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Andrew King, Adam Baskerville, Hazel Cox

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Author for correspondence: Hazel Cox [e-mail: h.cox@sussex.ac.uk](mailto:h.cox@sussex.ac.uk)

Hartree-Fock implementation using a Laguerre-based wavefunction for the ground-state and correlation energies of two-electron atoms

Andrew W. King 1,2 , Adam L. Baskerville 1 and Hazel Cox^1

 1 Department of Chemistry, School of Life Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K. ²Present Address: Department of Biochemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

An implementation of the Hartree-Fock (HF) method using a Laguerre-based wavefunction is described and used to accurately study the ground state of twoelectron atoms in the fixed nucleus approximation, and by comparison with fully-correlated (FC) energies, used to determine accurate electron correlation energies. A variational parameter A is included in the wavefunction and is shown to rapidly increase the convergence of the energy. The one-electron integrals are solved by series solution and an analytical form is found for the two-electron integrals. This methodology is used to produce accurate wavefunctions, energies and expectation values for the helium isoelectronic sequence, including at low nuclear charge just prior to electron detachment. Additionally, the critical nuclear charge for binding two electrons within the HF approach is calculated and determined to be Z_C^{HF} = 1.031 177 528.

1. Introduction

Hartree-Fock (HF) theory is the bedrock of conventional quantum chemistry. It is used as the reference wavefunction for electron-correlated methods, often referred to as post-HF methods, such as Møller-Plesset perturbation theory, coupled cluster theory, and configuration interaction [\[1\]](#page-14-0). The HF method treats the electron-electron interaction

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with a mean-field approach, i.e. each electron moves in the mean field generated by the other electron(s), and thus their motions are statistically independent and uncorrelated. Fermi correlation (which arises for electrons of the same spin) is accounted for through the antisymmetry of the HF wavefunction but Coulomb correlation (which is independent of spin) is missing. Löwdin defined this important missing Coulomb electron correlation, E_{corr} , as the difference between the exact non-relativistic energy E and the Hartree-Fock energy E_{HF} [\[2,](#page-14-1)[3\]](#page-14-2), i.e. $E_{corr} = E - E_{HF}$. The correlation energy E_{corr} is always negative as E_{HF} is an upper bound to E, the exact eigenvalue of the Hamiltonian for the state under consideration.

HF has also contributed to developments in approximate density functional theory (DFT). The basis of hybrid exchange-correlation (XC) functionals is the inclusion of some "exact" HF exchange. Additionally, HF has been the basis of some popular correlation functionals. For example, the renowned LYP correlation functional [\[4\]](#page-14-3), and subsequent functional developments e.g. [\[5](#page-14-4)[,6\]](#page-14-5), are based on the HF second order reduced density matrix and an exponential correlation factor following the approach of Colle and Salvetti [\[7\]](#page-14-6). The correlation factor was chosen to fulfil the nucleus-electron cusp condition and the constants in the final correlation energy formula were obtained by a fitting procedure using data for the helium atom. Therefore, the highly popular functional B3LYP, has a significant grounding in HF.

The aim of this paper is to present a simple, high-accuracy, implementation of HF theory. The accurate calculation of the HF energy for helium is an age-old problem. There have been many reports of high-accuracy computations using a variety of bases and techniques, for example [\[8](#page-14-7)[–11\]](#page-15-0). The present work is focused on implementing HF theory using a Laguerrebased wavefunction in perimetric coordinates. This basis is chosen for the following reasons (i) the Laguerre functions are orthogonal on the interval $[0, \infty)$, (ii) to use the elegant series solution method, where possible, to avoid costly explicit integration; it would also be possible to use the associated Laguerre polynomials but this is not necessary as the standard Laguerre recursion relations can be used to remove any variables and the orthogonality exploited, and (iii) to complement our work on fully-correlated systems, which uses a similar Laguerre-based wavefunction [\[12–](#page-15-1)[14\]](#page-15-2), and hence provide a balanced description of electron correlation.

In order to develop new correlation functionals, particularly incorporating the long-range behaviour of electronic motion, it is of benefit to be able to calculate the HF wavefunction accurately for any nuclear charge, including at low, non-integer values, and just prior to electron detachment. This is a key goal of the present work.

2. Method of Solution

The Schrödinger equation for two-electron atoms with a clamped nucleus, in atomic units, is

$$
\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\Psi = E\Psi
$$
\n(2.1)

where Z is the nuclear charge number and the r_i , $i = 1$ or 2, are the nucleus-electron distances and r_{12} the electron-electron distance.

(a) Choice of Coordinates

For atoms, it is usual to construct a solution for the translation-free problem directly, and integrate over the angular and radial coordinates. In the case of the ground state of helium, the angular part is a constant, $Y_{0,0}(\theta, \phi) = (2\pi)^{-1/2}$, and thus the wavefunction is independent of angle. To evaluate the $1/r_{12}$ term, arising in the Coulomb and exchange integral, $1/r_{12}$ is expanded by Legendre polynomials. The only terms that contribute to the integral are the ones with $l = m_l = 0$ and the radial integration is divided into two parts, one with $r_1 > r_2$ and the other with $r_2 > r_1$.

In the present work, we have chosen to follow our procedure for fully-correlated three-body systems [\[12](#page-15-1)[,13\]](#page-15-3) and separate off the angular momentum and solve a body-fixed problem. This is

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because there is a unique choice of body-fixed coordinates for a two-electron atom, namely the right-handed system in which two axes lie in the plane formed by the three particles with the third axis perpendicular to this plane [\[12\]](#page-15-1).

The three internal coordinates are chosen to be the interparticle distances, r_1 , r_2 and r_{12} . These are obtained by choosing the translationally invariant coordinates in terms of the Cartesian coordinates of the particles

$$
\underline{t}_1 = (\underline{x}_{electron_1} - \underline{x}_{nucleus}) \quad \text{and} \quad \underline{t}_2 = (\underline{x}_{electron_2} - \underline{x}_{nucleus}) \tag{2.2}
$$

to be

$$
r_i = |\underline{t}_i| \quad i = 1, 2 \quad \text{and} \quad r_{12} = |\underline{t}_2 - \underline{t}_1|.
$$
 (2.3)

The domains of the interparticle coordinates are not independent as the sides of a triangle are connected by the triangular condition. However, perimetric coordinates defined as $z_i = (r_i + \mathbf{I})$ $r_k - r_i$) where i, j, k are 1, 2 and 12 by cyclic permutation, are independent and each coordinate ranges from 0 to ∞ .

