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Abstract
We applied the finite-size scaling method using the B-splines basis set to construct the stability diagram for two-electron atoms with a screened Coulomb potential. The results of this method for two-electron atoms are very accurate in comparison with previous calculations based on Gaussian, Hylleraas and finite-element basis sets. The stability diagram for the screened two-electron atoms shows three distinct regions, i.e. a two-electron region, a one-electron region and a zero-electron region, which correspond to stable, ionized and double ionized atoms, respectively. In previous studies, it was difficult to extend the finite-size scaling calculations to large molecules and extended systems because of the computational cost and the lack of a simple way to increase the number of Gaussian basis elements in a systematic way. Motivated by recent studies showing how one can use B-splines to solve Hartree–Fock and Kohn–Sham equations, this combined finite-size scaling using the B-splines basis set might provide an effective systematic way to treat criticality of large molecules and extended systems. As benchmark calculations, the two-electron systems show the feasibility of this combined approach and provide an accurate reference for comparison.

(Some figures may appear in colour only in the online journal)

1. Introduction

Weakly bound systems represent an interesting field of research in atomic and molecular physics. The behaviour of systems near a binding threshold is important in the study of ionization of atoms and molecules, molecule dissociation and scattering collisions. Since the pioneering works of Bethe [1] and Hylleraas [2] confirming the existence of the negative hydrogen ion H^-, the study of the stability of the ground state of atomic and molecular negative anions becomes an active field of research. New phenomena appear when the Coulomb interaction is screened and the long-range electrostatic interactions turn to short-range potentials.

A simple model to describe the effect of the screening in the Coulomb potential is the Yukawa potential, where an exponential decay is introduced: $1/r \rightarrow \exp(-r/D)/r$, where D is a positive constant. The Yukawa potential has been used in many branches of physics, for example, to describe interactions in dusty plasmas where charged dust particles are surrounded by plasma [3], liquid metals [4] and charged colloidal particles [5]. Two-electron systems interacting via Yukawa potentials were the subject of recent research, studying the bound states using the Hylleraas basis set [6–10] and B-spline expansions [11]. Also, scattering processes were recently presented [12] using Yukawa potentials.

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To examine the near-threshold behaviour, the finite-size scaling (FSS) approach is needed in order to extrapolate results obtained from finite systems to the complete basis set limit. FSS is not only a formal way to understand the asymptotic behaviour of a system when the size tends to infinity, but a theory that also gives us numerical methods capable of obtaining accurate results for infinite systems by studying the corresponding small systems [13–24]. Applications include expansion in Slater-type basis functions [22], Gaussian-type basis functions [25] and, recently, finite elements [26].

Here, we combine FSS with the B-splines expansion to calculate the stability diagram for two-electron atoms with a screened Coulomb potential. The B-spline functions $B_i(r)$, $i = 1, n_s$, form a basis for piecewise polynomial functions that are polynomials of degree $(k_s - 1)$ in each interval and whose derivatives up to order $(k_s - 2)$ are continuous at the interior knots and have been increasingly used in atomic and molecular physics [27–31]. Our results show that the B-splines functions are very efficient in performing FSS to calculate the critical parameters and the stability diagram.

The rest of the paper is organized as follows. In section 2, we present FSS with a B-splines basis followed by the two-electron atom, as a benchmark calculation in section 3. In section 4, we present our main results for the screened two-electron atoms. Finally, in section 5, we discuss our results and conclusions.

2. Finite-size scaling with B-splines

Here, we briefly introduce the FSS (for more details, see [22]) and how to perform calculations using B-splines. The FSS method is a systematic way to extract the critical behaviour of an infinite system from an analysis on finite systems [22]. It is efficient and accurate for the calculation of critical parameters for a few-body Schrödinger equation.

In our study, we have a Hamiltonian of the following form:

$$\mathcal{H} = \mathcal{H}_0 + V_\lambda, \qquad (1)$$

where $\mathcal{H}_0$ is λ-independent term and V_λ is the λ-dependent term. We are interested in the study of how the different properties of the system change when the value of λ varies. A critical point λ_c will be defined as a point for which a bound state becomes absorbed or degenerate with a continuum. We also define a critical exponent α by the asymptotic behaviour of the ionization energy $E(\lambda) - \mathcal{E}_{th} \sim (\lambda - \lambda_c)^\alpha$, where we assume that the threshold energy $\mathcal{E}_{th}$ does not depend on λ. In the first example, the He-like atoms, we have only one parameter, λ while for the second case, the screened two-electron atoms, we have two parameters λ_1 and λ_2. To perform the FSS calculations, we expand the exact wavefunction in a finite basis set and truncate this expansion at some order N. The finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. The ground-state eigenfunction has the following expansion: $\Psi_\lambda = \sum_n a_n(\lambda)\phi_n$, where n is the set of quantum numbers. We have to truncate the series at order N,

