Scaling of the von Neumann entropy in a two-electron system near the ionization threshold

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The critical behavior of entanglement near a quantum phase transition has been studied intensely over the past few years. Few-body quantum systems show critical behavior near the ionization point. We investigate the scaling properties of the von Neumann entropy for an atomiclike system near the ionization threshold. Using finite size scaling methods we calculate the critical charge and the critical exponent associated to the von Neumann entropy. The parallelism between the behavior of entanglement near a quantum phase transition and the behavior of the von Neumann entropy in a critical few-body quantum system is analyzed.

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I. INTRODUCTION

In the past few years the relationship between quantum state entanglement and critical phenomena has received a lot of attention. The work of Osterloh *et al.* [1] signaled the opening of the field, which lies between quantum information theory and quantum critical phenomena. Since then the relationship has been made clear, in particular, Wu *et al.* [2] have shown that in quantum phase transitions (QPTs) the nonanalyticity of the reduced density matrix elements signaling the QPT is responsible for nonanalyticity of bipartite entanglement measures. The examples provided for them are quantum spin models, which are for many reasons the touchstone for any new theory.

Some of the topics concerning the relationship between entanglement and quantum phase transitions that have been studied previously include the behavior of thermal entanglement near a quantum phase transition [3], the scaling properties of entanglement measured by the *entropy of entanglement*, which allows one to consider not only bipartite subsystems but blocks of different sizes [4], the behavior of the entanglement on a disordered chain near a critical point [5], and the *localizable entanglement* used to observe diverging entanglement length [6]. Presently, there are a number of issues that wait for a better understanding, in particular: what happens in systems with continuous degrees of freedom?

The bipartite entanglement of distinguishable spins on a chain can be studied using well known entanglement measures as the entanglement of formation [7], random robustness of entanglement (or the modulus of separability) [8], which are useful for pure and mixed states. When considering systems with continuous degrees of freedom and identical particles one is faced with subtleties that are not present in models such as quantum spin chains. For a pure state $|\Psi\rangle$ the von Neumann entropy of the reduced state is a good entanglement measure [9], although other approaches are possible, for example, Shannon entropy has been used to study the two-electron atom [10] and a two-electron artificial atom [11], and the von Neumann entropy to study the dynamics of entanglement between two trapped atoms [12].

Gittings and Fisher [13] showed that von Neumann entropy for the reduced density matrix of half the system can be used as an entanglement measure for the case of indistinguishable particles.

At this point it is reasonable (and tempting) to ask which is the behavior of the von Neumann entropy in a system near the critical point of the ground-state energy, for example, in an atomic system near the ionization threshold. A critical point for a quantum few-body system is defined as a point for which a bound state becomes absorbed or degenerate with the continuum. For a two-electron atom the ionization point is a critical point with a bound state at the threshold [14]. We want to remark that the critical behavior of a few-body quantum system is not like the critical behavior of a quantum spin chain near a QPT. In the quantum Ising model with a transverse field [15], for example, the critical parameter can be changed at *both* sides of the critical point; however, a two-electron atom has a well defined bound (normalizable) state *at one side* of the ionization point. Nevertheless, there is a strong parallelism between both kinds of systems.

In this paper we will study the behavior of the von Neumann entropy for two electron atomiclike systems near the ionization point. As we shall show the nonanalyticity of the ground state energy at the critical point signals a corresponding nonanalyticity of the eigenvalues of the reduced density matrix and of the von Neumann entropy, which is reminiscent of the scenario proposed by Wu *et al.* [2] for quantum spin chain models. Moreover, we apply a finite size scaling (FSS) [16] method to the entropy in order to calculate the critical nuclear charge and critical exponent. We found that the critical behavior of the von Neumann entropy for these systems is similar to the behavior of other entanglement measures in systems that present quantum phase transitions [2].

