Critical Nuclear Charge for Two-Electron Atoms

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The critical nuclear charge Z_c required to bind a nucleus plus two electrons in a heliumlike atom has recently been an area of active study, resulting in a disagreement with earlier calculations and with the value obtained from the radius of convergence $1/Z^*$ of a $1/Z$ expansion of the energy. In order to resolve the disagreement, have performed high-precision variational calculations in Hylleraas coordinates. With the double basis set method, we have been able to obtain good convergence for Z very close to Z_c, which together with the Hellmann-Feynman theorem yields the value $Z_c = 0.911\,028\,224\,077\,255\,73(4)$, corresponding to $1/Z_c = 1.097\,660\,833\,738\,559\,80(5)$. This value is in agreement with the value obtained by Baker *et al.* [Phys. Rev. A **41**, 1247 (1990)]. A significant feature of the results is that the outer electron remains localized near the nucleus, even at $Z = Z_c$, and the bound state evidently changes smoothly into a shape resonance for $Z < Z_c$. A qualitative polarization potential is proposed to account for the resonance, and the radial distribution function for the electron density is calculated.

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The critical nuclear charge Z_c is the minimum charge required for an atomic system to have at least one bound state. For $Z < Z_c$, the ground state becomes unstable against electron detachment. For real physical systems, Z can only take on integer values, but there is great interest in studying the analytic properties of the function $E(Z)$, where E is the ground state energy and Z is a continuously variable parameter. At the outer fringes of stability near $Z = Z_c$, electron correlation effects play a crucial role in stabilizing the system, and from such studies one can learn about correlation effects in real physical systems. The passage from stability to instability can also be analyzed as a phase transition, as was emphasized by Kais and Shi [1].

Since hydrogenic atoms always have an infinity of Rydberg states, the simplest example is a heliumlike atom consisting of a nucleus of charge Ze and two electrons in a bound state. $Z = 2$ corresponds to neutral helium with an infinity of bound states, and $Z = 1$ to H^- which, as was proved by Hill [2,3], has only a single $1s^2\ ^1S$ bound state (the $2p^2\ ^3P$ state in the photodetachment continuum is also bound [4]). As Z is further reduced below $Z = 1$, one electron moves progressively further away until it becomes unbound at the critical value $Z_c \simeq 0.911$. At this point, the total nonrelativistic energy $E(Z)$ of the two-electron system is just the energy $E(Z) = -Z^2/2$ atomic units (a.u.) of the $1s$ core (assuming infinite nuclear mass). In constrast, the excited states become unbound at $Z = 1$, as studied by Katriel, Puchalski, and Pachucki [5].

Following early studies by Stillinger and co-workers [6–8], Baker *et al.* [9] performed extensive variational calculations to determine an accurate value for Z_c, and its relationship to the radius of convergence $\lambda^* = 1/Z^*$ for the $1/Z$ expansion

$$E(Z) = Z^2(E_0 + E_1/Z + E_2/Z^2 + \cdots). \tag{1}$$

Their work and subsequent analysis of the perturbation series by Ivanov [10] seemed to indicate that $Z^* = 0.911\,028$, and $Z_c = Z^*$ to within the accuracy of the calculation. However, recent calculations by Guevara and Turbiner [11] yielded the smaller value $Z_c = 0.910\,850$, in clear disagreement with Z^*. In addition, Zamastil *et al.* [12] obtained $Z^* = 0.9021$ from a new numerical analysis of only the first 20 coefficients (out of 400) of the perturbation series calculated by Baker *et al.* [9].

The purpose of the present work is to establish a definitive value for Z_c in order to resolve the existing contradiction in the literature, and to study the physical nature of the atomic system in the vicinity of Z_c. The early calculations by Stillinger [6–8] suggested that the system may persist as a bound state in the continuum, even for $Z < Z_c$. However, this possibility has been questioned by Reinhardt [13] in an analysis based on the complex rotation method. Our results indicate that the outer electron remains localized near the nucleus even for $Z = Z_c$, and that the system moves smoothly from a bound state for $Z > Z_c$ to a shape resonance just above threshold for $Z < Z_c$, in agreement with the analysis of [14] and [15].

