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# Quantum criticality at the infinite complete basis set limit: A thermodynamic analog of the Yang and Lee theorem

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**Abstract**

Finite size scaling for calculations of the critical parameters of the few-body Schrödinger equation is based on taking the number of elements in a complete basis set as the size of the system. We show in an analogy with Yang and Lee theorem, which states that singularities of the free energy at phase transitions occur only in the thermodynamic limit, that singularities in the ground state energy occur only in the infinite complete basis set limit. To illustrate this analogy in the complex-parameter space, we present calculations for Yukawa type potential, and a Coulomb type potential for two-electron atoms.


Phase transitions in statistical mechanical calculations arise only in the thermodynamic limit, in which the volume of the system and the number of particles go to infinity with fixed density. Only in this limit the free energy, or any thermodynamic quantity, is a singular function of the temperature or external fields [1–3]. Recently, a new classification scheme was developed [4] for phase transitions in finite systems like atomic and molecular clusters [5] based on the Yang–Lee zeros in the complex temperature plane. Finite size scaling, which was formulated by Fisher in 1971 and further developed by a number of people has been used in order to extrapolate the information available from a finite system to the thermodynamic limit [6–10]. However, in the last decade considerable attention has concentrated on a qualitatively different class of phase transitions, transitions which occur at the absolute zero of temperature. These are quantum phase transitions which are driven by quantum fluctuations as a consequence of Heisenberg's uncertainty principle [11,12]. These new transitions are tuned by parameters in the Hamiltonian. An example of this kind of transition is the melting of a Wigner crystal, orderly arrangement of electrons. As one make the crystal more dense, the electrons become more confined, the uncertainty principle takes over and the fluctuations in the momentum grow. Squeezing more on the crystal and eventually the system transform from insulator to conductor [13]. Other examples include the magnetic transitions of cuprates, superconductor-insulator transitions in alloys, metal-insulator transitions [12,14], cluster physics [15], electronic circuits [16] and deformed shape phase transition in nuclear physics [17].

In quantum mechanics, when using variation methods, one encounters the same finite size problem in studying the critical behavior of a quantum Hamiltonian $\mathscr{H}(\lambda_1, \ldots, \lambda_k)$ as a function of its set of parameters $\{\lambda_i\}$. In this context, critical means the values of $\{\lambda_i\}$ for which a bound state energy is nonanalytic. This nonanalytic behavior can be analysed using the theory of algebraic functions [18] and perturbation theory [19]. We have developed finite size scaling for quantum systems [20–22]. In this case, 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 wave function of a given Hamiltonian. This approach was very efficient and accurate for estimating the critical screening length for one-electron screened Coulomb potentials, the critical nuclear charges for two-electron and three-electron atoms [20,21], critical conditions for stable dipole and quadrupole-bound

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anions [24], simple diatomic molecules and three-body Coulomb systems [22].

Recently, Cejnar et al. [23] proposed a relationship between thermodynamic phase transitions and quantum phase transitions based on a link between zeros of the canonical partition function at complex temperatures and branch points of a quantum Hamiltonian in the complex-extended parameter space. Note also that in Ref. [23], the scaling factor $S$ in the specific heat analog turns out to be inversely proportional to the relevant Hilbert subspace dimension. This approach was applied to the interacting boson model. In this Letter, we show that singularities in the ground state energy occur only in the infinite complete basis set limit in an analogy with Yang and Lee theorem in classical statistical mechanics. Yang and Lee [25] developed a theory of equations of state and phase transitions that describes the condensed phases, the gas phases and the transition regions. A phase transition is related to a nonanalytical behavior of the free energy. Therefore, one can classify phase transition, if one finds the points where the free energy or the grand canonical potential becomes nonanalytical. However, this can be calculated from $F=-kT\ln Q$ with the grand partition function is written as $Q(z,V,T)=\sum_{N=0}^{\infty}z^{N}Z(N,V,T)$, where $Z(N,V,T)$ is partition function of the total system for a given number of particles $N$, Volume $V$ and temperature $T$ with the variable fugacity $z=\mathrm{e}^{\mu}/kT$ in term of the chemical potential $\mu$. Yang and Lee have shown rigorously by studying the grand partition function in the complex $z$-plane that nonanalyticity occurs only in the thermodynamic limit ($V\to\infty, N\to\infty, \frac{N}{V}=\text{constant}$).

Finite size scaling can be used to study the quantum criticality of Hamiltonians of the general form $\mathscr{H}=\mathscr{H}_0+\mathscr{V}_\lambda$, with $\mathscr{H}_0$ is $\lambda$-independent and $\mathscr{V}_\lambda$ is the $\lambda$-dependent term and $\lambda$ is a control parameter. At the critical value $\lambda_c$ some of the ground state energy derivatives of the Hamiltonian $\mathscr{H}$ change discontinuously. For a given complete orthonormal $\lambda$-independent basis set $\{\Phi_n\}$, the ground state eigenfunction takes the form, $\Psi_\lambda=\sum_n a_n(\lambda)\Phi_n$, where $n$ represents the adequate set of quantum numbers. In order to approximate the different quantities, we have to truncate the series at order $N$. Then the Hamiltonian is replaced by $M(N)\times M(N)$ matrix $\mathscr{H}^{(N)}$, with $M(N)$ being the number of elements in the truncated basis set at order $N$. Using the standard linear variational method, the $N$th-order approximation for the energies are given by the eigenvalues of the matrix $\mathscr{H}^{(N)}$.

