

**Quantum critical benchmark for electronic structure theory**Paul E. Grabowski<sup>1,\*</sup> and Kieron Burke<sup>2,†</sup><sup>1</sup>*Department of Chemistry, University of California, Irvine, California 92697, USA*<sup>2</sup>*Departments of Chemistry and Physics, University of California, Irvine, California 92697, USA*

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Two electrons at the threshold of ionization represent a severe test case for electronic structure theory. Variational methods can yield highly accurate energies, but may be less accurate for other operators of interest. A pseudospectral method yields very accurate expectation values for the two-electron ion with nuclear charge at and close to the critical value which yields zero ionization energy. As an illustration, the ground-state density is calculated and an extremely accurate parametrization is given. Other components in Kohn-Sham density functional theory are also calculated, and the efficacy of approximations is discussed.

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**I. INTRODUCTION**

The value of highly accurate benchmark calculations to first-principles electronic structure theory cannot be overstated. While comparison with experiment is the ultimate arbiter of the usefulness of prediction, the ability to control and eliminate multiple sources of error with a direct solution of the Schrödinger equation allows pure “apples-to-apples” comparisons. The two-electron atom is one of the simplest nontrivial quantum systems and so serves as a common test problem for electronic structure methods, from early variational [1] and computer [2] calculations to more recent basis set comparisons [3] and ultrahigh-precision calculations [4–6]. The special case when the ionization potential is precisely zero, i.e., the nuclear charge  $Z_c$  is the smallest value that binds two electrons, is the simplest case of a quantum-critical electronic problem [7]. Such systems have been mapped to phase transitions in statistical mechanics [8]. In this limit, the electron positions are most strongly correlated with each other and the decay of the electron density is slowest, two issues that are difficult for electronic structure methods to handle. Recently, high-precision variational calculations have greatly expanded the accuracy to which  $Z_c$  is known [9], and strong-correlation methods have been tested on this system [10].

For many  $N$ -electron atoms, there exists a minimum  $Z_c = N - 1 - \nu$ , with  $0 < \nu < 1$ , such that the ground state of  $\hat{H}(Z)$  has positive ionization energy for all nuclear charges  $Z > Z_c$ . It is thought that  $\lambda_c = 1/Z_c$  corresponds to the radius of convergence of the perturbative solution of the two-electron atom with the perturbation being the electron-electron interaction  $1/r_{12}$  [11]. Baker and co-workers used 401 orders of perturbation theory to obtain  $Z_c = 0.911\,03$  [11] and Ivanov later used better extrapolation techniques on their data to get  $Z_c = 0.911\,028\,26$  [12]. From a direct variational calculation to solve for the critical charge, Sergeev and Kais obtained  $Z_c = 0.911\,028\,225$  [13]. Recently, Estienne and co-workers [9] obtained  $Z_c = 0.911\,028\,224\,077\,255\,73(4)$ , far surpassing the prior estimates in precision. We obtain  $Z_c = 0.911\,028\,224\,07(6)$ , agreeing with Ref. [9] and an unpublished

figure by Schwartz [14]. Although our  $Z_c$  is not as precise, our wave function is roughly as accurate as our value of  $Z_c$  (to about  $10^{-10}$  of the maximum, even in the tail). Variational expansions typically have half as many accurate digits of accuracy in the wave function as in the energy [15]. Beyond ground-state energy comparisons, the density and expectation values can provide detailed information for strengths and weaknesses of electronic structure methods. The pioneering work of Umrigar and co-workers [16,17] for several spherical atoms is a case in point. The availability of the Kohn-Sham (KS) potential and its eigenvalues was useful for all of density functional theory (DFT), and especially for the development of linear-response time-dependent density functional methods for finding excited-state energies, where the ground-state orbitals and energies are vital inputs [18,19].

In this article, we give a high-order expansion for the electron density at large  $r$  for all  $Z \geq Z_c$ , including fits for the ionization energy and the normalization factor. This information encodes the quantum critical transition. We give a highly accurate fit to the density for  $Z = Z_c$  for all  $r$ , as well as precise expectation values. We conclude with an example from DFT. Common semilocal energy functionals fail to capture the qualitative behavior of the correlation energy as  $Z \rightarrow Z_c$ , but this error is almost perfectly canceled by their exchange approximations. We explain this cancellation in terms of the locality of the exchange-correlation holes.

