Value of interparticle interaction potential as a variable in solving many-body Schrödinger equation

V.M. Tapilin

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Abstract

A many-body wave function is approximated by a product of two functions: the wave function $\phi$ depending on the particle coordinates and the function $\chi$ depending only on the value of interparticle interaction potential. For the given $\phi$ an ordinary linear differential equation for $\chi$ is derived by averaging the Hamiltonian over the constant interparticle interaction potential surface. Generalized Hartree-Fock equations containing correlation effects are obtained. To test the proposed technique the ground $1^1S_0$ and excited $2^3S_1$ states of two-electron ions from H$^-$ up to Ne$^{8+}$ are calculated. In all cases the calculated energies are more accurate than those obtained with the Hartree-Fock theory even taking as $\phi$ the symmetrized product of electron wave functions in the Coulomb field of nucleus completely disregarding the electron-electron interaction. Variation of factors in the one-particle wave function exponents leads to the results close to those of configuration interaction approach.

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I. INTRODUCTION

Direct solution of the many-body Schrödinger equation has been performed only for two electron ions [1,2]. For more complicated cases dimensionality of the equation and impossibility to separate variables in it force to search for approximating solutions. There are two main approaches to find these solutions: the Hartree-Fock approximation (HF) [3,4], and the density functional theory (DFT) [5,6]. The first one is based on the approximation which considers electron moving in an average field of other electrons. The wave function in this approximation is presented by a symmetrized product of one particle functions, so the probability to find an electron at some space point does not depend on the positions of the rest electrons. To improve the Hartree-Fock theory one has to introduce this dependence known as the correlation in electron movement [7]. It can be achieved through configuration interactions, perturbations or coupled cluster theory [8]. DFT rests on the density functional theory where
exchange and correlation are introduced by a functional of electron charge density. Unfortunately, the exact form of the functional is not known and some approximations to it are used. In both approaches one needs to solve non-linear one-particle equations using an iteration procedure of the self-consistent field. In recent years, powerful computers and sophisticated computational algorithms have made a remarkable progress in this area. Nevertheless, the final solution of the problem has not been achieved yet, and developing new approaches, permitting to view this problem from another perspective, is being continued [9]. Searching for highly precise functions containing thousands variational parameters as well as simple but accurate functions for helium-like ions has not been stop yet also [10-25].

The aim of the present paper is to propose a new approach to solve the many-body Schrödinger equation going beyond HF theory. The idea of this work has been stated in [26]. We consider the value of the interparticle interaction potential as a variable and represent a many-body wave function as a product of a function \( \phi \) depending on particle coordinates and a function \( \chi \) depending only on the value of interparticle interaction potential. Function \( \chi \) due to its dependence on this potential introduces correlation in the many-body wave function omitted in \( \phi \). For a given \( \phi \), using averaging the many-particle Hamiltonian over constant interaction potential hypersurface, the Schrödinger equation is transformed into a one-dimensional linear differential equation for \( \chi \). In its turn, for any \( \chi \) one can find the best \( \phi \) which minimizes the total energy of the many-body system. Below, we develop the correspondent equations and apply them to calculate energies of two-electron ions.

### II. EQUATIONS

The Schrödinger equation of interacting particles can be written in the form

\[
[H_0(r) + v_{int}(r)]\Psi(r) = E\Psi(r),
\]

where \( H_0 \) and \( v_{int} \) are contributions to the Hamiltonian from non-interacting particles and the interparticle interaction, correspondently,

\[
H_0(r) = -\frac{1}{2} \sum_i \nabla_i^2 + V(r),
\]

\( r \) is a vector with components \( r_i, \) \( i \) numerates particles, \( V \) is a potential of an external field. For the Coulomb interaction

\[
v_{int}(r) = \frac{1}{\rho(r)} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \frac{1}{r_{ij}},
\]

where \( r_{ij} = |r_i - r_j| \).

