this form of points corresponds to that part of the (s,t,u) point set where $r_{12} = 0$). We will refer to the points of the two particle coalescences as singularity points or coalescence lines.

The local energy $E_{loc} = H\psi/\psi$ is suitable for measuring the quality of the wave function [18, 23, 24]. For the exact solution the local energy is a constant. In order to have finite local energy it is necessary that the numerators of right hand sides of (2) and (3) should be be zero at the corresponding singularity points. We get

$$\phi_s(s,-s,s) + \phi_t(s,-s,s) = -Z\phi(s,-s,s), \tag{7}$$

$$\phi_s(s,s,s) - \phi_t(s,s,s) = -Z\phi(s,s,s) \tag{8}$$

and

$$\phi_u(s,0,0) = \frac{1}{2}\phi(s,0,0). \tag{9}$$

The Kato's cusp conditions are usually given using the interparticle coordinates. Denoting the wave function by $\psi(r_1, r_2, r_{12})$ the e-n cusp conditions read $\psi_{r_1}(0, r_2, r_{12}) = -Z\psi(0, r_2, r_{12})$, $\psi_{r_2}(r_1, 0, r_{12}) = -Z\psi(r_1, 0, r_{12})$ and for the electrons $\psi_{r_{12}}(r_1, r_2, 0) = \frac{1}{2}\psi(r_1, r_2, 0)$. Due to the change of variables we have the transformation rules $\frac{\partial}{\partial r_1} \to \frac{\partial}{\partial s} + \frac{\partial}{\partial t}$, $\frac{\partial}{\partial r_2} \to \frac{\partial}{\partial s} - \frac{\partial}{\partial t}$ and $\frac{\partial}{\partial r_{12}} \to \frac{\partial}{\partial u}$. Using these simple rules we should get immediately Eqs. (7), (8) and (9). Our derivation however reveals that the finiteness of local energy leads to the Kato's cusp conditions in our problem.

In the Appendix we show that the coefficients $k_{l,m,n}$ of a Kinoshita-type wave function have to obey certain equations in order to satisfy the cusp conditions. The e-n cusp condition leads to

$$\sum_{m,n}(m+n)k_{0,m,n} = 0 \tag{10}$$

and

$$\sum_{m,n}[(m+n-l)k_{l,m,n} + (\alpha - Z)k_{l-1,m,n}] = 0, \quad l > 0. \tag{11}$$

The fulfilment of e-e cusp gives

$$k_{0,1,0} = 0 \tag{12}$$

and

$$k_{l,1,0} = \frac{1}{2}k_{l-1,0,0}, \quad l > 0. \tag{13}$$

To have correct cusp conditions with finite terms wave functions one needs two more additional constraints. The restriction

$$k_{l,0,n} = 0, \quad n > 0 \tag{14}$$

assures to have limit of the wave function at the singularity points $(s, 0, 0)$ $s \neq 0$. The second restriction

$$k_{l,1,n} = 0, \quad n \geq 2 \tag{15}$$

is necessary in order to have limit of ϕ_u at the e-e coalescence line $(s, 0, 0)$, $s > 0$. These conditions are in agreement with general considerations. Kinoshita only from the analysis of the recursion relation showed (15). According to Kinoshita the coefficients $k_{l,m,0}$ are undetermined by the recursion relation, so we may put $k_{0,1,0} = 0$ in order to satisfy the cusp condition. Equation (14) is also given in [15] but this condition was derived from other principles. We finally note that (13) corresponds to (A10) of [15] if (15) is considered.

We show in the Appendix that if we want the cusp condition to be satisfied in the triple coalescence point too we have severe restrictions for the terms with $l = 0$ and $l = 1$. The only possible terms are $[0, 0, 0], [1, 1, 0]$ and $[1, 0, 0]$. We will call this the $l = 0$ and $l = 1$ restrictions, respectively. In the case of Hylleraas-type function these are not restrictions but in the case of finite term Kinoshita wave function they are.

