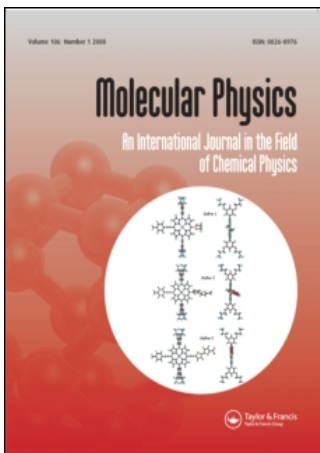


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## RESEARCH ARTICLE

### Finite size scaling with gaussian basis sets

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We combined finite size scaling method with the well-developed electronic structure methods, such as *ab initio* and density functional methods, to provide a systematic procedure for obtaining quantum critical parameters for atoms and molecules using Gaussian basis sets. The finite size scaling method is based on taking the number of elements in a complete basis set as the size of the system, to calculate the critical parameters for a given quantum system. We present results for the Yukawa potential and helium-like systems by expanding the wave function with a Gaussian basis. The finite size scaling approach was then used with the *ab initio* methods to find the critical parameters of two-electron atoms. The critical values of  $\lambda_c$  and  $\alpha$  were found to be 1.0578 and 1.0711 respectively using Møller–Plesset (MP2) level of theory. We then applied configuration interaction single and doubles excitation (CISD) to the helium system to improve upon the results. The critical parameters at the CISD level of theory were  $\alpha = 1.2891$  and  $\lambda_c = 1.1259$ . With time-dependent density functional theory (TDDFT) using the hybrid functional B3LYP resulted in  $\lambda_c = 1.0160$ . The *ab initio* results compare well with the exact results  $\alpha = 1$  and  $\lambda_c = 1.0971$ . The method is general and can be extended to calculate critical parameters for larger systems.

**Keywords:** Finite size scaling; Gaussian basis sets; Critical parameters

#### 1. Introduction

The behaviour of systems near the threshold, the separation of bound states from continuous states, is of great relevance to the behaviour of ionization in atoms and molecules, molecule dissociation, resonances and scattering collisions. The energy is non-analytical because a function of the system parameters or a bound state does not exist at the threshold energy. The study of quantum critical parameters is of increasing interest in atomic and molecular physics [1–5]. Phase transitions are associated with singularities of the free energy. These singularities occur only in the thermodynamic limit [6,7] where the dimension of the system approaches infinity. However calculations done are only on finite systems. A finite size scaling (FSS) approach is needed in order to extrapolate results from finite systems to the thermodynamic limit [8]. Finite-size scaling is not only a formal way to understand the asymptotic behaviour of a system when the size tends to infinity, but the theory also gives us numerical methods [9–16] capable of obtaining accurate results for infinite systems by studying the corresponding small systems.

Recently, we have developed finite size scaling for quantum systems [1,2,17–24]. In this approach, the finite size corresponds not to the spatial dimension, but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. This method is efficient and very accurate for estimating the critical screening length for one-electron screened Coulomb potentials [2], the critical nuclear charges for two-electron atoms [17,21] (which is in complete agreement with previous calculations [25,26]), three-electron atoms [18], critical conditions for stable dipole-bound anions [27], critical conditions for stable quadrupole-bound anions [28], simple diatomic molecules [29] and three-body Coulomb systems with charges ( $Q, q, Q$ ) and masses ( $M, m, M$ ) [30].

All of our previous finite size scaling calculations are done based on expanding the wave function in Hylleraas-type basis sets or more generally in Slater-type basis sets. In this paper, we will address the question of using Gaussian-type basis sets to perform finite size scaling calculations for criticality of atomic and molecular systems. This is very important

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in order to extend the finite size scaling calculations to large atomic and molecular systems.

In the following two sections, we will briefly review the finite size scaling method in quantum mechanics and the use of Gaussian basis sets in quantum chemistry calculations. In section 4, we will show how a Gaussian basis set can be used to obtain the criticality of the Yukawa potential. In section 5, we perform finite size scaling calculations for two-electron atoms using a Gaussian basis set and compare the results with the one using Hylleraas basis sets. In the last section we combined the finite size scaling method with standard *ab initio* methods and density functional methods.

## 2. Finite size scaling in quantum mechanics

In quantum mechanics, the finite size problem arises when looking at the critical behaviour of the Hamiltonian  $H(\lambda_1, \dots, \lambda_k)$ . The Hamiltonian is a function of its parameters  $\lambda_i$ . We are interested in values of  $\lambda_i$  that have bound state energies become non-analytical. This critical point is where the bound state becomes degenerate with the continuum. In this case the finite size corresponds to the number of elements in a complete basis set used to expand the exact wave function of the Hamiltonian [31]. The application of FSS to quantum mechanics concerns Hamiltonians with the form  $H = H_0 + V_\lambda$ , where  $H_0$  is the  $\lambda$ -independent term and  $V_\lambda$  is the  $\lambda$ -dependent term. We are interested to see the properties of the system as  $\lambda$  is varied, and assume that the Hamiltonian has a bound state for  $E_\lambda$  when  $\lambda > \lambda_c$  [32]. For quantum calculations the variation method is used to approximate the solution of the Schrödinger Equation [33]. For accurate results, the wave function is expanded in a complete basis set and the number of functions is taken to infinity. In practice, the expansion is truncated at order  $N$ . The ground state eigenfunction has the following expansion  $\Psi = \sum_n a_n \Phi_n$ , where  $n$  represents the set of quantum numbers. To approximate the different quantities, the series is truncated at order  $N$ . The Hamiltonian is replaced by a  $M(N) \times M(N)$  matrix, with  $M(N)$  being the number of elements in the expansion. The  $N$ th-order approximation for the expectation value of any operator  $O$  is then