In order to obtain accurate numerical results we will focus on the spherical heliumlike atom. This model has a long history and it has been used to study bound [17,18] and scattering [19] solutions of the two-electron atomic system. Moreover, recently it has been shown that the two-electron atom and its spherical approximation have the same near-threshold behavior, in particular, both systems have the same asymptotic expression for the ground-state energy with critical exponent $\alpha=1$ [20].

This paper is organized as follows. In Sec. II we give a short view about the spherical helium model. In Sec. III we

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discuss the properties of the von Neumann entropy and its near-threshold behavior. Our results are presented in Sec. IV. Finally, the conclusions are given in Sec. V.

II. MODEL

In the spherical helium model the Coulombic repulsion between electrons $1/r_{12}$ is replaced by its spherical average $1/r_>$, where $r_>=\max(r_1,r_2)$, then the Hamiltonian, in atomic units, and applying the standard transformation $\vec{r}\rightarrow\vec{r}/Z$; $H\rightarrow Z^2H$, takes the form [18]

$$H = h(1) + h(2) + \lambda V, \qquad (1)$$

where

$$h(i) = \frac{1}{2}p_i^2 - \frac{1}{r_i}, \quad \lambda = \frac{1}{Z}, \quad V = \frac{1}{r_>}, \qquad (2)$$

p_i and r_i are the momentum operator and the position operator of the $i=1,2$ electron, r_{12} is the distance between electrons, and Z is the nuclear charge.

As any two identical spin-1/2 fermionic system the total Hilbert space is the external product of the spin Hilbert space times the spatial Hilbert space. That is, the eigenfunctions of Hamiltonian Eq. (1) take the form

$$\Psi(1,2) = \Phi_{\substack{S\\A}}(\vec{r}_1,\vec{r}_2)\chi_{\text{trip}}^{\text{sing}}, \qquad (3)$$

where the spatial wave function Φ_S (Φ_A) is symmetric (antisymmetric) under permutation of the particles, and χ_{sing} and χ_{trip} are the singlet and triplet spinor, respectively. Note that, for $\lambda>0$, the eigenfunctions of the Hamiltonian Eq. (1) cannot be obtained by antisymmetrizing a factorized state, i.e., they cannot be written as a single Slater determinant [21]. Then, as established by Ghirardi and Marinatto [9], for values of $\lambda>0$ the states described by bound-state eigenfunctions are entangled states, and the greater is the von Neumann entropy, the larger is the amount of entanglement of the state.

In particular, the ground-state eigenfunction has the form

$$\Psi_0(1,2) = \Phi_0(\vec{r}_1,\vec{r}_2)\chi_{\text{sing}}, \qquad (4)$$

where Φ_0 is symmetric under permutation of the particles.

The advantage of the spherical-helium Hamiltonian is that the ground-state function depends only on the radial coordinates of the electrons $\Phi_0(\vec{r}_1,\vec{r}_2)=\Phi_0(r_1,r_2)$. Then this ground-state function could be written as an expansion in a complete basis set

$$\Phi_0(r_1,r_2) = \sum_{m,n}^{\infty} C_{m,n}\Phi_{m,n}(r_1,r_2). \qquad (5)$$

In particular, we choose the orthonormal basis set

$$\Phi_{m,n}(r_1,r_2) = \epsilon_{m,n}[\phi_m(r_1)\phi_n(r_2) + \phi_n(r_1)\phi_m(r_2)], \qquad (6)$$

where $\phi_m(r)$ are the one-electron orthonormal s-wave functions

$$\phi_m(r) = \sqrt{\frac{\beta^3}{4\pi(m+1)(m+2)}}e^{-\beta r/2}L_m^{(2)}(\beta r), \qquad (7)$$

$L_m^{(2)}$ are the Laguerre polynomials [22], β is a variational parameter that takes the value $\beta=1.3$ in all the calculations, and $\epsilon_{m,n}$ the matrix

$$\epsilon_{m,n} = \begin{cases} \dfrac{1}{2}, & m = n \\[2mm] \dfrac{1}{\sqrt{2}}, & m \neq n. \end{cases} \qquad (8)$$