Using the $l = 0$ restriction (10) becomes $0k_{0,0,0} = 0$ which can be fulfilled for arbitrary $k_{0,0,0}$. We take in the following $k_{0,0,0} = 1$ this choice effects only the normalization of the trial function. Using equations (14), (15) and (13) furthermore the $l = 0$ and $1 = 1$ restrictions we can turn (11) into the form

$$k_{l,0,0} = \sum_{m>1,n}\left[\left(\tfrac{m+n}{l} - 1\right)k_{l,m,n} + \tfrac{1}{l}(\alpha - Z)k_{l-1,m,n}\right] + \tfrac{1}{l}\left(\alpha - Z - \tfrac{l-1}{2}\right)k_{l-1,0,0} + \tfrac{\alpha - Z}{2l}k_{l-2,0,0}, \quad l > 0 \tag{16}$$

This is a recursive solution of the Kato's cusp equations.

For finite Kinoshita-type wave function which satisfies the e-e cusp conditions we have $k_{l_{max},0,0} = 0$, where the maximum of the l values of the ansatz is l_{max}. For finite trial functions from (11) it follows

$$(\alpha - Z)\sum_{m,n}k_{l_{max},m,n} = 0. \tag{17}$$

It was mentioned but the correct form was not given in [25] that equation (A9) of [15] generally does not correct. In the case of the He atom ($Z = 2$) it is customary to take $\alpha = 2$. In this case (10) and (11) goes into (A9) of Kinoshita's paper [15]. However, our equations (10) and (11) are valid for arbitrary Z and α. Since the energy is very sensitive to the value of the parameter α [21, 26, 27] it is important to have such a wave function with correct cusp conditions where the value of α can be freely changed.

In the rest of the paper we will consider Kinoshita-type wave functions with finite terms and impose the Kato's cusp conditions. For numerical calculations this means that the energy expectation value have to be minimized with respect to the parameters of the trial function but the constraints (13),(16) and (17) have to be taken into account.

IV. NUMERICAL RESULTS

An alternative and simple method to construct wave function with correct Kato's cusp condition is described in [18, 19]. Assume that a function $\psi(r_1, r_2, r_{12})$ with correct cusp conditions is given. We can get a better trial function if we take the following ansatz

$$\psi(r_1, r_2, r_{12})\dot{\sum_{i,j,k}} r_1^i r_2^j r_{12}^k, \tag{18}$$

where i, j, k are non-negative integers and the dot above the summation sign designates that the power series does not include the first power of the coordinates. If we make this restriction the new wave function is also satisfies the cusp conditions. We call this procedure as GR method. In the work [18, 19] the following standard separable choice was made for $\psi(r_1, r_2, r_{12})$

$$\psi(r_1, r_2, r_{12}) = e^{-2(r_1+r_2)}\frac{2\beta + 1 - e^{-\beta r_{12}}}{2\beta}, \tag{19}$$

where $\beta > 0$. This function satisfies the Kato's cusp conditions. We keep the notation of [18, 19] i.e. GR is the sign the wave function and the integer number attached to GR gives the number of independent parameters.

The excitation of atoms with photons gives a test for the wave function of the atom. The ratio of cross sections for double $\sigma^{++}(\omega)$ to single ionization cross sections ($\sigma^{+}(\omega)$, $\sigma^{+*}(\omega)$) by a photon is signed by $R = \sigma^{++}(\omega)/(\sigma^{+}(\omega) + \sigma^{+*}(\omega))$. For high photon energy and using only the so called shake off mechanism with dipole approximation it is derived [5, 6] that

$$R_d = \frac{\langle \delta(\mathbf{r_1}) \rangle}{\mathcal{N}} - 1, \tag{20}$$

where

$$\mathcal{N} = \sum_{nlm} \left| \int \phi(\mathbf{r_1}, \mathbf{0}) \psi_{nlm}(\mathbf{r_1}) d\mathbf{r_1} \right|^2 . \tag{21}$$