Evaluating the internal coordinate part of the Jacobian, the transformation from Cartesian coordinates, to interparticle coordinates, to perimetric coordinates is:

$$
dx_1^3 dx_2^3 = 8\pi^2 r_1 r_2 r_{12} dr_1 dr_2 dr_{12} = \frac{\pi^2}{4} (z_2 + z_3)(z_3 + z_1)(z_1 + z_2) dz_1 dz_2 dz_3 \tag{2.4}
$$

In the HF results to follow, we integrate over $dr_1 dr_2 dr_{12}$ (as the r_{12} term in the Jacobian conveniently cancels with the $1/r_{12}$ in the two-electron integrals, and also it facilitates easy conversion to the perimetrics). As we are dealing with the ${}^{1}S$ -state of the helium-like ions, and hence the wavefunctions are independent of angle, this gives the same result for the Coulomb integrals as integrating over the angles using the standard expansion of $1/r_{12}$ by Legendre polynomials.

(b) The Hartree-Fock Method

The HF wavefunction, Ψ_{HF} , is taken as the product

$$
\Psi_{HF}(r_1, r_2) = \psi(r_1)\psi(r_2),\tag{2.5}
$$

where r_1 and r_2 are the electron-nucleus distances defined in Eq. [2.3,](#page-3-0) and $\psi(r_i)$ has the form

$$
\psi(r_i) = e^{-\frac{1}{2}Ar_i} \sum_{q=0}^{\infty} C(q) L_q(Ar_i) \left(\approx \sum_{q=0}^{m-1} c_{qi} \phi_q \right), \qquad i = 1 \text{ or } 2.
$$
 (2.6)

Thus the infinite series is solved in truncated form with the m basis functions ϕ_q taken to be the Laguerre functions $e^{-x/2}L_q(x)$ where $L_q(x)$ is a Laguerre polynomial of degree q , which with the exponential weight factor, $e^{-x/2}$, form an orthogonal set defined for the range zero to infinity, i.e.

$$
\int_{0}^{\infty} e^{-x} L_p(x) L_q(x) dx = \delta_{pq}.
$$
\n(2.7)

The coordinate scale factor A is treated as a non-linear variational parameter (NLP). This Laguerre-based wavefunction was chosen to complement our work on fully-correlated (threebody) systems (see Section [\(d\)\)](#page-6-0) and hence provide a balanced description of electron correlation.

The expansion for the wavefunction ψ , Eq. [2.6,](#page-3-1) is substituted into the HF equations, $\hat{F}\psi(1)$ = $\epsilon_i\psi(1)$, to give the Roothaan-Hall equations which can be written compactly, in terms of $m \times m$ matrices, as

$$
\mathbf{FC} = \mathbf{SC}\epsilon \tag{2.8}
$$

where **is the Fock matrix,** $**C**$ **the matrix of wavefunction (orbital) coefficients,** $**S**$ **the overlap** matrix, and ϵ the diagonal matrix of the eigenvalues (orbital energies) ϵ_i . For a closed-shell system

of 2n−electrons the effective one-electron Fock operator, \hat{F} , has the form

$$
\hat{F} = \hat{H}^{core}(1) + \sum_{j=1}^{n} \left[2\hat{J}_j(1) - \hat{K}_j(1) \right], \text{ where } \hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}.
$$
 (2.9)

The Fock matrix elements have the form

$$
F_{pq} = \langle \phi_p(1) | \hat{H}^{core}(1) | \phi_q(1) \rangle + \sum_{j=1}^n \left[2 \langle \phi_p(1) | \hat{J}_j(1) | \phi_q(1) \rangle - \langle \phi_p(1) | \hat{K}_j(1) | \phi_q(1) \rangle \right] \tag{2.10}
$$

which we write as

$$
F_{pq} = H_{pq}^{core}(1) + G_{pq}, \text{ where } G_{pq} = \sum_{u,v=0}^{m-1} D_{u,v} \left[2(pq|uv) - (pv|uq) \right]. \tag{2.11}
$$

Here, $D_{u,v} = \sum_{j=1}^{n} c_{uj}^* c_{vj}$ represents the density matrix, $(pq|uv)$ the Coulomb integral J and $(pv|uq)$ the exchange integral K, and

$$
(pq|uv) = \int \int \phi_p^*(1)\phi_q(1)\frac{1}{r_{12}}\phi_u^*(2)\phi_v(2) dv_1 dv_2.
$$
 (2.12)

The HF energy is then calculated as

$$
E_{HF} = 2\sum_{i=1}^{n} \epsilon_i - \sum_{i=1}^{n} \sum_{j=1}^{n} (2J_{ij}(1) - K_{ij}(1))
$$
\n(2.13)

which removes the double-counting of the electron-electron energy in the expression

$$
\epsilon_i = \int \psi \hat{F} \psi dv = H_{ii}^{core} + \sum_{j=1}^{n} (2J_{ij}(1) - K_{ij}(1)).
$$
 (2.14)

However, in the present two-electron case, $n = 1$ and $2J - K$ reduced to J as the system is closedshell (so no parallel spins). Therefore,

$$
E_{HF} = 2\epsilon_i - J_{ij}, \quad \text{where} \quad i, j = 1 \text{ or } 2, i \neq j. \tag{2.15}
$$

(c) Implementation of the HF Method

First the one-electron matrix elements $H_{pq}^{core}(1)$ are calculated by series solution, and the wavefunction coefficients, obtained from solving $\hat{H}^{core}(1)\psi(1) = \epsilon^{core}\psi(1)$, used as the initial guess coefficients to calculate the two-electron matrix elements G_{pq} . The sum of the one electron H_{pq}^{core} and two-electron G_{pq} matrix elements are used to create the Fock matrix **F**, and Eq. [2.8](#page-3-2) is solved as a generalised eigenvalue problem, to acquire new wavefunction (orbital) coefficients. The convergence threshold for the SCF procedure is set at 3×10^{-15} and is performed using Direct Inversion of Iterative Space (DIIS). The HF energy is then calculated using Eq. [2.15.](#page-4-0) The non-linear variational parameter A is optimised using the built-in NLPSolve Maple command [\[15\]](#page-15-4) and the SCF procedure is repeated until A is also converged to within a tolerance of 3×10^{-15} .

