Multiply Charged Helium Isoelectronic Ions with Charge Z to 118: I. Ground State Energies, Mass Corrections, Mass Polarization

R.L. Pavlov[1,2], J. Maruani[2], L.M. Mihailov[3], Ch.J. Velchev[1], M. Dimitrova-Ivanovich[1], J.K. Stoianov[3], and D. Van Neck[4]

[1] Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

[2] Laboratoire de Chimie Physique, CNRS and UPMC, 11 Rue Pierre et Marie Curie, 75005 Paris, France

[3] Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

[4] University of Gent, Dept. of Subatomic and Radiation Physics, 86 Proeftuinstraat, 9000 Gent, Belgium

Abstract. Multiply charged Helium ions are strongly responsible for the properties and characteristics of high-temperature astrophysical and laboratory plasma, as well as for the processes within plasma.

Our previous works [1–3] present ground state electron energies, mass corrections and mass polarization effects of He isoelectronic ions, with charge from $Z = 2$ to $Z = 54$. Results were obtained by solving the two-electron Schrödinger equation in the explicitly correlated wave functions (ECWF) approach. The numerical procedure brings to a solving of algebraic system of non-linear integro-differential equations of 4th order.

The proposed work presents ground state electron energies, mass corrections and mass polarization effects of He isoelectronic ions with nuclear charge for the main nuclides from $Z = 2$ to $Z = 118$. The same type generalized Hylleraas' ECWF are used. The variational procedure for determination of the coefficients is discrete, leading to an eigenvalue problem. The developed analytical and numerical method allows to obtain numerical results, which are practically coinciding with those presented in [4,5]. Using of the same method, we have the same accuracy for ions with charge $Z > 10$. The dependence of the obtained energies versus Z is investigated, as well as the relative and complex contributions of mass corrections and mass polarization effects in formation of the ground state electron energies.

The approach developed may be regarded as a base for investigation of the relativistic corrections and QED effects at next stage. The accuracy of the obtained results allows directly usage in precise theoretical approaches [6,7] for plasma diagnostics.

1 Introduction

Multiply charged Helium ions and their interaction with photons and atomic particles (electrons, ions, atoms, molecules) are strongly responsible for the properties and characteristics of high-temperature astrophysical and laboratory plasma.

Multiply charged are ions [6] having spectroscopic symbol $z \geq 5$, where $z = Z - N_e + 1$, Z is the nuclear charge, N_e is the number of electrons. Helium multiply

charged ions possess all peculiarities, such as He and Helium low charged ions ($Z < 10$).

While for He and low-charged He ions, despite of the state (ground, excited, degenerated), the first electron always occupies $1s$ level, there exist states for He multiply charged ions, where both electrons can reside higher levels.

In addition to these peculiarities, multiply charged He ions ($Z > 10$) have specific properties, which are not appeared (or are slightly appeared) in low charged ions and neutral atoms. These properties are conditioned by non-compensated by electrons long-range Coulomb field of the nucleus. Ionic electrons in multiply ionized He ions already possess much higher orbital velocity comparing to the case of the neutral He atom, where $V_0 = 2.18 \times 10^6$ m/sek.

As a result, observed effects in low charged He ions become much more common. Mass-polarization and relativistic effects are already not negligible small corrections, and the bounding between spin and orbital electron moments cannot be described only with common LS interaction.

The relativistic corrections increase fast when the nuclear charge is increased. As a result, the probability of the low intensity radiation transitions for He and low charged He ions increases. For example, at $Z > 10$ the spectral line of $2^3P_1 - 1^1S_0$ transition possesses similar intensity as the intensity of the resonance line $2^1P_1 - 1^1S_0$. In addition to the allowed spectral transitions, there are appeared new high intensity lines for He atom (so called forbidden transitions), for example $1s2s\,^3S_1 - 1s^2\,^1S_0$. When the charge is increased, the relative part of the forbidden transitions increases also: the probability for allowed transitions increases as Z^4, and for the forbidden transitions as $Z^8 - Z^{10}$.

As a result of strong Coulomb field, and two electrons moving within it, the spectrum structure becomes H-like when Z increases. The strong Coulomb field determines the possibility for much higher absolute value of the energy of the electronic system compared to the ionization potential, and possibility for the two electrons occupation of highly excited (auto-ionized) states, outside the ionization limit. For these auto-ionized states, when Z increases, the probability for fast radioactive decay is raised. For low charged ions, the main decay channel is the auto-ionization. For $Z = 10 - 20$ the probabilities for radioactive decay and auto-ionizations are equal. For $Z > 30$ the radioactive decay is more probable. For much higher values of Z, the radioactive decay is the only main channel. For radioactive decay may be observed quasi-discrete states of the ions with transition states (one or both) disposed in the continuous spectrum.