$$\langle O \rangle^{(N)} = \sum_{nm} a_n^* a_n O_{nm}. \quad (1)$$

The expectation value of  $\langle O \rangle$  will be non-analytical at  $\lambda_c$ . The associated critical exponent  $\mu_0$  is defined by

$$\langle O \rangle_\lambda \underset{\lambda \rightarrow \lambda_c}{\sim} (\lambda - \lambda_c)^{\mu_0}. \quad (2)$$

However, the basis set is  $\lambda$  independent and  $N$  is finite, so it is easy to prove that any expectation value truncated at order  $N$  is analytical at the critical point  $\lambda_c$ . Just like in FSS for statistical mechanics, we assume an existing scaling function for the truncated magnitudes.

$$\langle O \rangle_\lambda^{(N)} \sim \langle O \rangle_\lambda F_O(N|\lambda - \lambda_c|^\nu). \quad (3)$$

with different scaling function  $F_O$  for different operators, but with the scaling exponent  $\nu$  being unique. With  $\langle O \rangle_\lambda^{(N)}$  being analytical at  $\lambda_c$

$$F_O \sim x^{-\mu_0/\nu}. \quad (4)$$

We can define the following function

$$o(\lambda; N, N') = \frac{\ln(\langle O \rangle_\lambda^{(N)} / \langle O \rangle_\lambda^{(N')})}{\ln(N'/N)}. \quad (5)$$

Then at the critical point  $\lambda_c$ , we obtain the equation for the ratio of the critical exponents

$$o(\lambda_c; N, N') = \frac{\mu_0}{\nu}, \quad (6)$$

which are independent of  $N$  and  $N'$ . Now for three different values of  $N$ ,  $N'$ , and  $N''$  the curves intersect at the critical point

$$o(\lambda_c; N, N') = o(\lambda_c; N'', N). \quad (7)$$

To obtain the critical exponent  $\alpha$  we can take  $O = H$  and  $\mu_0 = \alpha$ .

$$\Delta_H(\lambda_c; N, N') = \frac{\alpha}{\nu}. \quad (8)$$

Then by applying the Hellmann–Feynman theorem

$$\frac{\partial E_\lambda}{\partial \lambda} = \left( \frac{\partial H}{\partial \lambda} \right)_\lambda = \left( \frac{\partial V_\lambda}{\partial \lambda} \right)_\lambda. \quad (9)$$

We will now define the function  $\Gamma_\alpha$ :

$$\alpha(\lambda; N, N') = \frac{H(\lambda; N, N')}{H(\lambda; N, N') - \partial V_\lambda / \partial \lambda(\lambda; N, N')}. \quad (10)$$

The value of  $\Gamma_\alpha$  are independent of the values of  $N$  and  $N'$  at the critical point. Now the critical exponent  $\alpha$  is then

$$\alpha(\lambda_c; N, N') = \alpha. \quad (11)$$

These equations are valid only for the asymptotic limit  $N \rightarrow \infty$ , but for a finite basis set, values of  $\lambda_c$  can be obtained with a succession of values as a function of  $N$ ,  $N'$  and  $N''$ . The critical parameters are then obtained by a systematic extrapolation algorithm [31].

### 3. Gaussian basis sets

Modern quantum chemistry computations are generally carried out using mainly three types of basis sets: Slater orbitals, Gaussian orbitals, and plane waves, the last being reserved primarily for extended systems in solid state. Each of these has their advantages and disadvantages. The preferred type of functions in atomic and molecular computations are Slater-type functions due to their similarities to the atomic orbitals of hydrogen. The Slater-type orbitals (STO) are given by

$$\psi(\xi, n, l, m; r, \theta, \phi) = Nr^{n-1} \exp(-\xi r) Y_{lm}(\theta, \phi), \quad (12)$$

where  $(n, l, m)$  are integers,  $N$  is the normalization constant,  $r, \theta$  and  $\phi$  are the spherical coordinates, and  $Y_{lm}$  are the spherical harmonics. However, these STO do not allow for fast molecular calculations requiring the evaluation of many-centre two-electron integrals. To avoid the difficulty in computing molecular integrals, Boys suggested the use of the following functions [34]

$$g(\xi, l, m, n; x, y, z) = Nx^n y^l z^m \exp[-\xi(x^2 + y^2 + z^2)], \quad (13)$$

where  $N$  is the normalization constant and  $(n, l, m)$  are integers. The sum of the exponents  $L = n + l + m$  at the Cartesian coordinates designates the type of Gaussian that the function is. For example, s-type, p-type, d-type, and f-type is when  $L = 0, L = 1, L = 2$  and  $L = 3$  respectively, which is similar to the angular momentum quantum number. These functions are referred to as Gaussian functions. Notice that with Gaussian functions of d-type and higher, extra functions will be present. For d-type orbitals, there are six possible Cartesian Gaussians. If all six functions are to be used a 3s Gaussian function will be present since

$$3d_{xx} + 3d_{yy} + 3d_{zz} = N(x^2 + y^2 + z^2) \exp(-\xi r^2) = 3s. \quad (14)$$

For the f-type functions there are three spurious functions:  $4p_x, 4p_y$  and  $4p_z$ .