(i) One-electron integrals

To calculate the one-electron matrix elements $H_{pq}^{core}(1)$, the Laguerre-based wavefunction Eq. [2.6](#page-3-1) is substituted into

$$
(\hat{H}^{core}(1) - \epsilon^{core})\psi = 0.
$$
\n(2.16)

The Laguerre recurrence relations [\(2.17](#page-4-1)*a*) to [\(2.17](#page-4-2)*c*):

$$
xL_n(x) = -(n+1)L_{n+1}(x) + (2n+1)L_n(x) - nL_{n-1}(x)
$$
\n(2.17*a*)

$$
xL'_{n}(x) = nL_{n}(x) - nL_{n-1}(x)
$$
\n(2.17b)

$$
xL_{n}''(x) = (x - 1) L_{n}'(x) - nL_{n}(x)
$$
\n(2.17c)

are used to eliminate the derivatives and powers of the variable r_i , arising from the one-electron operators (kinetic energy and nucleus-electron potential energy) and the overlap. This leads to a 5-term recursion relation, between the coefficients $C(q)$ in the expansion Eq. [2.6,](#page-3-1) of the form:

$$
\sum_{\alpha=-2}^{+2} R_{\alpha}(q)C(q+\alpha) = 0.
$$
 (2.18)

The coefficients of the recursion relation are given in Table [1](#page-5-0) for the general case where Z (the nuclear charge) and A (the scale parameter) are arbitrary. The RR represents a set of linear

Table 1. Coefficients $R_{\alpha}(q)$ in the recursion relation given by Eq. [2.18](#page-5-1) for the nuclear charge Z and variational parameter A.

α	$R_{\alpha}(q)$
-2	$-q\pi(A^2q-A^2+8q-8)/2A^3$
-1	$4q\pi(AZ+4q)/A^3$
θ	$\pi (A^2q^2 + A^2q - 8AZq + A^2 - 4AZ - 24q^2 - 24q - 8)/A^3$
$+1$	$4\pi (AZq + AZ + 4q^2 + 8q + 4)/A^3$
$+2$	$-\pi(A^2q^2+3A^2q+2A^2+8q^2+24q+16)/2A^3$

equations for the determination of the coefficients $C(q)$, and the vanishing of their determinant yields the energy eigenvalues ϵ^{core} which can be used as a check given that the one-electron (hydrogenic) energy is known exactly. An example of a 3×3 determinant is given in Eq. [2.19.](#page-5-2)

$$
\det(H^{core} - \epsilon^{core}S) = \begin{vmatrix} \frac{\pi}{A} - \frac{4\pi Z}{A^2} - \epsilon^{core} \frac{8\pi}{A^3} & \frac{4\pi Z}{A^2} + \epsilon^{core} \frac{16\pi}{A^3} & -\frac{\pi}{A} - \epsilon^{core} \frac{8\pi}{A^3} \\ \frac{4\pi Z}{A^2} + \epsilon^{core} \frac{16\pi}{A^3} & \frac{3\pi}{A} - \frac{12\pi Z}{A^2} - \epsilon^{core} \frac{56\pi}{A^3} & \frac{8\pi Z}{A^2} + \epsilon^{core} \frac{64\pi}{A^3} \\ -\frac{\pi}{A} - \epsilon^{core} \frac{8\pi}{A^3} & \frac{8\pi Z}{A^2} + \epsilon^{core} \frac{64\pi}{A^3} & \frac{7\pi}{A} - \frac{20\pi Z}{A^2} - \epsilon^{core} \frac{152\pi}{A^3} \end{vmatrix}
$$
(2.19)

The RR is calculated once and then used to determine the m^2 matrix elements for any given m. These one electron terms are very fast to calculate compared to explicit integration (e.g. with a 20-term, i.e. $m=20$, wavefunction the one-electron terms take a tenth of a second using the series solution method and approximately 150 seconds with the "int" method of Maple on an iMac i5).

(ii) Two-electron integrals

The method of solution for the one-electron integrals described above is not amenable to the twoelectron integrals, as terms arise that do not satisfy the Laguerre orthogonality condition, Eq. [2.7.](#page-3-3) Integrals of the following form arise:

$$
\int_{0}^{\infty} \int_{0}^{\infty} \int_{|r_1 - r_2|}^{r_1 + r_2} e^{-r_1 - r_2} L_p(r_1) L_q(r_1) \frac{1}{r_{12}} L_u(r_2) L_v(r_2) \, dr_{12} \, dr_2 \, dr_1.
$$
 (2.20)

These can be solved analytically. First the integral is converted to perimetric coordinates to give independent integration domains. Next, the Laguerre polynomials are expressed in the form

$$
L_n(x) = \sum_{n_i=0}^{n} (-1)^{n_i} \binom{n}{n_i} \frac{x^{n_i}}{n_i!}
$$
\n(2.21)

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and the binomial expansion expanded. This then results in terms compatible with the known integral [\[16\]](#page-15-5)

$$
\int_{0}^{\infty} x^{n} e^{-ax} dx = \Gamma(n+1)a^{-n-1}.
$$
 (2.22)

Application of Eq. [2.22,](#page-6-1) provides an analytical expression for the two-electron integrals, for example the integral Eq. [2.20](#page-5-3) has the form:

$$
\sum_{p_i,q_i,u_i,v_i=0}^{p,q,u,v} \sum_{a_i=0}^{p_i+q_i} \sum_{b_i=0}^{u_i+v_i} 2^{a_i+b_i-\phi+1} (-1)^{\phi+1} \pi^2 \left(a_i^2 - 2a_i b_i + b_i^2 - p^2 - 2p_i q_i - 2p_i u_i - 2p_i v_i\right)
$$

$$
-q_i^2 - 2q_iu_i - 2q_iv_i - u^2 - 2u_iv_i - v^2 + a_i + b_i - 7\phi - 10\Big)\left(\phi - a_i - b_i\right)!(p_i + q_i)!(u_i + v_i)!
$$

$$
\times \frac{p!q!u!v!}{u_i!^2v_i!^2u_i!^2v_i!^2(p_i+q_i-a_i)!(q_i+u_i-b_i)!(p-p_i)!(q-q_i)!(u-u_i)!(v-v_i)!} \tag{2.23}
$$

where $\phi = p_i + q_i + u_i + v_i$. The m^4 two-electron integrals are reduced to $m(m+1)(m^2 + m +$ 2)/8 unique integrals by exploiting the 8-fold permutation symmetry of real basis functions, i.e. $(pq|uv) = (qp|uv) = (pq|vu) = (qp|vu) = (uv|pq) = (vu|qq) = (uv|qp) = (vu|qp)$, p.219 [\[1\]](#page-14-0).

