Effects induced by nuclear deformations and electron correlations on the ground-state energy of low and multiply charged helium like ions in high-temperature plasmas

R Pavlov$^1$, L Mihailov$^2$, Ch Velchev$^1$, M Dimitrova-Ivanovich$^1$, Zh Stoyanov$^2$, N Chamel$^3$ and J Maruani$^4$

$^1$Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria, E-mail: ropavlov@inrne.acad.bg

$^2$Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria, E-mail: lubomir.mihailov@gmail.com

$^3$Université Libre de Bruxelles, Institut d’Astronomie et d’Astrophysique, Boulevard du Triomphe, CP226, B-1050 Brussels, Belgium, E-mail: nchamel@ulb.ac.be

$^4$Laboratoire de Chimie Physique, CNRS and UPMC, 11 Rue Pierre et Marie Curie, 75005 Paris, France, E-mail: maruani@ccr.jussieu.fr

Abstract. The present work deals with the effects induced by nuclear deformations and electron correlations on the electron ground-state energies of low and multiply charged helium like ions. Numerical calculations of the ground state energies including mass corrections and polarization of the electronic system have been performed for such heliumoid ions with nuclear charge number from $Z=2$ to $Z=118$. A perturbation method has been developed based on a variational principle using explicitly correlated two-electron wave functions. The mass-polarization term accounting for correlation effects has been included for the first time in the minimization procedure. These effects have been found to be particularly pronounced for ions corresponding to nuclear magic numbers. The present method provides a general framework for high-precision calculations of plasma diagnostics.

1. Introduction

The properties and characteristics of high-temperature astrophysical and laboratory plasmas are determined by the interaction of low and multiply charged helium like ions (i.e. heliumoid ions) with electrons, ions, atoms, molecules and photons [1]. Heliumoid ions exhibit specific properties due to the unscreened long-range Coulomb field of their nucleus. High precision calculations of the electron ground-state energies of heliumoid ions requires to take into account the effects associated with nuclear deformations and electron correlations. The nuclear size effects increase steadily with increasing atomic number. The nuclear motion gives an even more significant correction to the electron energy [2,3]. This leads to two specific contributions: finite-mass effect (mass correction), electron-electron ($e-e$) and electron-nucleus ($e-n$) correlations (mass polarization). While the latter increases with increasing nuclear charge number $Z$, the former varies very little [4]. Relativity and quantum electrodynamics (QED) yield additional corrections which we do not include here.

A rich variety of resonant processes can be observed in high-temperature plasmas, due to multiply charged helium like ions [1,5]. In particular an isotope shift of the resonance lines has been recently observed [6,7] in radiative and dielectronic recombination processes. These shifts arise from changes in the charge distribution and in the nuclear mass with the neutron number $N$ [8]. This isotope shift thus indirectly reflects the variation of the mass excess with $N$.

The present work explores the contribution of both mass excess in the mass correction and mass polarization on the electron ground-state energies of heliumoid ions for the main nuclides with nuclear charge $Z=2\div118$. Effects associated with nuclear deformations are thus taken into account for the first time. A perturbation method for solving the 2-electron Schrödinger Equation (SE) has been developed.
based on a variational principle using Explicitly Correlated Wave Functions (ECWF) of a generalized Hylleraas type [9]. It is shown that the variational procedure leads to a generalized eigenvalue problem. This method has been applied to compute the electron ground-state energies taking into account both mass corrections and mass-polarization effects. This approach provides a general framework for including higher-order effects like for instance relativistic and QED corrections. This method is therefore very well-suited for high-precision calculations of plasma diagnostics.