Let us introduce a function of the form

\[
\psi(r) = \phi(r) \chi(p).
\]
The function $\phi$ is supposed to be symmetrized in respect to the particle permutations. The type of symmetrization must reflect the total spin of the considering system [27]. Substitution of (4) in (1) leads to

$$-rac{1}{2} \phi(r) \sum_i \left( \nabla_i p \right)^2 \frac{d^2 \chi(p)}{dp^2} - \left[ \frac{1}{2} \phi(r) \sum_i \nabla_i^2 p + \sum_i \nabla_i \phi(r) \nabla_i p \right] \frac{d \chi(p)}{dp}$$

$$+ (h(p) + 1/p)\phi(r)\chi(p) = E\phi(r)\chi(p) \quad (5)$$

It is easy to find

$$\nabla_i p = -\frac{1}{v_{int}^2} \nabla_i v_{int} = p^2 \sum_{j \neq i} \frac{r_{ij}}{r_{ij}^3} \quad (6)$$

$$\nabla_i^2 p = 2 \frac{v_{int}^2}{v_{int}^3} \left( \nabla_i v_{int} \right)^2 - \frac{1}{v_{int}^2} \nabla_i^2 v_{int} = 2p^2 \left( \sum_{j \neq i} \frac{r_{ij}^2}{r_{ij}^3} \right)^2 \quad (7)$$

In (7) it was taken into account that the Coulomb potential is satisfied to the Laplace equation.

The demands for function $\chi$ to minimize the value of the functional

$$E = \langle \psi | H_0 + v_{int} | \psi \rangle / \langle \psi | \psi \rangle \quad (8)$$

for a preset $\phi$ leads to the equation for $\chi$

$$-\frac{1}{2} \chi(p) \frac{d^2 \chi(p)}{dp^2} - u(p) \frac{d \chi(p)}{dp} + (h(p) + 1/p)\chi(p) = E\chi(p), \quad (9)$$

where

$$t(p) = s^{-1}(p) \int_{S(p)} d\phi^* \phi(r) \sum_i \left( \nabla_i p \right)^2,$$

$$u(p) = s^{-1}(p) \int_{S(p)} d\phi^* \phi(r) \left[ \frac{1}{2} \phi(r) \sum_i \nabla_i^2 p + \sum_i \nabla_i \phi(r) \nabla_i p \right],$$

$$h(p) = s^{-1}(p) \int_{S(p)} d\phi^* \phi(r) H_0 \phi(r),$$

$$s(p) = \int_{S(p)} d\phi^* \phi(r), \quad (10)$$

and the integration is performed over a constant interaction potential surface. The boundary conditions for $\chi$ follow from the demand for $\psi$ to be finite in the whole space.

Eq. (9) is a linear ordinary differential equation for $\chi$. The term $h(p)$ is the contribution of $H_0$ to the total energy when the system is in the state $\phi$. The first and the second terms describe additional contributions to kinetic energy which doesn’t enter $h(p)$ and appears due to the interparticle interaction $1/p$. If the interaction is absent and $\phi$ is an eigenstate of $H_0$ with energy $\epsilon$, the additional
contribution must be zero that occur when $\chi \equiv \text{const}$, $h$ is independent of $p$ and equals to $\epsilon$, and $E = \epsilon$. For interacting particles, $\chi$ can be a constant only if $φ$ would be an exact solution of the Schrödinger equation. The function $\chi$ we will name the correction function. The type of correction in $\chi$ depends on $φ$. If $φ$ corresponds to non-interacting particles $\chi$ contains corrections due to the whole interaction, in case of HF $φ$ only correlation part of the interaction, in the case of CI the part of correlation not taken into account in the used CI approximation.

Switching on the interaction between particles located on the same constant interaction potential surface does not change the particle motion on this surface and can accelerate the particles only along the normal to the surface. Eq. (9) takes into account this acceleration. However, the normal to the surface at point $r$ can not be parallel to the normal at point $r'$, so the acceleration obtained by the particle at $r$ can have a tangential component at $r'$. Eq. (9) disregards this effect and relative value in the change of the electron movement in normal and tangential directions due to electron-electron interaction for a given $\chi$ will determine the accuracy of the proposed approximation. To improve the approximation one can use common techniques choosing the better $φ$.