In order to explore the behavior of the system for values of the nuclear charge Z very close to Z_c, we have performed high-precision variational calculations in Hylleraas coordinates to solve the Z-scaled Schrödinger equation for a two-electron atom with infinite nuclear mass

$$\left[-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z}\frac{1}{r_{12}}\right]\psi = \tilde{E}\psi, \tag{2}$$

where r_i is the electronic distance for electron i and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The Z-scaled atomic unit of distance is a_0/Z, where a_0 is the Bohr radius, and $\tilde{E} = E/Z^2$.

The multiple basis set method described by Drake [16,17] was used for the present calculations. This method has been used by Drake and co-workers to calculate high-precision eigenvalues for He, H^-, and Ps^- [18], and especially the higher-lying Rydberg states [19]. In the present work, calculations were performed in quadruple precision arithmetic with double and triple basis sets, using wave functions of the symmetrized form

$$\psi(r_1, r_2, r_{12}) = \sum_{p=1}^{q} \sum_{i,j,k}^{i+j+k\le\Omega_p} c_{i,j,k}^{p} [r_1^i r_2^j r_{12}^k e^{-\alpha_p r_1} e^{-\beta_p r_2} + r_2^i r_1^j r_{12}^k e^{-\alpha_p r_2} e^{-\beta_p r_1}], \quad (3)$$

with $q = 2$ for a double basis set and $q = 3$ for a triple basis set. For fixed values of the nonlinear parameters α_p and β_p, we calculate the optimized linear parameters $c_{i,j,k}$ by use of the inverse iteration method to find the eigenvalues. In addition, the energy is minimized with respect to all four (for a double basis set) or six (for a triple basis set) nonlinear parameters, the derivatives of the energy with respect to these parameters being calculated analytically. As a consequence of the optimization, the nonlinear parameters separate naturally into blocks corresponding to different length scales of the physical problem. For a double basis set, for example, the parameters α_1 and β_1 describe the asymptotic behavior of the first and second electron respectively, while α_2 and β_2 describe the short-range behavior of the first and second electron. This feature allows one to track separately the behavior of each electron at different distance scales, making the use of the multiple basis set method especially suited to an investigation of the critical nuclear charge problem where the length scales for the two electrons are very different.

The ground-state energy of the system was calculated for values of Z between 1 and 0.910 (Fig. 1). With a double basis set, we set $\Omega_2 = \Omega_1$ with the additional truncation $i + j + k + |i - j| \le \Omega_2 + 7$ for $p = 2$ (the short-range sector). The convergence of the variational atomic energy as a function of the number of terms in the basis set degrades only slowly when the nuclear charge is decreased. Extrapolation to an infinite basis set gives 16 significant digits at $Z = 1$ and 13 significant digits close to the critical point. In addition, because the bound state gets exceedingly close to the detachment threshold when the nuclear charge approaches the critical value, basis sets with increasing sizes are needed to see it. It was found that a significant improvement in the rate of convergence could be achieved with a smaller number of basis functions if a triple basis set was used with $\Omega_2 = \Omega_1$ and $\Omega_3 = \Omega_1 - 8$ (Fig. 2). The most accurate results close to the critical point were obtained with triple basis sets containing up to 2276 terms (Table I).

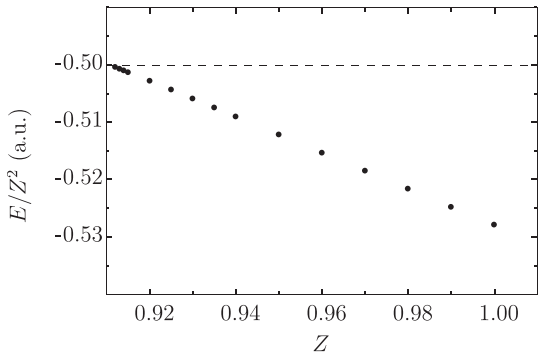

FIG. 1. Nonrelativistic atomic energy E (assuming infinite nuclear mass) for different values of the nuclear charge Z.