To maximise the size of the wavefunction m , the two-electron integrals were calculated using a dedicated C++ program and the results saved to disk to be read into Maple. The maximum value of m was limited only by the available random access memory (RAM) required for the large factorials in Eq. [\(2.23\)](#page-6-2) which can be much too big to be calculated with built in data types. Therefore the GNU Multiple Precision Arithmetic Library [\[17\]](#page-15-6) was used to perform the required arithmetic with large numbers, with the downside that it requires large amounts of RAM. These calculations were performed on an iMac i5 and due to limitations in RAM the largest value of m used in this work was 20.

The $(pq|uv)$ integrals arising in G_{pq} (defined in Eq. [2.11\)](#page-4-3), for the 2-term wavefunction ($m = 2$), i.e.

$$
\psi = e^{-\frac{1}{2}Ar_1} \sum_{q=0}^{\infty} C(q) L_q(Ar_1) = e^{-\frac{1}{2}Ar_1} \{ C(0) L_0(Ar_1) + C(1) L_1(Ar_1) \}
$$
(2.24)

requires the following six unique two-electron repulsion integrals:

$$
(0\ 0|0\ 1) = (0\ 0|10) = (0\ 1|0\ 0) = (1\ 0|0\ 0) = -\frac{925}{2}\pi^2
$$

$$
(0\ 1|0\ 1) = (0\ 1|1\ 0) = (1\ 0|1\ 0) = (1\ 0|0\ 1) = 485\pi^2
$$

$$
(0\ 1|1\ 1) = (1\ 1|0\ 1) = (1\ 0|1\ 1) = (1\ 1|1\ 0) = -\frac{4275}{4}\pi^2
$$

$$
(0\ 0|1\ 1) = (1\ 1|0\ 0) = \frac{2035}{2}\pi^2
$$

$$
(0\ 0|0\ 0) = 510\pi^2
$$

$$
(1\ 1|1\ 1) = \frac{19259}{8}\pi^2
$$

(d) The Fully-Correlated Method

To calculate the correlation energy E_{corr} , we subtract the HF energies from fully-correlated (FC) energies. Following our previous work on FC systems [\[14,](#page-15-2)[18](#page-15-7)[,19\]](#page-15-8), the wavefunction is expanded **6**

in a triple orthogonal set of Laguerre functions in scaled perimetric coordinates, i.e.

$$
\psi_{FC}(z_1, z_2, z_3) = e^{-\frac{1}{2}(\alpha z_1 + \alpha z_2 + \gamma z_3)} \sum_{l,m,n=0}^{\infty} A(l,m,n) L_l(\alpha z_1) L_m(\alpha z_2) L_n(\gamma z_3), \qquad (2.25)
$$

where α and γ are non-linear variational parameters. On substitution into the two-electron Schrödinger equation Eq. [2.1,](#page-2-0) a 33-term recurrence relation between the coefficients is generated which is used to form a sparse secular determinant that is solved in truncated form to give the eigenvalues as a function of basis set size N [\[12,](#page-15-1)[14](#page-15-2)[,20\]](#page-15-9). In the present work, a 4389-term wavefunction is used. This method can be applied to two-electron systems with any nuclear charge, including low Z , and the accurate wavefunctions obtained used to explore the properties of a fully-correlated system [\[18,](#page-15-7)[19\]](#page-15-8).

3. Results and Discussion

(a) Energy Convergence

The helium energy obtained from the solution of $\hat{H}^{core}(1)\psi(1) = \epsilon^{core}\psi(1)$ using the series solution implementation is provided in Table [2.](#page-7-0) In the absence of electron repulsion the exact two-electron energy should be $-Z^2$, as

$$
\epsilon^{core} \cong E_{hydrogenic} = -\frac{Z^2}{2}.\tag{3.1}
$$

Table [2](#page-7-0) shows that with just 3 terms ($m = 3$) the helium core energy, $2 \times \epsilon^{core}$, is exact to within a tenth of a μ -hartree. The ϵ^{core} energy is obtained by evaluating the determinant in Eq. [2.19](#page-5-2) with $Z = 2$ and $A = 3.841$ 765. Furthermore, with just 14 terms in the wavefunction the helium HF energy matches the exact numerical Hartree-Fock value [\[11\]](#page-15-0) to all significant figures available, and with just 18 terms the value of [\[9\]](#page-14-8). This gives us confidence that our implementation (series solution for the one-electron integrals and analytic integration for the two-electron integrals) is working effectively and can provide very accurate HF energies.

Table 2. The rate of convergence of the helium HF energy (hartree) with number of basis functions m. Digits in bold represent converged digits with respect to the numerical Hartree-Fock value [\[11\]](#page-15-0) and digits in bold-italic represent increased convergence exhibited by the method in this work in agreement with [\[9\]](#page-14-8). Also provided is the helium core energy, $2 \times e^{core}$, and the optimised value of the NLP A .

m	A	HF Energy / a.u.	$2 \times e^{core}$ a.u.
1	3.374 999	-2.847 656 249 999 999	-3.902 343 749 999 996
3	3.841765	-2.861 590 054 663 477	-3.999 999 993 527 671
5	3.933 089	-2.861679675254110	-3.999 999 999 999 999
8	4.683 471	-2.861 679 963 194 483	-3.999 999 999 999 999
10	4.997 241	-2.861 679 993 922 506	-3.999 999 999 999 999
12	5.217 990	-2.861 679 995 536 817	-3.999 999 999 999 999
14	5.383 991	-2.861 679 995 609 217	-3.999 999 999 999 999
16	5.506 436	-2.861 679 995 612 136	-3.999 999 999 999 999
18	5.581 394	-2.861 679 995 612 237	-3.999 999 999 999 999
20	5.581 838	-2.861 679 995 612 239	-3.999 999 999 999 999
Literature/Exact	N/A	$-2.8616799956122[9]$	-4

