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Non-conventional optimization procedure for mass effects investigation in the ground state energies of *1s* core-ionized helium-like atoms from helium to xenon

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The non-relativistic energy magnitudes for the ground state of He and He isoelectronic series with atomic numbers *Z*=3-54 are calculated. Calculations are performed using explicitly correlated trial wave-functions of the generalized Hylleraas type. A variational procedure is developed that allows solution of the two-particle Schroedinger equation for a practically unlimited number of parameters in a series of trial wave-functions along the positive degrees of the Hylleraas coordinates. Non-conventional optimization methods are developed and, in particular, applied nonlinear programming is used to solve the problem. The contributions to the energy for various parameters is analyzed. Mass corrections and polarizations to the non-relativistic energy are studied. The obtained results are compared to existing experimental data and available theoretical data by other authors. One should note that until now, such data have been computed only for atomic numbers *Z*=2-12. The behavior of the ground state energy versus *Z*, and the effects of mass corrections and polarizations, contributing to these effects in the electron system energies, are investigated.

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1. Introduction

Quite often, we apply "ab initio" approaches to analyze many-electron systems, when using a determinant class of trial Wave Functions (WF). In order to study an atomic system, we use Hartree-Fock methods which give good values for the ground state energies of atoms with atomic numbers *Z*>3. The results are unsatisfactory when the number of electrons is less. For He, the Hartree-Fock-Ruthaan method gives the ground state energy 2.861799a.u., while the experimental value is 2.9035621a.u.[1]. This disagreement is a result of various factors. For 1-electron approximation, just one electron always resides in the 1s level, which does not depend on the atomic state. The fact that the 1s particle orbitals are not zero in the nucleus center leads to some possible increase in the energy [2]. The nucleus size is finite and the charge inside is practically less than the number of protons *Z*. This energy change is 1.109454×10^{-10}a.u. [2].

In the case of atoms with a small number of electrons, the nuclear motion gives a substantial contribution [2], for a precise determination of the ground state energy. For this reason, two corrections are introduced: a finite mass correction and mass electron correlations. Regarding He and isoelectronic He ions, the behavior of one of the electrons strongly depends on the position of the other, and their relative dispositions. Both electrons influence the nuclear motion. Accounting for these processes, we have to exploit explicitly correlated trial WF, which depends on the distance between the electrons and their mutual disposition [2,3].

The explicitly correlated WF have broad application when studying the properties and characteristics of quantum systems [4]. There are precise numerical solutions of the wo-particle Schroedinger equation (SE) based on the functions of Hylleraas [3, 5], Pekeris [6, 7], generalized and modern WF introduced by other authors. Even though these are not precise WF of the SE, the results obtained for the energy characteristics of He practically coincide with the experimental data. There are 1S ground state calculations for the He and some ions of the He isoelectronic series with *Z*=3-12. For some of them, mass corrections and mass polarization effects are accounted for.

We use trial WF of generalized Hylleraas type to study He and He isoelectronic series with *Z*=2-54. The behavior of the ground state energy versus *Z*, effects of mass correction and mass polarization are investigated. The developed procedure allows us to solve the SE for practically an unlimited number of parameters in the series of trial WF upon positive degrees of the Hylleraas coordinates. Non-conventional optimization method is developed to solve the problem. We obtain the optimum energy when the number of coefficients is limited, evaluating their contribution, i.e. we do not need to discuss the open question [2, 8] of the divergence of the variational procedure with increasing the number of coefficients.

The obtained results are compared with experimental data and available theoretical data by other authors. Until now there are calculated data only for atomic numbers Z=2–12.

2. Variational procedure

Within the framework of the variational approach, a numerical solution of two particle stationary SE has been realized with the Hamiltonian

$$\mathrm{H} = -\frac{1}{2}\Delta_1^2 - \frac{1}{2}\Delta_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \qquad (1)$$

where r_1 and r_2 are the magnitudes of the electron radius-vectors in the coordinate system, set in the nucleus center, and r_{12} is the distance between them. The 2-particle wave function Ψ is defined in a 6-dimensional (6D) configurational space of the two electrons.