As in the finite size scaling ansatzs in statistical mechanics [26], we assume that there exists a scaling function $F_{\mathscr{H}}$ for the truncated magnitudes such that

$$\langle\mathscr{H}\rangle_\lambda^{(N)}\sim\langle\mathscr{H}\rangle_\lambda F_{\mathscr{H}}(N|\lambda-\lambda_c|^{\nu}) \tag{1}$$

with a unique scaling exponent $\nu$ defined by the singularity of the correlation length at the critical point. This is an analogous formula to the phenomenological renormalization equation developed by Nightingale in finite size scaling theory [7]. To obtain the critical parameters, we define the following function

$$\Delta_{\mathscr{O}}(\lambda;N,N')=\frac{\ln\left(\langle\mathscr{O}\rangle_\lambda^{(N)}/\langle\mathscr{O}\rangle_\lambda^{(N')}\right)}{\ln(N'/N)}, \tag{2}$$

such that for three different values $N$, $N'$, and $N''$ the curves defined intersect at the critical point,

$$\Delta_{\mathscr{O}}(\lambda_c;N,N')=\Delta_{\mathscr{O}}(\lambda_c;N'',N). \tag{3}$$

This formula is valid only as an asymptotic expressions, but unique values of $\lambda_c$, and the energy exponent $\alpha$, $\langle\mathscr{H}\rangle_\lambda\sim(\lambda-\lambda_c)^{\alpha}$, can be obtained as a succession of values as a function of $N$,$N'$ and $N''$ using the algorithm of Bulirsch and Stoer [27].

We propose in an analogy with Yang and Lee theorem, that singularities in the ground state energy occur only in the infinite complete basis set limit. To establish such an analogy we will focus on the distribution of branch points in the complex-parameter space as we increase the size of the basis set. These points are the simultaneous solutions of the two equations: $\det[E-\mathscr{H}(\lambda)]=0$ and $\frac{\partial}{\partial E}\det[E-\mathscr{H}(\lambda)]=0$, which yield the following condition [23,28,29]

$$D(\lambda)=(-1)^{N(N-1)/2}[E_j(\lambda)-E_i(\lambda)]^2=0, \tag{4}$$

where the discriminant $D(\lambda)$ is a polynomial of order $N(N-1)$ in $\lambda$, and $N$ is the dimension of the Hilbert space. From the hermiticity of $\mathscr{H}$ it follows that energy eigenvalues $E_i$ are real for real values of $\lambda$. We also assume $E_i(\lambda)\neq E_j(\lambda)$ for $i\neq j$ and for real $\lambda$. On the other hand the equation $E_i(\lambda)=E_j(\lambda)$ for given values of $i$ and $j$ must have a solution in the complex plane. Thus the discriminant roots occur as $N(N-1)/2$ complex conjugate pairs.

As an example, let us illustrate the link between the zeros of the canonical partition function at complex temperature and pseudosingular points, branch points, of the Yukawa potential in the complex-parameter space. The scaled Yukawa Hamiltonian for $l=0$ is given by

$$\mathscr{H}(\lambda)=-\frac{1}{2}\nabla^2-\lambda\frac{\mathrm{e}^{-r}}{r} \tag{5}$$

A convenient, orthonormal basis set is

$$\Phi_n(r)=\sqrt{\frac{1/4\pi}{(n+1)(n+2)}}\mathrm{e}^{-r/2}L_n^{(2)}(r). \tag{6}$$

where $n$ is the principle quantum number, $L_n^{(2)}(r)$ is the associated Laguerre polynomial of degree $n$ and order 2.

Using the finite size scaling equation, Eq. (2), we can define the following function:

$$\Gamma_\alpha(\lambda;N,N')=\frac{\Delta_{\mathscr{H}}(\lambda;N,N')}{\Delta_{\mathscr{H}}(\lambda;N,N')-\Delta_{\partial\mathscr{V}_\lambda/\partial\lambda}(\lambda;N,N')} \tag{7}$$

which is independent of the values of $N$ and $N'$ at the critical point $\lambda=\lambda_c$ and gives the critical exponent $\alpha=\Gamma_\alpha(\lambda_c;N,N')$. Using this function we can obtain successive curve crossings as the number of functions in the basis set increases. In Fig. 1, we show the pseudocritical points $\lambda_c^{(N)}$ as a function of $1/N$ for even and odd values of $N$. In the