and the expectation value of any general operator $\mathcal{O}$ at order N is given by

$$\langle \mathcal{O} \rangle^N = \sum_{n,m}^N a_n^{(N)} a_m^{(N)} \mathcal{O}_{n,m}, \qquad (2)$$

where $\mathcal{O}_{n,m}$ are the matrix elements of $\mathcal{O}$ in the basis set $\{\phi_n\}$.

In this study, we used the B-splines basis, the normalized one-electron orbitals are given by

$$\phi_n(r) = C_n \frac{B_{n+1}^{(k)}(r)}{r}, \quad n = 1, \dots, \qquad (3)$$

where $B_{n+1}^{(k)}(r)$ is a B-splines polynomial of order k. The numerical results are obtained by defining a cutoff radius R, and then, the interval $[0, R]$ is divided into I equal subintervals. B-spline polynomials [31] (for a review of applications of B-splines polynomials in atomic and molecular physics, see [33]) are piecewise polynomials defined by a sequence of knots $t_1 = 0 \leqslant t_2 \leqslant \cdots \leqslant t_{2k+I-1} = R$ and the recurrence relations

$$B_{i,1}(r) = \begin{cases} 1, & \text{if } t_i \leqslant r < t_{i+1}, \\ 0, & \text{otherwise,} \end{cases} \qquad (4)$$

$$B_{i,k}(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i,k-1}(r) \ (k > 1). \qquad (5)$$

In this work, we use the standard choice for the knots in atomic physics [33] $t_1 = \cdots = t_k = 0$ and $t_{k+I} = \cdots = t_{2k+I-1} = R$. Because we are interested in FSS, we choose an equidistant distribution of inside knots. The constant C_n in equation (3) is a normalization constant obtained from the condition $\langle n|n \rangle = 1$:

$$C_n = \frac{1}{\left[\int_0^{R_0} \left(B_{n+1}^{(k)}(r) \right)^2 \mathrm{d}r \right]^{1/2}}. \qquad (6)$$

Because $B_1(0) \neq 0$ and $B_{I+k-1}(R) \neq 0$, we have $N = I + k - 3$ orbitals corresponding to $B_2, \dots, B_{I+k-2}$. In all the calculations, we used the value $k = 5$, and we do not write the index k in the eigenvalues and coefficients.

To obtain the numerical values of the critical parameters (λ_c, α) for the energy, we define for any given operator $\mathcal{O}$ the function

$$\triangle_{\mathcal{O}}(\lambda; N, N') = \frac{\ln\left(\langle \mathcal{O}_\lambda^N \rangle / \langle \mathcal{O} \rangle_\lambda^{N'} \right)}{\ln(N'/N)}. \qquad (7)$$

If we take the operator $\mathcal{O}$ to be $H - \mathcal{E}_{th}$, and $\partial H/\partial \lambda$, we can obtain the critical parameters from the following function [22]:

$$\Gamma_\alpha(\lambda, N, N') = \frac{\triangle_H(\lambda; N, N')}{\triangle_H(\lambda; N, N') - \triangle_{\frac{\partial H}{\partial \lambda}}(\lambda; N, N')}, \qquad (8)$$

which at the critical point is independent of N and N' and takes the value of α. Namely, for $\lambda = \lambda_c$ and any values of N and N', we have

$$\Gamma_\alpha(\lambda_c, N, N') = \alpha. \qquad (9)$$

Because our results are asymptotic for large values of N, we obtain a sequence of pseudocritical parameters (λ_N, α_N) that converge to (λ_c, α) for $N \to \infty$.

3. Helium-like atoms

As a benchmark for FSS using B-splines, we calculate the critical parameters of the two-electron atom with a standard Coulomb potential. In this case, after a scaling with the nuclear charge, the system has a unique parameter $\lambda = 1/Z$:

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{1}{r_1} - \frac{1}{r_2} + \lambda\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}. \quad (10)$$

The ground-state energy $E_0(\lambda_1, \lambda_2)$ and its corresponding eigenvector $|\psi_0(1, 2)\rangle$ will be calculated within the variational approximation

$$|\psi_0(1, 2)\rangle \simeq |\Psi_0(1, 2)\rangle = \sum_{i=1}^{M} c_i^{(j)}|\Phi_i\rangle,$$

$$c_i^{(j)} = (\mathbf{c}^{(j)})_i; \quad j = 1, \ldots, M, \quad (11)$$

where $|\Phi_i\rangle$ must be chosen adequately and M is the basis set size.