To assess the effects of the non-linear variational parameter (NLP) A, Table [3](#page-8-0) provides the HF energy for helium, without the use of a parameter (i.e. $A = 1$), with a fixed value of $A = Z = 2$ (as the correct asymptotic behaviour of the solution of the Schrödinger equation for two-electron

* $A = 4.997 241 294$ for $m = 10$ and $A = 5.581 838 558$ for $m = 20$.

atoms at large r is $A = \sqrt{-E}$, [\[21\]](#page-15-10)), and with A fully optimised using the NPLSolve command of Maple. It is clear that optimisation of the NLP A greatly increases the rate of convergence of the calculated Hartree-Fock energy. The 10-term wavefunction gains an additional 4 converged digits and the 20-term wavefunction an extra 5-6 converged digits when relaxing any constraint on the value of A.

(b) HF Energy and Electron Correlation

The HF energies for the helium isoelectronic sequence $Z = 1$ to 18 are provided in Table [4.](#page-9-0) The energies are in excellent agreement with the most accurate literature values ([\[22\]](#page-15-11) for H−, [\[9\]](#page-14-8) for He, [\[23\]](#page-15-12) for Li⁺, [\[24\]](#page-15-13) for Be²⁺ to Ne⁸⁺, and [\[25\]](#page-15-14) for Na⁹⁺ to Ar¹⁶⁺), and offer increased accuracy for all of the cations. Additionally, we report the HF energy for a two-electron system with $Z = 0.911$ 028 224. This is the critical nuclear charge for binding two-electrons in a fullycorrelated system with infinite nuclear mass Z_C^{FC} [\[18,](#page-15-7)[26\]](#page-15-15).

The correlation energy, E_{corr} , is also provided in Table [4,](#page-9-0) where we have assumed $E_{FC} \approx$ E_{exact} . The data presented are in excellent agreement with previously reported correlation energies where available $[4,27,28]$ $[4,27,28]$ $[4,27,28]$. The correlation energy, as a fraction of the total energy, increases monotonically as Z decreases. For the system just prior to electron detachment, Z_C^{FC} , the correlation energy contributes almost 10 % of the total energy, and the correlation energy contribution (%) for the anions are orders of magnitude greater than that for the heavier cations.

However, the correlation energies exhibit an unexpected behaviour; they do not decrease monotonically. The magnitude of the correlation energy for Z_C^{FC} is greater than for H⁻. Evaluation of the correlation energy for the minimum nuclear charge for HF bound state stability Z_C^{HF} (see next section) reveals that the maximum in the correlation energy (smallest magnitude) occurs at this critical stability point.

(c) Z -Critical using the HF Method

The motivation for our implementation of HF was to have complete control over the optimisation of the wavefunction for low and/or non-integer nuclear charge Z so that we can calculate highaccuracy electron correlation data for all values of Z. The critical nuclear charge Z_C is the minimum charge required for an atomic system to have at least one bound state, i.e. to be stable against electron detachment. Previously we [\[18\]](#page-15-7) and others [\[26,](#page-15-15)[29,](#page-15-18)[30\]](#page-15-19) have calculated the critical nuclear charge for binding two-electrons in a fully-correlated system with an infinite nuclear mass, which has a value of $Z_C^{FC} = 0.911$ 028 224 077 255 73 [\[26\]](#page-15-15). The HF data for this system has been calculated and is presented, along with the electron correlation energy, in Table [4.](#page-9-0)

However, HF theory predicts the hydride ion to be unbound, i.e. $E_{HF}(\overline{H}^-) > E(\overline{H})$, but it is known that the hydride ion has a single bound state [\[31\]](#page-15-20), demonstrating the crucial role electron correlation effects play in stabilizing anionic systems. Thus the HF critical nuclear charge for binding two electrons must necessarily be greater than unity and so we have calculated the critical nuclear charge Z_C^{HF} required for the two-electron system to have at least one bound state

System	E_{HF}	${\cal E}_{FC}$	E_{corr}
Z_C^{FC}	-0.37390622	-0.41498621	-0.041 079 99
H^-	-0.4879297343	-0.52775101654	-0.039821282
He	-2.861 679 995 612	-2.903 724 377 034 0	-0.042044381422
$Li+$	-7.236 415 201 452 2	-7.279 913 412 66	-0.043 498 211 20
Be^{2+}	-13.611 299 430 619 1	-13.655 566 238 42	-0.04426680780
B^{3+}	-21.986 234 466 824 34	-22.030 971 580 24	-0.044 737 113 41
C^{4+}	-32.361 192 875 718 01	-32.406 246 601 89	-0.045 053 726 17
N^{5+}	-44.736 163 964 942 47	-44.781 445 148 7	-0.0452811837
O^{6+}	-59.111 142 701 913 658	-59.156 595 122 7	-0.0454524207
F^{7+}	-75.486 126 406 260 515	-75.531 712 363 9	-0.045559576
Ne^{8+}	-93.861 113 519 231 344	-93.9068065150	-0.0456929957
Na^{9+}	-114.236 103 072 533 87	-114.281 883 776 0	-0.045 780 703 4
Mg^{10+}	-136.611 094 432 922 60	-136.656 948 312	-0.0458538790
Al^{11+}	-160.986 087 168 814 85	-161.0320030260	-0.0459158571
$Si12+$	-187.361 080 975 930 946	-187.407 049 998 6	-0.0459690226
P^{13+}	-215.736 075 633 578 38	-215.782 090 763 5	-0.046 015 129 9
S^{14+}	-246.111 070 977 793 26	-246.157 126 474	-0.046055496
$Cl15+$	-278.486 066 884 212 90	-278.532 158 015	-0.046091130
Ar^{16+}	-312.861 063 256 800 63	-312.907 186 076 5	-0.046 122 819 6

Table 4. The Hartree-Fock energy E_{HF} , fully-correlated energy E_{FC} , and the correlation energy $E_{corr} = E_{FC}$ – E_{HF} , accurate to the number of digits presented, calculated using the Laguerre-based wavefunctions described in the text. All energies are given in a.u.

within the HF approach. It is not possible to use the direct variational method we developed for calculating Z_C^{FC} [\[18\]](#page-15-7) due to the SCF procedure. Therefore, we have varied the nuclear charge until E_{HF} equals the lowest continuum threshold (which is simply the hydrogenic energy, $E_{hydrogenic} = -Z^2/2$ a.u.), and found that Z_C^{HF} = 1.031 177 528. The HF energy is therefore -0.531 663 547 020 a.u., and calculating the fully-correlated energy for this system, gives $E_{corr} = -0.039$ 715 117 4 a.u.