In order to obtain an approximate ground-state function we apply the Ritz variational method [23]. The expansion shown in Eq. (5) is truncated at order $N=$maximum value of m and n, which corresponds to $(N+1)(N+2)/2$ functions in the expansion as shown in Eq. (5). The lowest eigenvalue of the finite Hamiltonian matrix $\langle\Phi_{m,n}|H|\Phi_{m',n'}\rangle$ is a variational upper bound for the ground-state energy and the corresponding eigenvector gives the coefficients $C_{mn}^{(N)}$ for the Nth-order variational wave function

$$\Phi_0^{(N)}(r_1,r_2) = \sum_{m,n}^{N} C_{m,n}^{(N)}\Phi_{m,n}(r_1,r_2). \qquad (9)$$

Explicit expressions for the Hamiltonian matrix elements are given in the Appendix.

This model has at least one bound state for $\lambda \leq \lambda_c \simeq 1.054$, and the asymptotic behavior of the ground-state energy is

$$E_0(\lambda) - E_{th} \sim (\lambda_c - \lambda)^{\alpha} \quad \text{for } \lambda \rightarrow \lambda_c^-, \qquad (10)$$

where $E_{th}=-1/2$ is the threshold energy and $\alpha=1$ [20].

III. VON NEUMANN ENTROPY

For a two-particle system in a pure state $|\Psi\rangle$ the density operator ρ takes the form

$$\rho = |\Psi\rangle\langle\Psi|. \qquad (11)$$

The reduced density operator is [24,25]

$$\hat{\rho}^{\text{red}}(\vec{r}_1,\vec{r}_1') = \text{tr}_2|\Psi\rangle\langle\Psi|. \qquad (12)$$

Here the trace is taken over one electron.

The von Neumann entropy is given by

$$\mathbf{S} = -\text{tr}(\hat{\rho}^{\text{red}}\log_2\hat{\rho}^{\text{red}}). \qquad (13)$$

As the ground-state wave function is given by Eq. (4), the von Neumann entropy separates in two contributions, one corresponding to the spin degrees of freedom plus one corresponding to the spatial degrees of freedom. For spin-independent Hamiltonians the spin degrees of freedom contribution is equal to one; then the entropy could be written as

$$\mathbf{S} = 1 + S = 1 - \sum_i \Lambda_i \log_2(\Lambda_i), \qquad (14)$$

where Λ_i are the eigenvalues of the spatial part of the reduced density operator

$$\int d^3x_1' \int d^3x_2 \Phi_0(r_1,r_2)\Phi_0^*(r_1',r_2)\varphi_i(r_1') = \Lambda_i\varphi_i(r_1).$$
$$(15)$$

Here, we want to stress that the ground state is a singlet and the total wave function is the product of the spatial and the spin wave functions. For this reason the spin wave function contributes only with an additive constant to the entropy (equal to one). Clearly the additive constant does not change the behavior of the von Neumann entropy near the critical point, nor its scaling properties. Then from here we will refer to the spatial contribution S in Eq. (14) as the von Neumann entropy.

In this paper we give evidence that the von Neumann entropy for the ground state has a singular behavior at the critical point λ_c,

$$S(\lambda) - S(\lambda_c) \sim (\lambda_c - \lambda)^\mu \quad \text{for } \lambda \to \lambda_c^-, \qquad (16)$$

with a critical exponent $\mu=0$ corresponding to a discontinuity of the entropy at $\lambda=\lambda_c$.