**II. METHOD**

Standard quantum methods typically have trouble calculating states near the ionization threshold because of their much more diffuse and, hence, spatially correlated wave function,  $\Psi$ , and the accidental mixing of energetically similar continuum states into the ground state. For example, diffusion Monte Carlo calculations take advantage of the separation in energy between the ground and excited states and fail to separate degenerate states. However, the pseudospectral method used here is a nonvariational collocation method in which the value of  $\Psi$  is calculated on a grid in such a way that the *local* error in  $\Psi$  becomes exponentially small with increasing grid resolution. We accurately calculate the bound state right on the threshold of the continuum by automatically selecting normalizable states. Thus our method is particularly well

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suited to produce benchmark expectation values for quantities not directly related to the energy at the critical value.

Pseudospectral methods [20] have their origins in fluid dynamics [21], where they are used to evolve systems without shocks because their convergence properties hold only for  $C^\infty$  functions. They have been extended to solving Einstein's field equations for colliding black holes by the excision of the singularities from the computational domain [22,23]. In quantum chemistry, Friesner and others have shown orders of magnitude improvement in speed for a wide variety of methods [24–32]. Direct solution of Schrödinger's equation has been performed for one-electron problems [33,34], but only recently has a sufficient representation of the computational domain been demonstrated for fully correlated, two-electron atoms [35,36]. We use the implementation of Ref. [36].

### III. ASYMPTOTIC BEHAVIOR AND DENSITY FIT

A difficult test for any method is the large- $r$  behavior of the density. As  $r \rightarrow \infty$ , for  $Z > Z_c$ , the well-known analysis of the exponential decay of the density [37] yields  $n(r) \rightarrow \exp(-2\sqrt{2I}r)$ , where  $I$  is the ionization energy. However, for  $Z = Z_c$ , the behavior differs qualitatively [ $n(r) \rightarrow \exp[-4\sqrt{2(1-Z_c)r}]$ ; note that  $r$  is inside the square root]. For low values of  $Z$ , the asymptotic value is not approached until very large  $r$ . So one must use higher-order expansions to connect the limits with our numeric results.

To analyze these results, we review well-known facts from KS DFT [38]. The KS equations describe fictitious noninteracting fermions sitting in a potential,  $v_s(\mathbf{r})$ , whose density matches the real one. For two spin-unpolarized electrons, one orbital is doubly occupied and the KS equation in atomic units is

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}), \quad (1)$$

where  $\phi = \sqrt{n(r)}/2$  and  $\epsilon = -I = E + Z^2/2$  are the KS orbital and its energy, respectively, while  $v_s(r)$  is the Kohn-Sham potential given by

$$v_s(\mathbf{r}) = -\frac{Z}{r} + v_h(\mathbf{r}) + v_x(\mathbf{r}) + v_c(\mathbf{r}). \quad (2)$$

For two electrons, the Hartree and exchange potentials are trivially related,

$$v_h(\mathbf{r}) = -2v_x(\mathbf{r}) = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

and the correlation potential is defined so as to make Eq. (1) exact. For large  $r$ , the exchange potential behaves as  $-1/r$ , while the correlation potential decays much faster as  $-\alpha/2r^4$ , where  $\alpha$  is the dipole polarizability of the  $N - 1$  system, here equal to  $9/2Z^4$  [16]. Amovilli and March [39] derived the asymptotic behavior of the density at large  $r$  for  $Z = 2$ . We extend their work to any  $Z > Z_c$  and to the next highest order in  $1/r$  by solving Eq. (1) order by order:

$$\sqrt{n_Z(r)} \sim \frac{x^\beta \sqrt{A_Z}}{e^x} \left[ \sum_{k=0}^4 \frac{a_k}{x^k} - \frac{3r^{-2}}{4Z^4} \sum_{k=1}^2 \frac{\tilde{a}_k}{x^k} + O(x^{-5}) \right], \quad (4)$$

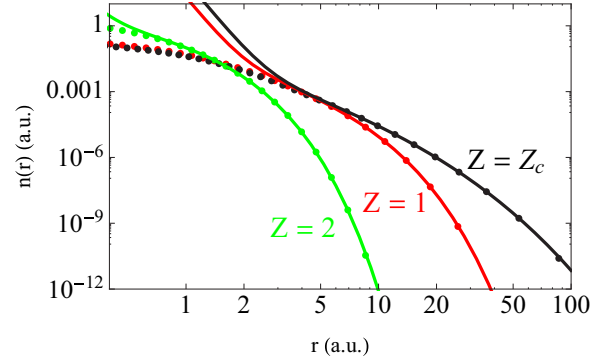


FIG. 1. (Color online) Exact (dots) and asymptotic ( $A_1 = 5.528 \times 10^{-3}$ ,  $A_2 = 1.517$ , and  $B = 0.1375$ ) densities (solid line) for  $Z = 1, 2$ , and  $Z_c$ .