The variational equation has the form [1,2]:

$$\delta E = \delta \frac{\int\left[\frac{1}{2}(\Delta_1\Psi)^2 + \frac{1}{2}(\Delta_2\Psi)^2 + U\Psi^2\right] d\mathbf{r}_1 d\mathbf{r}_2}{\langle\Psi|\Psi\rangle} = 0 \qquad (2)$$

For trial wave functions, we use explicitly correlated WF of generalized Hylleraas type [4,9]

$$\Psi(ks,kt,ku) = e^{-\frac{ks}{2}} F(ks,kt,ku),\ F(s,t,u) = \sum_{nlm=0}^{\infty} c_{nlm} s^n t^{2l} u^m \qquad (3)$$

where s,t,u are the generalized Hyllleraas coordinates: $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$, c_{nlm} are coefficients of the series in powers of s,t,u, and k is a scalar factor (effective charge of the nuclei). $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ can be reduced to the definition in 3D space of the variables s,t,u. After substitution of r_1,r_2,r_{12} with s,t,u, differentiating by k, and long analytical transformations, the following expression for the energy functional in a form suitable for solving numerically is obtained: $E = -E_P^2/(4E_KE_N)$, where E_K/E_N and E_P/E_N are the kinetic and potential energies,

$$E_L = \sum_{r,p,q=0}^{\infty} (c_{rpq}^2 R_{rpq}^L + \sum_{n,l,m} c_{nlm} c_{rpq} S_{nlmrpq}^L),\quad L = P,K,N, \qquad (4)$$

where

$$\sum_{\substack{n,l,m\\rpq}} = \sum_{n=0}^{r-1}\sum_{l=0}^{p-1}\sum_{n=0}^{r-1} + \sum_{n=0}^{r-1}\sum_{\substack{l=0\\m=q}}^{p-1} + \sum_{n=0}^{r-1}\sum_{\substack{m=0\\l=p}}^{q-1} + \sum_{l=0}^{p-1}\sum_{\substack{m=0\\n=r}}^{q-1} + \sum_{\substack{n=0\\l=p\\m=q}}^{r-1} + \sum_{\substack{l=0\\n=r\\m=q}}^{p-1} + \sum_{\substack{m=0\\n=r\\l=p}}^{q-1}$$

$$S_{nlmrpq}^K = 2(mr + nr - 4lp - 2mp + nq - 2lp)\, I_{m+q+1}^{2r+2p,\,n+r} + 2nr\, I_{m+q+1}^{2l+2p+2,\,n+r-2} - (n+m+r+q)\, I_{m+q+1}^{2l+2p,\,n+r+1} + (n+r)\, I_{m+q+1}^{2l+2p+2,\,n+r-1} + 0.5\, I_{m+q+1}^{2l+2p,\,n+r+2} - 0.5\, I_{m+q+1}^{2l+2p+2,\,n+r} + 8lp\, I_{m+q+1}^{2l+2p-2,\,n+r+2} + 2(mq + 2mp + 2lq)\, I_{m+q-1}^{2l+2p,\,n+r+2},\ S_{nlmrpq}^N = I_{m+q+1}^{2l+2p,\,n+r+2} - I_{m+q+1}^{2l+2p+2,\,n+r}$$

$$S_{nlmrpq}^P = 4Z\, I_{m+q+1}^{2l+2p,\,n+r+1} - I_{m+q}^{2l+2p,\,n+r+2} + I_{m+q}^{2l+2p+2,\,n+r}$$

$$R_{rpq}^P = 4Z\, I_{2q+1}^{4p,\,2r+1} - I_{2q}^{4p+2,\,2r+2} + I_{2q}^{4p+2,\,2r},\ R_{rpq}^N = I_{2q+1}^{4p,\,2r+2} - I_{2q+1}^{4p+2,\,2r}$$

$$R_{rpq}^K = (r^2 - 4p^2 + 2rq - 4pq)\, I_{2q+1}^{4p,\,2r} - r^2 I_{2q+1}^{4p+2,\,2r-2} + 0.25\, I_{2q+1}^{4p,\,2r+2} - 0.25\, I_{2q+1}^{4p+2,\,2r} + 4p^2 I_{2q+1}^{4p-2,\,2r+2} + (q^2 + 4pq)\, I_{2q-1}^{4p,\,2r+2} - (q^2 + 2rq)\, I_{2q-1}^{4p+2,\,2r} - (r+q)\, I_{2q+1}^{4p,\,2r+1} + r\, I_{2q+1}^{4p+2,\,2r-1} + q\, I_{2q-1}^{4p+2,\,2r+1}$$

$$I_m^n = \int_0^{\infty} ds \int_0^{s} du \int_0^{u} e^{-s} s^n t^l u^m dt = \frac{(n+l+m+2)!}{(l+1)(l+m+2)}$$

The determination of c_{nlm} is brought to the solution of the system $\partial E/\partial c_{nlm}$=0 (a non-linear algebraic system). Strict examination of the convergence, depending on the number of the coefficients in (3), have not been realized. The energy minimization was performed using elaborated by us of an algorithm and program for numerical solution of non-linear systems. The reason is that the existing standard programs do not allow the solution of the system for an arbitrary number of coefficients.