Introducing the Nth-order variational approximation to the ground state function [Eq. (9)] in the integral equation (15), we obtain

$$\int d^3x_1' \int d^3x_2 \Phi_0^{(N)}(r_1,r_2)(\Phi_0^{(N)}(r_1',r_2))^*\varphi_i^{(N)}(r_1')$$
$$= \Lambda_i^{(N)}\varphi_i^{(N)}(r_1), \quad i = 1, \ldots, N. \qquad (17)$$

The exact eigenfunctions $\varphi_i^{(N)}$ of this integral equation can be written as a linear combination of the functions ϕ_m, $m = 1, \ldots, N$ [26]. Then Eq. (17) can be recast as an algebraic eigenvalue problem for a $N \times N$ matrix. The conservation of the probability

$$\sum_{i=1}^{N} \Lambda_i^{(N)} = 1 \qquad (18)$$

is satisfied for all values of N. In consequence the Nth-order approximation to the entropy is

$$S^{(N)} = -\sum_{i=1}^{N} \Lambda_i^{(N)} \log_2(\Lambda_i^{(N)}). \qquad (19)$$

Now we study the scaling of $S^{(N)}(\lambda)$ with the size of the basis set N applying standard finite size scaling methods for quantum few-body systems [10,16], i.e., we assume the scaling form for the singular part of the entropy,

$$S(\lambda_c) - S^{(N)}(\lambda) \sim [S(\lambda_c) - S(\lambda)]F_S[N(\lambda_c - \lambda)^\nu] \quad \text{for } \lambda \to \lambda_c^-, \qquad (20)$$

where $\nu=1$ was calculated in Ref. [27], and

$$F_S(x) \sim x^{-\mu/\nu} \quad \text{for } x \to 0, \qquad (21)$$

where the critical exponent μ was defined in Eq. (16). Now, we can obtain the critical parameters (λ_c,μ) by defining the function [28]
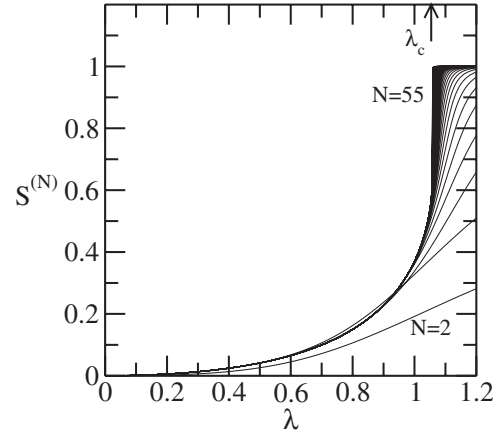

FIG. 1. $S^{(N)}$ vs λ for $N=2,\ldots,55$. The convergence of $S^{(N)}$ to a nonanalytic function at $\lambda=\lambda_c \simeq 1.054$ is clear.

$$\Delta_S(\lambda,N,N') = \frac{\ln[S_c - S^{(N)}(\lambda)] - \ln[S_c - S^{(N')}(\lambda)]}{\ln(N') - \ln(N)}, \quad (22)$$

where $S_c = \log_2 2 = 1$ is the limit value of $S^{(N)}(\lambda)$ for $N \to \infty$ and $\lambda > \lambda_c$. At the critical point we have

$$\Delta_S(\lambda_c,N,N') = \frac{\mu}{\nu}, \qquad (23)$$

independent of the values of N and N'. Thus, for three different values N, N', and N'' the curves defined by Eq. (22) intersect at the critical point

$$\Delta_S(\lambda_c,N,N') = \Delta_S(\lambda_c,N'',N). \qquad (24)$$

Expression (23) is asymptotic, therefore we calculate (λ_c,μ) as an extrapolation from a sequence of values $(\lambda^{(N)},\mu^{(N)})$ for $N \to \infty$, where $(\lambda^{(N)},\mu^{(N)})$ are the solutions to Eq. (24) with $N'=N-1$ and $N''=N+1$ [28].