Since we are interested in the behaviour of the system near the ground-state ionization threshold, we choose as a basis set the s-wave singlets given by

$$|\Phi_i\rangle \equiv |n_1, n_2; l\rangle = (\phi_{n_1}(r_1)\phi_{n_2}(r_2))_s \mathcal{Y}_{0,0}^l(\Omega_1, \Omega_2)\chi_s, \quad (12)$$

where $n_2 \leqslant n_1 \leqslant N$. Also, we introduce a cutoff value $l_{\max}$ for the angular momentum $l \leqslant l_{\max}$ and denote χ_s as the singlet spinor, and $\mathcal{Y}_{0,0}^l(\Omega_1, \Omega_2)$ are given by

$$\mathcal{Y}_{0,0}^l(\Omega_1, \Omega_2) = \frac{(-1)^l}{\sqrt{2l+1}}\sum_{m=-l}^{l}(-1)^m Y_{lm}(\Omega_1)Y_{l-m}(\Omega_2), \quad (13)$$

i.e. they are eigenfunctions of the total angular momentum with zero eigenvalue, and the Y_{lm}'s are the spherical harmonics. Note also that $\mathcal{Y}_{0,0}^l$ is a real function since it is symmetric in the particle index. The radial term $(\phi_{n_1}(r_1)\phi_{n_2}(r_2))_s$ has the appropriate symmetry for a singlet state:

$$(\phi_{n_1}(r_1)\phi_{n_2}(r_2))_s = \phi_{n_1}(r_1)\phi_{n_2}(r_2) + \phi_{n_1}(r_2)\phi_{n_2}(r_1). \quad (14)$$

In general, the size M of a basis set defined for equations (11)–(14) is $M = N(N+1)(l_{\max}+1)/2$. For the radial orbitals, we used normalized B-splines polynomial of order k

$$\phi_n(r) = C_n\frac{B_{n+1}^{(k)}(r)}{r}; \quad n = 1, \ldots, N = k + I - 3. \quad (15)$$

The calculations in this section were performed with $k = 5$, $R = 30$ and $l_{\max} = 3$.

In order to calculate the Hamiltonian matrix elements, we expand the electronic Coulomb interaction in spherical harmonics

$$\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} = \sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}\sum_{m=-l}^{l}Y_{l,m}^*(\Omega_1)Y_{l,m}(\Omega_2). \quad (16)$$

Because of the cutoff $l_{\max}$, the matrix elements of this expansion are nonzero only for $l \leqslant 2l_{\max}$.

In our previous studies, the critical behaviour of the two-electron atom was obtained by using the FSS approach with Hylleraas [34] and Gaussian basis sets [35]. The FSS was performed with a finite small basis set and then increased the number of basis functions N in a systematic way. The B-splines
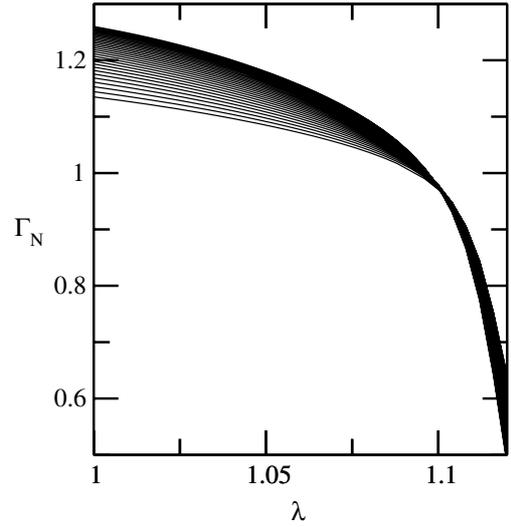