The single particle Coulomb wave function $\psi_{nlm}(\mathbf{r_1})$ describes an electron in the field of the nucleus. The notation $\langle \delta(\mathbf{r_1}) \rangle$ stands for the mean value of the operator $\delta(\mathbf{r_1})$ using the ground state wave function of the atom. Correction to the ratio of the double-to-single electron photo-ionization cross section due to the quasifree mechanism for small values of ω/c can be written [5, 8] in the form $R(\omega) \approx R_d + \frac{\sqrt{128}}{5Z^2} \frac{\omega}{c} C$ where

$$C = \frac{\langle \delta(\mathbf{r_{12}}) \rangle}{\mathcal{N}}. \tag{22}$$

A. Trial function with correct cusp conditions

Now we outline our strategy how to modify a given Hylleraas- or Kinoshita-type wave function in order to satisfy the cusp conditions. First a starting wave function is borrowed from the literature. We want to keep all terms of the starting function because they are optimized. However, if it contains such terms which do not satisfy equations (14), (15) or the $l = 0, 1$ restrictions we have to drop them. Unfortunately, the published Kinoshita-type functions are such that they contain a few forbidden terms. For example the ten terms wave function in [21] contains the terms $[0, 3, 0], [1, 2, 0]$ and $[1, 1, 2]$, the twenty terms ansatz from the same paper includes the terms $[0, 3, 0], [1, 2, 0], [1, 1, 2]$ and $[1, 2, 2]$. These terms and the action of Hamiltonian onto them are square integrable so it is legitimate to use them in a trial function. However, the presence of these terms prevent to satisfy the cusp conditions. Since we did not want to find the optimal replacements so we decided to use Hylleraas-type function for the starting wave function. We take the ten and twenty term optimal Hylleraas wave functions of the work [27].

The e-e cusp conditions are very simple so we follow a very straightforward procedure. If the starting wave function contains both the $[l, 1, 0]$ and $[l-1, 0, 0]$ terms we have nothing to do. Very frequently happens that the starting wave function contains the term $[l-1, 0, 0]$ ($[l, 1, 0]$) but does not contain $[l, 1, 0]$ ($[l-1, 0, 0]$). There are two solutions to fulfill the e-e cusp conditions. We either delete the problematic term or we add the missing one. Since we do not want to get energetically worse wave function than the starting one so we always add the missing term to the starting wave function.

Using equation (11) with $l = 1$ and the $l = 0$ and $l = 1$ restrictions we get $-k_{1,0,0} + (\alpha - Z)k_{0,0,0} = 0$. It follows if $\alpha = Z$ then $k_{1,0,0} = 0$ and (13) implies $k_{2,1,0} = 0$. This also means that if we want use an arbitrary value for α then the terms $[2, 1, 0]$ and $[1, 0, 0]$ have to be present in the trial wave functions.

To satisfy the e-n cusp condition is not as straightforward as the previous case. We have large freedom how to correct the starting wave function in order to fulfill the cusp equations. If we have to add a new term to the ansatz we have chosen a simple strategy. We looked for what is the optimal term concerning the energy (including the cusp conditions). We searched for the term in the following set of non-negative integer triplets $\{[l, m, n] | l = 1, \cdots, l_{max}, m = 0, \cdots, 7, n = 0, \cdots, 7\}$. We did not re-optimize the previously fixed terms.

Using the outlined strategy we set up the following trial functions. We take the ten term Hylleraas wave function of [27]. We added the terms $[3, 1, 0]$ and $[1, 0, 0]$ to satisfy the e-e cusp conditions. To get better energy we added two more terms $[4, 2, 0]$ and $[3, 2, 0]$. This function is denoted by K10M14 and it is a Hylleraas-type trial function. We use the following abbreviation system for wave functions. First we sign somehow the original wave function in the present example K10. If we add few terms to the original ansatz it is denoted by K10M, the total number of terms is attached to K10M. If the the cusp conditions are imposed it is denoted by attaching capital letter C to the end of the notation.