The channels for radioactive decay in this case may be: braking radiation – electron transition between states in the continuous spectrum, or the contrary process – braking absorption. For transitions from the continuous to the discrete spectrum, the final state can be excited or ground. For this transition there is a photon emission – radiative recombination (photorecombination). It is possible also the reverce process – photoionisation. A special case of photorecombination is the dielectron photorecombination – electron trapping from an ion and exciting of the ion. The channels for decomposition of excited ion are two: autoionisation with electron emission and

radiative with photon emission and transition of the ion in stable state – dielectron recombination. This process is accompanied by additional dielectron satellite spectral lines.

The important role of the correlation interactions and their contribution to the electron energy in low and multiply charged He ions requires using of approaches, accounting for the correlation between particles. In such approaches wave functions are not represented as anti-symmetrized multiplications of one-electron functions. Hartree-Fock results can be improved by applying configuration interaction, coupled cluster or other schemes to account for electron correlation. But for atoms with few electrons, the best account of correlation is obtained using explicitly correlated wave functions [8–10].

2 Method

2.1 Hylleraas Wave Function

Ingenious explicitly correlated wave function proposed by Hylleraas [11,12] is formulated in terms of elliptical coordinates:

$$s = r_1 + r_2; \quad t = r_2 - r_1; \quad u = r_{12} = |\vec{r_2} - \vec{r_1}|, \tag{1}$$

where $\vec{r_1}$ and $\vec{r_2}$ are the radius-vector of two electrons in the Decarts-coordinate system with the zero point in the nuclear center and r_1 and r_2 are their magnitudes.

The generalized Hylleraas-type 2-electron wave functions we consider have the form [8]

$$|\Psi\rangle = \sum_{STU} C_{STU} |STU\rangle \tag{2}$$

where

$$\langle \vec{r_1}\vec{r_2}|STU\rangle = \frac{1}{\pi\sqrt{2}} \mathrm{e}^{-s/2} s^S t^T u^U. \tag{3}$$

The S, T, U are positive integers, with T even as a consequence of the symmetry requirement of the spatial wave function.

The phase space in these elliptical coordinates is well known. For a normalizable function $F(s, t, u)$ symmetric in t one has

$$\int d^3 r_1 d^3 r_2 \delta(r_1 + r_2 - s)\delta(r_2 - r_1 - t)\delta(r_{12} - u)F(s, t, u) =$$

$$= 2\pi^2 \int_0^{+\infty} ds \int_0^s du \int_0^u dt u(s^2 - t^2)F(s, t, u). \tag{4}$$

The overlap of two Hylleraas wave functions is therefore given by

$$\langle STU|S'T'U'\rangle = \int_0^{+\infty} ds \int_0^s du \int_0^u dt \, u(s^2 - t^2)\mathrm{e}^{-s} s^{S+S'} t^{T+T'} u^{U+U'} \tag{5}$$

With the standard integral

$$I(k, l, m) = \int_0^{+\infty} ds \int_0^s du \int_0^u dt \, \mathrm{e}^{-s} s^k t^l u^m = \frac{(k + l + m + 2)!}{(l + 1)(l + m + 2)}, \quad (6)$$

the overlap matrix becomes

$$\langle STU | S'T'U' \rangle = I(\mathcal{S} + 2, \mathcal{T}, \mathcal{U} + 1) - I(\mathcal{S}, \mathcal{T} + 2, \mathcal{U} + 1)), \quad (7)$$

where $\mathcal{S} = S + S'$, $\mathcal{T} = T + T'$, $\mathcal{U} = U + U'$. To avoid numerical roundoff error it is advisable to calculate this difference analytically,

$$\langle STU | S'T'U' \rangle = (\mathcal{S} + \mathcal{T} + \mathcal{U} + 5)! \frac{2(2\mathcal{T} + \mathcal{U} + 6)}{(\mathcal{T} + 1)(\mathcal{T} + 3)(\mathcal{T} + \mathcal{U} + 3)(\mathcal{T} + \mathcal{U} + 5)}. \tag{8}$$

2.2 Matrix Elements of the Hamiltonian

The non-relativistic Hamiltonian is the sum of the kinetic energy, the Coulomb attraction to the central charge, and the inter-electron repulsion. In atomic units:

$$H = T + V_c + V_e = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z(\frac{1}{r_1} + \frac{1}{r_2}) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (9)$$

The potential terms are easily written in elliptical coordinates. Combined with the phase space element one has

$$u(s^2 - t^2)V_c = (-Z)4su \tag{10}$$
$$u(s^2 - t^2)V_e = s^2 - t^2. \tag{11}$$

The kinetic term requires a bit more work. In general a matrix element can be written as

$$\int d^3 r_1 d^3 r_2 \psi_L(\vec{r}_1, \vec{r}_2)[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2)]\psi_R(\vec{r}_1, \vec{r}_2) =$$
$$= \frac{1}{2}\int d^3 r_1 d^3 r_2 [(\nabla_1 \psi_L).(\nabla_1 \psi_R) + (\nabla_2 \psi_L).(\nabla_2 \psi_R)]. \quad (12)$$