2. Method

2.1. Hylleraas wave functions and Hamiltonian
Let us consider two electrons with position vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) in the Decart's coordinate system with the zero point in the nuclear centre. Introducing elliptical coordinates, \( s = r_1 + r_2 \), \( t = r_1 - r_2 \), \( u = r_{12} = |r_1 - r_2| \), the Hylleraas-type 2-electron wave functions that we consider have the form

\[
|\psi\rangle = \sum_{STU} C_{STU} |STU\rangle = \sum_{STU} C_{STU} \frac{1}{\pi^{3/2}} e^{-s^2/2} s^S t^T u^U
\]

where \( S, T, U \) are positive integers, with \( T \) even as a consequence of the symmetry requirement of the spatial wave function. The overlap of two Hylleraas wave functions is therefore given by

\[
\langle STU | S'T'U' \rangle = \frac{2(2S + U + 6)(2S + T + U + 5)!}{(T + 1)(T + 3)(T + U + 3)(T + U + 5)}, \quad S = S + S', \quad T = T + T', \quad U = U + U'.
\]

These quantities are evaluated analytically in order to avoid numerical roundoff errors.

The non-relativistic Hamiltonian is the sum of the kinetic energy \( T \), the Coulomb attractive potential \( V_{en} \) due to the central charge, and the electron-electron repulsive potential \( V_{ee} \) [10].

2.2. Scaling
If the Hylleraas wave function (1) is subject to a coordinate scaling transformation

\[
\langle \tilde{r}_1, \tilde{r}_2 | \psi_0 \rangle = \sum_{STU} C_{STU} \alpha^{-S/2} (\alpha S)^S (\alpha T)^T (\alpha U)^U
\]

\( \alpha \) being a scaling factor, then the overlap, kinetic, and potential matrix elements transform as

\[
\langle \psi_a | \psi_a \rangle = \langle \Psi | \Psi \rangle / \alpha^6, \quad \langle \psi_a | T | \psi_a \rangle = \langle \Psi | T' | \Psi \rangle / \alpha^6, \quad \langle \psi_a | V | \psi_a \rangle = \langle \Psi | V' | \Psi \rangle / \alpha^5,
\]

with \( V = V_{en} + V_{ee} \). The expectation value of the energy thus scales as

\[
\langle \psi_a | H | \psi_a \rangle = \alpha^2 \langle \Psi | T' | \Psi \rangle + \alpha \langle \Psi | V' | \Psi \rangle \langle \Psi | \Psi \rangle
\]

3. Mass corrections
The variational calculation of the ground state energy using ECWF as trial 2-electron wave functions yields a lower bound to the exact energy. To obtain a better estimate, it is necessary to include mass correction and mass polarization. The first-order correction is given by [2,4]:

\[
\varepsilon_1 = -\frac{\varepsilon}{1 + \varepsilon} E_0 \approx -\varepsilon E_0
\]
where $E_0$ is the electron ground-state energy and $\varepsilon = m_e/M$ ($m_e$ being the electron mass and $M$ the nuclear mass). This correction is independent of the atomic state. The second-order perturbation correction given by

$$\varepsilon_2 = \epsilon \int \nabla \Psi^* (\mathbf{r}_1, \mathbf{r}_2) \nabla \cdot \Psi (\mathbf{r}_1, \mathbf{r}_2) d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 = \langle \Psi | \varepsilon | \Psi \rangle,$$  

(7)

depends on the atomic state as it involves the two-electron wave function. The matrix elements of $\varepsilon_2$ can be obtained in an analogous manner as those of the kinetic energy operator and can be found in [10]. After a scaling transformation, the mass polarization (7) becomes

$$\langle \Psi_a | \varepsilon | \Psi_a \rangle = \langle \Psi | \varepsilon | \Psi \rangle / \alpha^4.$$  

(8)

4. Variational method

The energy is minimized by varying the Hylleraas wave function with respect to both the expansion coefficients $C_{STU}$ and the scaling factor $\alpha$. Variation with respect to the expansion coefficients leads to the generalized eigenvalue problem,

$$(\alpha^2 [T] + \alpha [V]) C_a = E_\alpha [O] C_a$$  

(9)

where $T$, $V$, $O$ are the kinetic, potential, and overlap (symmetric) matrices respectively and $C_a$ is the column vector containing the expansion coefficients. The lowest eigenvalue $E_{\alpha}^0$ obtained for a fixed value of $\alpha$ defines a function of one variable. Its minimum which can be found using standard techniques yields the best estimate of the ground-state energy.