The ground state energies of the He atom using different wave functions are given in Table I. The wave function K10M14 contains fourteen variational parameters thirteen linear ones and one non-linear parameter, α. The number of cusp conditions for the wave function K10M14C is 8 so the wave function K10M14C contains only 6 free parameters. This is the reason why the energy of K1014MC deteriorates comparing it with K10M14.

Next we take the twenty terms Hylleraas wave function of [27] as starting wave function. We have to add the terms $[3, 1, 0], [3, 0, 0]$ and $[5, 1, 0]$ to satisfy the e-e cusp conditions. Adding more terms to improve the energy we observed that we have to use Kinoshita-type terms. We added three more terms $[5, 2, 0], [3, 5, 0]$ and $[2, 7, 0]$. Our twenty six terms wave function K20M26C contains only 14 free parameters. If we compare the ground state energies of wave functions with correct cusp conditions we can notice that our procedure to enforce the cusp conditions gives better results than the GR method. This is best salient in the case K20M26C and GR29. Our wave function not only has fewer terms but and one has to

TABLE I. Global properties of different wave functions. Ground state energy, mean values of the operators $\delta(\mathbf{r_1})$ and $\delta(\mathbf{r_{12}})$ are given. The ν_{en} and ν_{ee} values measure the fulfillment of the cusp conditions. Quantities (R and C) characterizing the double photo-ionization are displayed. For comparison results of large basis size calculations which can be considered exact are also showed.

	E	$\langle\delta(\mathbf{r_1})\rangle$	$\langle\delta(\mathbf{r_{12}})\rangle$	ν_{en}	ν_{ee}	R	C
K10M14	-2.903566	1.803	0.107	-1.98405	0.48289	0.017	0.0604
K10M14C	-2.903482	1.815	0.107	-2.00000	0.49999	0.016	0.0596
GR14	-2.90342[d]	1.801	0.107	-2	0.5	0.016	0.0605
K20M26	-2.903720	1.810	0.107	-1.99685	0.47113	0.017	0.0600
K20M26C	-2.903712	1.811	0.106	-1.99999	0.50000	0.016	0.0596
GR29	-2.90360[d]	1.807	0.107	-2	0.5	0.016	0.0602
exact	-2.903724[a]	1.810[a]	0.106[a]	-2	0.5	0.01645[b]	0.0597[c]

[a] Ref. [9]
[b] Ref. [6]
[c] Ref. [8]
[d] Ref. [19]

remember that the GR29 function has 29 free parameters where as our has only 14 ones.

B. Global and local characteristics

A global approximate measure of the fulfillment of the cusp conditions are the following ratios of mean values [4, 9]

$$\nu_{en} = \frac{\langle\delta(\mathbf{r_1})\frac{\partial}{\partial r_1}\rangle}{\langle\delta(\mathbf{r_1})\rangle} \quad \nu_{ee} = \frac{\langle\delta(\mathbf{r_{12}})\frac{\partial}{\partial r_{12}}\rangle}{\langle\delta(\mathbf{r_{12}})\rangle}. \tag{23}$$

The calculated values for different wave functions are given in Table I. In order to completely characterize the fulfillment of the Kato's cusp conditions one has to study the cusp ratio functions

$$\frac{\psi_{r_1}(0, r_2, r_{12})}{\psi(0, r_2, r_{12})} \tag{24}$$

and

$$\frac{\psi_{r_{12}}(r_1, r_2, 0)}{\psi(r_1, r_2, 0)}. \tag{25}$$

In the case of the exact solution these functions are constant for all over the configuration space and its values are $-Z$ and $\frac{1}{2}$, respectively. In terms of Hylleraas variables the definitions are

$$C_{en}(s) = \frac{\phi_s(s, -s, s) + \phi_t(s, -s, s)}{\phi(s, -s, s)} \tag{26}$$