The use of these types of functions simplify the evaluation of molecular integrals significantly. All integrals needed for molecular computation can be done analytically. The drawback in using these functions concerns the accuracy of the calculations. The Gaussian functions are not as suitable for expanding the wave functions of atoms and molecules compared to Slater functions. To obtain better results, the use of a larger set of Gaussian functions are needed. When comparing Slater functions to Gaussian functions, the Slater functions of 1s, 2s, 3s, ... functions have the behaviour of  $\exp(-\xi r), r \exp$

$(-\xi r), r^2 \exp(-\xi r)$  respectively while all  $s$  Gaussian functions have the behaviour of  $\exp(-\xi r^2)$ . The  $p_z$  functions are all taken to be in the form  $z \exp(-\xi r^2)$ ; similarly all  $d_{xy}$  functions have the form  $xy \exp(-\xi r^2)$ . As a result of removing the  $r^{n-1}$  term, the Gaussian functions only approximate the 1s, 2p, 3d, 4f... orbitals. Even though the Gaussian functions have been limited, the functions are still sufficient even for higher atomic orbitals [35].

### 4. Finite size scaling for the Yukawa potential using Gaussian basis-set

This section will discuss using the finite size scaling ansatz to obtain the critical parameters for the Yukawa potential using a Gaussian basis and compare the results with an  $s$ -wave complete orthonormal basis set. The Hamiltonian (in atomic units) is given by

$$H(\lambda) = -\frac{1}{2} \nabla^2 - \lambda \frac{\exp(-r)}{r}. \quad (15)$$

The FSS ansatz was applied directly to calculate the critical parameters for this Hamiltonian. This approach assumes that the asymptotic behaviour of the mean values near the critical point have an explicit form. The critical parameters are then found by systematic expansion in a finite basis using an  $s$ -wave complete orthonormal basis set of the form [20]

$$n(r) = \frac{1}{[4\pi(n+1)(n+2)]^{1/2}} \exp\left(-\frac{r}{2}\right) L_n^{(2)}(r). \quad (16)$$

Due to the spherical symmetry of the potential, the exact ground state wave function only has a radial dependence, the basis functions with angular dependence will be orthogonal to the ground state wave function. Then, for potentials with spherical symmetry, instead of the basis set Equation (16) we are going to use only symmetric Gaussian functions

$$m(\beta; r) = C_m \exp(-\beta r^2/2) r^m. \quad (17)$$

The different functions are not orthogonal, but by using again the spherical symmetry we can use an orthonormal basis set that is a linear combination of functions Equation (17)

$$\phi_N(\beta; r) = \frac{1}{2^N [4\pi(2N+1)!]^{1/2}} \left(\frac{\beta}{\pi}\right)^{1/4} \times \frac{\exp(-\beta r^2/2)}{r} H_{2N+1}(\beta^{1/2} r), \quad (18)$$

where  $H_{2N+1}$  are the usual Hermite polynomials. These functions are orthonormal,  $(M|N) = \delta_{M,N}$ .

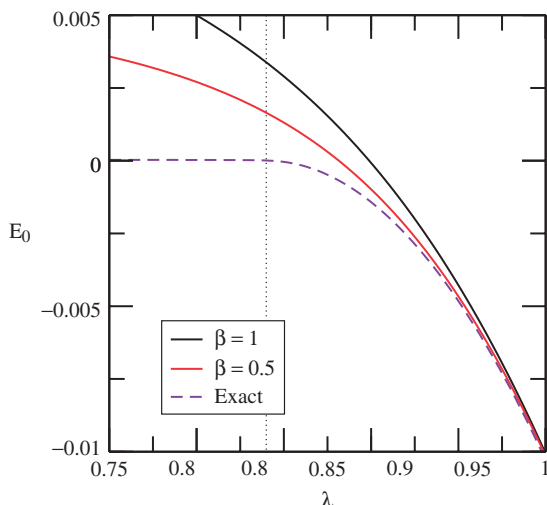


Figure 1. Ground state energy of the Yukawa potential as a function of  $\lambda$  for  $N = 100$ . The values obtained with  $\beta = 1$  and  $\beta = 0.5$  are compared with accurate values of the energy obtained from a 1500 Slater-type basis function expansion.

Now, we have to calculate  $\langle M|H|N\rangle$ ; the matrix elements for the kinetic energy are just the harmonic oscillator matrix elements. The potential energy matrix elements are more complicated, but they can still be calculated analytically.

We use FSS to calculate the critical parameters  $\lambda_c$  and  $\alpha$ . In order to compare with the values using Slater type orbitals as shown in [20,21], we did FSS calculations using Gaussian type functions with  $N=0, 1, \dots, 500$ .

