Upper bound to the critical binding nuclear charge for a three-electron atomic system

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Abstract
The three-electron ground state atomic energy in the $Z \to 2$ limit, where Z is the nuclear charge, is studied using high precision Hylleraas-type calculations, with the objective to investigate the stability of the ground state of the helium negative ion. Finite nuclear mass effects and relativistic corrections are incorporated in the computations. The calculations reveal that the critical binding nuclear charge, Z_c, the value below which the three-electron system is no longer stable, is bounded above by $Z_c = 2.000\,001$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The atomic helium negative ion, He$^-$, has been of considerable theoretical and experimental interest [1–37]. Atomic negative ions tend to form very few, and often no, bound states. The helium negative ion is known to form two metastable excited states [18], but the consensus opinion in the literature is that the helium negative ion does not have a stable ground state. The helium negative ion has attracted attention because of the nature of the decay of its metastable states: the 1s2s2p $^4P^o_{5/2}$ state cannot autoionize via a Coulomb interaction, so the state is bound in the nonrelativistic level of theory [18, 34]. The possibility of forming a stable helium negative ion in very intense laser fields [35] or in the presence of extremely large magnetic fields, such as those likely to arise in astrophysical situations [36], have been topics of recent research interest. Correlation effects play a key role in the calculations on this system, and this is generally the case for the stability of atomic negative ions, so this species has been of interest for testing post Hartree–Fock theories. The few-electron nature of this atomic species makes it particularly amenable to high-precision calculations.

The focus of this work is an attempt to provide an understanding of the stability issues associated with this ion, and in the process, fix an upper bound on the critical binding nuclear charge for the ground state of an atomic three-electron system. We also explore the nature of the interactions that impact the question of stability for this ion. We examine the impact of finite nuclear mass corrections, and evaluate relativistic corrections through order α^2, where α is the fine structure constant, in order to assess the importance of these contributions to the stability of the helium negative ion ground state. Our calculations indicate a bound state exists for a three-electron atomic system at a nuclear charge of 2.000 001, but efforts to decrease the nuclear charge below this value lead to numerical stability issues. Extensive calculations on the three-electron atomic system at exactly $Z = 2$ gave no evidence for a bound state of this system.

2. Computational approach

The computational approach employed is as follows. The variational calculations were carried out for the three-electron system in an S state, using a Hylleraas basis of the form [38]

$$\psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = A \sum_{s=1}^{N} c_s r_1^{i_s} r_2^{j_s} r_3^{k_s} r_{12}^{l_s} r_{13}^{m_s} r_{23}^{n_s}$$
$$\times \, \mathrm{e}^{-\alpha_s \, r_1 - \beta_s \, r_2 - \gamma_s \, r_3} \chi_s, \tag{1}$$

where A is the three-electron antisymmetrizer, c_s denotes the expansion coefficients, χ_s is a spin eigenfunction, r_i designates

the electron–nuclear separation distance for electron i, r_{ij} is the inter-electronic separation distance and N represents the number of terms in the expansion. The nonlinear exponents α_s, β_s, and γ_s are each > 0, and the integer indices $\{i_s, j_s, k_s, l_s, m_s, n_s\}$ are each $\geqslant 0$. For the calculations in the range $Z = 2.000\,001$–3, the infinite nuclear mass nonrelativistic approximation was employed. Below $Z = 2.01$, the finite nuclear mass approximation was also employed using the Hamiltonian (for the three-electron system in atomic units (a.u.))

$$H = -\frac{1}{2\mu}\sum_{i=1}^{3}\nabla_i^2 - \frac{1}{M}\sum_{i=1}^{3}\sum_{j>i}^{3}\nabla_i \cdot \nabla_j$$

$$-Z\sum_{i=1}^{3}\frac{1}{r_i} + \sum_{i=1}^{3}\sum_{j>i}^{3}\frac{1}{r_{ij}}, \tag{2}$$

where μ is the reduced mass $\mu = M/(1+M)$, and M is the nuclear mass of ^{4}He in a.u.