IV. NUMERICAL RESULTS

Figure 1 shows the behavior of the von Neumann entropy $S^{(N)}$ vs λ, for different values of the basis set size $N = 2, \ldots, 55$. The behavior of the von Neumann entropy can be understood as follows. For $\lambda \to 0$ the two electrons become independent since the Coulomb repulsion between electrons goes to zero [see Eq. (1)]. In that situation the spatial wave function can be written as a simple product, giving $S^{(N)}=0$. For $\lambda > \lambda_c$ the system consists of one electron bounded to the central charge, and one unbounded electron. In this case the spatial wave function can be written as a symmetrized product of one-electron wave functions so $S = S_c = 1$.

The scenario described in the previous paragraph can be better understood looking at Fig. 2, which shows the behavior of the first and second largest eigenvalues $\Lambda_1^{(N)}$ and $\Lambda_2^{(N)}$, respectively. For $\lambda \to 0$ there is only one nonzero eigenvalue: $\Lambda_1^{(N)} \to 1$, hence it is clear that $S^{(N)} \to 0$. For $\lambda > \lambda_c$ only the two largest eigenvalues are significant, they become degenerate and equal to $1/2$, therefore the value of $S = \log_2 2 = S(\lambda_c)$.
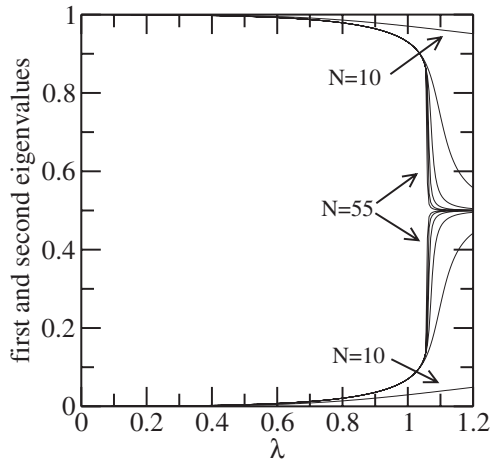
FIG. 2. First and second largest eigenvalues of the reduced density matrix against λ for $N=10$, 20, 30, 40, 50, and 55.

Figure 3 shows the derivative of the von Neumann entropy $\frac{dS^{(N)}}{d\lambda}$ for different values of N. When N is increased the maximum of the derivative gets increased while the position of the maximum changes and tends towards the critical point λ_c. This figure is similar to the corresponding figure obtained by Osterloh *et al.* [1] for the derivative of the concurrence between nearest neighbors in a spin chain. They were considering the quantum phase transition that occurs in an Ising model with transverse external magnetic field. Until the work of Wu *et al.* [2] there was not a systematic way to relate quantum phase transitions characterized by nonanalyticities of the energy and the behavior of bipartite entanglement. Anyway, using finite size scaling Osterloh *et al.* showed that the divergence of the derivative of the concurrence is logarithmic with the size of the spin chain (i.e., the number of quantum spins on the chain).

The critical parameters $(\lambda_c^{(N)}, \mu^{(N)})$ vs $1/N$ are shown in Fig. 4. Figure 4(a) shows that the finite size scaling provides values for the critical parameter $\lambda_c^{(N)}$ below and above λ_c, i.e., Eq. (24) has two solutions for each N. The extrapolation of the values of $\lambda_c^{(N)} > \lambda_c$ gives $\lambda_c \simeq 1.0539$ which is in very
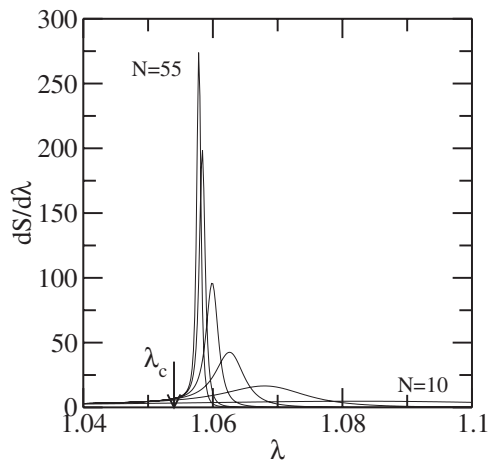