Figure 1. Γ_N versus λ for two-electron atoms, for $N = 20, \ldots, 50$.
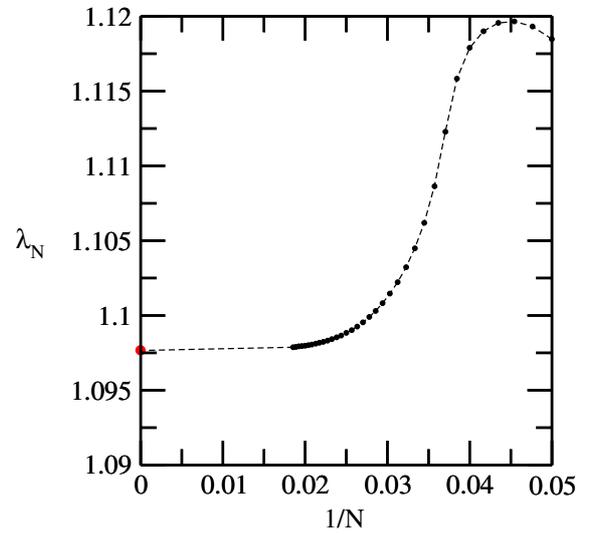

Figure 2. λ_N versus $1/N$ for $N = 20, \ldots, 55$ for the two-electron atom. The red point is the value of λ_c from [34].

Table 1. Comparison of λ_c and α for the ground-state energy of the two-electron atom.

	This work	FSS (Hylleraas) [22]	[37]	Exact
λ_c	1.097 76	1.0976	1.097 88	–
α	0.9947	1.04	–	1

basis set in this sense is different. When N is changed, we are not adding new functions, but the complete basis set is changed in a way which is similar to the finite-element method [36].

Figure 1 shows the results for the plot Γ_N as λ varies for different values of N. Successive curves cross at pseudocritical points. In figures 2 and 3, we observed the behaviour of the pseudocritical parameters, λ_N and α_N as a function of $1/N$. The two curves converged to the exact values, in complete agreement with our previous [17, 22, 25] and recent results [37]. The numerical values are shown in table 1. These accurate results indicate that FSS can be combined with B-spline basis
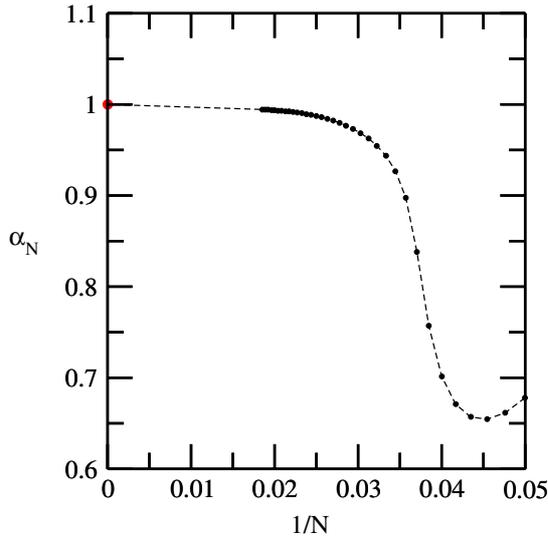
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Figure 3. Critical exponent α_N versus $1/N$ for $N = 20, \ldots, 55$ for the two-electron atom. The red point is the exact value $\alpha = 1$.
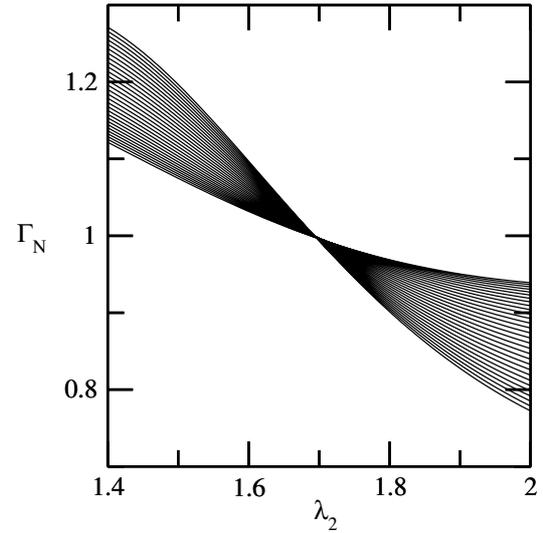

Figure 4. $\Gamma_N(\lambda_1 = 1.5; \lambda_2)$ versus λ_2 for the screened two-electron atom, for $N = 20, \ldots, 50$.

to obtain critical parameters for the few-body Schrödinger equation.