The conversion to s, t, u variables proceeds with the chain rule,

$$\frac{\partial}{\partial(x_\alpha)_i} = \left(\frac{\partial s}{\partial(x_\alpha)_i}\right)\frac{\partial}{\partial s} + \left(\frac{\partial t}{\partial(x_\alpha)_i}\right)\frac{\partial}{\partial t} + \left(\frac{\partial u}{\partial(x_\alpha)_i}\right)\frac{\partial}{\partial u} =$$
$$= \frac{(x_\alpha)_i}{r_\alpha}\left(\frac{\partial}{\partial s} + (-1)^\alpha\frac{\partial}{\partial t}\right) + (-1)^\alpha\frac{(x_2)_i - (x_1)_i}{r_{12}}\frac{\partial}{\partial u}, \quad (13)$$

$\alpha = 1, 2, \quad i = 1, 2, 3.$

Using L, R indices to indicate that the derivative operators act on the left or right wave function, one obtains

$$\nabla_{1L}.\nabla_{1R} + \nabla_{2L}.\nabla_{2R} =$$
$$= (\frac{\partial}{\partial s_L} - \frac{\partial}{\partial t_L})(\frac{\partial}{\partial s_R} - \frac{\partial}{\partial t_R}) + (\frac{\partial}{\partial s_L} + \frac{\partial}{\partial t_L})(\frac{\partial}{\partial s_R} + \frac{\partial}{\partial t_R}) + 2\frac{\partial}{\partial u_L}\frac{\partial}{\partial u_R} +$$
$$+ \frac{r_1^2 - \vec{r}_1.\vec{r}_2}{r_1 r_{12}}\{(\frac{\partial}{\partial s_L} + \frac{\partial}{\partial t_L})\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}(\frac{\partial}{\partial s_R} + \frac{\partial}{\partial t_R})\} +$$
$$+ \frac{r_2^2 - \vec{r}_1.\vec{r}_2}{r_2 r_{12}}\{(\frac{\partial}{\partial s_L} - \frac{\partial}{\partial t_L})\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}(\frac{\partial}{\partial s_R} - \frac{\partial}{\partial t_R})\}. \quad (14)$$

After simplification, using *e.g.*

$$\frac{r_1^2 - \vec{r}_1.\vec{r}_2}{r_1 r_{12}} \pm \frac{r_2^2 - \vec{r}_1.\vec{r}_2}{r_2 r_{12}} = \frac{(r_1 \pm r_2)(2r_1 r_2 \pm [r_{12}^2 - r_1^2 - r_2^2])}{2 r_1 r_2 r_{12}} \quad (15)$$

the operator of kinetic energy can be rewritten as

$$T = T_{ss} + T_{tt} + T_{uu} + T_{su} + T_{tu} \quad (16)$$

where

$$u(s^2 - t^2)T_{ss} = u(s^2 - t^2)\frac{\partial}{\partial s_L}\frac{\partial}{\partial s_R} \quad (17)$$

$$u(s^2 - t^2)T_{tt} = u(s^2 - t^2)\frac{\partial}{\partial t_L}\frac{\partial}{\partial t_R} \quad (18)$$

$$u(s^2 - t^2)T_{uu} = u(s^2 - t^2)\frac{\partial}{\partial u_L}\frac{\partial}{\partial u_R} \quad (19)$$

$$u(s^2 - t^2)T_{su} = s(u^2 - t^2)\{\frac{\partial}{\partial s_L}\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}\frac{\partial}{\partial s_R}\} \quad (20)$$

$$u(s^2 - t^2)T_{tu} = t(s^2 - u^2)\{\frac{\partial}{\partial t_L}\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}\frac{\partial}{\partial t_R}\}, \quad (21)$$

i.e. $T_{\mu\nu} = f(h, \mu, \nu)D_{\mu\nu}$, where $f(h, \mu, \nu)$ is square function of (h, μ, ν), $D_{\mu\nu}$ are derivative operators of first order and $h, \mu, \nu = s, t$ or u.

It is now possible to calculate the matrix elements of the Hamiltonian. Using the notations of the expressions (7), (8) and $\mathcal{V} = \mathcal{T} + \mathcal{U}$ $\mathcal{W} = \mathcal{S} + \mathcal{V}$, one finds the matrix elements of kinetic energy:

$$\langle STU|S'T'U'\rangle = (\mathcal{W}+5)!\frac{2(\mathcal{T}+\mathcal{V}+6)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+3)(\mathcal{V}+5)} \tag{22}$$

$$\langle STU|T_{ss}|S'T'U'\rangle = \{SS'(\mathcal{W}+3)! - \frac{S+S'}{2}(\mathcal{W}+4)! + \frac{1}{4}(\mathcal{W}+5)!\} \times$$
$$\times \frac{2(\mathcal{T}+\mathcal{V}+6)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+3)(\mathcal{V}+5)} \tag{23}$$