and

$$C_{ee}(s) = \frac{\phi_u(s, 0, 0)}{\phi(s, 0, 0)}. \tag{27}$$

The cusp ratio functions are two variable functions in interparticle coordinates but they are simpler, one variable functions in Hylleraas coordinates so it is easy to display them. In Figure 1 these cusp ratio functions are shown using different wave functions without imposing the Kato's cusp conditions. This Figure shows that it is misleading to pick up a given point and give the cusp ratio only at that point. For example, the total variation of the function $C_{ee}(s)$ in the case of K10M14 is roughly 0.2 if $s \in [0, 6]$. Of course if the cusp conditions are imposed for approximate wave functions like K10M14C and K20M26C the cusp ratio functions are constants for every s value ($\nu_{en}(s) = -Z, \nu_{ee}(s) = 1/2$).

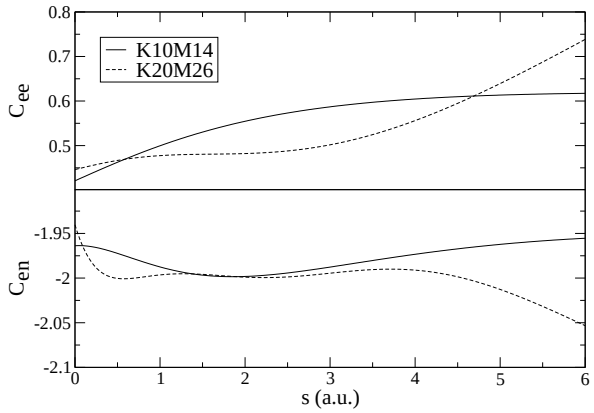

FIG. 1. The cusp ratio functions for the trial functions K10M14 and K20M26 functions. The upper part shows the e-e the lower part displays the e-n cusp ratio functions.

The ν_{en} and ν_{ee} values in Table I and the Figure 1 shows that with increasing basis size one can improve the fulfilment of the cusp conditions. However for an approximate wave functions to get correct cusp conditions one has to explicitly force the fulfilment of the cusp conditions.

It is obvious that the mean values of the operators $\delta(\mathbf{r_1})$ and $\delta(\mathbf{r_{12}})$ are sensitive to the cusp conditions. This can be noticed in Table I when the mean values of different wave functions are compared to the exact ones. When the cusp conditions are imposed the mean values

becomes closer to the exact ones. One can observe also that our method gives better results than the GR prescription.

As for the problem of the double photo-ionization it was demonstrated by Åberg [2] that the R quantity of the double photo-ionization is very sensitive to the Kato's cusp conditions. Now we have calculations for this quantity which can be considered exact thanks to the works [6, 8]. In these papers the authors applied the hyperharmonics method. Our results for the quantities R and C which determine the ratio of the cross section for double photo-ionization to single photo-ionization are given in Table I. The effect of the fulfilment of the cusp conditions onto the observables R and C is striking. We can not only observe that the correct cusp conditions influence the result but it has large positive effect on these quantities. Concerning the quantity C the fourteen terms wave function K10M14C gives almost identical result with the hyperharmonics method which uses several hundred basis functions. One can notice that the RG method gives good result for R but fails to describe the quantity C.

Next we consider the local energy which checks the local accuracy of the approximate wave function. A good mean energy does not say too much about the quality of the wave function a smooth local energy is much stronger quality test [18, 23, 24]. When the local energy of different wave functions are compared it is better to take into account the energy differences of the model functions so we follow the suggestion of [23] and we will plot the errors in the local energy $\Delta E_{loc} = E_{loc} - E$, which should be zero for the exact solution. In the graphical demonstration we follow the standard way, the first electron is at a distance r_1 from the nucleus, the distance of the second electron is r_2. The r_1 and r_2 values are fixed and the local energy is plotted as the function of θ, where θ is the angle between the vectors $\mathbf{r_1}$ and $\mathbf{r_2}$. If $r_1 = r_2 \neq 0$ then the $\theta = 0$ value corresponds the e-e coalescence. It is well know that the local energy is infinite at the two particle coalescence points unless the Kato's cusp conditions are imposed. The upper part of Figure 2 shows the errors of the local energy for the wave functions K10M14, K10M14C and GR14 of Ref [19]. The same quantity for the wave functions K20M26, K20M26C and GR29 are displayed at the lower part of Figure 2. The divergence of the local energy at the point $\theta = 0$ can be observed in the case of the wave functions K10M14 and K20M26. However if we impose the cusp conditions there are no divergences for the very simple wave functions K10M14C, K20M26C, GR14 and GR29. The inset at the lower part of Figure 2 shows the divergent and non-divergent properties of the wave functions more clearly since the region around $\theta = 0$ is enlarged.