4. The screened two-electron atom

The Hamiltonian, in atomic units, takes the form

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{Z e^{-r_1/D}}{r_1} - \frac{Z e^{-r_2/D}}{r_2} + \frac{e^{-|\mathbf{r}_2 - \mathbf{r}_1|/D}}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{17}$$

where Z is the nuclear charge and $D > 0$ is the Debye screening length. The Hamiltonian takes a form more convenient for our purposes after scaling with D, $r \rightarrow r/D$ and $H \rightarrow D^2 H$:

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \lambda_1 \left(\frac{e^{-r_1}}{r_1} + \frac{e^{-r_2}}{r_2} \right) + \lambda_2 \frac{e^{-|\mathbf{r}_2 - \mathbf{r}_1|}}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{18}$$

where $\lambda_1 = ZD$, and $\lambda_2 = D$. The numerical results are obtained using the same basis set as the Coulomb case described in section 3, except the value of the cutoff radius, that for the Yukawa potential we set $R = 20$.

For the Yukawa potential, we use Gegenbauer's expansion in spherical harmonics:

$$\frac{e^{-|\mathbf{r}_2 - \mathbf{r}_1|}}{|\mathbf{r}_2 - \mathbf{r}_1|} = \sum_{l=0}^{\infty} 4\pi \frac{I_{l+1/2}(r_<)}{\sqrt{r_<}} \frac{K_{l+1/2}(r_>)}{\sqrt{r_>}}$$

$$\times \sum_{m=-l}^{l} Y^*_{l,m}(\Omega_1) Y_{l,m}(\Omega_2), \tag{19}$$

where $I_{l+1/2}$ and $K_{l+1/2}$ are the modified Bessel functions of the first and the second kind, respectively [38].

Since $\mathcal{E}_{th}$ does not depend on λ_2, we calculate the scaling function Γ_N for given values of λ_1 as a function of λ_2. Figure 4 shows the results for the plot $\Gamma_N(\lambda_1 = 1.5; \lambda_2)$ as λ_2 varies for different values of N. All of the curves cross very close to the critical point. In figure 5, we present the phase diagram for the screened two-electron atoms with three distinct phases:
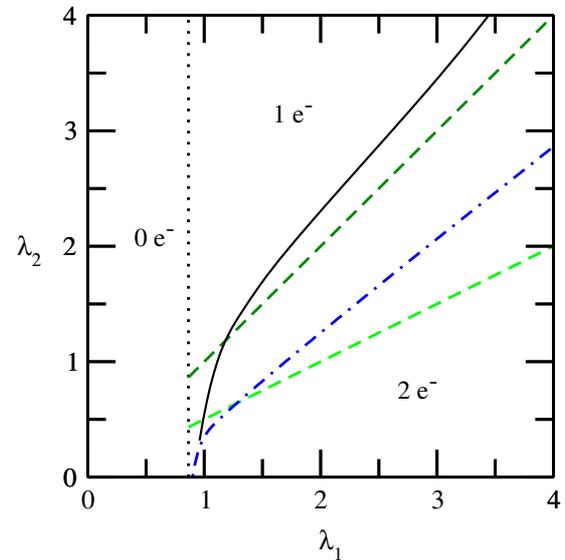

Figure 5. Ground-state stability diagram for the screened two-electron atom, the black line denotes the critical $2e^- - 1e^-$ line calculated with FSS with $N = 40$, the dotted line denotes the $1e^- - 0e^-$ critical line and the dashed blue line denotes the lower bound for the $2e^- - 1e^-$ line of [32]. The dot-dashed lines correspond to the helium (dark green) and hydrogen (light green) atoms, respectively.

the two-electron phase ($2e^-$), one-electron phase ($1e^-$) and zero-electron phase ($0e^-$), corresponding to stable, ionized and double ionized atoms, respectively.

The dotted line $\lambda_1 = \lambda_1^{(c)} \simeq 0.84$ corresponds to the critical value of the one-electron Yukawa potential. Therefore, there are no bound states for $\lambda_1 \leqslant \lambda_1^{(c)}$. For $\lambda_1 \gtrsim \lambda_1^{(c)}$, the one-body bound state is extended, and the method is applicable until the size of the one-body state becomes of the order of the cutoff radius R. For the value $R = 20$, we calculate the $1e^-$ stability line for $\lambda_1 \geqslant 0.95$.