$$\langle STU|T_{tt}|S'T'U'\rangle = TT'(\mathcal{W}+3)!\frac{2(\mathcal{T}+\mathcal{V}+2)}{(\mathcal{T}-1)(\mathcal{T}+1)(\mathcal{V}+1)(\mathcal{V}+3)} \tag{24}$$

$$\langle STU|T_{uu}|S'T'U'\rangle = UU'(\mathcal{W}+3)!\frac{2(\mathcal{T}+\mathcal{V}+4)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+1)(\mathcal{V}+3)} \tag{25}$$

$$\langle STU|T_{su}|S'T'U'\rangle = \{(SU'+US')(\mathcal{W}+3)! - \frac{U+U'}{2}(\mathcal{W}+4)!\} \times$$
$$\times \frac{2}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+3)} \tag{26}$$

$$\langle STU|T_{tu}|S'T'U'\rangle = (TU'+UT')(\mathcal{W}+3)!\frac{2}{(\mathcal{T}+1)(\mathcal{V}+1)(\mathcal{V}+3)} \tag{27}$$

$$\langle STU|V_c|S'T'U'\rangle = (-Z)(\mathcal{W}+4)!\frac{4}{(\mathcal{T}+1)(\mathcal{V}+3)} \tag{28}$$

$$\langle STU|V_e|S'T'U'\rangle = (\mathcal{W}+4)!\frac{2(\mathcal{T}+\mathcal{V}+5)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+2)(\mathcal{V}+4)}. \tag{29}$$

2.3 Scaling

If the Hylleraas wave function in Eq. (3) is subjected to a coordinate scaling transformation

$$\langle \vec{r}_1\vec{r}_2|\Psi_\alpha\rangle = \sum_{STU} C_{STU}\, \mathrm{e}^{-\alpha s/2}(\alpha s)^S(\alpha t)^T(\alpha u)^U \tag{30}$$

then the overlap, kinetic, and potential matrix elements have definite scaling,

$$\langle \Psi_\alpha|\Psi_\alpha\rangle = \langle \Psi|\Psi\rangle/\alpha^6 \tag{31}$$

$$\langle \Psi_\alpha|T|\Psi_\alpha\rangle = \langle \Psi|T|\Psi\rangle/\alpha^4 \tag{32}$$

$$\langle \Psi_\alpha|V|\Psi_\alpha\rangle = \langle \Psi|V|\Psi\rangle/\alpha^5. \tag{33}$$

The expectation value of the energy then becomes

$$\frac{\langle \Psi_\alpha|H|\Psi_\alpha\rangle}{\langle \Psi_\alpha|\Psi_\alpha\rangle} = \frac{\alpha^2\langle \Psi|T|\Psi\rangle + \alpha\langle \Psi|V|\Psi\rangle}{\langle \Psi|\Psi\rangle}. \tag{34}$$

2.4 Variational Procedure

The energy will be minimized by varying the Hylleraas wave function to both the expansion coefficients C_{STU} and the scaling factor α.

One first determines, for fixed α, the best linear combination. Variation with respect to the expansion coefficients in Eq. (34) leads to the generalized eigenvalue problem,

$$(\alpha^2[T] + \alpha[V])C_\alpha = E_\alpha[M]C_\alpha. \tag{35}$$

where the square symmetric matrices $[T]$, $[V]$, $[M]$ are the kinetic, potential, and overlap matrices as derived above in the basis of the $|STU\rangle$ states, and C_α is the column matrix containing the expansion coefficients. The lowest eigenvalue E_α^0 defines a function of one variable, the minimum of which can be obtained using standard techniques. This minimum is finally the best variational approximation for the ground-state energy.

In practice one calculates the matrices $[T]$, $[V]$ and $[M]$ only once. We use Lövdin's orthogonalization [13]. Solving the generalized eigenvalue problem in Eq. (35)proceeds by first diagonalizing the overlap matrix $[M]$, with resulting eigenvalues d_i and eigenvectors Z_i. In a next step one constructs the matrices $[T']_{ij} = (Z_i^T[T]Z_j)/\sqrt{d_id_j}$ and $[V']_{ij} = (Z_i^T[V]Z_j)/\sqrt{d_id_j}$. This has the advantage that it is possible to introduce a threshold for the eigenvalues of $[M]$. A large basis of polynomials may be almost linearly dependent in the limited volume around the atom. This results in very small eigenvalues d_i of $[M]$, and numerically instable results. Such instabilities can be simply avoided by omitting the corresponding eigenvectors Z_i in the construction of $[T']$ and $[V']$. Finally one has to solve, for various values of α, the lowest eigenvalue of the eigenvalue problem

$$(\alpha^2[T'] + \alpha[V'])C'_\alpha = E_\alpha C'_\alpha. \tag{36}$$

This determines the function E_α^0 of which the minimum has to be determined.