where  $x = \eta r$ ,  $\eta = \sqrt{2I}$ ,  $\beta = \xi/\eta - 1$ , and  $\xi = Z - 1$ . The normalization factor  $A_Z$  is defined as  $A_Z = \lim_{r \rightarrow \infty} n_Z(r) e^{2x}/x^{2\beta}$ . The formula

$$A_Z = \alpha_1 \delta + \alpha_2 \delta^2 + \alpha_3 \delta^3, \quad (5)$$

with  $\delta = Z - Z_c$ ,  $\alpha_1 = 0.00667448$ ,  $\alpha_2 = 0.567102$ , and  $\alpha_3 = 2/\pi$ , fits our densities over the entire  $Z$  range to within 0.2%, with the maximum error occurring around  $Z = 1$ . The value of  $\alpha_3$  comes from the large- $Z$  limit of the density. Likewise,

$$I = \{1 + \beta_1 \exp[-\beta_2 \ln^2(\beta_3 \delta)]\}(\beta_4 \delta + \delta^2/2), \quad (6)$$

with  $\beta_1 = 0.0857048$ ,  $\beta_2 = 0.166941$ ,  $\beta_3 = 5.097253$ , and  $\beta_4 = 2(1/r_1)_{Z=Z_c} - Z_c = 0.24518901$  has a maximum error of 0.3% occurring around  $Z = 0.92$ . The coefficients in the large- $r$  expansion are given recursively as  $a_0 = 1$ ,  $a_k = -a_{k-1}[\xi - k\eta][\xi - (k-1)\eta]/(2k\eta^2)$ , and  $\tilde{a}_1 = 1$  and  $\tilde{a}_2 = -(\beta^2 + \beta + 3)/2$ .

At  $Z_c$ , the long-range behavior changes [10,39,40]. Here we extend such asymptotic forms to higher order:

$$\sqrt{n_{Z_c}(r)} \sim \frac{\sqrt{B}e^{-y}}{r^{3/4}} \left[ \sum_{k=0}^8 \frac{b_k}{y^k} - \frac{9r^{-2}}{4Z_c^4} \sum_{k=1}^4 \frac{\tilde{b}_k}{y^k} + O(y^{-9}) \right], \quad (7)$$

where  $B = \lim_{r \rightarrow \infty} n_{Z_c}(r) e^{2y} r^{3/2} \approx 0.1375$ ,  $y = 2\sqrt{2|\xi_c|r}$ ,  $\xi_c = Z_c - 1$ , and  $b_0 = 1$ ,  $b_k = -b_{k-1}(2k+1)(2k-3)/8k$ , while  $\tilde{b}_1 = 4/5$ ,  $\tilde{b}_2 = -17/10$ ,  $\tilde{b}_3 = 1107/224$ , and  $\tilde{b}_4 = -30489/1792$ . These asymptotic expressions are shown with our calculated densities in Fig. 1 for  $Z = Z_c, 1$  and  $2$ . See Appendix A for the errors in this expansion.

TABLE I. Parameters for Eq. (8) in atomic units.

$n_0$	0.23819008067	$B$	0.1375
$c_1$	0.0610986	$c_2$	0.0352145
$c_3$	-0.0494222	$c_4$	0.123575
$c_5$	-0.212456	$c_6$	0.308266
$c_7$	-0.328053	$c_8$	0.219550
$d_1$	$7.82582 \times 10^{-5}$	$d_2$	3.79484
$s$	4.19599		

TABLE II. Expectation values in atomic units. Uncertainties in the last digit(s) are given by the number in parentheses.

	$Z = Z_c$	$Z = 2$ (Ref. [36])
$\langle r_1^2 \rangle$	39.779 95(20)	1.193 482 995 30(16)
$\langle r_{12}^2 \rangle$	81.303 37(40)	2.516 439 313 8(6)
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$	-0.871 728 2(66)	-0.064 736 661 60(25)
$\langle r_1 \rangle$	4.146 972 44(58)	0.929 472 295 02(6)
$\langle r_{12} \rangle$	7.083 427 6(12)	1.422 070 255 93(38)
$\langle 1/r_1 \rangle$	0.578 108 619(11)	1.688 316 800 5(6)
$\langle 1/r_{12} \rangle$	0.223 374 112(19)	0.945 818 448 5(6)
$\langle 1/r_1^2 \rangle$	0.873 035 760 4(46)	6.017 408 866 1(36)
$\langle 1/r_{12}^2 \rangle$	0.085 788 151 9(80)	1.464 770 922 4(15)
$\langle 1/r_1 r_2 \rangle$	0.239 016 167(21)	2.708 655 473 6(20)
$\langle 1/r_1 r_{12} \rangle$	0.154 038 646(14)	1.920 943 921 1(13)
$\langle \delta(r_1) \rangle$	0.157 506 390 55(31)	1.810 429 318 2(12)
$\langle \delta(r_{12}) \rangle$	0.001 473 985 59(13)	0.106 345 370 53(33)