The best $φ$ for independent particle approximation can be obtained by minimization of functional (8) considering $χ$ as a known function. Presenting $φ$ by a determinant of one-particle functions $ϕ_i$, one can obtain a set of equations analogous to the Hartree-Fock ones

$$\left[ -\frac{1}{2} \nabla^2 + V(r_1) \right] ϕ_i(r_1) + \sum_{jk} \tau_{ik}^{-1} [u_{kj}(r_1) \nabla_1 ϕ_i(r_1) + \sum_k υ_{ij}(r_1) ϕ_j(r_1)] = Eϕ_i(r_1),$$

(11)

where

$$υ_{ij}^{\text{eff}}(r_1) = \langle ϕ_i | χ^* | χ | ϕ_j \rangle_1,$$

$$τ_{ij}(r_1) = \langle ϕ_i | χ^* | χ | ϕ_j \rangle_1, \quad u_{ij}(r_1) = \langle ϕ_i | \sum_k χ^* \nabla_k p \frac{dχ}{dp} | ϕ_j \rangle_1,$$

(12)

and $τ^{-1}$ is the reverse matrix to $τ$. Integration in (12) is performed over coordinates of all particles except particle 1, $ϕ_i$ means that function $φ_i$ in $φ$ is replaced by unity. The set of equation (11) resembles the Hartree-Fock equations. A difference arises from the fact that minimization in respect to one-particle functions is performed with weighted function $χ$ depending on the coordinates of all particles. It leads to the appearance of non-diagonal matrix elements in $τ$ and replacing the interparticle Coulomb interaction $1/r_{12}$ of the Hartree-Fock equations by the screened interaction $υ^{\text{eff}}$. Through this interaction the correlation in the Hartree-Fock equations is introduced. For $χ \equiv 1$, equations (11) are common Hartree-Fock equations.

Another possibility to improve $φ$ avoiding the need to solve HF equation occurs for $φ$ depending on some parameters. In this case eigenvalues of (9) can
be considered as the functional on these parameters and their values can be find minimizing the functional. This technique will be used in section 3.

Constructing interaction potential surface, it is useful to note that the form of the interparticle interaction \( W \) allows to carry any set of particle positions \( \mathbf{r} \) belonging to constant interparticle interaction potential surface \( 1/p \) to another set \( \mathbf{r}' \) belonging to surface \( 1/p' \) by coordinate scaling with factor \( p'/p \). It makes the generating points for any surface an easy task and restricts itself for initial generation by the surface, for example, \( p = 1 \). To obtain the point for any other surface one can use coordinate scaling again. Besides, the construction of the constant interaction potential surface can be presented in a recurrent form. For this purpose let us introduce notations

\[
\frac{1}{q_n} = \sum_{i=1}^{n-1} \frac{1}{r_{in}}, \quad (13)
\]

where \( n \) is the number of particles, and express the interaction potential as contributions from \( n - 1 \) particles and interaction of the \( n \)th particle with the rest

\[
\frac{1}{p_n} = \frac{1}{p_{n-1}} + \frac{1}{q_n}. \quad (14)
\]

Then integration over the constant interaction potential surface \( S(p_n) \) for \( n \) particles can be presented in the form

\[
\int_{S(p_n)} d\mathbf{R}_n = \int_{S(p_{n-1})} d\mathbf{R}_{n-1} \int_{S(q_n)} d\mathbf{r}_n \quad (15)
\]

where \( d\mathbf{R}_n = d\mathbf{r}_1 \ldots d\mathbf{r}_n \). For a given \( \mathbf{R}_{n-1} \equiv \{ \mathbf{r}_1, \ldots, \mathbf{r}_{n-1} \} \) integration over \( \mathbf{r}_n \) is performed over the surface determined in 3-dimension space by \( (14) \). For two particles it is the sphere of radius \( p \) around position of the first particle, for three particles it is a circle formed by crossing the sphere of radius \( r_{13} \) around \( \mathbf{r}_1 \) with the sphere of radius \( r_{23} \) around \( \mathbf{r}_2 \), for four particles it is only two points at the circle, etc. In addition one can restrict itself by irreducible part of the surface results from the identity of the particles. Evidently, with the help of particle numeration one can always satisfy the condition

\[
\sum_i^1 \frac{1}{r_{il}} \leq \sum_i^n \frac{1}{r_{ik}} \quad \text{if} \quad l < k, \quad (16)
\]

and it will be enough to consider only the part of the whole surface, satisfying to \( (16) \).

As an example, we represent the integral over the constant interaction potential surface for two particles

\[
\int_{S(p)} d\mathbf{R}_2 = \int_0^\infty r_1^3 d\mathbf{r}_1 \int_0^{2\pi} d\varphi_1 \int_0^\pi \sin \theta_1 d\theta_1 \int_0^\infty \delta(r_{12} - p) r_{12}^2 d\mathbf{r}_{12} \int_0^{2\pi} d\varphi_2 \int_0^\pi \sin \theta_2 d\theta_2, \quad (17)
\]
where the integration over the coordinates of the 1st particle is performed over the whole space, while the integration over the coordinates of the 2nd particle for a given \( r_1 \) is reduced to the integration over a sphere of radius \( r_{12} = p \) around the first particle.