The computational strategy employed is as follows. The calculations were commenced at the nuclear charge $Z = 3$, which corresponds to the next member of the helium negative ion isoelectronic series. The nuclear charge was then reduced down in suitable steps from $Z = 3$ to $Z \rightarrow 2$. When $2 < Z < 3$ we are dealing with a pseudo-negative ion. In the course of changing Z, the basis set was systematically refined and expanded. For the four smallest values of Z for which a bound state was found for the three-electron system, the following Breit–Pauli relativistic corrections were evaluated using first-order perturbation theory based on the Hamiltonian in au:

$$H_{REL} = -\frac{\alpha^2}{8}\sum_{i=1}^{3}\nabla_i^4 + \frac{1}{2}\alpha^2 Z\pi\sum_{i=1}^{3}\delta(\mathbf{r}_i) - \pi\alpha^2\sum_{i=1}^{3}\sum_{j>i}^{3}\delta(\mathbf{r}_{ij})$$

$$-\frac{8\pi\alpha^2}{3}\sum_{i=1}^{3}\sum_{j>i}^{3}\mathbf{s}_i\cdot\mathbf{s}_j\delta(\mathbf{r}_{ij})$$

$$+\frac{1}{2}\alpha^2\sum_{i=1}^{3}\sum_{j>i}^{3}\left\{r_{ij}^{-1}\nabla_i\cdot\nabla_j + r_{ij}^{-3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_i)\nabla_j\right\},$$

$$\equiv H_{mass} + H_{enD} + H_{eeD} + H_{ssc} + H_{oo}, \tag{3}$$

where H_{mass} represents the kinetic energy mass correction, H_{enD} is the electron–nuclear Darwin term, H_{eeD} denotes the electron–electron Darwin term, H_{ssc} is the spin–spin contact interaction and H_{oo} designates the electron–electron orbit interaction, $\delta(\mathbf{r})$ is a Dirac delta function and $\mathbf{s}_i$ is an electron spin operator.

To calculate the ionization energies for each value of Z investigated, two-electron counterparts to equations (1)–(3) were employed. The ionization energy was evaluated in terms of the two- and three-electron energies $E_2(Z)$ and $E_3(Z)$, respectively, as

$$I(Z) = E_2(Z) - E_3(Z). \tag{4}$$

The approximate rate of change of the ionization energy with respect to the nuclear charge was evaluated from the Hellmann–Feynman theorem, using

$$\frac{\partial I}{\partial Z} = \langle\psi_3|\sum_{i=1}^{3}\frac{1}{r_i}|\psi_3\rangle - \langle\psi_2|\sum_{i=1}^{2}\frac{1}{r_i}|\psi_2\rangle, \tag{5}$$
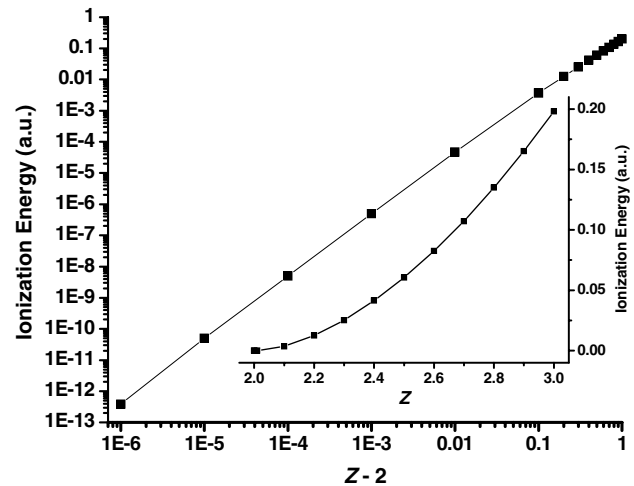

Figure 1. Ionization energy of the three-electron ground state as a function of $Z - 2$ on a log–log scale. The inset shows the ionization energy as a function of the nuclear charge on a linear scale.

where ψ_2 is the two-electron wavefunction. In addition to the small contributions arising from relativistic terms, there are small corrections to consider that arise from quantum electrodynamic contributions (QED). At $Z = 3$, the quantum electrodynamic correction to the ionization energy is an order of magnitude smaller than the relativistic contribution to the ionization energy. For values of Z very close to $Z = 2$, we expect this situation to prevail, and consequently have ignored these QED corrections. For smaller values of Z_c than found in the present work, it might be necessary to consider the QED contributions. The reader interested in the nature of these small QED corrections could see, for example, [39].