We observed rather poor values near the threshold energy because of the use of Gaussian functions to approximate the exact wave function. The exact ground wave function decays slowly in comparison to the much faster decaying Gaussian functions. However, better near-threshold results are obtainable by adjusting  $\beta$  to a smaller value. Figure 1 shows the behaviour of the energies with  $\beta=0.5$  and  $\beta=1$  with the exact energy. The dashed vertical line in Figure 1 indicates where the threshold energy  $E_{\text{th}}(\lambda_c)=0$  occurs for  $\lambda_c \simeq 0.8399$ . Comparing the two values  $\lambda_c$  obtained with  $\beta=0.5$  and  $\beta=1$ ,  $\lambda_{100}(\beta=0.5) \simeq 0.865$  while  $\lambda_{100}(\beta=1) \simeq 0.899$ ;  $\lambda_{500}(\beta=1) \simeq 0.866$ . The accurate value of  $\lambda_c \simeq 0.839904$  [36] compared well with our FSS values  $\lambda_c^{100} \simeq 0.839\,903\,15$  and  $\lambda_c^{500} \simeq 0.839\,903\,88$ .

In Figure 2, we compared the behaviour of  $\Gamma$  as a function of  $\lambda$  with both Gaussian-and Slater-type functions. At the critical point ( $\lambda_c$ ),  $\Gamma$  is defined to be the critical exponent  $\alpha$  (Equation (10)). We observe that fewer Slater-type functions are needed to converge to the correct values of  $\lambda_c$  and  $\alpha$ . The Gaussian-type functions needed a larger  $N$  to converge to the correct values of  $\lambda_c$  and  $\alpha$ .

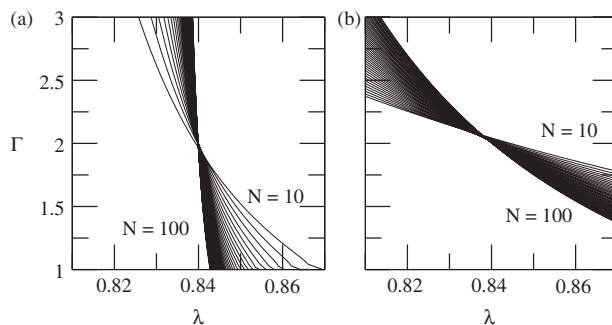


Figure 2. Finite size scaling calculations of the critical  $\lambda$  for the Yukawa potential using (a) Gaussian functions and (b) Slater functions.  $N$  is the number of functions and  $\Gamma$  is defined in such a way that one can read from the crossings the critical exponent  $\alpha$  for the energy and the critical value  $\lambda_c$ , see the text equation (10). The accurate value is  $\lambda_c = 0.839\,904$ .

The best values for  $\lambda^{(N)}$  and  $\alpha^{(N)}$  as shown in Figures 3 and 4 are obtained with  $\beta=1$ . As in previous papers [20,21], we also find a parity effect with Gaussian functions, therefore FSS equations are applied using  $N' = N + 2$ . As before, different curves are obtained for even and odd values of  $N$ . As shown in Figure 3, for  $\beta=1$  the upper (lower) curve corresponds to odd (even) values of  $N$ . A similar effect for  $\alpha$  is shown in Figure 4.

By switching to a Gaussian basis, we found that a large number of functions was needed to obtain good convergence. When we applied the Gaussian basis to a non-symmetric many-electron system we needed up to  $N \simeq 10$ . These results are very encouraging and show that one can use Gaussian basis sets to obtain critical parameters of the Yukawa potential.

## 5. Finite size scaling for the helium-like atoms using a Gaussian basis set

We have applied FSS to study the critical properties of two-electron atoms. The scaled Hamiltonian is given by

$$H(\lambda) = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \lambda \frac{1}{r_{12}}. \quad (19)$$

The basis set is a set of Gaussian functions symmetric in  $\mathbf{x}_1, \mathbf{x}_2$ , these functions are a complete set for  $s$ -waves

$${}_{i,j,k}(\beta; \mathbf{x}_1, \mathbf{x}_2) = C_{ijk} \exp(-\beta(u^2 + v^2)/2) u^i v^{2j} r_{12}^k, \quad (20)$$

where  $u = (r_1 + r_2)/2$ ;  $v = (r_1 - r_2)/2$ ;  $C_{ijk}$  is the normalization constant, and  $\beta$  is a free parameter. Note that these functions are symmetric. Antisymmetric wave functions are obtained using odd powers of  $v$ .

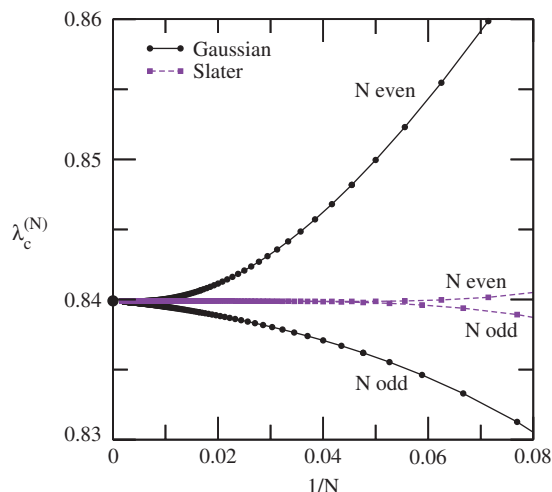


Figure 3.  $\lambda_c^{(N)}$  as a function of  $1/N$  for the Yukawa potential for both even and odd basis functions of Gaussian and Slater types.