### III. HELIUMLIKE IONS

As an application of the developed technique we calculated the ground \(^1S_0\) and excited \(^3S_1\) states electronic structure of heliumlike ions from \( H^- \) up to \( \text{Ne}^{8+} \). For these ions \( p \equiv r_{12} \) and (4) is reduced to the form used in a number of papers [1, 2, 17, 22, 23, 25]. The difference between those and the present paper consists in the different ways of the wave function calculation.

We represent

\[
\phi(r_1, r_2) = \frac{\varphi_1(r_1) \varphi_2(r_2) \pm \varphi_2(r_1) \varphi_1(r_2)}{\sqrt{2(1 \pm S^2)}} \quad (18)
\]

where \( S = \langle \varphi_1 | \varphi_2 \rangle \), for \(^1S_0\)

\[
\varphi_1(r) = 2Z_i^{3/2} \exp(-Z_i r) \quad (19)
\]

is 1s function of the electron in the field of nucleus with the charge \( Z_i \). For \(^3S_1\) the function of type (19) was used for \( \varphi_1 \), whereas

\[
\varphi_2(r) = Z_2^{3/2}(1 - Z_2 r/2) \exp(-Z_2 r/2) / \sqrt{2} \quad (20)
\]

is the 2s function of the electron in the field of nucleus with the charge \( Z_2 \). Factor \( Z_i \) in function (19) or (20) is known as an efficient nuclear charge seeing by the electron in the corresponding state, \( Z \) without subscript we save for the real nuclear charge. For function (18) Eq. (5) can be written in the form

\[
-\phi \frac{d^2 \chi}{dp^2} - \left[ \frac{p^2 + r_1^2 - r_2^2}{2pr_1} \frac{\partial \phi}{\partial r_1} + \frac{p^2 + r_2^2 - r_1^2}{2pr_2} \frac{\partial \phi}{\partial r_2} + \frac{2}{p} \frac{\partial \phi}{\partial r} \right] \frac{d\chi}{dp} - \left[ \frac{1}{2} \frac{\partial^2 \phi}{\partial r_1^2} + \frac{1}{2} \frac{\partial^2 \phi}{\partial r_2^2} + \frac{1}{r_1} \frac{\partial \phi}{\partial r_1} + \frac{1}{r_2} \frac{\partial \phi}{\partial r_2} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Zp} \right] \chi = E\phi\chi \quad (21)
\]

Here \( Z \) is the nuclear charge, the length unit is Bohr/\( Z \), and atomic units are used for other values.

Integration in (17) over a constant potential surface, when calculating expressions (10) for these case, is reduced to

\[
\int_{S(p)} d\mathbf{R}_2 = 4\pi p \int_0^\infty r_1 dr_1 \int_{|r_1-p|}^{r_1+p} r_2 dr_2 \quad (22)
\]

and can be performed analytically. The results are cumbersome and we present only their common form

\[
\sum_k c_{1,k} p^k e^{-2Z_1 p} + \sum_l c_{2,l} p^l e^{-(Z_1+Z_2)p} + \sum_m c_{3,m} p^m e^{-2Z_2 p} \quad (23)
\]
Eq. (9) with coefficients (23) can be solved analytically for asymptotic cases $p \to 0$ and $p \to \infty$. The finite asymptotic solutions are

$$
\lim_{p \to 0} \chi(p) \to \chi(0)(1 + \frac{p}{2Z} + \frac{p^2}{12Z^2} + O(p^3)), \quad (24)
$$

$$
\lim_{p \to \infty} \chi(p) \to \exp \left[ \left( -Z_{\text{min}} - \sqrt{Z_{\text{min}}^2 - E + E_0} \right) p \right], \quad (25)
$$

where $Z_{\text{min}} = \min(Z_1, Z_2)$. $E_0$ is energy in state $\phi$.

