New method of solving the many-body Schrödinger equation.

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A method of solving the Schrödinger equation based on the use of constant particle-particle interaction potential surfaces (IPS) is proposed. The many-body wave function is presented in a configuration interaction form, with coefficients depending on the total interaction potential. The corresponding set of linear ordinary differential equations for the coefficients was developed. To reduce the computational work, a hierarchy of approximations based on interaction potential surfaces of a part of the particle system was worked out. The solution of a simple exactly solvable model and He-like ions proves that this method is more accurate than the conventional configuration interaction method and demonstrates a better convergence with a basis set increase.

Introduction.— Møller-Plesset perturbation theory and configuration interactions (CI) are the conventional methods of treating electron-electron correlation in the theory of atoms and molecules [1]. Unfortunately, due to the presence of the correlation cusp [2, 3] in the wave function, both of them reveal slow convergence of electron energy with basis set increasing.

Density functional theory (DFT) [4–7] is another approach for the solution of a quantum many-body problem. Based on solving Kohn-Sham equations [5], it has been successfully applied to many problems [7]. Unfortunately, the exact form of this functional is still unknown, and its approximated forms do not always provide needed accuracy, for example, in treating the systems with strong electron-electron correlations [8–10].

All these arguments give reasons to search for other ways of treating the correlation problem. To speed up the convergence, explicitly correlated have been developed over the last two decades [11–13] in which the wave function explicitly depends on electron-electron spacing. Iterative complement interaction method has been formulated in [14, 15].

This paper is aimed at developing another way of treating the correlation problem presented in [16]. The theory is based on the introduction of constant particle-particle interaction potential surfaces (IPS). From the definition of such surfaces it follows that particle-particle interaction acts along the normal to the surface and, therefore, does not influence particle motion on the surface. Further a new form of many-body wave function and equations to find it will be proposed and applied to a simple model system and He-like ions.

Configuration weight functions and equations determining them.— Consider the Schrödinger equation of \( n \) interacting particles and introduce a collective variable

\[
\frac{1}{p(R)} = V(R) = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \frac{1}{r_{ij}} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} v_{ij}. \tag{1}
\]

Here \( R \) stands for a set of particle coordinates \( r_1, ..., r_n \), \( r_{ij} = |r_i - r_j| \).

A constant IPS \( V(R) = 1/p \) selects a subspace of particle coordinates in which particle motion is correlated \( ab \) origin due to the demand remaining at the surface rather than particle interaction. The resulting interaction force does not act on particle movement along the surface, therefore, the movement can be described by a function \( \Phi_i(R) = \phi_{i_1}(r_1) \cdots \phi_{i_n}(r_n) \) satisfying to the Schrödinger equation of non-interacting particles \( H(R) \). Here we introduced vectors \( i \) with components \( i_1, ..., i_n \). To satisfy the Schrödinger equation of interacting particles we represented the wave function in the form

\[
\Psi(R) = \sum_i \chi_i(p(R))\Phi_i(R). \tag{2}
\]

Function (2) has the form of CI function in which constant coefficients are replaced by functions \( \chi_i(p(R)) \) depending on interaction potential at points \( R \).

Energy minimization in respect to \( \chi_i \) leads to equations

\[
\sum_j \left[ -\frac{t_{ij}(p)}{2} \frac{d^2 \chi_j(p)}{dp^2} - \left( \frac{t_{ij}(p)}{p} + \frac{u_{ij}(p)}{2} \right) \frac{d \chi_j(p)}{dp} + \left( \frac{h_{ij}(p)}{p} + \frac{1}{p} \right) \chi_j(p) \right] = E \sum_j s_{ij}(p)\chi_j(p),
\]

where

\[
t_{ij}(p) = \langle \Phi_i(R)(\nabla R)^2\Phi_j(R) \rangle_p, \tag{4}
\]

\[
u_{ij}(p) = \langle \Phi_i(R)\nabla R^2\Phi_j(R) \rangle_p, \tag{5}
\]

\[
h_{ij}(p) = \langle \Phi_i(R)H(R)\Phi_j(R) \rangle_p, \tag{6}
\]

\[
s_{ij}(p) = \langle \Phi_i(R)\Phi_j(R) \rangle_p. \tag{7}
\]