If approximate wave functions are used and the cusp conditions are not enforced in some way, divergence in the local energy always appears no matter how good wave functions are used. This is true even if logarithmic terms are present. The triple coalescence point is well described using the complicated Fock-expansion of order $O\left(r_1^2 + r_2^2\right)$ in Ref.[23] but as the authors showed the local energy of the second order Fock-expansion diverges at the two particle coalescence points, and only the exponentiated second order Fock form is free from divergence.

We present results for the errors in local energy away from the two-particle coalescence lines in Figure 3. Both Figures 2 and 3 show that our wave functions produce smoother local energy than the wave functions of the GR method. However concerning numerical computational point of view the GR method is simpler than ours.

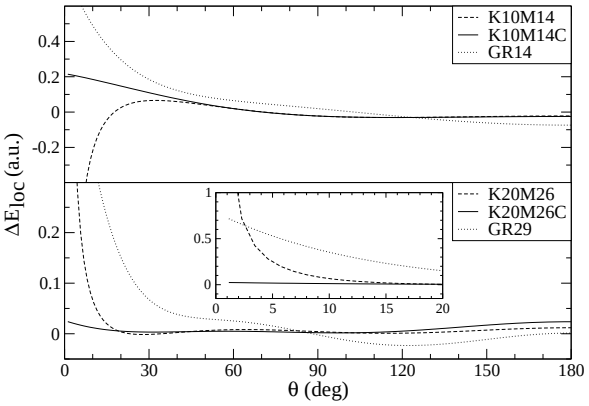

FIG. 2. Errors in the local energy as the function of θ when $r_1 = r_2 = 1$ a.u. Divergence at $\theta = 0$ can be noticed for wave functions K10M14 and K20M26. For wave functions with correct cusp conditions there are no divergence at the two particle coalescence point. The inset shows an enlarged region around $\theta = 0$.

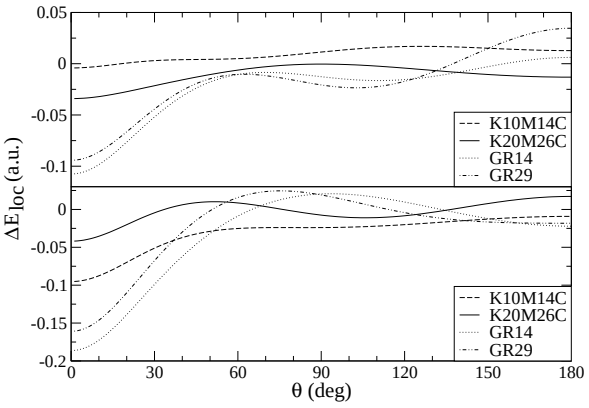

FIG. 3. Errors in the local energy away from the two-particle coalescence lines as the function of θ, in the upper part $r_1 = 1$ a.u. and $r_2 = 2$ a.u. and in the lower part $r_1 = 0.5$ a.u. and $r_2 = 1$ a.u.

V. CONCLUSIONS

We gave the correct form of the Kato's cusp equations expressed by the linear expansion coefficients of

the Hylleraas- or Kinoshita-type wave functions. A recursion-type solution of the cusp equations is determined. We showed that the fulfillment of the cusp equations restrict the allowed form of the terms in the variational wave function. In order to fulfill the cusp equations at the triple coalescence point one has to very heavily restrain the $l = 0$ and $l = 1$ terms which can be allowed in a finite Kinoshita-type wave functions. For terms with $l = 0$ and $l = 1$ negative powers of the variables s and u are not allowed.