The variational calculation giving an upper limit to the true energy, the smallest value of Z at which the calculated energy lies below the detachment threshold gives an upper bound to the exact value of the critical charge Z_c. It was found by Baker *et al.* [9] that $Z_c < 0.911\,03$. As shown in Table I we find $Z_c < 0.911\,028\,224\,0773$, which is consistent with [9], but more restrictive.

A better determination of Z_c can, in principle, be obtained by extrapolation. In the work of Guevara and Turbiner [11], a set of nine values of the atomic energy calculated to 12 digits for values of Z between 0.95 and 1.35 was fitted to a Puiseux series with half-integer powers of $(Z - Z_c)$ to yield $Z_c = 0.910\,850$ (with no estimate of the uncertainty). The variational energies were calculated with the quasirandom method described by Korobov [20], with wave functions of the form $\sum_{i=1}^{N} c_i \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})$, where the nonlinear parameters α_i, β_i, and γ_i are chosen randomly from

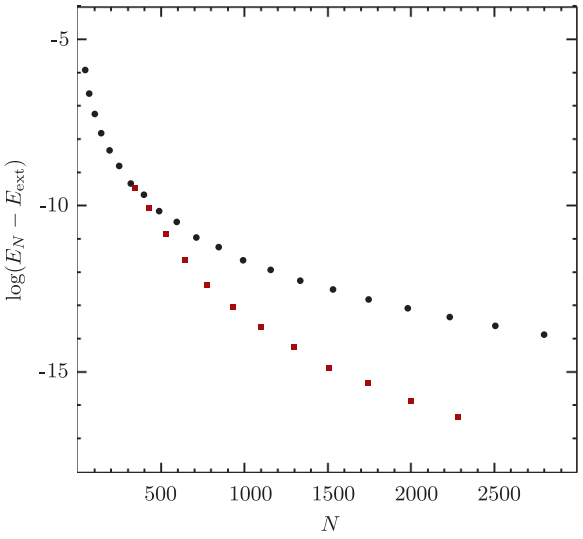

FIG. 2 (color online). Convergence behavior at $Z = 0.911\,028\,224\,0773$ for double (black circles) and triple (red squares) basis sets containing N functions (E_N is the variational energy from a set of N functions, $E_{\rm ext}$ the energy extrapolated to $N = \infty$).

specified intervals. The authors mention that the calculation could not be performed for $Z < 0.95$ due to a dramatic decrease in the rate of convergence below this point.

We do reproduce this result if we use the same data set and the same fit function, but we are also able to show that the accuracy of the above extrapolation is rather poor. Indeed, the multiple basis set method allows a much closer approach to the critical point, with the benefit of a more controlled extrapolation. A linear extrapolation using the first six points in Table I (where a bound state still exists) gives $Z_c = 0.911\,028\,224\,077\,255\,73(8)$. The uncertainty was evaluated by predicting the value of Z at the sixth point from a linear extrapolation using the other five points. Including higher powers of Z does not improve the accuracy. Another approach is to note that by the Hellmann-Feynman theorem

$$\frac{dE}{d(1/Z)} = \int \psi^* \frac{\partial H}{\partial(1/Z)} \psi dv = \left\langle \frac{1}{r_{12}} \right\rangle, \tag{4}$$

where H is the Hamiltonian of the system, ψ the wave function, and dv the volume element. Expression (4) can be evaluated with the variational wave function calculated at a given Z. At $Z = 0.911\,028\,224\,0773$, we obtain $dE/d(1/Z) = 0.245\,189\,0639(1)$. This value agrees with a direct evaluation of the slope from our data set, which gives $dE/d(1/Z) = 0.2452(1)$, in agreement with the value 0.245 obtained by Baker *et al.* [21]. Furthermore, the use of a linear extrapolation close to the critical point is substantiated by the Hellmann-Feynman theorem, together with the proof by the Hoffmann-Ostenhof's and Simon [22] that the wave function remains square integrable at the critical point, as was already pointed out by Baker *et al.* [9]. A linear extrapolation with the value of the slope obtained from the Hellmann-Feynman theorem yields $Z_c = 0.911\,028\,224\,077\,255\,73(4)$, or $1/Z_c = 1.097\,660\,833\,738\,559\,80(5)$, in agreement with the direct linear extrapolation but with a slightly smaller error bar. This is our final recommended value for Z_c.