Eq. (3) is a set of linear ordinary differential equation with eigenvalues equal to the system energy. The terms
containing derivatives of $\chi$ describe additional contributions to kinetic energy arising when redistribution of electrons between different interaction potential surfaces occurs. There is no such redistribution for non-interacting particles. For this case functions $\chi$ are constant and differential equations (3) reduce to the Schrödinger equations of non-interacting particles. Beside electron redistribution between different $p$, functions $\chi$ determine the contributions of different configurations for constant $p$, hence referred to as configuration weight function.

The boundary conditions for $\chi$ follow from the demand for $\Psi$ to be finite in the whole space $\chi_i(p)s_{ij}(p)\chi_j(p) < \infty$. For small $p$ Eqs. (3) can be approximated by $2d\chi/\text{dp} + \chi = 0$ with solution $\chi(p) \approx e^{2p/2}$ which provides the boundary conditions for solutions of (3). Determine functions $\omega^l_{ij}(p, E)$ which are solutions of (3) for energy $E$ with different boundary conditions $\omega^l_{ij}(0) = \delta_{ij}$, and $d\omega^l_{ij} / dp = Z\delta_{ij}/2$. The common solution of (3) can be presented in the form $\chi^l_{ij}(p, E) = \sum k c^l_k \omega^l_{ij}(p, E)$.

Since particle-particle interaction tends to separate the particles, it can be expected that $\chi(p)$ is a growing function of $p$, with the growth being not too fast to prevent total function divergence. The valid boundary conditions depend on the behavior of $\Omega_{ij}$ and $\Omega_{ij}$ when $p \to \infty$ and should be discussed for particular problems.

The particle-particle IPS.— The constant particle-particle IPS is a plane in the space of the pair potentials $v_{ij} = 1/r_{ij}$, which will be refer to as $v$-space. The dimensionality of $v$-space is $n(n-1)/2$. Each point of $v$-space determines the relative particle positions $r_{ij}$ in the usual space, which we call $r$-space, so the set of $\mathbf{R}$ belonging to the same surface can be easily determined. Not all of $r_{ij}$ are independent because all of them are determined by $3(n-1)$ particles coordinates placing the 1st particle at the coordinate system origin. Due to the multidimensionality of the plane and a dependence of integration limits of a particle on position of the other particles the numerical integration over the surface can be performed only for several particle systems. It means that the developed theory can be applied at the best only for such systems, and an extension of the theory to bigger systems needs to be simplified. Possible simplifications are proposed below.

At first, one can introduce a set of approximations to the theory based on the lowering the dimension of IPS by averaging over the coordinates of $m$ particles. Correspondent surfaces will be denoted $S_m$, the dimension of such IPS is $3(n - m - 1)$. Averaging over all particles but two describes the motion of exactly correlating particle pairs in the middle field of other particles can be called independent pair approximation. The same way can be introduced independent triplet, quadruple, etc. approximations. Introducing IPS for potential acting on a particle from the other ones, each $S_m$ IPS can be reduced to $S_{1m}$ with dimension $n - m - 1$. For a particle at $r_1$ it consists of $n - m - 1$ spheres of radius $r_{3i}$.

A simple exactly solvable model. To test the developing theory, we considered a simple model, three particles in one dimensional infinite square potential well, and solved the Schrödinger equation directly, with configuration interaction method and with different approximations of the developing theory. To avoid errors in derivatives approximation by finite differences we ab origin used the discrete space containing ten points together with the border ones in which kinetic energy operator acting on a particle at point $i$ is $\delta_{ij} - \delta_{ij}|i_+1|$, and the interaction between a pair of particles $v_{ij} = 1/\sqrt{r_{ij} + 1}$ with $\lambda = 0.1$ to prevent $v$ from becoming infinity at $i = j$. The total matrix of 512x512 order constructed from these matrix elements for three particles has been diagonalized.