(d) HF Bound State Properties

To determine the quality of the HF wavefunctions obtained, various expectation values have been calculated using the best 20-term wavefunction in each case. The properties presented in Table [5](#page-11-0) include the expectation values of r_i , r_i^{-1} , r_i^2 and the two-particle Dirac delta functions $\delta(r_i)$, for $r_i = r_1$ the nucleus-electron distance or r_{12} the electron-electron distance. The extent to which the virial condition $\big<\hat{V}\big>=-2\,\big<\hat{T}\big>$ is satisfied is presented to provide a measure of the quality of the solution. It was found that for all systems, including at Z_C (HF and FC), the factor η defined as

$$
\eta = \left| \frac{\left\langle \hat{V} \right\rangle}{\left\langle \hat{T} \right\rangle} + 2 \right| \tag{3.2}
$$

where $\big\langle \hat{V} \big\rangle$ and $\big\langle \hat{T} \big\rangle$ are the expectation values of the potential and kinetic energy, respectively, was calculated to be less than 6×10^{-14} , which is close to the exact value of zero.

At particle coalescence, the potential energy becomes singular, however must remain selfadjoint and bounded [\[32\]](#page-15-21). Kato showed how the kinetic energy compensates for this change in . rsta.royalsocietypublishing.org Phil. Trans. R. Soc0000000

potential energy at the singularity [\[32\]](#page-15-21). The two-body cusp ratios were determined using [\[32](#page-15-21)[,33\]](#page-15-22):

$$
\nu_{ij} = \langle \hat{\nu_{ij}} \rangle = \frac{\langle \delta(r_{ij}) \frac{\partial}{\partial r_{ij}} \rangle}{\langle \delta(r_{ij}) \rangle}.
$$
\n(3.3)

The exact value of the nucleus-electron cusp ν_{31} is $-Z$ for the infinite nuclear mass systems, and the exact value of the electron-electron cusp ν_{12} is 0.5, but for Hartree-Fock calculations ν_{12} is zero [\[34\]](#page-15-23). The data presented in Table [5](#page-11-0) demonstrate that the HF Laguerre-based wavefunction is capable of producing accurate nucleus-electron cusps.

Table 5. Various expectation values of nucleus-electron r_1 and inter-electronic r_1 ₂ distances, virial η , and nuclearelectron cusp ν_{31} , accurate to the number of digits presented, for the helium iso-electronic sequence using a 20-term Laguerre-based HF wavefunction.