3. Mass corrections and mass correlations

Taking into account the nuclear motion in two-electron SE [2], we introduce corrections to the unperturbed electron system energy E_0 due to the mass correction and mass electron correlations:

$$\varepsilon_1 = \frac{M}{m_e + M} E_0,\quad \varepsilon_2 = \frac{m_e}{M} \int \nabla_1\Psi^* \nabla_2\Psi\, d\mathbf{r}_1 d\mathbf{r}_2 \qquad (5)$$

where m_e is the electron mass and M is the nuclear mass. ε_1 reduces $|E|$ for all levels, approximately as $(m_e/M)E_0$. For a fixed Z, $|E|$ increases with the growth of M. ε_1 does not depend on the atomic state (degenerate, excited or ionized).

When we depart from the one-particle SE, accounting for the nuclear motion leads to changes in the two-particle SE: (i) In the kinetic energy, we have the reduced mass instead of the electron mass, as happens in the one-particle case. (ii) Mass correlation correction ε_2 appears, corresponding to a change in the energy [2], which accounts for the electron mass polarization. ε_2 is different for various atomic states, as a result of mutual disposition and space correlations between electrons. The treatment of ε_2 is based on the Pauli principle and electrostatic interactions. The Pauli principle does not give a contribution to ε_2 for ground states. The electrostatic repulsion provokes polarization effects in a two-electron

system. These effects require accounting for the dependence of the WF upon r_{12}. For the ground state, both electrons are located with a very small distance between them, and polarization effects are not negligible. ε_2 is a perturbation term, calculated by the unperturbed WF Ψ_0 (the solution of (1) without taking into account the nuclear motion). Following the procedure in sec.2, after changing the variables and substitution of the WF, (3) ε_2 becomes:

$$\varepsilon_2 = \frac{1}{E_N} \sum_{r,p,q=0}^{\infty} \left(c_{rpq}^2 R_{rpq}^Q + \sum_{n,l,m}^{} c_{nlm} c_{rpq} S_{nlmrpq}^Q \right) \qquad (6)$$

where

$$R_{rpq}^Q = \left(r^2 - 4p^2 - 2rq + 4pq\right) I_{2q+1}^{4p,2r} + r^2 I_{2q+1}^{4p+2,2r-2} + 0.25 I_{2q+1}^{4p,2r+2}$$
$$+ 0.25 I_{2q+1}^{4p+2,2r} - 4p^2 I_{2q+1}^{4p-2,2r+2} + \left(q^2 + 4pq\right) I_{2q-1}^{4p,2r+2} +$$
$$\left(q^2 + 2rq\right) I_{2q-1}^{4p+2,2r} + (q-r) I_{2q+1}^{4p,2r+1} - r I_{2q+1}^{4p+2,2r-1} - q I_{2q-1}^{4p+2,2r+1}$$
$$- 2r^2 I_{2q+3}^{4p,2r-2} - 0.5 I_{2q+3}^{4p,2r} + 2r I_{2q+3}^{4p,2r-1} + 2p^2 I_{2q+3}^{4p-2,2r}$$

$$S_{nlmrpq}^Q = 2\left(nr - mr - 4lp + 2mp - nq + 2lq\right) I_{m+q+1}^{2l+2p,n+r}$$
$$+ 2nr I_{m+q+1}^{2l+2p+2,n+r-2} + (m - n + q - r) I_{m+q+1}^{2l+2p,n+r+1} - (n+r) I_{m+q+1}^{2l+2p+2,n+r-1}$$
$$+ 0.5 I_{m+q+1}^{2l+2p,n+r+2} + 0.5 I_{m+q+1}^{2l+2p+2,n+r} - 8lp I_{m+q+1}^{2l+2p-2,n+r+2} + 16lp I_{m+q+3}^{2l+2p-2,n+r}$$
$$- 2(mq + 2mp + 2lq) I_{m+q-1}^{2l+2p,n+r+2} + 2(mq + mr + qn) I_{m+q-1}^{2l+2p+2,n+r}$$
$$- (m+q) I_{m+q-1}^{2l+2p+2,n+r+1} - 4nr I_{m+q+3}^{2l+2p,n+r-2} + 2(n+r) I_{m+q+3}^{2l+2p,n+r-1} - I_{m+q+3}^{2l+2p,n+r}$$

The nuclear masses are calculated using Kravcov's tables [10]. In order to calculate ε_2, we substitute in (6) values of c_{nlm}, obtained after minimisation of E.