A complete orthonormal basis functions set turn into zero at the border points is

$$\varphi_\alpha(i) = \sqrt{\frac{2}{\pi^2}} \sin \frac{\alpha \pi i}{9}, \quad i = 0, \ldots, 9, \quad \alpha = 1, \ldots, 8,$$

where $\alpha$ numerates functions and $i$ numerates points. From these functions a set of configurations can be constructed $\Phi_\alpha(i) = \varphi_\alpha(i_1) \varphi_\alpha(i_2) \varphi_\alpha(i_3)$. To check the convergence of CI method the problem has been solved for different number $n_f$ of functions (8) used to configuration construction. The four lowest eigenvalues for different $n_f$ are shown in Table 1, columns CI.

The IPS has been constructed for the total interaction, $S_3$, for the potential $v_{12} + v_{13}, S_{13}$, and for $v_{12}, S_{2}$. On some surfaces functions (8) are linear dependent and for such surfaces a new orthonormal set of one-particle functions has been constructed. The matrix corresponding to $\chi$ has been obtained and diagonalized. The four lowest eigenvalues for different $n_f$ are shown in Table 1 in columns $S_3, S_{13}$ and $S_2$.

The results show that all of the applied methods for $n_f = 8$ give exactly the same results for the ground and exited states. This situation continues in $S_3$ and $S_{13}$ cases up to $n_f = 4$ for all states, and up to $n_f = 3$ for the ground state in spite of one-body basis set reduction. The result is a sequent that up to $n_f = 4$ the number of linear independent functions constructed with (8) remains unchanged. The basis set decrease leads to the decrease of linear independent functions, and the accuracy of calculations drops significantly, faster for CI method.

He-like ions. Solving the Schrödinger equations for He-like ions it is convenient to use for length and energy corresponding atomic units divided by nuclear charge $Z$ and $Z^2$, respectively. For description of 1S states we used $2e^{-r}, (1 - r/2)e^{-r^2/2}/\sqrt{2}$ and $2(1 - 2r^2 + 2r^4/27)e^{-r^2/3}/\sqrt{27}$ wave functions corresponding to 1s, 2s and 3s states of an electron in the nuclear field. From these function 3 configuration with the lowest energy, $\Phi_1(r_1, r_2) = \phi_1(r_1)\phi_1(r_2), \Phi_2(r_1, r_2) = (\phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1))/\sqrt{2}$ and $\Phi_3(r_1, r_2) = (\phi_1(r_1)\phi_3(r_2) + \phi_1(r_2)\phi_3(r_1))/\sqrt{2}$.

He-like ions. Solving the Schrödinger equations for He-like ions it is convenient to use for length and energy corresponding atomic units divided by nuclear charge $Z$ and $Z^2$, respectively. For description of 1S states we used $2e^{-r}, (1 - r/2)e^{-r^2/2}/\sqrt{2}$ and $2(1 - 2r^2 + 2r^4/27)e^{-r^2/3}/\sqrt{27}$ wave functions corresponding to 1s, 2s and 3s states of an electron in the nuclear field. From these function 3 configuration with the lowest energy, $\Phi_1(r_1, r_2) = \phi_1(r_1)\phi_1(r_2), \Phi_2(r_1, r_2) = (\phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1))/\sqrt{2}$ and $\Phi_3(r_1, r_2) = (\phi_1(r_1)\phi_3(r_2) + \phi_1(r_2)\phi_3(r_1))/\sqrt{2}$.
The common solution of (3) can be presented in the form

\[ r_ω e^{t} \quad \text{and} \quad s_1, s_3, s_2 \text{and CI matrices.} \]

\[ \sum_{j=1}^{n} \left[ -\lambda^2 s_{ij}(p) - \lambda(2s_{ij}(p)/p + u_{ij}(p)) + h_{ij}(p) \right] \]

\[ + s_{ij}(p)/Zp - E s_{ij}(p) \chi_j(p) = 0, \quad i = 1, \ldots, n, \]