FSS for this Hamiltonian were done in detail in [22] using the complete non-orthonormal Hylleraas basis set for  $s$ -waves

$$ijk(\mathbf{x}_1, \mathbf{x}_2) = C_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha r_1) \exp(-\beta r_2). \quad (21)$$

Gaussian basis-set Equation (20), as Hylleraas, are non-orthonormal and complete for  $s$ -waves. In order to make FSS calculations, we truncate the basis set at order  $N$ , where  $N = \max(i, 2j, k)$ , then the matrices are  $M(N) \times M(N)$ , with  $M(N) = ([N/2] + 1)(N + 1)^2$ . Now, we have to calculate the overlap  $\langle m|n \rangle$  and the Hamiltonian matrix  $\langle m|H|n \rangle$ . All the matrix elements could be calculated analytically.

In Figure 5 we show the energy versus the variational parameter  $\beta$  for  $\lambda = 0.5$  (He), for  $\lambda = 1$  ( $H^-$ ) and for the near-threshold value  $\lambda = 1.05$ , both calculated with  $N = 10$ . All the curves present a plateau for  $\beta \simeq (0.15, 0.6)$ , therefore the values of the energies are not very sensitive with  $\beta$ . In all the calculations we used  $\beta = 0.25$ .

In Figure 6 we compared the ground state energy  $E_0^{(N)}$  as a function of  $\lambda$  for  $N = 10$  using both the Gaussian and the Hylleraas basis sets. We obtain good values for the energy for small values of  $\lambda$ , but for the near-threshold behaviour the Hylleraas basis set gives a better result.

In many FSS calculations we found parity effects, which made taking  $N' = N + 2$  necessary. However parity effects were not reported for the helium atom in [22]. Strong parity effects are present in our calculations with the Gaussian basis set. It is possible that parity effects are present when using Hylleraas functions, but the effect was too small for

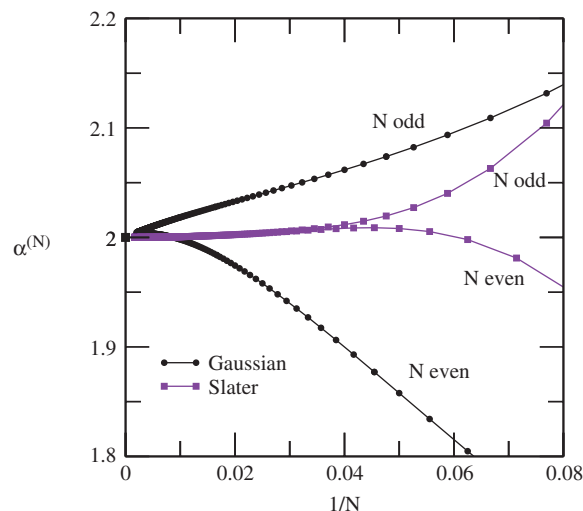


Figure 4.  $\alpha^{(N)}$  as a function of  $1/N$  for the Yukawa potential for both even and odd basis functions of Gaussian and Slater types.

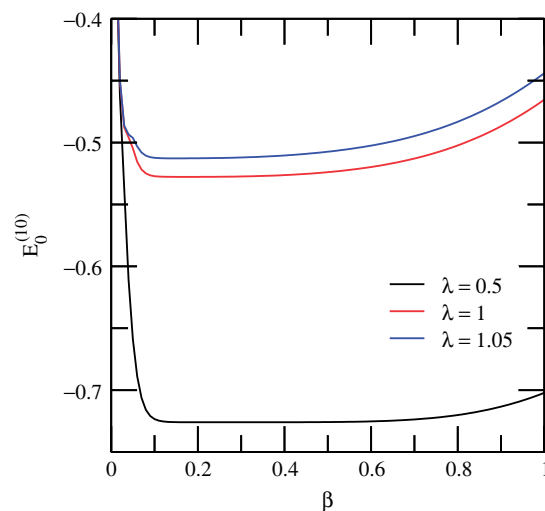


Figure 5. Ground state energy for the two-electron atom as a function of  $\beta$  for  $N = 10$  and three values of  $\lambda$ .

observation in this case. Therefore we calculated critical values using Equation (16) from [20] with  $N' = N + 2$ , and different curves are obtained for even and odd values of  $N$ . Figures 7 and 8 shows  $\Gamma$  as a function of  $\lambda$ . Figure 7 uses even values of  $N$ , while Figure 8 uses odd values of  $N$ .

In Figure 9, we observe the behaviour of  $\lambda^{(N)}$  as a function of  $1/N$ ; because of the parity effect the even and odd values of  $N$  are plotted separately. Once again there is a need for larger  $N$  to converge to the correct value of  $\lambda$ , which is the same behaviour as before from the Yukawa example.