A fourteen terms Hylleraas-type wave function and twenty six terms Kinositha-type wave function with correct cusp conditions are introduced for the description of the ground state of the He atom. It was showed the imposition of the Kato's cusp conditions has large and positive effect on the quality of the description of the double photo-ionization.

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Appendix A: Derivation of the cusp conditions for Kinoshita-type functions

First we start with the e-n cusp condition. Substituting the Kinoshita wave function (6) into right hand side of the equation (7) we get

$$-Ze^{-\alpha s}\sum_{l,m,n} k_{l,m,n}s^l. \tag{A1}$$

Direct calculation of the left hand side of (7) gives

$$e^{-\alpha s}\sum_{l,m,n}\left[(l-m-n)-\alpha s\right]k_{l,m,n}s^{l-1}. \tag{A2}$$

With these results the e-n cusp equation (7) can be turned into the form

$$\sum_{l,m,n}\left[(m+n-l-1)k_{l+1,m,n}+(\alpha-Z)k_{l,m,n}\right]s^l=0. \tag{A3}$$

We can conclude that for each l the coefficients in front of s^l should be zero and this leads to (10) and (11). The second e-n cusp equation (8) furnishes also (10) and (11).

The e-e cusp equation can be derived also with simple manipulations but it needs more considerations. The e-e cusp condition refers to the points $(s, 0, 0)$, $s > 0$. Since in a Kinoshita-type wave function u with negative power can be present these points are not in the domain of definition of the trial function (6). A finite limit of ϕ at these points may exist. In case when negative power of u appears in the trial function the e-e cusp condition (9) has to be interpreted in limit sense

$$\lim_{\underline{P}\to(s,0,0)}\phi_u(s,t,u)=\frac{1}{2}\lim_{\underline{P}\to(s,0,0)}\phi(s,t,u). \tag{A4}$$

The Kinoshita wave function (6) is finite superposition of the functions $w_{l,m,n}(s,t,u)$. We determine the limits of $w_{l,m,n}(s,t,u)$ and $\partial w_{l,m,n}/\partial u$ at the points $(s,0,0)$, $s>0$ and from these we can simply construct (A4).

From the definition of $w_{l,m,n}$ it follows if $m = 0$ and $n > 0$ the limit of $w_{l,0,n}$ at the singularity points does not exist. This means that in the Kinoshita wave function $k_{l,0,n} = 0$, $n > 0$. Let's take two zero sequences t_k and u_k as $k \to \infty$. When $m > 0$ we have the following estimate $|w_{l,m,n}(s,t_k,u_k)| \le s^{l-m}u_k^m$ since $|t_k/u_k| \le 1$. We can conclude that the limit of $w_{l,m,n}$ is zero when $m > 0$. We can establish that

$$\lim_{\underline{P}\to(s,0,0)}\phi = e^{-\alpha s}\sum_l k_{l,0,0}s^l, \quad s>0. \tag{A5}$$

For the e-e cusp equation (9) we need the partial derivative of $w_{l,m,n}$ with respect to u. To determine the limit of this function at the points $(s,0,0)$, $s > 0$ we dissect the inspection according to the value of m.

If $m > 1$ the searched limit is zero since we have the evaluation $|\partial w_{l,m,n}(s,t_k,u_k)/\partial u| \le s^{l-m}u_k^{m-1}|m-n|$. In the case of $m = 1$ and $n \ge 2$ the function $\partial w_{l,m,n}(s,t_k,u_k)/\partial u$ does not have a limit at the points $(s,0,0)$, $s > 0$ so in the Kinoshita wave function we have $k_{l,1,n} = 0$ if $n \ge 2$. It remains to consider the case when $m = 1, n = 0$ and obviously the considered limit is zero. Finally we consider the case $m = 0$. If $m = 0$ we have already established that $k_{l,0,n} = 0$, $n > 0$ so the only case remained is $w_{l,0,0}$ and the considered limit is zero. Taking into account all the considerations we get for the Kinoshita wave function

$$\lim_{\underline{P}\to(s,0,0)}\frac{\partial\phi}{\partial u} = e^{-\alpha s}\sum_l k_{l,1,0}s^{l-1}, \quad s>0 \tag{A6}$$