TABLE I. Extrapolated nonrelativistic atomic energy E (assuming infinite nuclear mass) from a triple basis set including up to 2276 terms for different values of the nuclear charge Z.

Z (a.u.)	E/Z^2 (a.u.)
0.911 028 224 077 8	−0.500 000 000 000 160 79(1)
0.911 028 224 077 7	−0.500 000 000 000 131 25(1)
0.911 028 224 077 6	−0.500 000 000 000 101 71(1)
0.911 028 224 077 5	−0.500 000 000 000 072 17(1)
0.911 028 224 077 4	−0.500 000 000 000 042 64(2)
0.911 028 224 077 3	−0.500 000 000 000 013 08(1)
0.911 028 224 077 2	−0.499 999 999 999 983 54(1)
0.911 028 224 077 1	−0.499 999 999 999 954 00(1)
0.911 028 224 077 0	−0.499 999 999 999 924 46(1)

Finally, we find that well-defined eigenvalues continue to appear for $Z < Z_c$, corresponding to positive energies for the outer electron (Table I). Furthermore, the nonlinear parameter β_1 describing the asymptotic behavior of the outer electron does not tend to zero as $Z \to Z_c$, as would happen if the outer electron would move to infinity at the critical point. On the contrary, as shown in Fig. 3, β_1 still stabilizes to a well-defined value, independent of the size of the basis set and of its structure (double or triple). The fact that the outer electron remains characterized by a finite length scale at the critical point indicates that the wave function not only is square-integrable at this point, as was proven by the Hoffmann-Ostenhof's and Simon [22], but also remains localized at a finite distance from the nucleus.

These observations point to the existence of resonances induced by the shape of the atomic potential. In a simplified model, we consider the combination of a long-range Coulomb repulsion of the form $-(Z-1)/r$ and a short-range attraction due to the polarization of the core, corresponding to a charge-dipole interaction of the form $-\alpha_d/r^4$ (where α_d is the dipole polarizability, with $\alpha_d = 9/(2Z^4)$ for a hydrogenic ion [23]), resulting in the potential

$$V(r) = -\frac{Z-1}{r} - \frac{9}{2Z^4 r^4}. \tag{5}$$

Strictly speaking, the polarization model does not apply to an S state, due to the divergence of the $1/r^4$ operator in this

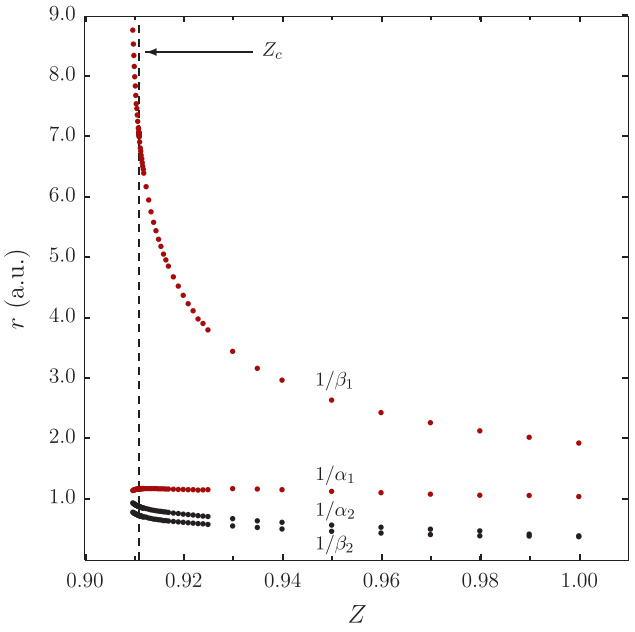

FIG. 3 (color online). Inverse nonlinear parameter r as a function of the nuclear charge Z for $0.910 < Z < 1$ (0.910 is the smallest value of Z at which β_1 still stabilizes to a well-defined value).