In Figure 10, we plot the values of  $\alpha^{(N)}$  as a function of  $1/N$ ; once again because of the parity effect

the even and odd values of  $N$  are plotted separately. Just as before, we notice the need for larger values of  $N$  to converge for  $\alpha$ . The exact value is  $\alpha = 1$ . The results indicate that Gaussian basis sets can be used to obtain accurately the critical parameters for two-electron atoms.

## 6. Finite size scaling and traditional electronic structure methods

We have demonstrated that a Gaussian basis will indeed allow us to obtain the critical exponents needed for FSS calculations. Now, we are in a position to

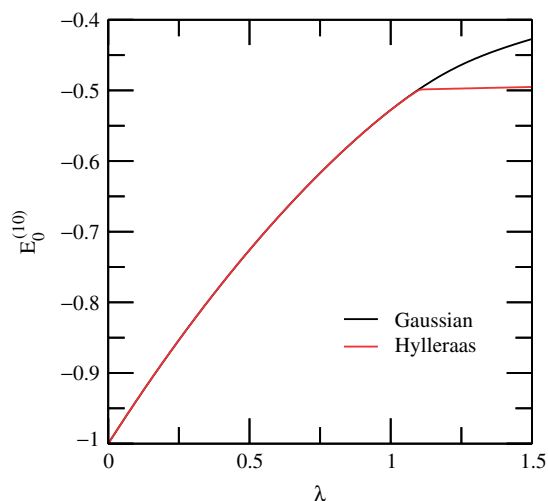


Figure 6.  $E_0^{(N)}$  as a function of  $\lambda$  for  $N = 10$  for the two-electron atom obtained with the Gaussian and the Hylleraas basis set.

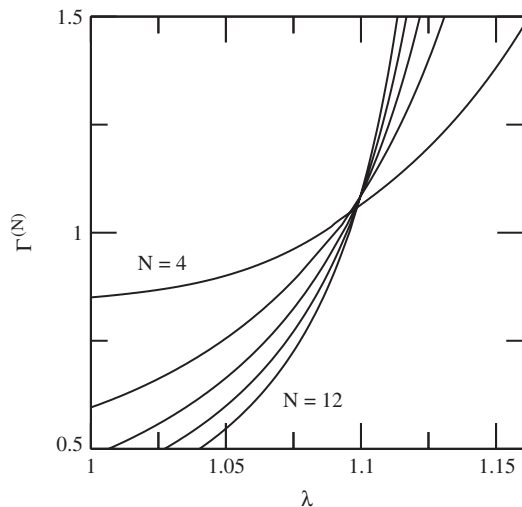


Figure 7.  $\Gamma^{(N)}$  as a function of  $\lambda$  for the two-electron atom with even values of  $N$  obtained with the Gaussian basis set.

propose a generalization of this method for larger systems. In order to calculate the matrix elements needed for finite size scaling one can use traditional electronic structure methods (depending on the complexity of the system) such as *ab initio* [37], density functionals [38] and density matrices [39,40], semi-empirical, quantum Monte Carlo [41–43], and electron propagator methods [44,45]. As an initial test, we consider the two-electron atoms. The basis set used is Dunning's correlation consistent basis set. These basis sets give results that can recover much of the correlation energy.

The selection of a convenient basis is a little more tricky for this system. We elected to use basis sets that are readily available to *ab initio* packages.

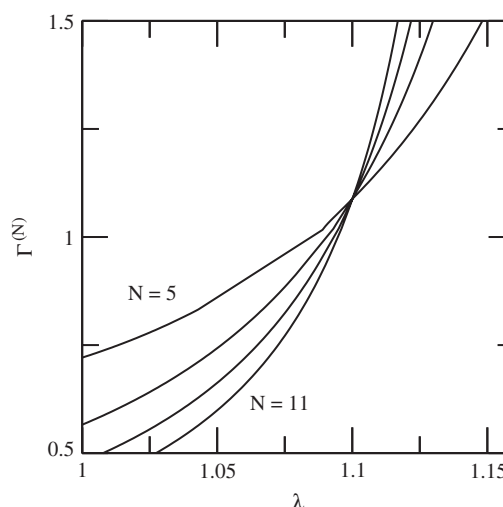


Figure 8.  $\Gamma^{(N)}$  as a function of  $\lambda$  for the two-electron atom with odd values of  $N$  obtained with the Gaussian basis set.

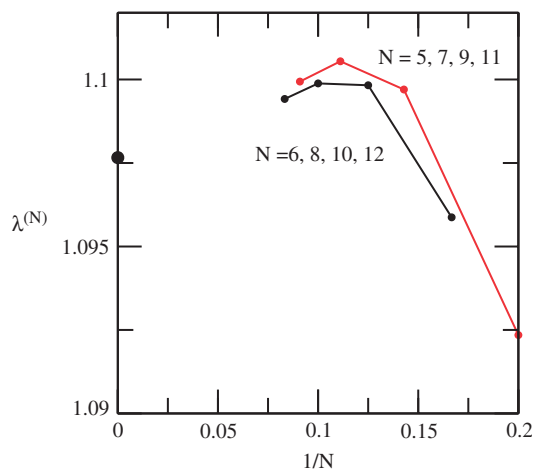


Figure 9.  $\lambda^{(N)}$  as a function of  $1/N$  for the two-electron atom obtained with the Gaussian basis set for even and odd values of  $N$ . The exact value 1.097 66 is showed by a dot.