Extensive preliminary calculations were made for the three-electron system at $Z = 2$. No evidence for a bound ground state for the three-electron system was found, and our best result obtained indicates that at this value of Z the system is unbound by an upper bound of approximately 0.25 picohartree. These calculations did however provide a guide to the critical need for very careful exponent optimization, particularly for the third electron in the system. As the nuclear charge is reduced from $Z = 3$ to $Z \rightarrow 2$, the valence electron cloud, not surprisingly, take on an increasingly diffuse Rydberg-like character. The optimal nonlinear parameters change significantly from $Z = 3$ to $Z = 2$, particularly the γ_i values. Below $Z \approx 2.001$ the results are as expected, particularly sensitive to the values of γ_i, and the optimal γ_i value becomes $\approx Z - 2$. As a result, it was essential to carry out the calculations in quadruple precision, in order to avoid numerical stability issues. We also note that as the optimal γ_i values change so rapidly near $Z = 2$, simple Z-scaling has extremely limited effectiveness.

3. Results

In figure 1, we show the variation of the ionization energy as a function of Z, calculated in the nonrelativistic infinite nuclear mass approximation. The results in figure 1, which
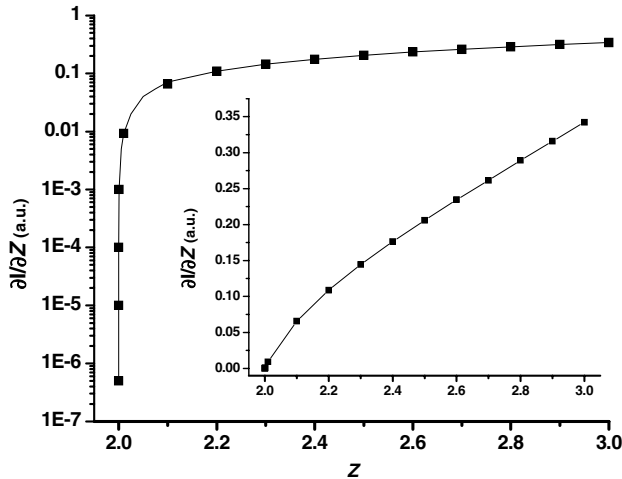
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Figure 2. Derivative of the ionization energy as a function of atomic number Z as calculated using equation (5). The inset shows the data on a linear scale.

represent a lower bound to the nonrelativistic component of the ionization energy, make it clear that for all values of Z slightly larger than 2, the three-electron ground state system is stable. The three-electron ground state system is still stable at $Z = 2.000\,001$. Attempts to execute the calculations for values of Z below those presented in figure 1 led to numerical stability issues, which we surmise could only be resolved by working in higher precision arithmetic beyond the quadruple precision (30–35 digits, depending on the machine) we employed for all the calculations.

In order to clarify the term $\lim_{Z \to 2} I(Z)$, we examined the behaviour of $\partial I / \partial Z$ as a function of Z. The results are indicated in figure 2. As $Z \to 2$, $\partial I / \partial Z \to 0$, which is very suggestive that the critical nuclear charge Z_c, lies in very close proximity to the value 2.

In order to ascertain the importance of finite nuclear mass effects, calculations were carried out using the Hamiltonian given in equation (2). Relativistic effects through order α^2 were evaluated using first-order perturbation theory. Some of the results for the three smallest values of Z are summarized in table 1. An approximate error estimate for the total relativistic correction was based on an examination of the convergence characteristics for the two- and three-electron relativistic contributions. For the lowest value of Z examined, the estimated uncertainty in the relativistic correction to $I(Z)$ is too large to draw a definite conclusion about the impact of the relativistic correction to the stability of the three-electron system. However, the results are at least suggestive that Z_c lies below the value $2.000\,001$.