In practice the matrices $T$, $V$ and $O$ are calculated only once. Solving the eigenvalue problem in (9) proceeds by first diagonalizing the overlap matrix $O$, with resulting eigenvalues $d_i$ and eigenvectors $Z_i$. We use Löwdin's orthogonalization. If the number of terms in the expansion (1) is too large, the set of polynomials could be overcomplete. As a consequence the overlap matrix may have very small eigenvalues which could lead to numerical instabilities. Such instabilities can be avoided by constructing the matrices $T'_{ij} = Z_i^T \cdot T \cdot Z_j \sqrt{(d_i \cdot d_j)}$ and $V'_{ij} = Z_i^T \cdot V \cdot Z_j \sqrt{(d_i \cdot d_j)}$ in which the small eigenvalues and their corresponding eigenvectors are omitted. Finally one has to solve the eigenvalue problem

$$(\alpha^2 [T'] + \alpha [V']) C'_a = E_\alpha C'_a$$  

(10)

for various values of $\alpha$ in order to find the lowest energy $E_{\alpha}^0$. After substitution into (8) the values of the expansion coefficients $C_{STU}$ and scale parameter $\alpha$, corresponding to $E_{\alpha}^0$, we obtain mass polarization $\varepsilon_2$ (7). In order to include $\varepsilon_2$ in the variational procedure, the operator of mass-polarization $\varepsilon$ is added to the Hamiltonian. Then the expectation value of the energy becomes

$$\frac{\langle \Psi_a | H | \Psi_a \rangle}{\langle \Psi_a | \Psi_a \rangle} = \alpha^2 \langle \Psi | T | \Psi \rangle + \alpha \langle \Psi | V | \Psi \rangle + \alpha^2 \langle \Psi | \varepsilon | \Psi \rangle.$$  

(11)

The variational equations (9) and (10) correspondingly are replaced by

$$(\alpha^2 [T + \varepsilon] + \alpha [V]) C_a = E_\alpha [O] C_a \quad \text{and} \quad (\alpha^2 [T' + \varepsilon'] + \alpha [V']) C'_a = E_\alpha C'_a$$  

(12)
The nuclear masses $M$ in (6, 7) are calculated using the well-known relation $M = \Delta + A - Z m_e + b_e$ [11], where $\Delta$ is the mass excess, $A$ is the nuclear mass number and $b_e$ is the mass equivalent of the binding energy which is neglected here. Values of $\Delta$ are taken from recent mass excess tables [12].

5. Results and discussion
The electron ground-state energies for the lightest heliumoid ions are indicated in Table 1. For comparison we have also shown the results obtained from calculations using different methods.

| Z  | A  | $E_0$ [14] | $E_0$ [2]* | $E_0$ [13]* | $E_0$ [14] | $E_0$ [16]* | $E_0$ [15] | $E_0$ [16]* |
|----|----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 2  | 4  | 2.9037283 | 2.9037244 | 2.9037242 | 2.9037244 | 2.8616800 | -0.0000002 | 0.0420442 |
| 3  | 7  | 7.2799088 | 7.2799088 | 7.2799132 | 7.2799134 | 7.2364152 | -0.0000002 | 0.0434980 |
| 4  | 9  | 13.655565 | 13.655565 | 13.655566 | 13.655566 | 13.611299 | -0.0000002 | 0.0442666 |
| 5  | 11 | 22.030973 | 22.030972 | 22.030972 | 22.030972 | 21.986234 | -0.0000006 | 0.0457365 |
| 6  | 12 | 32.406248 | 32.406246 | 32.406246 | 32.406247 | 32.361193 | -0.0000006 | 0.0450532 |
| 7  | 14 | 44.781447 | 44.781445 | 44.781445 | 44.781445 | 44.736164 | -0.0000001 | 0.0452811 |
| 8  | 16 | 59.156596 | 59.156595 | 59.156595 | 59.156595 | 59.111114 | -0.0000001 | 0.0454523 |
| 9  | 19 | 75.531713 | 75.531712 | 75.531712 | 75.531712 | 75.486126 | -0.0000003 | 0.0455856 |
| 10 | 20 | 93.906806 | 93.906807 | 93.906807 | 93.906807 | 93.861113 | -0.0000005 | 0.0456925 |