Expectation Value	Z_{C}^{FC}	H	Z_c^{HF}	He
$\langle r_1\rangle$	2.989 00	2.503 959	2.372 691	0.927 273 404 7
$\left\langle r_1^{-1}\right\rangle$	0.595 799 1	0.685 672 15	0.717 056 3	1.687 282 215 281
$\left\langle r_1^2\right\rangle$	13.9768	9.411 09	8.370 83	1.184 828 479
	4.4939	3.739 273	3.537 395	1.362 124 383 6
$\langle r_{12} \rangle$				
(r_{12}^{-1})	0.337 767	0.395 484 84	0.415 497 75	1.025 768 869
$\left\langle r_{12}^2\right\rangle$	27.953	18.8221	16.741 67	2.369 656 959
$\langle \delta(r_1) \rangle$	0.1084	0.154	0.1734	1.797 959
$\langle \delta(r_{12}) \rangle$	0.008 601 2	0.012 983 476 3	0.014 816 097 5	0.190 603 997 806
η	$2.20\!\times\!10^{-15}$	$5.34\!\times\!10^{-14}$	$5.68\!\times\!10^{-14}$	4.53×10^{-17} -1.9999994
ν_{31} Expectation Value	-0.91111 $Li+$	-1.00004 $Be2+$	-1.0312 B^{3+}	$\overline{C^{4+}}$
	0.572 366 815 001	0.414 140 615 568 1	0.324 489 369 182 71	0.266 757 615 135 3
$\langle r_1\rangle$ $\left\langle r_1^{-1} \right\rangle$	2.687 419 466 644	3.687 458 389 249 97	4.687 474 643 446 75	5.687 482 944 834 96
$\left\langle r_1^2\right\rangle$	0.445 320 566 921	0.231 830 322 853 3 0.605 815 984 796	0.141 884 348 144 6	0.095 701 924 976 5
$\langle r_{12} \rangle$	0.838 314 780 311		0.474 345 724 536 7	0.389 782 153 288 89
$\binom{r-1}{12}$	1.651 686 396 960	2.277 068 252 761 5	2.902 277 500 818 8	3.527 409 586 583 50
$\left\langle r_{12}^2\right\rangle$	0.890 641 133 84	0.463 660 645 706	0.283 768 696 289	0.191 403 849 953 1
$\langle \delta(r_1) \rangle$	6.836 07	17.17874	34.73581	61.417 162
$\langle \delta(r_{12}) \rangle$	0.770 240 340 922 7.12×10^{-19}	1.990 626 059 609 1.41×10^{-19}	4.090 493 547 1	7.308 575 204 423
η	-2.999 999 2	-3.999 999 4	4.58×10^{-20} -4.999 999 5	1.9×10^{-20} -5.999996
ν_{31} Expectation Value	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
$\langle r_1 \rangle$	0.226 470 429 279 68	0.196 757 446 644 138	0.173 937 927 216 261	0.155 862 014 215 682
$\langle r_1^{-1} \rangle$	6.687 487 748 026 931 5	7.687 490 774 592 685	8.687 492 803 873 803 2	9.687 494 230 378 304 7
$\left\langle r_{1}^{2}\right\rangle$	0.068 885 369 277 05	0.0519 445 884 305 9	0.040 564 077 503 4	0.032 551 993 163 717
$\langle r_{12} \rangle$	0.330 815 397 642 55	0.287 348 866 910 399	0.253 979 884 030 87	0.227 555 582 436 616
r_{12}^{-1}	4.152 500 542 492 09	0.045 063 429 955 47	5.402 617 657 207 43	6.027 657 569 103 412
$\left\langle r_{12}^2\right\rangle$	0.137 770 738 554 10	0.103 889 176 861 18	0.081 128 155 006 91	0.065 103 986 327 43
$\langle \delta(r_1) \rangle$	99.132 630	149.792 081	215.305 375	297.582 370
$\langle \delta(r_{12}) \rangle$	11.883 603 439 511	18.054 310 663 495 6	26.059 429 289 010	36.137 691 729 472
η	9.18×10^{-21}	4.95×10^{-21}	2.89×10^{-21}	$8.31\!\times\!10^{-21}$
ν_{31} Expectation Value	-6.999996 $Na9+$	-7.999 999 7 Mg^{10+}	-8.999 999 7 $Al11+$	-9.999 999 7 $Si12+$
$\langle r_1 \rangle$	0.141 189 717 906 113 7	0.129 042 354 514 559	0.118 819 751 815 005 3	0.110 097 996 941 252 4
$\left\langle r_1^{-1}\right\rangle$	10.687 495 271 199 216	11.687 496 053 813 491 2	12.687 496 657 071 361 4	13.687 497 131 869 626
$\left\langle r_{1}^{2}\right\rangle$	0.026 699 076 885 451	0.022 293 792 594 156	0.018 895 284 789 469	0.016 218 589 707 459 0
$\langle r_{12} \rangle$	0.206 112 102 776 530	0.188 362 335 342 144	0.173 427 508 025 716	0.160 687 143 008 656 4
$\binom{r-1}{12}$	6.652 689 821 315 019	7.277 716 425 678 5	7.902 738 746 225 69	8.527 757 740 487 65
$\left\langle r_{12}^2\right\rangle$	0.053 398 153 770 902	0.044 587 585 188 31	0.037 790 569 578 939	0.032 437 179 414 918
$\langle \delta(r_1) \rangle$	398.532926	520.066 902	664.094 15	832.524 55
$\langle \delta(r_{12}) \rangle$	48.527 830 398 735	63.468 577 710 913	81.198 666 080 277	101.956 827 921 204
η	4.78×10^{-21}	5.46×10^{-22}	5.46×10^{-22}	3.93×10^{-22}
ν_{31}	-10.999 999 7 P^{13+}	-11.999 999 7 S^{14+}	-12.999 999 7 Cl^{15+}	-13.999 999 7 Ar^{16+}
Expectation Value	0.102 569 153 766 943 1	0.096 004 138 194 073 8	0.090 228 996 519 663 6	0.085 109 261 715 179
$\langle r_1 \rangle$ $\left\langle r_1^{-1} \right\rangle$	14.687 497 512 252 545 6	15.687 497 821 690 245 1	16.687 498 076 788 450	17.687 498 289 564 019 5
$\left\langle r_{1}^{2}\right\rangle$	0.014 072 873 510 907	0.012 326 442 221 612	0.010 886 037 250 214	0.009 684 119 549 269 3
$\langle r_{12} \rangle$	0.149 690 648 009 823 7	0.140 102 895 398 260	0.131 669 462 386 735 6	0.124 193 715 644 530
$\binom{r-1}{12}$	9.152 774 100 419 603	9.777 788 338 501 332	10.402 800 842 381 50	11.027 811 910 703 449
$\langle r_{12}^2\rangle$	0.028 145 747 021 815	0.246 528 844 432 2	0.021 772 074 500 429	0.019 368 239 098 538 7
$\langle \delta(r_1) \rangle$	1027.26794	1250.234 19	1503.333 15	1788.474
$\langle \delta(r_{12}) \rangle$	125.981 795 648 139	153.512 301 675 576	184.787 078 418 042	220.044 858 290 089
η	2.95×10^{-22}	2.17×10^{-22}	1.62×10^{-22}	-2.82×10^{-22}
ν_{31}	-14.999 999 7	-15,999 999 7	-16.999 999 7	-17,999 999 7

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(e) Behaviour Near Z-Critical

For $Z < Z_C^{HF}$, the ground state becomes unstable against electron detachment. The convergence of the variational atomic energy as a function of the number of terms degrades only slowly as the nuclear charge approaches Z_C^{HF} . In fact, at Z=0.85 the HF energy is still converged to 7-8 significant figures, but as Z decreases further the convergence deteriorates rapidly as shown in Table [6.](#page-12-0) Furthermore, the convergence of the bound state properties deteriorates much more rapidly than the energy, to the extent that for $Z = 0.80$ the expectation values are erratic and basis-size dependent. However, for $Z \geq 0.85$ the data appears to converge.

Table 6. Energy and radial expectation value convergence for low, non-integer, nuclear charge Z as a function of basis set size m compared to helium, where bold digits represent converged digits. The threshold energy E_{th} for each system is also provided. All energies and radial expectation values in a.u. (i.e. hartree and bohr).

Ζ	E_{th}	m	E_{HF}	$\langle r_1 \rangle$	$\langle r_{12} \rangle$
$\overline{2}$	-2	12	-2.861 679 995 536	0.927 273 403 133	1.362 124 380 627
		16	-2.861 679 995 612	0.927 273 404 727	1.362 124 383 668
		20	-2.861 679 995 612	0.927 273 404 731	1.362 124 383 676
Z_C^{HF}	-0.531663547	12	-0.531 663 542 501	2.372 690 028	3.537 391 966
$=1.031$ 177 528		16	-0.531 663 546 953	2.372 691 771	3.537 395 323
		20	-0.531 663 547 396	2.372 691 816	3.537 395 411
$\mathbf{1}$	-0.5	12	-0.487 929 728 147	2.503 956 640	3.739 268 219
		16	-0.487 929 734 257	2.503 959 062	3.739 272 889
		20	-0.487 929 734 369	2.503 959 636	3.739 273 998
Z_C^{FC}	-0.414986212	12	-0.373 906 208 969	2.988 986 931	4.493 907 504
$= 0.911$ 028 224		16	-0.373 906 226 807	2.989 002 458	4.493 937 611
		20	-0.373 906 227 545	2.989 003 842	4.493 940 297
0.9	-0.405	12	-0.360 888 381 644	3.065 294 750	4.614 076 439
		16	-0.360 888 402 143	3.065 313 178	4.614 112 237
		20	-0.360888403143	3.065 315 315	4.614 116 388
0.85	-0.36125	12	-0.304 973 717 153	3.487 529 820	5.288 177 405
		16	-0.304 973 760 265	3.487 705 173	5.288 517 822
		20	-0.304 973 765 993	3.487 732 757	5.288 571 638
0.80	-0.32	12	-0.254 204 267 742	4.213 237 569	6.507 070 336
		16	-0.254217315751	5.130 527 896	8.313 287 004
		20	-0.254245116965	6.474 496 685	10.968 420 616