We then chose the correlation consistent basis sets: aug-cc-pVTZ ( $N=4$ ), aug-cc-pVQZ ( $N=5$ ), aug-cc-pV5Z ( $N=6$ ) and aug-cc-pV6Z ( $N=7$ ) [46,47]. These basis sets were then chosen to be optimized for helium. The *ab initio* program that was used is PC GAMESS version 7.0 [48]. For the calculations, MP2, DFT(B3LYP) and CISD levels of theory were used.

Figure 11 shows  $\Gamma^{(N)}$  as a function  $\lambda$ . The exact  $E_0$  is also plotted using the Hylleraas basis set with  $N=10$ , and is compared with the value of  $E_0$  using

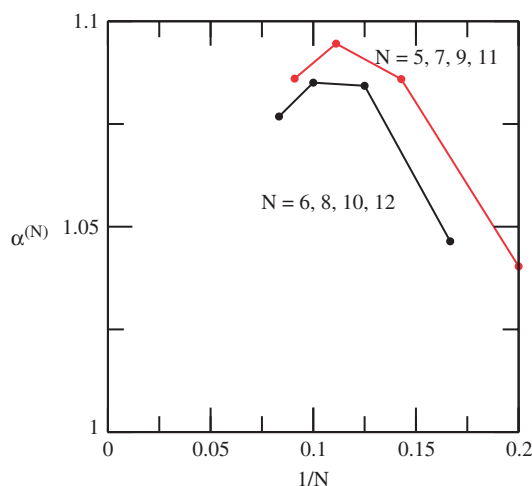


Figure 10.  $\alpha^{(N)}$  as a function of  $1/N$  for the two-electron atom obtained with the Gaussian basis set with even and odd values of  $N$ . The exact value is  $\alpha = 1$ .

MP2 level of theory with the correlation consistent basis set from  $N=4, \dots, 7$ . The energy of the exact results approach zero after  $\lambda_c$ . The results of MP2 indicate the  $\lambda_c = 1.0578$  and  $\alpha = 1.0711$ .

Next we used CISD to calculate for  $\Gamma$ . In Figure 12, the two highest values of  $N$  intersect at  $\lambda = 1.1259$  and with  $\Gamma = 1.2891$  at the intersection. The plot of  $\Gamma^{(5)}$  crossed the other to  $N$  values. Again we plot exact  $E_0$  using the Hylleraas basis set with  $N=10$  and compared the result of  $E_0$  with CISD using the correlation consistent basis set from  $N=4, \dots, 7$ .

For the DFT level of theory, we used a different equation [17] to obtain the value of  $\lambda_c$ . The ratio  $(E_1/E_0)^N$  is plotted as a function of  $\lambda$  in Figure 13. The intersection of the lines predicted the value of  $\lambda_c$  to be 1.0160. We also plotted the exact  $E_0$  using the Hylleraas basis set with  $N=10$  and compared the result of  $E_0$  with DFT using the correlation consistent basis set from  $N=4, \dots, 7$ . The *ab initio* methods did not provide exact results, but predicted correctly that  $H^-$  is a stable anion. These results clearly indicate that one can use standard *ab initio* and density functional methods to perform finite size scaling calculations using Gaussian basis sets.

## 7. Discussion and future directions

We have shown the results for FSS using Gaussian-type functions for the Yukawa potential and results for the helium atom. We observed the following from

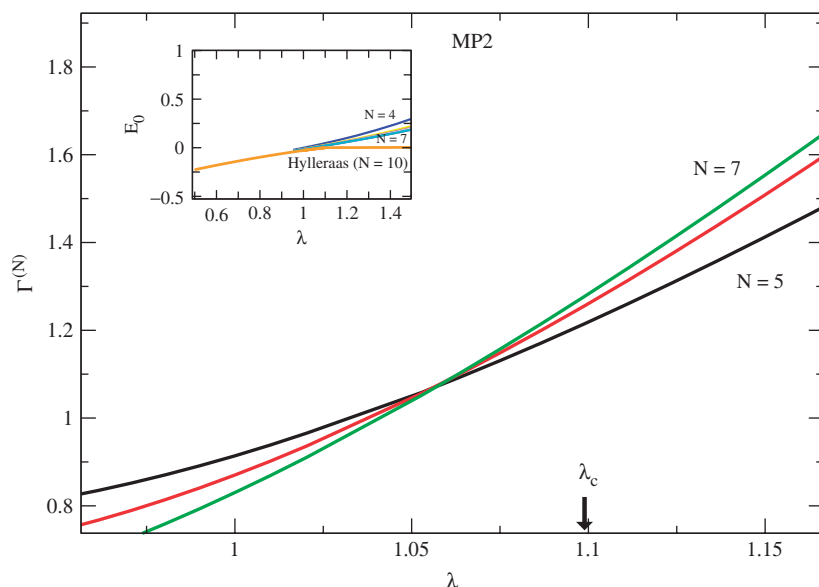


Figure 11. Plot of  $\Gamma^{(N)}$  as a function of  $\lambda$  for the two-electron atom using MP2 level of theory. The behaviour of the ground state energy as a function of  $\lambda$  is shown in the window. The exact energy as a function of  $\lambda$  using the Hylleraas basis set with  $N=10$  is also shown in the window.