Eqs. (24) and (25) were taken as the boundary conditions in the numerical solution of (9). For the numerical calculations the differential operators were approximated with finite differences. Adopting

$$
\frac{d\chi_i}{dp} \approx \frac{\chi_{i+1} - \chi_{i-1}}{2\Delta p}, \quad (26)
$$

$$
\frac{d^2\chi_i}{dp^2} \approx \frac{\chi_{i-1} + \chi_{i+1} - 2\chi_i}{\Delta p^2}, \quad (27)
$$

where $i$ numerates points of discrete set $\{p_i\}$, $\chi_i = \chi(p_i)$, $\Delta p = p_i - p_{i-1}$. Eq. (9) can be represented by $n \times n$ tridiagonal matrix with $n$ is the number of points in $\{p_i\}$

$$
H_{ii} = \frac{t_i}{2\Delta p^2} + \frac{1}{Zp_i} + h_i, \quad (28)
$$

$$
H_{i,i\pm1} = -\frac{t_i}{2\Delta p^2} \pm \frac{u_i}{2\Delta p} \quad (29)
$$

for $1 < i < n$, and

$$
H_{11} = \frac{t_1}{2\Delta p^2} + \frac{1}{Zp_1} + h_i + \left( -\frac{t_1}{2\Delta p^2} + \frac{u_1}{2\Delta p} \right) / (1 + \Delta p/2Z + \Delta p^2/12Z^2), \quad (30)
$$

$$
H_{n,n} = \left( -\frac{t_n}{2\Delta p^2} + \frac{u_n}{2\Delta p} \right) \exp \left[ \left( -Z_{\text{min}} - \sqrt{Z_{\text{min}}^2 - E + E_0} \right) \Delta p \right] \quad (31)
$$

in accordance with (24), (25). Because boundary condition (31) depends on calculating eigenvalue, it is satisfied in the iteration process. Eigenvalues and eigenfuctions of (9) were approximated by eigenvalues and eigenvectors of matrix $H$ in interval $0 < p < 20/Z$ with 200 points at the interval. The value of interval and the number of points guarantee all significant numbers in the results presented below.

For $1^1S_0$ states the calculations were performed for three sets of function (19): a) $Z_1 = Z_2 = Z$; b) $Z_1 = Z_2$, however, the value is chosen from energy minimum; c) $Z_1 \neq Z_2$ and each the value is chosen from energy minimum. For $2^3S_1$ only the first and the third cases were considered. The calculated energies of these states together with those of HF theory for $1^1S_0$, and configuration interaction for $1^1S_0$ and $2^3S_1$ are shown in Table 1.

As it is seen in Table 1 in all cases the energies of $1^1S_0$ states calculated with Eq. (9) are less than the energies calculated with HF theory. Even for functions
\[ \phi \] completely disregard the interaction between electrons the correction function \[ \chi \] capable to take into account electron-electron interaction more accurate than it is done in HF approximation. However, the achieved accuracy is still far from the accuracy obtained by configuration interaction calculations \[ 29 \] or calculations which explicitly introduce the distance between electrons in the wave function \[ 1,2,23,25 \]. It is due to correction function \[ \chi \] describe the electron motion only between different electron-electron potential surface keeping the motion on a surface determined by function \[ \phi \].

The results can be improved by choosing the best \[ \phi \] solving Eq. \( 11 \). However, we attempt to use another way. Function \( 18 \) depends on two parameters, \( Z_1 \) and \( Z_2 \), so eigenvalues of \( 9 \) are the functionals of these parameters. The best one-particle functions of the form \( 19 \) and \( 20 \) minimize the functional. It permits us to avoid the solution of non-linear HF equations and makes technique based on \( 9 \) self-sufficient. Table I contains obtained results. We observe a slight improvement when both electrons are seeing an equal nucleus electric charge. Considerable improvement is observed when different electrons are seeing different effective nucleus charges. These charges and their dependence on \( Z \) are presented in Fig. 1.

As for \( 1^1S_0 \) the results for \( 2^3S_1 \) obtained with \( Z_1 = Z_2 = Z \) can be significantly improved by introducing different effective nuclear charges for the electrons. As it is seeing in Table I, in this case the results are close to those, obtained with configuration interaction. The charges and their dependence on \( Z \) are presented in Fig. 2.