Intuitively, it is reasonable to expect that the outer electron moves to infinite distance becoming unbound at the critical point, leaving behind a hydrogenic 1s electron. However, it was shown previously for the fully-correlated system with infinite mass that for $0.910 \leq Z \leq Z_C^{FC}$ the outer electron remains localized at a finite distance from the nucleus [\[26\]](#page-15-15). For $Z\,{<}\,Z_C^{FC}$ it was surmised that the quasibound particle can tunnel through the barrier, formed by a combined effect of the long-range Coulomb repulsion and short-range polarization attraction, and escape to produce a shape resonance [\[26\]](#page-15-15). A similar localisation behaviour near the nucleus was indicated in our own work [\[18\]](#page-15-7) (despite our wavefunction being constrained to be symmetrical in the two electrons, as in the present work); it was also shown that this feature near $Z = Z_C^{FC}$ was independent of the nuclear motion.

Gridnev has studied this behaviour mathematically in great detail [\[35\]](#page-15-24). He has proven that the bound state, as it approaches the threshold, does not spread and eventually becomes the bound state at threshold, i.e. the Hamiltonian has an eigenstate even when $Z = Z_C^{FC}$ and the wavefunction does not spread [\[35\]](#page-15-24). In the case when the charge is exactly equal to the critical value the wave function decays exponentially according to the law $Ae^{-B\sqrt{r}}$, where A and B are constants and r is the distance from the nucleus to the outer electron [\[36\]](#page-15-25). This is to be compared to the standard decay law $A\mathrm{e}^{-B r}$, when the binding energy is not zero.

Figure [1](#page-13-0) shows the expectation value of the nucleus-electron distance and the electron-electron distance using the HF wavefunction, as a function of nuclear charge Z. Also, shown (vertical dotted line) is the position of the critical nuclear charge Z_C^{HF} . There is no change in behaviour as Z passes through the critical point, the point at which the energy becomes greater than the lowest continuum threshold and thus corresponds to electron detachment. Given that the electronic motions are statistically independent and uncorrelated in the HF method, and that in the present work both electrons are constrained to the same spatial "orbital", it is perhaps not surprising that the wavefunction is unable to capture the physics of the electron detachment process. However, if we assume that the poor convergence at $Z < 0.85$ and large erratic radial expectation values reflects the inadequacy of the wavefunction to model one of the electrons moving to infinite distance as it becomes unbound (c.f. $[18]$), it would indicate that the mean-field approach allows the detaching electron to remain quasi-bound for a significant finite length scale. This exploratory result warrants further rigorous investigation.

Figure 1. The expectation value of the nucleus-electron distance $\langle r_1 \rangle$, and the electron-electron distance $\langle r_{12} \rangle$, as a function of nuclear charge, Z. The HF critical nuclear charge value is shown by the vertical red dotted line.

4. Conclusion

The HF method has been implemented using a Laguerre-based wavefunction. This implementation is used to study the ground state of two-electron atoms and ions within the clamped nucleus approximation. By exploiting the properties of the Laguerre polynomials, which are orthogonal on the interval $[0, \infty)$ with an exponential weight function, the oneelectron equations are solved by series solution method and the two-electron integrals are solved analytically. It is found that a 20-term wavefunction with a single variational parameter is sufficient to provide extremely accurate energies (accurate to the pico-hartree or better for $Z = 2$ to 18, to one tenth of a nano-hartree for $Z = 1$, and to one hundredth of a μ -hartree for the critical nuclear charge systems), and the wavefunctions are shown to provide accurate nucleuselectron cusps and expectation values of the interparticle distances for all systems considered. These HF energies, along with energies calculated using a wavefunction that depends explicitly on the inter-electronic distance, were used to calculate accurate correlation energies. Of particular interest was the critical nuclear charge for which a two-electron system remains bound. Bound state properties of both the HF critical nuclear charge and the fully-correlated critical nuclear . rsta.royalsocietypublishing.org Phil. Trans. R. Soc0000000

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charge systems were calculated using the HF method. The critical nuclear charge for the Hartree-Fock method was calculated by varying the nuclear charge Z until the ionisation energy was zero, and was found to be Z_C^{HF} = 1.031 177 528. This critical nuclear charge is greater than that of the hydride ion and reinforces the crucial role electron correlation effects play in stabilizing anionic systems. The radial behaviour near Z_C^{HF} was investigated and the results suggest that the nucleus-electron and electron-electron distances vary smoothly with decreasing Z indicating that the electrons, in a mean-field potential, remain quasi-bound for $Z \geq 0.85$. A more detailed study of the variational wave function at and below the critical point, for both the correlated FC method and the uncorrelated HF method, should shed more light on the behaviour of these systems. In particular, a stability analysis of the HF wavefunction will be performed to test for stability both internally and externally (i.e. with some constraints removed) [\[37\]](#page-16-0). This further work is under-way.

Supplementary Material

The Supplementary Material contains (i) energy convergence data as a function of basis set size and (ii) the HF wavefunction coefficients.

Data Accessibility. A Maple script containing all the HF wavefunctions can be accessed via the Dryad Digital Repository: doi:10.5061/dryad.fr34t

Authors' Contributions. AWK developed and implemented the HF code, ALB optimised it and calculated the HF critical nuclear charge for binding, HC conceived and devised the study. All authors contributed to the writing, critical reading, and approved the final version of the manuscript.

Competing Interests. The authors declare that they have no competing interests.

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