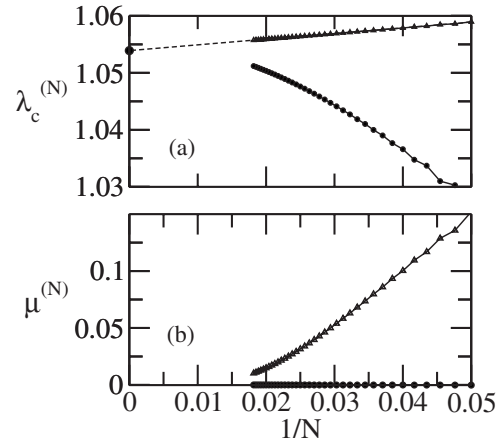FIG. 3. Derivatives of $S^{(N)}$ vs λ for $N=10$, 20, 30, 40, 50, and 55.

FIG. 4. (a) Critical parameter $\lambda^{(N)}$ against $1/N$ for $N=20,\ldots,55$ for the two solutions of Eq. (24). The extrapolated value for λ_c is also shown with a filled dot. (b) Critical exponent $\mu^{(N)}$ for the two solutions displayed in (a) against $1/N$ for $N=20,\ldots,55$. For the lower curve $\mu^{(N)} \leqslant 10^{-4} \; \forall \; N$.

good agreement with the value obtained using the finite size scaling method with the energy of the ground state (see [20]) $\lambda_c^E \simeq 1.054$. The convergence of the data below the critical point is not as good as the convergence of the data above the critical point. It seems that it is necessary to perform the calculations using larger basis set sizes to get a good convergence, besides it is not clear how to extrapolate the $\lambda_c^{(N)}$ obtained below λ_c. On the contrary, above the critical point, $\lambda_c^{(N)} = \text{const } 1/N + \lambda_c$ gives a very good fit of the data. The extrapolated value is also shown.

The behavior of the critical exponents $\mu^{(N)}$ is shown in Fig. 4(b). The filled dots correspond to the values calculated using finite size scaling above the critical point; the empty dots correspond to the values obtained using FSS below the critical point. Both sets of data seem to support that the critical exponent $\mu=0$. As it is well known, a zero critical exponent is compatible with a discontinuous or a logarithmic behavior, and it is very difficult to elucidate from finite size scaling the right asymptotic form. Our assumption that the entropy has a discontinuity at $\lambda=\lambda_c$ is based on the existence of a normalizable wave function at the threshold [14]. The kernel of the integral equation (15) still is a L_2 kernel at $\lambda=\lambda_c$ and therefore we expect an infinite number of nonzero eigenvalues [26].

V. CONCLUSIONS

The results presented show that all the key ingredients of the finite size scaling are present in the von Neumann entropy for the spherical helium model. Preliminary results obtained for the heliumlike atom, i.e., taking into account the full Coulombic repulsion, show the same qualitative behavior as that observed for the spherical approximation, in particular, the von Neumann entropy saturates to the same value above λ_c, and the eigenvalues of the reduced matrix operator show a similar critical behavior near the ionization point.

For quantum spin chains there is a general theory linking quantum phase transitions and bipartite entanglement [2]. It

sums up that a nonanalytical point in a bipartite entanglement measure (or its derivative) is necessary and sufficient to signal a QPT, assuming suitable conditions over the elements of the two-spin reduced density matrix. Moreover, the order of the QPT is related to the kind of singularity of the entanglement measure: for a first-(second-) order QPT corresponds a discontinuity (discontinuity or divergence of the first derivative of) of the entanglement measure. For quantum spin chains like the Ising model, or the frustrated two-leg spin-1/2 ladder, a detailed study of the coefficients of the two-spin reduced density matrix can be carried through since these models are exactly solvable. The model that we consider in this paper, or other atomiclike systems, lacks this advantage, so it is more difficult to show that a nonanalyticity on the von Neumann entropy, or in the coefficients of the reduced density matrix, is necessary or sufficient to have a critical point.