The function \[ \phi \] obtained by minimization of \( E(Z_1, Z_2) \) can be considered as HF function. Thus, the correction function \[ \chi \] can be regarded as correlation functions. These functions, normalized so that integral \( \chi(p)s(p)\chi(p) \) over interval \( 0 \leq p \leq 20 \) equals to 1, are presented in Fig. 3. The functions reduce the probability of electrons to be at a short distances showing monotonic growth with the distance between the electrons. The behavior of \[ \chi \] for all ions is similar, however, the functions become smoother with the growth of \( Z \) and tend to some limit. The deviation \[ \chi \] from the unity for \( 2^3S_1 \) states is less then for \( 1^1S_0 \) state suggesting a decrease of correlation effects. It is known to occur due to the exchange hole appearing for antisymmetric \[ \phi \]. The function \[ \chi \] changes this hole, with this change being more significant at electron-electron distances \( p \leq 1/Z \) reducing further the small probability to find electrons at these distances.

The function \( s(p) \) determined in \( 10 \) is the distribution function of \( r_{12} \) for wave function \( \phi \), and function \( \chi s \chi \) is the distribution function for \( \phi \chi \). These function for \( 1^1S_0 \) states for \( H^- \) and \( Ne^{8+} \) are shown in Fig. 4. Besides, Fig. 4 shows the corresponding correlation holes determined as \( s(\chi^2 - 1) \). In general, the form of the correlation holes is the same as in \( 30 \). However, the depths of the holes decreases from \( H^- \) to \( Ne^{8+} \). The distribution functions and correlations holes for \( 2^3S_1 \) of \( He \) and \( Ne^{8+} \) are shown in Fig. 5. As for \( 1^1S_0 \) states the depths of the holes decreases with nuclear charge growth and the holes become more shallow in comparison with \( 1^1S_0 \).

Until now we have considered only the lowest eigenstates of \( 9 \). However, for given the \( \phi \) we can calculate higher eigenstates for \( \chi \). We will demonstrate how
these states correspond to real excited states on the example of non-interacting electron for which the exact results have been available. In Fig. 6 functions \( \chi \) for the lowest three solutions of (9) for non-interacting electrons are shown. As it is seen, higher eigenfunctions exhibit nodes due to which function \( \phi \) based on 1s functions is transformed in function \( \phi \) similar to the function based on 2s or 3s functions. However, the energies corresponding to these function are \( E = -0.440 \) and \(-0.245 \) instead of exact energies -0.625 and -0.555 a.u. The source of pure accuracy is the conservation 1s function in computations (10). The use of proper function in (10) makes it possible to obtain the exact results for the excited states. As such, we can use higher eigenstates of (9) only for a crude estimation of exited states energies and use proper \( \phi \) to obtain more accurate results.

IV. CONCLUSIONS

Eq. (9) reduces the many-body Schrödinger equation to the 2nd order linear ordinary differential equation for the correction function. It describes the changes in electron movement between constant interaction potential surfaces due to electron-electron interaction. The changes in electron movement along the surface are disregarded in (9).

Solutions of the (9) for two electron ions give the total energies more accurate than HF theory does. It is true even in the simplest case where wave functions of non-interacting electrons are used for function \( \phi \). For \( \phi \) containing only two variations parameters, efficient nuclear charges visible by the electrons, the results are close to those obtained by configuration interaction or explicit dependence of the wave function on the distance between electrons where tens parameters are used. It means that the electron-electron interaction changes the electron motion of independent particle mainly between different constant interaction potential surfaces affecting the movement along the surfaces to a lesser degree. Nevertheless, to improve the accuracy it is needed, in one or another way, to take into account the changes in electron movement along the surfaces.

Considering eigenvalues of (9) as a functional of parameters determining \( \phi \), it seems possible to avoid the solution of non-linear HF equation when finding the best \( \phi \) by solving iterative Eq. (9). Hopefully, Eq. (9) can also replace the HF equations for system with more then two electrons. The main effort in the proposed technique application is the integration over constant interaction potential surface. For a two electron system it can be done analytical. It doesn’t seem difficult to solve this problem for a several electron system. However, computation efforts will grow with the increasing number of electrons and, eventually, the direct integration in (10) will be inefficient. We will put off discussion the possible ways to solve this problem after solving it for several electron systems.