3 Mass Corrections

In a system described by a two-electron Schrödinger equation, taking into account nuclear motion entails two mass corrections [9,10]:

(i) As in the one-electron case, the mass correction

$$\varepsilon_1 = -\frac{\varepsilon}{1+\varepsilon}E_0 \approx -\varepsilon E_0, \tag{37}$$

where $\varepsilon = m_e/M$ (m_e is the electron mass and M is the nucleus mass). The accounting of mass correction leads to increasing of the atomic energy approximately by $\varepsilon|E_0| = (m_e/M)|E_0|$, independently of the atomic state.

(ii) An additional perturbation correction, 'mass polarization'

$$\varepsilon_2 = \varepsilon \int \nabla_1 \Psi^*(\vec{r}_1, \vec{r}_2)\nabla_2\Psi(\vec{r}_1, \vec{r}_2)d\vec{r}_1 d\vec{r}_2, \tag{38}$$

is different for various atomic states, as it depends on the mutual disposition and space correlation of the electrons.

Within ECWF approach, the mass corrections ε_1 and ε_2 are positive. For example, the order of ε_1 for Helium is 1.22×10^{-4} [11], and the order of ε_2 is 2.18×10^{-5} [4]. There exist experimental data for some values of the nucleus charge Z. Regarding the ground state energy of He and isoelectronic He ions, variational solving of two-particle Schrödinger equation using trial ECWF, gives energy values, which are lower than the experimentally observed ones. In order to be able to compare these values to the experimental data, obligatory condition is to add mass corrections ε_1 and ε_2 to ground state energy. Exact coincidence with the experiment is expected after addition of relativistic and QED corrections as well.

For the ground state, the electrons are located at relatively small distance from each other, and this effect may be significant. The term ε_2 can be derived by perturbation from the unperturbed ψ_0. Following the procedure described in Section 2, we obtain:

$$(\nabla_1 \psi_L) \cdot (\nabla_2 \psi_R) = \frac{1}{2} \Big\{ \frac{(r_1^2 + r_2^2 - r_{12}^2)}{r_1 r_2} \frac{\partial \psi_L}{\partial r_1} \frac{\partial \psi_R}{\partial r_2} + \frac{(r_2^2 - r_1^2 - r_{12}^2)}{r_1 r_{12}} \frac{\partial \psi_L}{\partial r_1} \frac{\partial \psi_R}{\partial r_{12}} + $$
$$+ \frac{(r_1^2 - r_2^2 - r_{12}^2)}{r_2 r_{12}} \frac{\partial \psi_L}{\partial r_{12}} \frac{\partial \psi_R}{\partial r_2} \Big\} - \frac{\partial \psi_L}{\partial r_{12}} \frac{\partial \psi_R}{\partial r_{12}} \tag{39}$$

$$\mathcal{E} = \int (\nabla_1 \psi_L) \cdot (\nabla_2 \psi_R) d\mathbf{r}_1 d\mathbf{r}_2 = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \psi_L \times$$
$$\times (\mathcal{E}_{ss} + \mathcal{E}_{tt} + \mathcal{E}_{uu} + \mathcal{E}_{st} + \mathcal{E}_{su} + \mathcal{E}_{su}^A + \mathcal{E}_{tu} + \mathcal{E}_{tu}^A) \psi_R u(s_2 - t_2), \tag{40}$$

where

$$u(s^2 - t^2)\mathcal{E}_{ss} = u(s^2 + t^2 - 2u^2)\frac{\partial}{\partial s_L}\frac{\partial}{\partial s_R}, \tag{41}$$

$$u(s^2 - t^2)\mathcal{E}_{tt} = -u(s^2 + t^2 - 2u^2)\frac{\partial}{\partial t_L}\frac{\partial}{\partial t_R}, \tag{42}$$

$$u(s^2 - t^2)\mathcal{E}_{uu} = -u(s^2 - t^2)\frac{\partial}{\partial u_L}\frac{\partial}{\partial u_R}, \tag{43}$$

$$u(s^2 - t^2)\mathcal{E}_{st} = u(s^2 + t^2 - 2u^2)\Big\{\frac{\partial}{\partial s_L}\frac{\partial}{\partial t_R} - \frac{\partial}{\partial t_L}\frac{\partial}{\partial s_R}\Big\}, \tag{44}$$

$$u(s^2 - t^2)\mathcal{E}_{su} = t(s^2 - u^2)\Big\{\frac{\partial}{\partial s_L}\frac{\partial}{\partial u_R} - \frac{\partial}{\partial u_L}\frac{\partial}{\partial s_R}\Big\}, \tag{45}$$

$$u(s^2 - t^2)\mathcal{E}_{su}^A = s(t^2 - u^2)\Big\{\frac{\partial}{\partial s_L}\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}\frac{\partial}{\partial s_R}\Big\}, \tag{46}$$

$$u(s^2 - t^2)\mathcal{E}_{tu} = -s(t^2 - u^2)\Big\{\frac{\partial}{\partial t_L}\frac{\partial}{\partial u_R} - \frac{\partial}{\partial u_L}\frac{\partial}{\partial t_R}\Big\}, \tag{47}$$

$$u(s^2 - t^2)\mathcal{E}_{tu}^A = -t(s^2 - u^2)\Big\{\frac{\partial}{\partial t_L}\frac{\partial}{\partial u_R} + \frac{\partial}{\partial u_L}\frac{\partial}{\partial t_R}\Big\}. \tag{48}$$