To make our results more immediately useful, we created a fit to the critical density:

$$n_{Z_c}(r) = \left[ n_0 e^{-2Z_c r} \left( 1 + \sum_{k=1}^8 \frac{c_k}{2k^{2/4}} r^{k+1} \right) + B \frac{r^3}{s^3 + r^3} \left( \frac{a}{\tilde{y}} \right)^3 \right. \\ \left. \times \frac{e^{-\tilde{y}}}{1 - \frac{3}{2\tilde{y}} + \frac{21}{8\tilde{y}^2} - \frac{87}{16\tilde{y}^3} + \frac{1755}{128\tilde{y}^4}} \right] \left[ 1 + \frac{d_1 r^{10}}{1 + d_2 r^{29/2}} \right], \quad (8)$$

where  $\tilde{y} = (2y)^4 / \sqrt{1 + (2y)^6}$ ,  $a = 4\sqrt{2|\xi_c|}$ ,  $n_0 = 2\langle \delta(r_1) \rangle$ , and the fit parameters ( $c_k$  and  $d_k$ ) are given in Table I. The short-range part is exact to first order in  $r$  and along with the long-range part contains higher-order corrections to order  $r^9$  by fitting to the pseudospectral density. The long-range part is chosen to reproduce Eq. (5) to order  $r^{-2}$  (second order), while the last term is a Padé approximant to the remaining error. Our numerical densities appear in Appendix B. We believe that there is great value in parametrizations that capture asymptotic limits, which is why we constructed our critical density in such detail. Analytic forms can be applied in almost any context, and guarantees of asymptotic correctness can be useful in testing methods.

TABLE III. Normalization and energy components (total, Hartree, Kohn-Sham kinetic, nuclear, correlation, and kinetic correlation) of the critically bound system in atomic units. Uncertainties in the last digit(s) are given by the number in parentheses.

	Pseudospectral	Fit
$N$	1.9999118	1.99757
$E$	-0.414 986 212 52(5)	
$E_H$	0.595 467(52)	0.595 038
$T_s$	0.389 857(17)	0.389 873
$E_n$	-1.053 346 537(20)	-1.053 176
$E_c$	-0.049 240(39)	-0.049 202
$T_c$	0.025 129(17)	0.0251 133

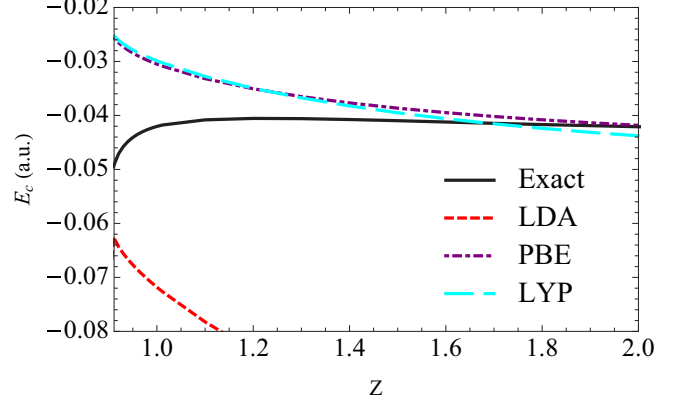


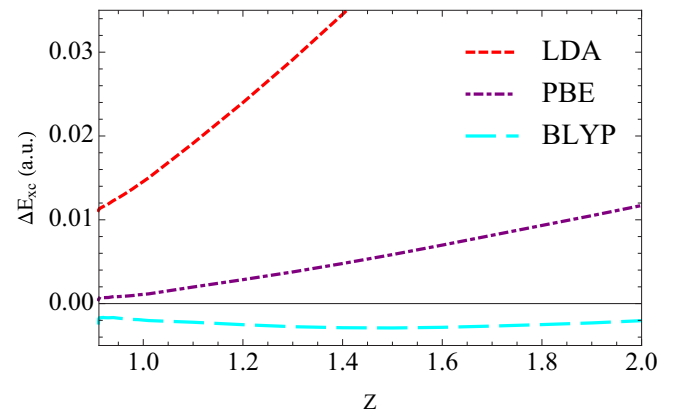
FIG. 2. (Color online) Exact and approximate correlation energies, evaluated with the exact densities.