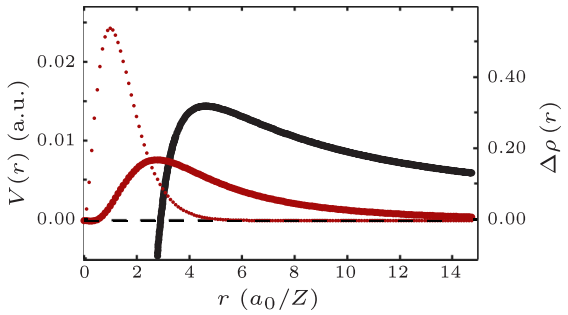

FIG. 4 (color online). Variation of the model potential $V(r)$ from Eq. (5) with $Z = 0.9$. Also shown is the electron density $\rho_{1s}(r)$ for a hydrogenic $1s$ electron (red dotted line), and the change in electron density $\Delta\rho(r) = 2\rho(r) - \rho_{1s}(r)$ (red solid line) due to the second electron (at $Z = Z_c$).

case. However, when this model potential is evaluated at $Z = 0.9$ (Fig. 4), it does exhibit a potential well with a peak around 5 a.u., in qualitative agreement with the distance scale found by the variational calculation (Fig. 3). Hence, we believe that this model potential supports the claim that for $Z < Z_c$ the system exhibits shape resonances just above threshold.

To further elucidate the electronic structure near the critical nuclear charge, we have calculated the radial electron density distribution function

$$\rho(r_1)dr_1 = r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|\mathbf{r}_1-\mathbf{r}_2|}^{r_1+r_2} r_{12} dr_{12} |\psi(r_1, r_2, r_{12})|^2 \tag{6}$$

at $Z = Z_c$, such that $\int_0^\infty \rho(r_1)dr_1 = 1$ is the complete three-dimensional normalization integral over both electrons. The results are included in Fig. 4. To show directly the effect of the outer electron on the density distribution, the quantity plotted is

$$\Delta\rho(r) = 2\rho(r) - \rho_{1s}(r), \tag{7}$$

where $\rho_{1s}(r)dr = r^2 dr|2e^{-r}|^2$ is the radial density distribution in Z-scaled atomic units for a hydrogenic $1s$ electron. Both curves are plotted in the figure for comparison. Since $2\rho(r) \simeq \rho_{1s}(r)$ for $r \ll 1$, the two terms nearly cancel in (7) and so $\Delta\rho(r)$ is very small near the nucleus. One might intuitively expect that $\Delta\rho(r) \to 0$ for all r as $Z \to Z_c$, corresponding to the outer electron moving out to infinite distance and becoming unbound, while leaving behind a hydrogenic $1s$ electron. The actual curve is profoundly different, with $\Delta\rho(r)$ remaining localized behind the potential barrier formed by the combined effect of the long-range Coulomb repulsion and short-range polarization attraction, as shown in the figure. The exponential decrease is consistent with Eq. (19) of Ref. [9]. For $Z < Z_c$, the quasibound particle can tunnel through the barrier and escape to produce a shape resonance in the elastic scattering cross section.

To conclude, we have shown that the multiple basis set method is especially suited to an investigation of the critical nuclear charge problem for two-electron atoms. From high-precision variational calculations with triple basis sets, together with the Hellmann-Feynman theorem, we obtain $Z_c = 0.911\,028\,224\,077\,255\,73(4)$ which is by far the most accurate value in the literature. It confirms the value found by Baker *et al.* [9] but excludes the value obtained by Guevara and Turbiner [11]. We also observe the transition of the system from a bound state to a shape resonance as the nuclear charge goes through the critical point. A simplified model potential is proposed to explain the formation of these resonances. A more detailed study of the structure of the variational wave function at and below the critical point, and the inclusion of mass polarization effects, should shed more light on the physical nature of the system in this region of parameter space. In addition, we now plan a new calculation of the coefficients of the $1/Z$ expansion.

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Note added in proof.—We have recently learned that Schwartz [24] has obtained a value for Z_c that agrees with ours to 12 significant figures.

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