\[ n \quad \text{is the number of configuration taking into account. Set} \]

\[ \text{(9)} \]

\[ \text{has non-zero solution if } \det(\Lambda) = 0 \text{ where matrix } \Lambda \]

\[ \text{is determined by the expressions in the square brackets of (9). Determine functions } \omega_{ij}(p, E) \]

\[ \text{which are solutions of (3) for energy } E \text{ and satisfy boundary conditions} \]

\[ \omega_{ij}(p, E) = \delta_{ij}, \text{ and } d\omega_{ij}(p, E)/dp = \lambda(E)\delta_{ij}, \text{ where } \lambda \]

\[ \text{is a root of } \det(\Lambda) \text{ satisfying condition } e^{2\lambda p} s_{ij}(p) < \infty. \]

The common solution of (3) can be presented in the form

\[ \chi^s_i(p, E) = \sum_{j=1}^{n} c^s_j \omega^s_{ij}(p, E). \]

\[ \text{Coefficients } c^s_i, c^s_p \text{ and energy } E \text{ are determined from the demand that functions} \]

\[ \chi^s_i \text{ must continuously pass to functions } \chi^s_i \text{ at a matching point } p \text{ together with their 1st derivatives.} \]

To solve (3) the Runge-Kutta 4th-order method was employed. The energies obtained for the ground states of He-like ions are shown in Tables II together with CI and results. The use of only one-configuration approximation gives energies slightly below Hartree-Fock limit. Inclusion of the second configuration gives results comparable with those of CI with 35 configurations [18].

Our results are slightly above the CI results from \( H^- \) up to \( B^3+ \) and below CI results for the rest of calculated ions. Inclusion of the third configuration gives the lowest energies presented in the table. More over the energies of ions up to \( Be^2+ \) turn out to be below experimental values. However, accounting mass correction factors for these ions \( M/(M + m) \), gives energies for \( He \) -2.903501, for \( Li^+ \) -7.280415 and \( Be^2+ \) -13.656841.

The configuration weight functions for 1-, 2- and 3-configuration approximation are shown in Fig. 1, Fig. 2, and Fig. 3 and Fig. 4, correspondingly.

\[ \phi_1(r_2) \phi_3(r_1)/\sqrt{2}, \text{ have been constructed. Matrix elements between these functions can be obtained analytically.} \]

To define the boundary condition when \( p \to \infty \) we represent the solution of (3) at a point \( p \) as \( e^{λp} \). Substitution of this representation in (3) leads to

\[ \text{FIG. 1. 1s1s configuration weight functions for } H^-,...,Ar^{16+} \]

\[ \text{in 1-configuration approximation.} \]

In all cases 1s1s configuration weight functions are increasing functions. The functions growth slows down with increasing nuclear charges and tends to be constant. The growing weight function decreases the probability of finding an electron at a small separation which increases for a bigger separation in comparison with a non-interacting case. For 2-configuration approximation 1s2s functions have noticeable values at small \( p \) decreasing with the growth of \( p \) and atomic charges (Fig. 2). 1s3s configuration weight function for \( He \) (Fig. 3) in small \( p \) region significantly exceeds 1s1s and 1s2s configuration weight functions, however, with the growth of \( p \)
### Table II: The ground states energies of He-like ions.