#### IV. EXPECTATION VALUES

We give expectation values of some simple operators in Table II, compared to those for the helium atom. At  $Z_c$ , the two-electron atom is much fatter than for  $Z = 2$ . Furthermore, the two electrons are much more likely to be on opposite sides of the nucleus than for  $Z = 2$ , as the expectation value of  $\mathbf{r}_1 \cdot \mathbf{r}_2$  is more than an order of magnitude greater. We challenge any other method to match the precision of this table.

#### V. EXAMPLE BENCHMARKS FOR DENSITY FUNCTIONAL THEORY

To illustrate the usefulness of these results, we examine the behavior of the critical ion in KS DFT. For two unpolarized electrons, the ground-state energy and all exact KS energy components can be extracted directly from the density and external potential without solving an interacting problem by using the asymptotic decay of the density to determine the ionization potential and the virial theorem [16,41]. We perform this procedure here as a test of the accuracy of our densities. These energies are listed in Table III for  $Z = Z_c$  for both our pseudospectral density and our parametrized form [Eq. (8)]. The errors in the fit components are  $\sim 0.1\%$  or less.


 FIG. 3. (Color online) Error in approximations evaluated with the exact densities. For PBE at  $Z = Z_c$ , the error is 0.6 millihartree.

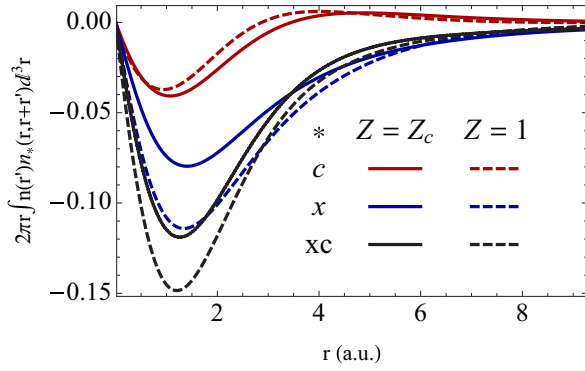


FIG. 4. (Color online) Exact density-weighted holes for  $Z = Z_c$  and 1. The magnitude of the exchange hole decreases as  $Z \rightarrow Z_c$ , allowing for the error cancellation.

Next, we illustrate the usefulness of our method in explaining the behavior of approximations to DFT. At first glance, this system appears as a disaster for commonly used approximations, since their self-consistent densities will not bind the electrons. However, this is solely due to failures in the approximate  $v_{xc}(\mathbf{r})$ , while the energy itself remains highly accurate [42]. Evaluation on the accurate density circumvents this (important) distraction. In Fig. 2, we show several common  $E_c$  functionals for the two-electron ions, showing how unusual this system is. The local-density approximation (LDA) usually overestimates  $E_c$  by a factor of 2–3 (as it does for He), but here is *more accurate* than the “better” generalized gradient approximations (GGAs) of Perdew, Burke, and Ernzerhof (PBE) [43] and Lee, Yang, and Parr (LYP) [44,45]. This is clearly due to the sharp dip in the exact curve which occurs only for  $Z \leq 1$ . This oddness is also reflected in the ratio of  $T_c/|E_c|$ , which is close to 1 for He, close to 0 for stretched  $H_2$ , but close to 1/2 at  $Z_c$ .

But DFT requires approximating both  $E_x$  and  $E_c$  simultaneously, and is notorious for cancellations of errors. In Fig. 3, we plot the exchange-correlation (XC) errors, showing a very different picture. The GGA’s are absurdly accurate, with errors that are far less than for  $E_x$  or  $E_c$  separately. How can

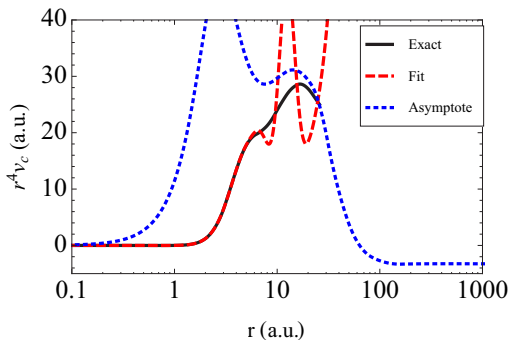


FIG. 5. (Color online) The correlation potential times  $r^4$  calculated with our numerical density (exact, black line), Eq. (8) (fit, dashed red line), and using the asymptotic form (7) for the local noninteracting kinetic energy and the fit for the exchange energy (dotted blue line). Only by combining the asymptote with our exact data can we extract the behavior for all  $r$ .