3.1 Matrix Elements

For the matrix elements of mass polarization ε_2 by analogical of the kinetic energy, we obtain:

$$\langle STU|\mathcal{E}_{ss}|S'T'U'\rangle = \frac{(\mathcal{W}+3)!}{2}\frac{[(S-S')^2-(\mathcal{V}+4)^2-(\mathcal{W}+4)]\mathcal{U}}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+3)(\mathcal{V}+5)}, \quad (49)$$

$$\langle STU|\mathcal{E}_{tt}|S'T'U'\rangle = 2(\mathcal{W}+3)!\frac{TT'\mathcal{U}}{(\mathcal{T}-1)(\mathcal{T}+1)(\mathcal{V}+1)(\mathcal{V}+3)}, \quad (50)$$

$$\langle STU|\mathcal{E}_{uu}|S'T'U'\rangle = -(\mathcal{W}+3)!\frac{2UU'(\mathcal{T}+\mathcal{V}+4)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+1)(\mathcal{V}+3)}, \quad (51)$$

$$\langle STU|\mathcal{E}_{st}|S'T'U'\rangle = 0, \quad (52)$$

$$\langle STU|\mathcal{E}_{su}|S'T'U'\rangle = 0, \quad (53)$$

$$\langle STU|\mathcal{E}_{su}^A|S'T'U'\rangle = (\mathcal{W}+3)!\frac{(S-S')(U-U')+\mathcal{U}(\mathcal{V}+4)}{(\mathcal{T}+1)(\mathcal{T}+3)(\mathcal{V}+3)}, \quad (54)$$

$$\langle STU|\mathcal{E}_{tu}|S'T'U'\rangle = 0, \quad (55)$$

$$\langle STU|\mathcal{E}_{tu}^A|S'T'U'\rangle = -2(\mathcal{W}+3)!\frac{TU'+T'U}{(\mathcal{T}+1)(\mathcal{V}+1)(\mathcal{V}+3)}, \quad (56)$$

where by analogical of the equations (16–21),

$$\mathcal{E}_{\mu\nu} = f_\mathcal{E}(h,\mu\nu)D_{\mu\nu}^\mathcal{E},$$

$f_\mathcal{E}(h,\mu\nu)$ are again square functions and $D_{\mu\nu}^\mathcal{E}$ are derivative operators; index A notes anti-commutator.

In order to obtain mass polarization ε_2 of Eq. (38), after scaling:

$$\langle \Psi_\alpha|\mathcal{E}|\Psi_\alpha\rangle = \langle \Psi|\mathcal{E}|\Psi\rangle/\alpha^4, \quad (57)$$

where $\langle \Psi|\mathcal{E}|\Psi\rangle$ is sum of the matrix elements Eqs. (49–56) we substitute in Eq. (57) the values of the expansion coefficients C_{STU} and scale parameter α determined by variational equation (36).

The nuclear masses used in our computations were derived from recent tables of mass exess Δ [14], using the known relation:

$$M_{NUC} = \Delta + A - Zm_e + b_e$$

The main isotope is chosen for each element, using the data in [14].

4 Results

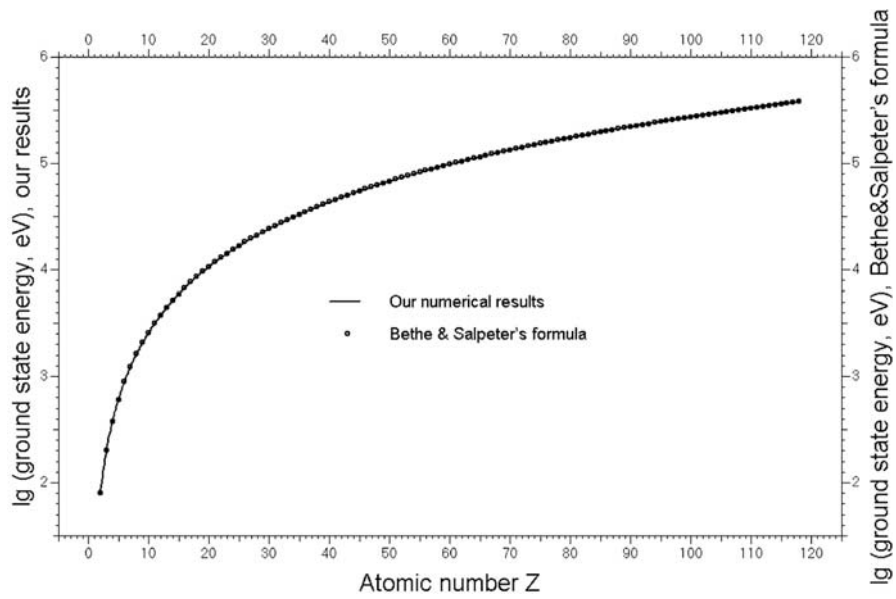The obtained results are presented in following tables and pictures:

Figure 1. Correlated ground-state energies E_0 [eV] of Helium isoelectronic ions with $Z = 2 \div 118$, omitting mass corrections: $E_0(BS)$ – computed using Bethe and Salpeter's semi-empirical formula [8] and our results.
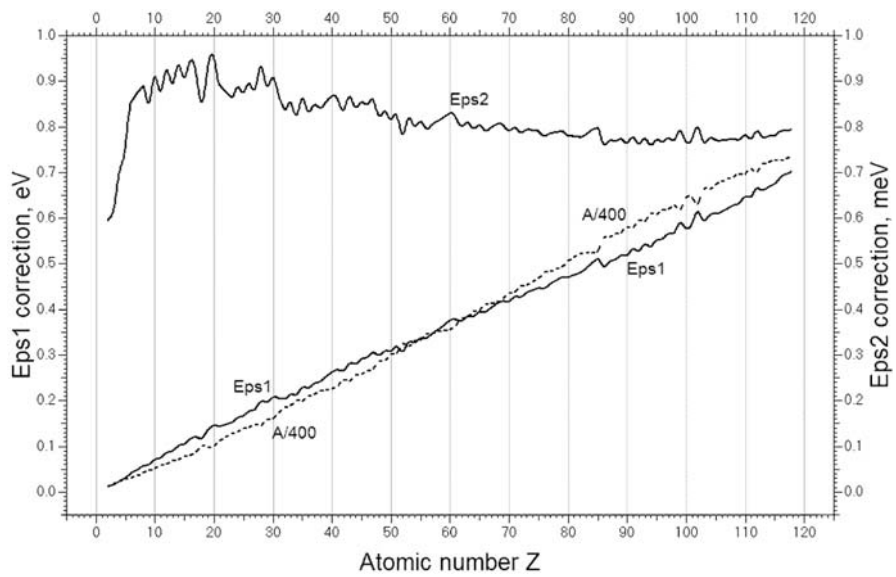

Figure 2. Various corrections to the ground-state energy of He isoelectronic ions, with $Z = 2 \div 118$: respective variations of our overall mass corrections and isotope number A.
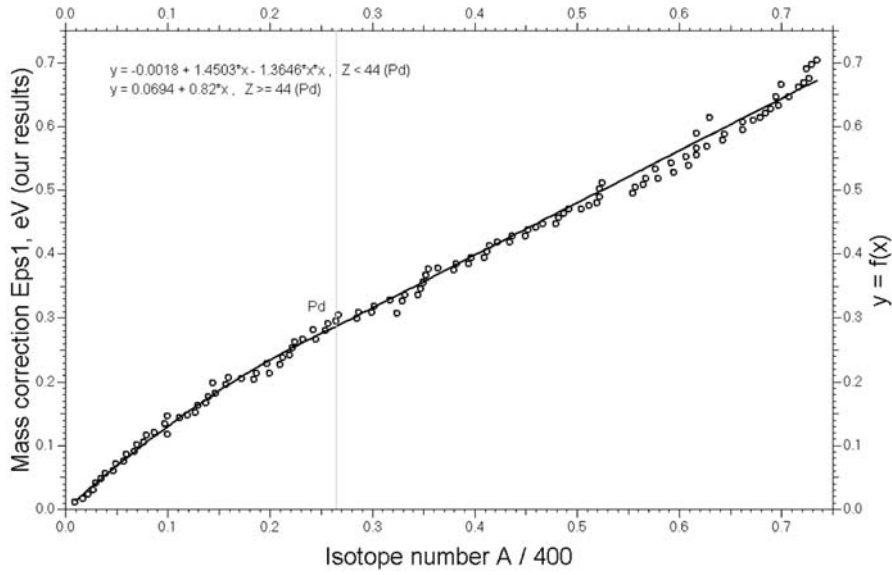
Figure 3. Our mass correction ε_1 [eV] dependence from the isotope number A for Helium isoelectronic ions with $Z = 2 \div 118$ and corresponding quadratic fit.

Table 1. Correlated ground-state (nonrelativistic) energies $E_0[au]$ for Helium isoelectronic ions, omitting mass corrections with $Z = 2 \div 10$: E_0 (Pk) Pekeris' results [4], E_0 (TK) yielded by Thakkar and Koga's [5], E_0 (PM – Pavlov, Maruani, Mihailov $at\ al.$) – our computed results (the sign '−' is omitted).