In order to satisfy the e-e cusp equation (9) the comparison of (A6) and (A5) shows that $k_{0,1,0} = 0$ and then we get for (9)

$$\sum_{l\ge1}\left[2k_{l,1,0}-k_{l-1,0,0}\right]s^l=0 \tag{A7}$$

and this proves (13).

Since in Kinoshita-type wave function negative powers of s and u can be present at the triple coalescence point equations (7), (8) and (9) have to be considered in limit sense

$$\lim_{\underline{P}\to\underline{0}}\left(\phi_s(s,t,u)\pm\phi_t(s,t,u)\right) = -Z\lim_{\underline{P}\to\underline{0}}\phi(s,t,u) \tag{A8}$$

and

$$\lim_{\underline{P}\to\underline{0}}\phi_u(s,t,u)=\frac{1}{2}\lim_{\underline{P}\to\underline{0}}\phi(s,t,u). \tag{A9}$$

First we inspect the right hand side of (A9). Let's take three sequences s_k, t_k, u_k converging to zero as $k \to \infty$. We have the estimate $|w_{l,m,n}| \leq s_k^l$ since the sequences satisfy the relation $s_k \geq u_k \geq |t_k| \geq 0$. From the estimate it follows

$$\lim_{\underline{P} \to \underline{0}} w_{l,m,n} = 0, \quad l > 0. \tag{A10}$$

In the case $l = 0$ it is obvious that the limit $\underline{P} \to \underline{0}$ exists if and only if $m = 0$ and $n = 0$. This means that $k_{0,m,n} = 0$ if $(m, n) \neq (0, 0)$. Other words in the case of $l = 0$ the only term that is possible is $[0, 0, 0]$. All type of partial derivatives of the function [0,0,0] exists so in the rest of the Appendix we do not have to consider the $l = 0$ case.

Now we consider the limit of $\partial w_{l,m,n}/\partial u$ at $\underline{0}$. If $m = 0$ and $n > 0$ there is no finite limit i.e. $k_{l,0,n} = 0, \quad n > 0$. Since earlier we have found this rule this result gives no new restrictions. If $l, m > 0$ we have the estimate $|\partial w_{l,m,n}/\partial u| \leq s^{l-1}|m - n|$. It follows

$$\lim_{\underline{P} \to \underline{0}} \frac{\partial w_{l,m,n}}{\partial u} = 0, \quad l > 1, m > 0. \tag{A11}$$

It is trivial if $l = 1$ and $m > 1, m \neq n$ the considered limit does not exist and it is also obvious if $l = m = 1$ and $n \geq 2$ finite $\underline{P} \to \underline{0}$ limit does not exist. We get that (A9) restraints the $l = 0$ and $l = 1$ terms to the forms: $[0, 0, 0], [1, 0, 0], [1, 1, 0]$ and $[1, n, n], n \geq 2$. Simple direct calculation gives that the e-n cusp condition (A8) does not allow the terms $[1, n, n], n \geq 2$. We find that due to the cusp conditions at the triple coalescence point the only possible $l = 0, 1$ terms in a finite Kinoshita-type function are $[0, 0, 0], [1, 0, 0]$ and $[1, 1, 0]$. It remains to check whether (A8) in the case of $l \geq 2$ gives restrictions or not. In this case we find for the l.h.s of (A8)

$$\lim_{\underline{P} \to \underline{0}} \exp(-\alpha s) s^{l-2} \left(\frac{u}{s}\right)^{m-1} \left(\frac{t}{u}\right)^{n-1} (-mt \pm ns). \tag{A12}$$

and from this it follows that we do not get new restrictions.

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