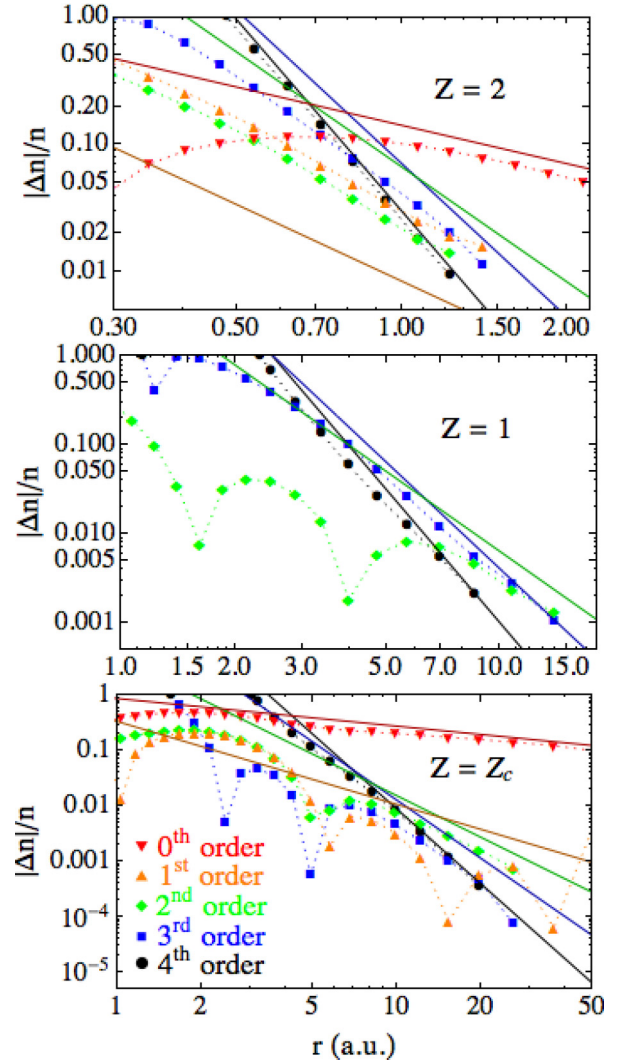


FIG. 6. (Color online) Relative error in the asymptotic densities [Eqs. (4) and (7)] compared to the exact densities (points) from zeroth to fourth order in  $1/r$ . The leading-order correction to these formulas is calculated with higher-order terms and plotted as dark solid lines, except for the fourth-order error which is made with a fit. These lines indicate whether or not the errors have reached the asymptotic regime. Note that for  $Z = 1$ , the zeroth, first, and second order are the same. There does not appear to be a general pattern. Deviations from limits at very large  $r$  are due to the limits in machine-precision arithmetic in calculating  $\Psi$  in the tail.

we understand this? The clue is in the LDA result, which is remarkably accurate. For large  $Z$  (even He),  $E_x/E_c \gg 1$ , so any cancellation is negligible. As  $Z$  reduces to  $Z_c$ ,  $E_x$  becomes much smaller, allowing a much greater cancellation. To see why this is so, in Fig. 4, we plot the system-averaged X, C, and XC holes of  $Z = Z_c$  and  $Z = 1$  [46]. The much smaller X hole at  $Z_c$  is much more greatly affected by the addition of the C hole, and the extent of the XC hole is much more short ranged than that of X (or C) alone. Bringing the XC hole inwards makes it more amenable to local approximation because of the accuracy of the on-top hole and cusp condition satisfied by LDA and PBE. This is why these approximations work unusually well for such a strongly correlated system.

TABLE IV. Density at the pseudospectral grid points and quadrature weights.