In figures 3(a) and (b) we show a breakdown of the potential and kinetic contributions to the ionization energy as a function of Z and $Z - 2$, respectively. The ionization energy components are computed in the nonrelativistic infinite nuclear mass approximation. These contributions are defined by $I_{KE} = \langle KE \rangle_2 - \langle KE \rangle_3$, $I_{vee} = \langle vee \rangle_2 - \langle vee \rangle_3$, and $I_{ven} = \langle ven \rangle_2 - \langle ven \rangle_3$, where $\langle \rangle_2$ and $\langle \rangle_3$ denote the two-electron and three-electron expectation values, respectively,
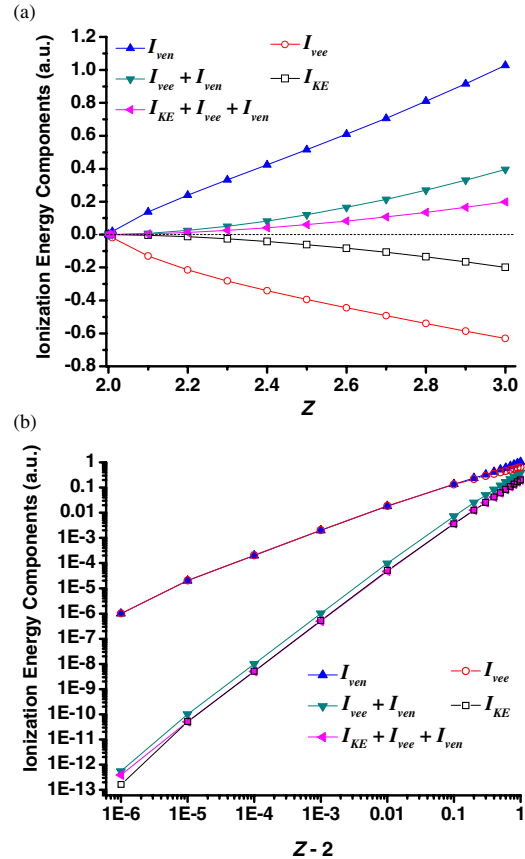

Figure 3. The ionization energy components as a function of (a) Z and (b) $Z - 2$. In (b), the absolute value of the ionization energy components is presented. Open symbols denote negative quantities in both (a) and (b).

Table 1. Nonrelativistic, finite nuclear mass and relativistic contributions to the ionization energy, for Z near the value 2.

Ionization energy contributions μ hartree	Z values		
	2.0001	2.000 01	2.000 001
$\langle H_{\text{inf}} \rangle$	0.004 992 988	0.000 049 963	0.000 000 375
$\langle H_{\text{finite}} \rangle$	0.004 992 304	0.000 049 955	0.000 000 385
$\langle H_{\text{enD}} \rangle$	−0.000 20	−0.000 09	−0.000 04
$\langle H_{\text{eeD}} \rangle$	0.000 005	−0.000 001	−0.000 0014
$\langle H_{\text{ssc}} \rangle$	−0.000 008	0.000 002	0.000 002
$\langle H_{\text{mass}} \rangle$	0.000 40	0.000 18	0.000 09
$\langle H_{\text{oo}} \rangle$	0.000 000 16	−0.000 000 02	−0.000 000 01
$\langle H_{\text{REL}} \rangle$	0.000 20(40)	0.000 09(40)	0.000 05(40)
I (total)	0.005 19(40)	0.000 14(40)	0.000 05(40)

and KE, vee and ven refer to kinetic energy, electron–electron, and electron–nuclear potential terms of the Hamiltonian, respectively. In figure 3(b), the curves for I_{vee} and $|I_{ven}|$ are essentially superimposed upon one another, as $Z \to 2$. As a direct consequence, the curves for I_{KE} and $I_{KE} + I_{vee} + I_{ven}$ in figure 3(b) are also almost superimposed upon one another.

To rationalize the behaviour observed in figure 3, suppose in the limit $Z \to 2$ that the third electron becomes 'Rydberg-like' which we know, in part, from the very diffuse nature

of the basis functions required to obtain an accurate energy. Then $r_3 \gg r_1$, $r_3 \gg r_2$, $\psi_3(r_1, r_2, r_3) \approx \psi_2(r_1, r_2)\phi(r_3)$, with $\phi(3) \approx N r_3^{n-1} e^{-\zeta r_3}$, where n is the principal quantum number of a Rydberg valence ns orbital and N is a normalization constant. We have assumed that n is sufficiently large so that the interaction of the Rydberg electron with the core electrons is extremely small. Set $V = \left(\frac{1}{r_{13}} + \frac{1}{r_{23}} - \frac{Z}{r_3}\right)$, and let H_2 and H_3 denote the two- and three-electron infinite nuclear mass Hamiltonians, respectively, then in the limit $Z \to 2$