4. Algorithm and program

The energy of the ground state of the He isoelectronic series without mass corrections is obtained by solving the system $\partial E/\partial c_{nlm}=0$. For this purpose, an algorithm and program for solving non-linear algebraic system of integro-differential equations is developed. The optimization methods are non-conventional, and in particular, applied nonlinear programming is used. The effective algorithm includes a few known methods and algorithms: a 1D search; a many-D random searching including some elements of the cluster analysis; a gradient search with variable metric. All programs are written in C++ object-oriented language using object-oriented programming.

There are many deep minima without physical meaning in the objective function. Thus, the minimization procedure was complicated in order to fit the correct energy local minimum. First of all, we are searching for a minimum by varying the parameters one by one. Then we switch to the many-D optimization method, varying c_{nlm} in a small range around the best values. An important feature in this calculation is that the energy is quite sensitive to some of the coefficients. In such cases, we perform a more careful calculation, searching for a local minimum around the zero value for the corresponding coefficient. Such a procedure allows the discovery of small scratches that are local minima in a large slope.

The obtained values differ from the experimental and other theoretical data after the 3rd to 5th digit. Investigation of the nuclear motion influence on the electron system energy is correct, because the precision is the same at any Z. More precise results will be obtained, accounting for relativistic effects.

5. Results and discussion

Table 1 presents energies of the ground state of He and He isoelectronic series for the most naturally distributed isotopes with Z=2-26: experimental data E_e [11], data from an empirical-approximate formula E_f which give good values for larger Z [1, 2, 5], the results of Pekeris E_P [7], Thakkar&Koga [9] E_{0TK}, and data calculated by us E. The index "0" indicates the unperturbed energy, excluding the corrections ε_1 and ε_2.

Our calculations do not include relativistic corrections, which would reduce the energy absolute value by about 10^{-6}a.u. The results of Pekeris are closer to the experimental data for Z=2-6, while our results coincide practically with the experimental ones for Z=7-10. Thus, we are allowed to consider that our algorithm can be successfully applied for ground state energy calculations at Z>10. The results for E_0 coincide with E_{0f} better than other theoretical results E_{0TK}.

Table 1. Ground state energy of He and He isoelectronic series.

Z	E_{0f}	E_{0TK}	E_0
2	2.903569712	2.903724377	2.903859033
3	7.279731109	7.279913413	7.280128956
4	13.655671100	13.655566238	13.66150342
5	22.031955620	22.030971580	22.03847579
6	32.408915410	32.406246601	32.41414303
7	44.788167426	44.781445149	44.79071755
8	59.170005660	59.156595122	59.16850584
9	75.555238590	75.531712364	75.55334187
10	93.945924160	93.906806515	93.92942094

Z	E_e	E_f	E_P	E
2	2.9035697	2.903347	2.903592	2.90333013
3	7.2797311	7.279340	7.279673	7.27949855
4	13.6556711	13.65473	13.655177	13.66064732
5	22.0319556	22.029877	22.030421	22.03736246
6	32.4089154	32.404766	32.405474	32.41264980
7	44.7881674	44.779692	44.780491	44.78895435
8	59.1700057	59.154567	59.155450	59.16646921
9	75.5552386	75.529531	75.530425	75.55115486
10	93.9459247	93.904229	93.905257	93.92683874

Z	E_e	E_f	E
11	114.34206237	114.279156	114.3022518
12	136.74585816	136.653821	136.6800979
13	161.15878149	161.028727	161.0528331
14	187.58303730	187.403372	187.4307364
15	216.01825810	215.778266	215.8049685
16	246.47510110	246.152899	246.4657676
17	278.94254160	278.527784	278.8648468
18	313.43160430	312.902886	313.2627015
19	349.94596410	349.277289	349.6615098
20	388.48194610	387.651907	388.05640500
21	429.04690010	428.027026	428.46484350
22	471.64817590	470.401885	470.86667080
23	516.27842370	514.776741	515.26049990
24	562.95601800	561.151372	561.66119940
25	611.67360900	609.526227	610.05739720
26	662.42017200	659.900737	660.45642840

6. Conclusion

The dependencies of $E_0(Z)$ and $E(Z)$ are almost linear at $Z>40$. Considerably non-linear is the increasing of E for $Z<35$. The dependence E-$E_0(Z)$ shows that the contribution of the mass correction/polarization increases with Z, keeping a linear tendency. This indicates an increasing role of the nuclei motion in the electron system energy when Z increases. A similar dependence appears in the isoelectronic H series [2,11]. The existing fluctuations around the approximate line are due to the difference between the numbers of neutrons and protons within the nuclei. For example, this difference for Z=52 is 26. Our calculations at Z=2-30 for nuclides with equal numbers of neutrons and protons, or having a difference of 1 for $Z>30$, shows that the contribution of these effects increases linearly. Anomalies appear at Z=30,33,36,42,52.

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