$r_j$ (a.u.)	$x_j$ (a.u.)	$n_j/Z_c^3$ (a.u.)	$w_j$ (a.u.)
0.0005759641912909017	0.9989511111039503	0.314682351915279	$4.660741235847267 \times 10^{-9}$
0.00303925808565137	0.9944775909292161	0.3132732840892592	$3.0300099503007153 \times 10^{-7}$
0.007489495670215863	0.9864461956515499	0.3107441016739011	$2.9066843483625716 \times 10^{-6}$
0.013959796221790716	0.9748838842217445	0.30710436909115857	0.000013877890940302966
0.02249735397316229	0.9598318269330866	0.3023689171597749	0.00004612340448161165
0.03316494107684804	0.9413438536413591	0.29655769404226007	0.00012288064229107963
0.046041970051123156	0.9194861289164246	0.28969610387322686	0.00028224923029420383
0.061225781649952314	0.8943368905344953	0.2818154628129142	0.0005832308520293945
0.07883324279239258	0.8659861628460676	0.27295353887455004	0.0011139006628788277
0.09900270777331016	0.8345354323267345	0.2631551627930131	0.0020025658396714803
0.12189640224230178	0.8000972834304684	0.252472896572073	0.0034331010464428006
0.147703303023036	0.7627949951937449	0.24096774168832766	0.005666131691016764
0.17664260478943944	0.7227620997499832	0.22870986212496724	0.009068430900444735
0.2089678872961224	0.6801419042271677	0.21577928855460538	0.014153905827555817
0.24497212550105105	0.6350869776952459	0.20226655892230294	0.021641025428937748
0.28499372130027406	0.5877586049795791	0.18827323726105366	0.032533717316659924
0.32942378214164697	0.5383262092858274	0.17391223683317283	0.04823599283798371
0.3787149317776135	0.48696674569809606	0.15930785598077488	0.07071540224691103
0.43339201631982543	0.4338640677187617	0.14459541626218037	0.10273774745849322
0.4940651706915445	0.3792082691160937	0.12992037421715608	0.1482066729138109
0.5614458450037321	0.32319500343480784	0.11543676326001442	0.21265904048506942
0.6363665691262939	0.2660247836050018	0.10130481511247609	0.30399399290119455
0.7198054734468116	0.20790226415636606	0.0876876171812794	0.43355629325257544
0.8129169082310087	0.14903550860694917	0.07474669189818135	0.6177628843571673
0.9170699472802668	0.08963524464890056	0.06263644690028392	0.8805726039488526
1.033897173471482	0.029914109797338766	0.05149755279322456	1.2572818945152056
1.1653569976191294	-0.029914109797338766	0.04144946858019295	1.800435561708559
1.3138139675134421	-0.08963524464890056	0.032582558170176246	2.5891630981063303
1.4821432470208165	-0.14903550860694917	0.02495051560492449	3.744155528864454
1.6738679412287918	-0.20790226415636606	0.018564108415709536	5.452097769788892
1.8933416121746534	-0.2660247836050018	0.013387488441818883	8.006263376861513
2.145993806251467	-0.32319500343480784	0.009338394879270824	11.875328334071545
2.4386647296695396	-0.3792082691160937	0.006293338088208658	17.822611142279463
2.7800680689846717	-0.4338640677187617	0.004097904475823055	27.117747215953976
3.1814412499350295	-0.48696674569809606	0.0025830926921683018	41.92262357320114
3.657475177082267	-0.5383262092858274	0.0015807827534237687	66.01620223603643
4.2276696497961455	-0.5877586049795791	0.0009415599134492133	106.20157190068788
4.9183526634276635	-0.6350869776952459	0.0005453042282610736	175.1405955662702
5.76576296728434	-0.6801419042271677	0.0003049997869381752	297.30896094699824
6.820887335531765	-0.7227620997499832	0.00016242082753832506	522.1176753124039
8.157294259937565	-0.7627949951937449	0.00008077588981359748	954.4527398959269
9.884289312564363	-0.8000972834304684	0.00003665063488089955	1830.417963708067
12.169963155779914	-0.8345354323267345	0.000014740319797992315	3719.7467675090556
15.28364511271759	-0.8659861628460676	$5.054109250994349 \times 10^{-6}$	8117.066837845993
19.678953431941505	-0.8943368905344953	$1.3947108874720773 \times 10^{-6}$	19366.157899552323
26.168717467688783	-0.9194861289164246	$2.8316551169626493 \times 10^{-7}$	51822.50322060266
36.329306394116436	-0.9413438536413591	$3.6357597278623005 \times 10^{-8}$	161516.57680062292
53.55560068801603	-0.9598318269330866	$2.2296122675325307 \times 10^{-9}$	622216.7754332445
86.30923308485625	-0.9748838842217445	$3.32223667644662 \times 10^{-11}$	$3.2798803957197545 \times 10^6$
160.8732228413056	-0.9864461956515499	0	$2.880656250507084 \times 10^7$
396.4320475486722	-0.9944775909292161	0	$6.724307713324147 \times 10^8$
2091.8996773448594	-0.9989511111039503	0	$2.2330122223506357 \times 10^{11}$