$^Z El^+$	E_0 (Pk)	E_0 (TK)	E_0 (PM)
$^2 He^*$	2.903 724 228 18289	2.903 724 377 03389	2.903 724 372 00350
$^3 Li^{1+*}$	7.279 913 245 93142	7.279 913 412 66914	7.279 913 405 98892
$^4 Be^{2+*}$	13.655 566 064 04600	13.655 566 238 42343	13.655 566 230 53670
$^5 B^{3+*}$	22.030 971 401 91010	22.030 971 580 24262	22.030 971 571 41920
$^6 C^{4+*}$	32.406 246 420 82860	32.406 246 601 89837	32.406 246 592 31340
$^7 N^{5+*}$	44.781 444 965 94940	44.781 445 148 77254	44.781 445 138 54710
$^8 O^{6+*}$	59.156 594 939 48940	59.156 595 122 75776	59.156 595 111 98040
$^9 F^{7+*}$	75.531 712 179 79520	75.531 712 363 95932	75.531 712 352 69580
$^{10} Ne^{8+*}$	93.906 806 328 80690	93.906 806 515 03737	93.906 806 503 34240

Table 2. Mass corrections in a.u.: mass correction ε_1 and 'mass polarization' correction ε_2 for Helium isoelectronic ions with $Z = 2 \div 10$ (Pk – Pekeris' results; PM – our results).

$^Z El^+$	$\varepsilon_1(\text{PM}) \times 10^{-4}$	$\varepsilon_2(\text{PM}) \times 10^{-5}$	$\varepsilon_2(\text{Pk}) \times 10^{-5}$
$^2He^*$	3.980 268 125 186	2.180 438 608 687	2.180 243 296 004
$^3Li^{1+*}$	5.693 040 027 525	2.259 849 702 947	2.260 004 093 439
$^4Be^{2+*}$	8.313 789 194 329	2.560 214 458 570	2.560 412 988 624
$^5B^{3+*}$	10.979 947 476 630	2.754 847 205 670	2.755 165 781 146
$^6C^{4+*}$	14.817 902 631 770	3.133 725 061 288	3.134 318 923 867
$^7N^{5+*}$	17.547 562 500 285	3.205 789 953 211	3.206 359 899 811
$^8O^{6+*}$	20.293 898 928 876	3.262 542 671 668	3.263 644 518 290
$^9F^{7+*}$	21.814 864 741 131	3.130 849 920 246	3.131 334 938 233
$^{10}Ne^{8+*}$	25.773 803 005 157	3.340 413 124 123	3.341 560 695 814

Acknowledgements

References

1. R. L. Pavlov, J. Maruani, L. M. Mihailov, Ch. J. Velchev and M. Dimitrova-Ivanovich, In Progress in Theoretical Chemistry and Physics, Ed. St. Wilson, Springer, The Nederlands 269–285, 2008 (in print).

2. L. M. Mihailov, R. L. Pavlov, Ch. Velchev, L. I Pavlov, M. Dimitrova-Ivanovich and J. Maruani, Journal of Optoelectronics and Advanced Materials **9**, 390–393 (2007).

3. R. L. Pavlov, J. Maruani, L. M. Mihailov, L. I. Pavlov, Ch. J. Velchev, M. Dimitrova-Ivanovich and V. O. Nesterenko, Proceedings of the 25th International Workshop on Nuclear Theory, ed. S. Dimitrova, Rila-Bulgaria, June 26 – July 1 (2006) pp. 335–347.

4. C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); in ibid. **115**, 1216 (1959); in ibid. **126**, 1470 (1962).

5. A. J. Thakkar, T. Koga, Phys. Rev. A **50**, 854 (1994).

6. L.P. Presnyakov, V.P. Shevelko, R.K. Yanev, *Elementary processes with multiply charged ions*, Energoatomizdat Moskva, 1986 (in Russian).

7. P.G. Burke, W.B. Eissner, D.G. Hummer and I.C. Percival, *Atoms in Astrophysics*, Plenum Press: New York and London, 1983.

8. J. Rychlewski (Ed.), *Explicitly Correlated Wavefunctions in Chemistry and Physics*, Progress in Theoretical Chemistry and Physics **13**, Kluwer, Dordrecht (2003).

9. H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Springer, Berlin (1967).

10. von P. Gombas, *Theorie und Losungsmethoden des Mehrteilchenproblems der Wellenmechanik*, Basel (1950).

11. E. A. Hylleraas, Z. Phys. **48**, 469 (1928); in ibid. **54**, 347 (1929).

12. E. A. Hylleraas, Z. Phys. in ibid. **60**, 624 (1930); in ibid. **63**, 291 (1930); in ibid. **65**, 209 (1930).

13. P. O. Lövdin, J. Chem. Phys. **18**, 365 (1950).

14. J. K. Tuli, *Nuclear Wallet Cards*, National Nuclear Data Center (Upton, NY, 2005), pp. 1–77.