| Ion       | HF<sup>a</sup> | 1    | 2   | 3    | CI<sup>b</sup> | CI<sup>c</sup> | Exp.<sup>d</sup> |
|-----------|----------------|------|-----|------|----------------|----------------|-----------------|
| H<sup>+</sup> | -0.498665   | -0.527171 | -0.527768 | -0.52760 | -0.527730 |
| He        | -2.86171    | -2.880042 | -2.901782 | -2.903896 | -2.90325  | -2.9037236 | -2.9038 |
| Li<sup>2+</sup> | -7.27633   | -2.57493 | -7.278072 | -7.280982 | -7.27928  | -7.279819  | -7.2804 |
| Be<sup>2+</sup> | -13.61130  | -13.633947 | -13.654148 | -13.657667 | -13.65485  | -13.655551  | -13.6574 |
| B<sup>3+</sup>    | -21.98067   | -22.010000 | -22.030959 | -22.034159 | -22.03020  | -22.030875  | -22.0360 |
| C<sup>4+</sup>    | -32.36137   | -32.385852 | -32.405967 | -32.405454 | -32.40544  | -32.406070  | -32.4174 |
| N<sup>5+</sup>    | -44.73618   | -44.761590 | -44.781795 | -44.78061  | -44.781141 | -44.784114  | -44.8035 |
| O<sup>6+</sup>    | -59.11159   | -59.137256 | -59.157592 | -59.15574  | -59.156222 | -59.1958    |
| F<sup>7+</sup>    | -75.48702   | -75.512875 | -75.533370 | -75.539432 | -75.5308   | -75.531401  | -75.5970 |
| Ne<sup>8+</sup>   | -93.86174   | -93.888460 | -93.909133 | -93.915678 | -93.906452 | -94.0086    |
| Na<sup>9+</sup>   | -114.264020 | -114.284885 | -114.291910 | -114.28165 |
| Mg<sup>10+</sup> | -136.639562 | -136.660629 | -136.668132 | -136.6572  |
| Al<sup>11+</sup> | -161.015090 | -161.036367 | -161.044346 | -161.03180 |
| Si<sup>12+</sup> | -187.390605 | -187.412100 | -187.420554 | -187.40687 |
| P<sup>13+</sup>   | -215.766116 | -215.787829 | -215.796757 | -215.78191 |
| S<sup>14+</sup>   | -246.141617 | -246.163554 | -246.172956 | -246.15697 |
| Cl<sup>15+</sup> | -278.517113 | -278.539277 | -278.549152 | -278.53201 |
| Ar<sup>16+</sup> | -312.929603 | -312.941998 | -312.925344 | -312.90704 |

<sup>a</sup> Ref. [17].
<sup>b</sup> Ref. [18].
<sup>c</sup> Ref. [19].
<sup>d</sup> Ref. [20, 21].

1s1s function dominating. For Ar<sup>16+</sup> 1s2s and 1s3s configuration weight functions are similar to those of He, whereas their relative values in comparison with 1s1s function decrease significantly (Fig. 4). All configuration weight function exhibit monotonic gradual changes with the increase in nuclear charge.

**Summary.** The proposed theory can be considered as an extension of configuration interaction method in which configuration weights depend on the values of the interaction potential, which makes the wave function more flexible and eliminates the influence of the wave function cusps on the convergence of the wave function to the exact one with an increase in a basis set. At the same time, the theory can be compared with explicitly correlated methods since configuration weight functions explicitly depend on a particle-particle separation. The main difference between these theories is the form of the dependence which is prescribed in explicitly correlated theories, whereas in the suggested theory it is obtained by the solution of the corresponding equations.

The solution of the model example with CI method and with the proposed theory shows that the convergence of the proposed theory even in the lowest approximation is faster than in CI method. The performed calculations of He-like ions show that the developed theory gives accuracy, at least, none the worse than the accuracy of the most precise techniques but with much less computational efforts. The use of only three configurations constructed from 1s, 2s, and 3s wave functions of non-interacting electrons in the nuclear field gives ground state energies of He-like ions lower than those of CI wave function with 35 configurations constructed from seven s, p, d, f, and g Slater type orbitals [18], and lower than those of configuration interaction wave function with 15 configuration constructed from 5 Slater orbitals and explicit r<sup>12</sup> terms up to 5 order [19], lower than Hylleraas-type wave function with more than three hundred terms. The results were obtained without iteration procedure of self-consistent field because the developed theory does not presuppose the use of the Hartree-Fock approximation as a preliminary step for precise calculations.

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FIG. 2. 1s1s and 1s2s configuration weight functions from He to Ar$^{16+}$ for even atomic numbers in 2-configuration approximation.