VI. CONCLUSIONS

We close with a clear illustration of the demands of this system, and the limits of even this method. Although the dependence of  $v_s(\mathbf{r})$  is notoriously sensitive to  $n(\mathbf{r})$ , a plot of  $v_c(\mathbf{r})$  for our fit density is indistinguishable from the numerical

result. But in Fig. 5, we show  $r^4 v_c(r)$ , which is known to approach  $-9/(4Z_c^4)$  as  $r \rightarrow \infty$ . Our numerical density is accurate just far enough (to  $r \approx 40$ ) to roughly meet the asymptote for  $v_c(r)$ , and suggests the final value is not reached even at  $r = 100$ . For this quantity, our fit fails around  $r \approx 8$ , despite the care in its construction.

In summary, we have shown that pseudospectral methods yield highly accurate densities, even at and near a quantum critical transition, allowing unprecedented evaluation of densities in the tail and of other position expectation values for such a situation. We have constructed high-order asymptotic forms for all  $Z \geq Z_c$  and used our densities to give accurate fits of the ionization energy and normalization factors in such expressions as a function of  $Z$ . A highly accurate fit for the critical density has been given to make this benchmark easier to use for other electronic structure theorists, and we demonstrate how this system can be used to evaluate and learn about errors with density functional theory examples. We have shown a remarkable cancellation of exchange and correlation errors for local and semilocal functionals at the critical density and explain this cancellation in terms of the exchange and correlation holes.

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#### APPENDIX A: ERRORS IN ASYMPTOTIC DENSITIES

We have given the asymptotic densities at large  $r$  for all  $Z \geq Z_c$  in Eqs. (4) and (7). These along with our fit to the normalization factors [Eq. (5) and  $B = 0.1375$ ] and ionization energies [Eq. (6)] are useful for checking the accuracy of the electronic structure of any two-electron atom. Although these are exact expressions (up to the fits), there is still the open question of how accurate each order is as a function of  $r$ . We answer this question in detail in Fig. 6 for  $Z = Z_c, 1$ , and 2. There is no easily discernible pattern other than that lower  $Z$  implies larger  $r$  for a given order. It is of note that the most well-known asymptotic form (the zeroth-order expression) is relatively slow to converge to the exact density. For example, at  $Z = Z_c$ , it still yields a 10% error at  $r = 50$  a.u.

#### APPENDIX B: RAW DENSITY DATA

In the main body of the paper, we gave a fit to our density at  $Z = Z_c$ . This fit gave DFT energies to 0.1% or

less. For those readers requiring more accuracy, we provide our best calculation of the one-electron density in Table IV. The accuracy of these data can be inferred from the value of our normalization in Table II, which is off by  $9 \times 10^{-5}$ . The majority of this error comes from the relatively large errors in the tail of the density. Since the weight for the density at the furthest-out nonzero value is about  $3 \times 10^6$ , the error in the density values is about  $3 \times 10^{-11}$ , comparable to the error in our value of  $Z_c$ .

In order to obtain a functional form that can be easily evaluated off the grid or used to calculate derivatives, one should construct the Cardinal functions,

$$C_j(x) = \prod_{k=1, k \neq j}^N \frac{x - x_k}{x_j - x_k}, \quad (\text{B1})$$

where  $x = (1 - Z_c r)/(1 + Z_c r)$  and  $N = 52$ , which have the property of being equal to one at one grid point and zero at all the others. The density at an arbitrary value of  $x$  can then be obtained by

$$n(x) = \sum_{k=1}^N n_j C_j(x). \quad (\text{B2})$$

The explicit values used for  $n_j$  are in Table IV (note that values in the table are divided by  $Z_c^3$ ).

Integration can be performed via quadrature. The values of  $x_j$  are the Gaussian quadrature points (roots of the 53rd-order Legendre polynomial). For example,

$$\int dr n(r) = \frac{1}{Z_c^3} \sum_{j=1}^N w_j n_j, \quad (\text{B3})$$

where the values of  $w_j$  can be found in Table IV. Note that the volume element  $4\pi r^2 dr$  and the conversion from the  $r$  coordinate to the  $x$  coordinate have already been taken into account by the values of  $w_j$ . Since the weights get rather large when  $r_j$  is big and the precision of the density is not very good in the tail, one should be careful about including such points in the quadrature. Usually some sort of truncation scheme is needed, chosen at a value of  $r$  such that contributions from larger  $r$  should be negligible.

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