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TABLE I. Energies of Heliumlike ions (a.u.): HF - HF approximation; Z - Eq. \( \text{(9)} \) with effective nuclear charges equal to \( Z \), \( Z_1 = Z_2 \neq Z \), \( Z_1 \neq Z_2 \neq Z \); CI - configuration interaction.

| Ion | \( 1^1S_0 \) | \( 2^1S_1 \) | Ion | \( 1^1S_0 \) | \( 2^1S_1 \) |
|-----|-------------|-------------|-----|-------------|-------------|
| \( H^- \) | HF | -0.49843 | \( C^+ \) | HF | -32.36137<sup>a</sup> | \( Z \) | Z | -32.38345 | -21.40351 |
| \( Z \) | Z | -0.50936 | \( Z_1 = Z_2 \) | Z | 32.39605 |
| \( Z_1 \neq Z_2 \) | -0.52623 | \( Z_1 \neq Z_2 \) | Z | -32.40493 | -21.41659 |
| CI | -0.52760<sup>b</sup> | CI | -32.40544<sup>b</sup> | -21.42249<sup>c</sup> |
| He | HF | -2.86171<sup>a</sup> | \( N^5^+ \) | HF | -44.73618<sup>a</sup> | \( Z \) | Z | -44.75873 | -29.34061 |
| \( Z \) | -2.87940 | -2.15491 |
| \( Z_1 = Z_2 \) | -2.89142 | \( Z_1 = Z_2 \) | -44.77422 |
| \( Z_1 \neq Z_2 \) | -2.90208 | \( Z_1 \neq Z_2 \) | -44.78001 | -29.35355 |
| CI | -2.90325<sup>b</sup> | -2.17521<sup>c</sup> | CI | -44.78061<sup>b</sup> | -29.36118<sup>c</sup> |
| Li<sup>+1</sup> | HF | -7.23633<sup>a</sup> | \( O^6^+ \) | HF | -59.11159<sup>a</sup> | \( Z \) | Z | -59.13392 | -38.52770 |
| \( Z \) | -7.25642 | -5.09213 |
| \( Z_1 = Z_2 \) | -7.26856 | \( Z_1 = Z_2 \) | -59.15135 |
| \( Z_1 \neq Z_2 \) | -7.27829 | -5.10636 | \( Z_1 \neq Z_2 \) | -59.15543 | -38.54054 |
| CI | -7.27928<sup>b</sup> | -5.11075<sup>c</sup> | CI | -59.15574<sup>b</sup> | -38.55098<sup>c</sup> |
| Be<sup>2+</sup> | HF | -13.61130<sup>a</sup> | \( F^7^+ \) | HF | -75.48702<sup>a</sup> | \( Z \) | Z | -75.50906 | -48.96479 |
| \( Z \) | -13.63244 | -9.27928 |
| \( Z_1 = Z_2 \) | -13.64393 | \( Z_1 = Z_2 \) | -75.52834 |
| \( Z_1 \neq Z_2 \) | -13.65406 | -9.29290 | \( Z_1 \neq Z_2 \) | -75.53066 | -48.97754 |
| CI | -13.65485<sup>b</sup> | -9.29739<sup>c</sup> | CI | -75.53083<sup>b</sup> | -48.99223<sup>c</sup> |
| B<sup>3+</sup> | HF | -21.98607<sup>a</sup> | \( Ne^{8^+} \) | HF | -93.86174<sup>a</sup> | \( Z \) | Z | -93.88415 | -60.65187 |
| \( Z \) | -22.00805 | -14.71640 |
| \( Z_1 = Z_2 \) | -22.02112 | \( Z_1 = Z_2 \) | -93.90520 |
| \( Z_1 \neq Z_2 \) | -22.02934 | -14.72969 | \( Z_1 \neq Z_2 \) | -93.90577 | -60.66457 |
| CI | -22.03020<sup>b</sup> | -14.73463<sup>c</sup> | CI | -93.90592<sup>b</sup> | -60.68527<sup>c</sup> |

<sup>a</sup>Ref. [28]
<sup>b</sup>Ref. [29]
<sup>c</sup>Ref. [12]
FIG 1. Efficient charges for $1^1S_0$ states.
FIG 2. Efficient charges for $2^3S_1$ states.
FIG 3. Functions $\chi$ for $1^1S_0$ and $2^3S_1$ states.
FIG 4. Distribution of the electron-electron distance (solid and dash lines for the HF approximation and present calculation, correspondently) and correlation holes for $1^1S_0$ states.
FIG 5. Distribution of the electron-electron distance (solid and dash lines for the HF approximation and present calculation, correspondently) and correlation holes for $2^3S_1$ states.
FIG 6. Function $\chi$ of the ground state and excited states for non-interacting particles.