$$
\begin{aligned}
I &= \langle \psi_2(\mathbf{r}_1, \mathbf{r}_2)|H_2|\psi_2(\mathbf{r}_1, \mathbf{r}_2)\rangle \\
&\quad - \langle \psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)|H_3|\psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\rangle \\
&\approx \frac{1}{2}\langle \phi(\mathbf{r}_3)|\frac{1}{2}\nabla_3^2|\phi(\mathbf{r}_3)\rangle \\
&\quad - \langle \psi_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_3)|V|\psi_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_3)\rangle \\
&= -\frac{1}{2}\frac{\zeta^2}{(2n-1)} + \frac{\zeta(Z-2)}{n} \\
&\quad - \langle \psi_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_3)|O\left(\frac{1}{r_3^2}\right)|\psi_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{r}_3)\rangle \\
&\approx -\frac{1}{2}\frac{\zeta^2}{(2n-1)} + \frac{\zeta(Z-2)}{n}
\end{aligned}
\tag{6}
$$

When $\zeta \approx (Z-2)$, which corresponds to a fully screened valence electron, the sum of the $\langle vee \rangle + \langle ven \rangle$ contributions to $I(Z)$ will be similar in size, but of the opposite sign to the $\langle KE \rangle$ contribution to $I(Z)$, which is the approximate behaviour exhibited in figure 3. The magnitudes of the individual terms contributing to $\langle V \rangle$ are each proportional to ζ, and would thus be expected to be about an order of ζ^{-1} larger than $\langle KE \rangle$ in the limit $Z \to 2$, which is the behaviour illustrated in figure 3. If the selected Z exceeds the value 2 by an amount ε, then it is advantageous to carry out the calculations with exponents for the valence electron bounded above by $2(2 - n^{-1})\varepsilon$. Upon inserting $(Z-2)$ for ζ in equation (6), and then letting $Z \to 2$, the potential and kinetic energy contributions go to zero at approximately the same rate. The preceding simplified model of the Z behaviour near $Z = 2$ would be insufficient to explore the detailed Z dependence of $I(Z)$ below the critical Z_c found in this study. Additional terms in the expansion of the matrix element of V, together with an improved decomposition for $\psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, would be required for a more detailed analysis.

There is one reported prediction of a stable state for the helium negative ion by Guo *et al* [26], with a proposed stability of the order of a few millihartree, and a rebuttal of this work has also appeared [30]. The results of the present calculations make it clear that the helium negative ion is not stable by a few millihartree.

Serra *et al* [31] have performed a nonrelativistic calculation (in the infinite nuclear mass approximation) and determined the value $Z_c = 2.01 \pm 0.03$ using a Hylleraas approach, but without exponent optimization. These authors attempt an analogy of the behaviour of $E(Z)$ near Z_c with the behaviour of continuous phase transitions. We have been able to significantly improve upon their result for $(Z - Z_c)$ by a factor of 10^4, by carrying out a careful optimization of the exponents. An extrapolation of the ionization energy based on the lowest values of Z yields the extrapolated upperbound

result $Z_c = 2.000\,0005$. This estimate makes it clear that we have $Z_c = 2.000\,001$ as a true upper bound estimate to the critical binding nuclear charge. Furthermore, the behaviour of $\partial I/\partial Z$ indicates that we have not in fact reached the true minimum result for Z_c, which also implies that we have an upper bound for this quantity.

The results of the present work suggest that with a highly optimized description of correlation effects, a stable ground state for the helium negative ion may exist for weaker laser fields [35] or magnetic fields [36, 37] than have recently been proposed to support a bound state for this anion.

4. Conclusion

In summary, we have determined that the critical nuclear charge for a stable three-electron system is bounded above by the value $Z_c = 2.000\,001$. For this value of the nuclear charge the valence electron is best described as having considerable Rydberg-like character. We hope the extreme proximity of Z_c to the nuclear charge of He found in the present work will stimulate theoretical and experimental investigations of the helium negative ion, particularly in intense laser fields or in very large magnetic fields, such as those likely to arise in astrophysical situations.

Acknowledgments

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