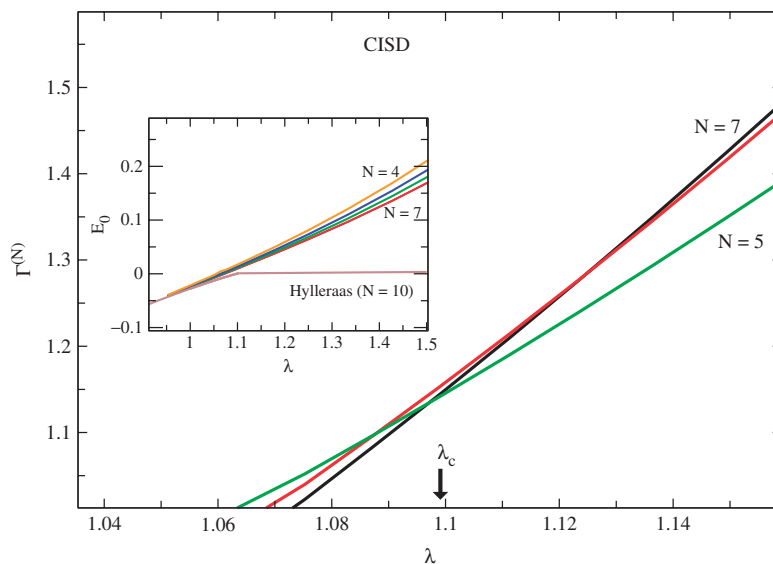


Figure 12. Plot of  $\Gamma^{(N)}$  as a function of  $\lambda$  for the two-electron atom using CISD level of theory. The behaviour of the ground state energy as a function of  $\lambda$  is shown in the window. The exact energy as a function of  $\lambda$  using the Hylleraas basis set with  $N = 10$  is also shown in the window.

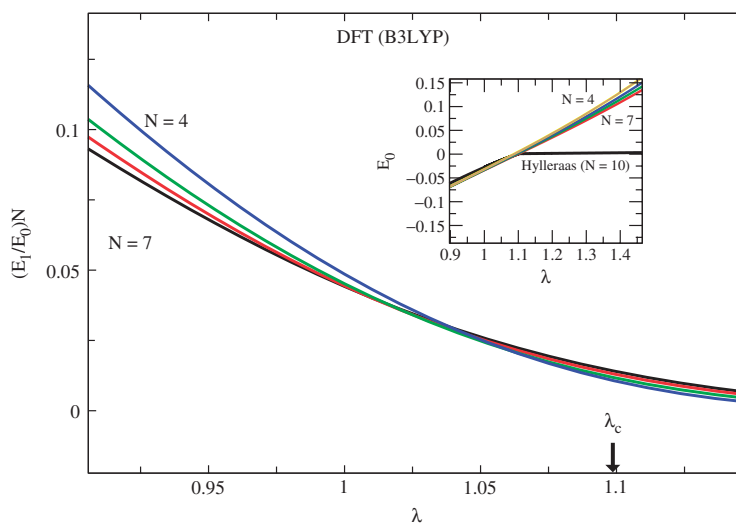


Figure 13. Plot of the ratio of the ground state energy,  $E_0$ , and the first excited state,  $E_1$ , raised to the power  $N$  as a function of  $\lambda$  for the two-electron atom using B3LYP level of theory. The behaviour of the ground state energy as a function of  $\lambda$  is shown in the window. The exact energy as a function of  $\lambda$  using the Hylleraas basis set with  $N = 10$  is also shown in the window.

using a Gaussian basis set: (i) the basis set required more functions for a good convergence; (ii) the values obtained for the critical parameters agree well with previous studies using Slater- and Hylleraas-type basis functions; (iii) the energies near the threshold value were good at describing the criticality of the systems.

After showing that a Gaussian basis is acceptable for FSS calculations, we moved on to using the *ab*

*initio* package PC GAMESS to perform the calculations necessary for FSS. We observed that critical parameters obtained from MP2, DFT and CISD gave good estimations for  $\lambda_c$  and the critical exponent for the energy  $\alpha$ . We expect that better values will be obtained by using a higher level of theory and larger basis sets.

The method for FSS with *ab initio* is simple to apply. In general, we need only to identify the

parameter to manipulate for our calculations. We have shown that the Gaussian-type functions produce acceptable results. With that in mind, we can move on to larger systems of interest. For example, many molecular systems with an excess electron are known to have localization and delocalization of the electron as a parameter changes, such as the torsion angle. By analysing the behaviour of the system as the ring torsion angle varies, we may be able to predict the critical angle of localization and delocalization. Electronic structure calculations for large molecular systems are done everyday using standard *ab initio* packages. We have shown for helium that FSS calculations can be done using such software packages. The accuracy afforded from a Slater-type basis function is definitely preferred over Gaussian-type basis functions, however the former, while more accurate, requires large amounts of disk space for the calculation of integrals. With the use of Gaussian-type basis functions, it is now possible to study critical phenomena in larger systems of interest.

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