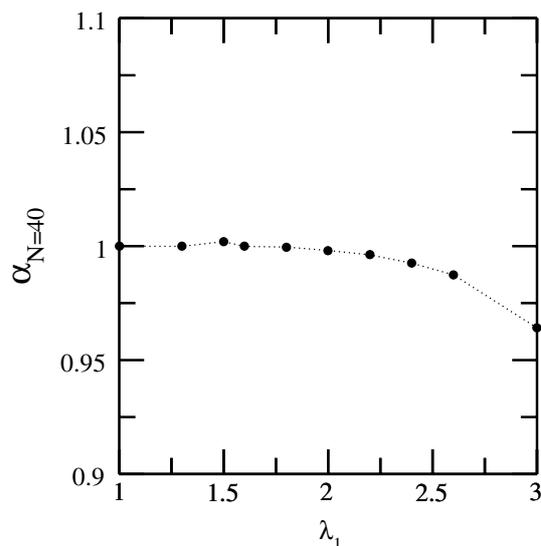The authors of [32] described the three different ground-state stability diagrams that a two-parameter Hamiltonian with

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Figure 6. Critical exponent α_N versus λ_1 for $N = 40$ for the screened two-electron atom. The exact value is $\alpha = 1$.

a short-range one-body potential could present. These cases are (see figure 1 of this reference) (a) no $2e^- - 0e^-$ line, (b) exists a finite $2e^- - 0e^-$ line for $0 \leqslant \lambda_2 \leqslant \lambda_2^{(mc)}$ and (c) the $2e^- - 0e^-$ line is infinite. Also in this reference rigorous lower and upper bounds for the $2e^- - 1e^-$ stability line are established. We calculate these bounds for the Hamiltonian equation (18). The lower bound is shown in figure 5. For the Yukawa potential, the upper bound diverges for $\lambda_1 \rightarrow \lambda_1^{(c)}$, and then, it is not useful in this case.

Even our results suggest that the ground-state stability diagram is of type (a). Large numerical instabilities could appear for $\lambda_1 \rightarrow \lambda_1^{(c)}$, and then, we can discard a type (c) diagram, but we can not discard a type (b) diagram with a small value of $\lambda_2^{(mc)}$.

We note that the H^- atom corresponds to the line $\lambda_2 = \lambda_1$ and the He atom to the line $\lambda_2 = \lambda_1/2$. These lines are also indicated in figure 5. The critical screening values for H$^-$ and He are $D_{H^-} \simeq 1.2969$ and $D_{He} \simeq 0.4934$, respectively.

In figure 6, we show how the critical exponent α^N versus λ_1 for $N = 40$ for the screened two-electron atom converges to the exact value, $\alpha = 1$ [32].

5. Summary and conclusions

We have shown that the introduction of B-spline basis sets in FSS calculations is very powerful in obtaining critical parameters and stability diagrams for few-body systems.

This basis set presents very different characteristics than the standard basis sets previously used in FSS-like Hylleraas or Slater-type basis sets. B-splines are non-zero only on a small interval, and changing the FSS parameter N (number of basis functions) changes the complete basis set. In particular, we used this basis set together with FSS to calculate the critical parameter of the helium-like atom as a benchmark, finding very accurate results. We then applied the method to the important case of the ground-state stability diagram for a two-electron atom interacting via a screened Coulomb potential. Also in this

case, FSS with a B-spline basis set proves to be an excellent approach to obtain the critical behaviour for this two-parameter Hamiltonian.

Our results show that the ground-state diagram of two-electron atoms interacting via Yukawa potentials does not present a $2e^- - 0e^-$ line. That is, the systems always undergoes a $2e^- - 1e^-$ transition before losing both electrons as the screening grows. Even the numerical results are not accurate enough to discard a small $2e^- - 0e^-$ line. We discard the existence of an infinite $2e^- - 0e^-$ line.

We have shown in previous works that FSS combined with different basis functions (Hylleraas, Gaussian, Slater) is a powerful method to obtain quantum critical parameters for few-body systems [22]. However, these basis sets are not useful to calculate critical parameters for large systems, or for quantum phase transitions in infinite systems. A possible way to apply FSS to study quantum phase transitions in materials is to combine FSS with Hartree–Fock or density functional approaches. In this direction, new efficient methods to solve the Hartree–Fock equations using B-splines expansions were recently established [39], and numerical codes are available [27]. As a benchmark system, we started with the two electron atoms. We show that indeed this can be done, and we obtained very accurate quantum critical parameters. Then, we went to a more difficult case, two-electron atoms with screened Coulomb potentials. Getting all of the stability and transition lines from two electrons to one electron to zero electrons is numerically difficult to calculate. We have shown that FSS with B-spline basis functions can construct the full stability diagram. Our work is in progress to calculate critical parameters for large i molecular and extended systems by applying FSS with B-spline expansions of Hartree–Fock equations.

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