Table 1. Absolute value of electron ground-state energies $E_0$ in atomic units (on the left panel) for heliumoid ions with $Z=2$ to $Z=10$ with corrections: from Bethe and Salpeter’s semi-empirical formula [2], from Thakkar and Koga [13], from Pekeris [14], from our calculations, from Karwowski [15] and from Hartree-Fock (HF) calculations using Froese-Fischer’s code [16]. Differences between $E_0$ from Pekeris and from other calculations are shown on the right panel. Results marked with an asterisk do not include the correlation term $\epsilon_2$.

In particular, the right panel of Table 1 shows that our results are in excellent agreement with those from Pekeris[14] which are currently regarded as being the most precise. However unlike Pekeris calculations, our calculations have been carried out not only for $Z<10$ but also for heavier ions. Complete tables for the most abundant or stable isotopes can be found in [12].

![Figure 1](image-url)

Figure 1. Comparison between different non-relativistic calculations of the electron ground state energy (in keV) of heliumoid ions for $Z=2$ to $Z=118$. 
Figure 1 shows the electron ground-state energies as obtained from our calculations, from non-relativistic calculations of Karwowski [15] and from HF calculations using Froese–Fischer’s code [16]. The curves are barely distinguishable because of the small differences between the different calculations. Figure 2 compares our results with those obtained from relativistic calculations. The Karwowski’s results [17] are obtained in the scheme of relativistic Hylleraas-CI method using 2-component wave functions. HF results are relativistic, realized using the one-component scheme (Breit-Pauli) which is correct at the L-S binding level, while the two-component scheme is correct at the j-j coupling level. Figure 3 shows the effects on $\varepsilon_2$ and $E_0$ of including or not $\varepsilon_2$ in the minimization. Green lines indicate magic proton numbers. For all magic numbers up to $Z=54$, there is a peak of e-e and e-n correlations, caused by $\varepsilon_2$ (50 is an unstable magic number as observed experimentally [18]). At higher $Z$, the peaks are shifted by 2 from the magic numbers 80 and 100. Exact coincidences are expected to be found when relativistic effects are included. At $Z>114$ fluctuations in the energy disappear, which corresponds to the nuclear area of stability [18]. The peak values arise from the sphericity of magic nuclei.

![Figure 2. Comparison between our calculations and different relativistic calculations of the electron ground-state energy (in keV) of heliumoid ions for $Z=2$ to $Z=118.$](image)

In conclusion, we have studied the effects of nuclear deformations and electron correlations on the electron ground-state energy of heliumoid ions for $Z=2$ to $Z=118$ using a variational-perturbation method with explicitly correlated trial wave functions of a generalized Hylleraas type. For the first time, we have included mass polarization in the minimization procedure which is found to decrease the ground-state energy. For $Z<10$, our results are in excellent agreement with Pekeris’s results [14]. This demonstrates the high accuracy of our method. The direct inclusion of the mass excess in the calculation has revealed a new correlation between the ground state energy and proton magic numbers, thus showing the influence of the nuclear shape on the electronic structure. We have recently extended the calculations to all known isotopes [to be published] in order to further investigate this feature which is expected to be found in other ionic species and also in solids. Because of the restricted space available here, results will be discussed elsewhere. The explicitly correlated 2-electron wave functions that we have obtained are valid up to second-order in the perturbation theory and therefore provide a basis for calculating the higher-order relativistic corrections [2]. In future works, we will include these corrections which can be comparable to the mass polarization contribution for large $Z$. These high-precision calculations will provide reliable inputs in precise approaches for plasma diagnostics, for example in the spectral analysis of high-temperature plasmas, in deformation wave and tight-binding methods used for studying electron-ion plasma processes.
Figure 3. The upper (lower) curve shows the difference between $\varepsilon_2$ ($E_0$) obtained without and with including $\varepsilon_2$ in the minimization.

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