[1] C. D. Sherrill, J. Chem. Phys. 132, 110902 (2010).
[2] T. Kato, Commun. Pure Appl. Math. 10, 151 (1957).
[3] H. King, Theor. Chim. Acta 94, 345 (1996).
[4] P. Hohenberg and W. Kohn, Physical Review 136, B864 (1964).
[5] W. Kohn and L. J. Sham, Physical Review 140, A1133 (1965).
[6] P. Hohenberg and W. Kohn, J. Phys. Chem. 100, 12974 (1996).
[7] C. Christopher and D. Truhlar, Phys. Chem. Chem. Phys. 11, 10757 (2009).
[8] N. Ivanova, S. Ovchinnikov, M. Korshunov, I. Eremin, and N. Kazak, Physics-Uspekhi 179, 837 (2009).
[9] F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamasaki, and O. K. Andersen, Phys. Rev. B 74, 125120 (2006).
[10] E. Dagotto, Science 309, 257 (2005).
[11] K. E. Yousaf and K. A. Peterson, Chemical Physics Letters 476, 303 (2009).
[12] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem 25, 427 (2006).
[13] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chemical Reviews 112, 4 (2012), http://pubs.acs.org/doi/pdf/10.1021/cr200168z.
[14] H. Nakatsuji, Phys. Rev. Lett. 93, 030403 (2004).
[15] H. Nakatsuji, Phys. Rev. A 72, 062110 (2005).
[16] V. Tapilin, J. Struct. Chem. 49, 409 (2008); arXiv:0809.1478v1 [quant-ph] (2008).
[17] E. Clementi and C. Roetti, Atomic data and Nuclear data Tables 14, 177 (1974).
[18] A. Weiss, Phys. Rev. 122, 1826 (1961).
[19] B. Saha, S. Bhattacharyya, T. K. Mukherjee, and P. K. Mukherjee, Int. J. Quantum Chem. 92, 413 (2003).
[20] C. Moore, Atomic Energy Levels, Vol. 1 (NSRDS-NBS 35, 1971).

FIG. 3. 1s1s, 1s2s and 1s3s configuration weight functions for He in 3-configuration approximation.

[1] C. D. Sherrill, J. Chem. Phys. 132, 110902 (2010).
[2] T. Kato, Commun. Pure Appl. Math. 10, 151 (1957).
[3] H. King, Theor. Chim. Acta 94, 345 (1996).
[4] P. Hohenberg and W. Kohn, Physical Review 136, B864 (1964).
[5] W. Kohn and L. J. Sham, Physical Review 140, A1133 (1965).
[6] P. Hohenberg and W. Kohn, J. Phys. Chem. 100, 12974 (1996).
[7] C. Christopher and D. Truhlar, Phys. Chem. Chem. Phys. 11, 10757 (2009).
[8] N. Ivanova, S. Ovchinnikov, M. Korshunov, I. Eremin, and N. Kazak, Physics-Uspekhi 179, 837 (2009).
[9] F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamasaki, and O. K. Andersen, Phys. Rev. B 74, 125120 (2006).
[10] E. Dagotto, Science 309, 257 (2005).
[11] K. E. Yousaf and K. A. Peterson, Chemical Physics Letters 476, 303 (2009).
[12] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem 25, 427 (2006).
[13] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chemical Reviews 112, 4 (2012), http://pubs.acs.org/doi/pdf/10.1021/cr200168z.
[14] H. Nakatsuji, Phys. Rev. Lett. 93, 030403 (2004).
[15] H. Nakatsuji, Phys. Rev. A 72, 062110 (2005).
[16] V. Tapilin, J. Struct. Chem. 49, 409 (2008); arXiv:0809.1478v1 [quant-ph] (2008).

FIG. 4. 1s1s, 1s2s and 1s3s configuration weight functions for Ar$^{16+}$ in 3-configuration approximation.

[21] S. Bashkin and J. Stoner, Jr., Atomic Energy Levels and Grotrian Diagrams, Vol. I and II (North-Holland, Amsterdam, 1975, 1978).