For quantum few-body systems it is well known that the critical behavior of the energy near the ionization threshold depends on the existence (or not) of a normalizable bounded state at the threshold [16,29]. The He-like atom and the spherical He-like atom considered in this paper have normalizable bounded state at the threshold and the critical exponent asociated to the energy is $\alpha=1$. The Li atom does not possess a normalizable bounded state at the threshold and $\alpha=2$ [16]. Then, it is reasonable to expect that the behavior of an entanglement measure near the ionization threshold will depend on which kind of critical point is under consideration. Also, it is reasonable to expect that the critical behavior of the entanglement measure does not depend on the particular measure used, since the critical behavior of the concurrence or the negativity is the same in quantum spin chains [2]. Anyway, it is necessary to calculate the critical behavior of another measure, and not only the critical behavior of the von Neumann entropy, to be sure about this point. Work is in progress on these relevant topics.

APPENDIX

In this Appendix we give the explicit expression for the matrix elements $\langle\Phi_{m,n}|H|\Phi_{m',n'}\rangle$ used in the variational calculations, where H is the Hamiltonian defined by Eqs. (1) and (2), and the basis functions are defined by Eqs. (6)–(8). Using the symmetry under permutation of the particles, a matrix element takes the form

$$\langle\Phi_{m,n}|H|\Phi_{m',n'}\rangle = 2\epsilon_{m,n}\epsilon_{m',n'}(h_{mm'}\delta_{n,n'} + h_{mn'}\delta_{n,m'} + h_{nm'}\delta_{m,n'} + h_{nn'}\delta_{m,m'} + \lambda V_{mn,m'n'}),$$

(A1)

where $h_{mm'}$ is the one-electron matrix element $h_{mm'} = \langle\phi_m|h|\phi_{m'}\rangle$, and $V_{mn,m'n'} = \langle\phi_m\phi_n|1/r_>|\phi_{m'}\phi_{n'}\rangle$. The integrals involved in the calculation of $h_{mm'}$ are tabulated [30], and we obtain

$$h_{mm'} = \frac{\beta[(2m'+1)\beta-6]}{12}\sqrt{\frac{(m'+1)(m'+2)}{(m+1)(m+2)}}$$
$$-\frac{\beta^2}{8}\delta_{m,m'} \quad \text{for } m \leq m'; \quad h_{m'm} = h_{mm'}. \quad \text{(A2)}$$

Using the explicit expression for the Laguerre polynomials $L_m^{(2)}(r)$ [22], the calculation of the two-electron potential matrix elements $V_{mn,m'n'}$ is cumbersome but straightforward, giving

$$V_{mn,m'n'} = \frac{\beta}{\sqrt{m(m+1)n(n+1)m'(m'+1)n'(n'+1)}}\sum_{s=0}^{m-1}\sum_{t=0}^{n-1}\sum_{u=0}^{m'-1}\sum_{v=0}^{n'-1} \times \frac{(-1)^{s+t+u+v}}{s!t!u!v!}\binom{m+1}{s+2}\binom{n+1}{t+2}\binom{m'+1}{u+2}\binom{n'+1}{v+2}I_{s+u,t+v}^{(>)},$$

(A3)

where

$$I_{i,j}^{(>)} = \int_0^\infty r_1^2\,dr_1 \int_0^\infty r_2^2\,dr_2 \frac{r_1^i r_2^j}{r_>}e^{-(r_1+r_2)} = \frac{(i+1)!(j+2)!(2^{i+2}-1)}{2^{i+2}} - (j+1)!\sum_{u=1}^{j+1}\frac{u(i+j+3-u)!}{(j+2-u)!2^{i+j+4-u}}.$$

(A4)

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