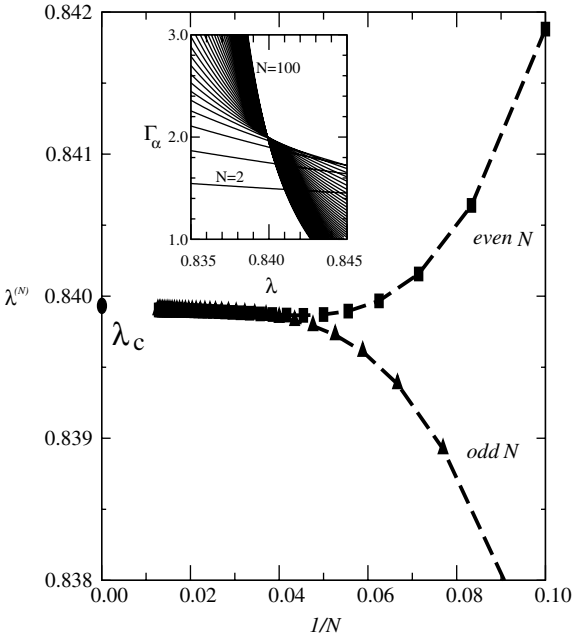


Fig. 1. $\lambda^N$ as a function of $1/N$, for the ground state of the Yukawa potential. The points were obtained from the curve crossings shown in the window.

upper window we show the curve crossings as $N$ increases and the value of the extrapolated $\lambda_c = 0.839903$ is shown by a dot. In the complex-$\lambda$ plane, the critical value of $\lambda$ at each order, $\lambda_c^{(N)}$, is calculated by first obtaining the Hamiltonian matrix in an analytical form, with the elements as functions of $\lambda$ only. The Hamiltonian matrix elements are given by

$$H_{a,b} = \left\langle \Phi_a \left| -\frac{1}{2}\nabla^2 - \lambda\frac{e^{-r}}{r} \right| \Phi_b \right\rangle = -\frac{1}{2}\left\langle \Phi_a \left| \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + 2\lambda\frac{e^{-r}}{r} \right| \Phi_b \right\rangle. \quad (8)$$

By expanding the first two terms with the differentiation properties of the Laguerre polynomials and integration of the Hamiltonian matrix elements one obtain the general formula

$$\begin{aligned} H_{a,b} = & -\frac{1}{2\sqrt{(a+1)(a+2)(b+1)(b+2)}} \\ & \times \left\{ \frac{1}{4}\frac{\Gamma(a+3)}{a!}\delta(a,b) + 2\lambda\sum_{i=0}^{a}\sum_{j=0}^{b} f_a^{(2)}(i) f_b^{(2)}(i) \right. \\ & \times \frac{(i+j+1)!}{2^{(i+j+2)}} - (b+1)\frac{\Gamma(\min(a,b)+3)}{2\min(a,b)!} \\ & - b\frac{\Gamma(\min(a,b)+3)}{6\min(a,b)!}(2[a+b-2\min(a,b)+1] \\ & + (a+b+1)) + (b+2)\frac{\Gamma(\min(a,b-1)+3)}{6\min(a,b-1)!} \\ & \left. \times (2[a+b-1-2\min(a,b-1)+1] + (a+b)) \right\}, \end{aligned} \quad (9)$$

where $\Gamma(x)$ is the Euler gamma function of $x$, $\delta(n_1,n_2)$ is the Kronecker delta of $n_1$ and $n_2$, and $f_n^{(2)}(m)$ is the $m$th coefficient of the Laguerre polynomial of degree $n$ and order 2. It is given by a minor modification to the series definition of the Laguerre polynomial

$$f_n^k(m) = (-1)^m \frac{(n+k)!}{(n-m)!(k+m)!m!}. \quad (10)$$

The eigenvalues are obtained by solving the characteristic equation of the matrix,

$$\det(\mathscr{H} - \mathscr{E}) = 0, \quad (11)$$

where $E$ is used for the matrix eigenvalues.

The characteristic equation is simply a polynomial in $E$, and analytical forms for all of the roots can be obtained. The value of $\lambda_c^{(N)}$ is found by numerically solving the equation

$$E_i^{(N)}(\lambda) = E_j^{(N)}(\lambda) \quad (12)$$

for $\lambda$ for all combinations of $i$ and $j$ where $i \neq j$ and $i,j \leqslant N$. In the case of $N = 2$, there are only two eigenvalues so there is only one possible solution for $\lambda_c^{(N)}$. For higher-order calculations, the desired value of $\lambda_c^{(N)}$ is the one which follows the trend from the previous order calculations; specifically, the magnitude of both the real and imaginary components decreases as $N \to \infty$ and $\lambda_c^{(N)} \to \lambda_c$. These calculations were performed with the computational package MATHEMATICA [30]. The results are given in Table 1. In Fig. 2, we show the pairwise complex conjugated pseudocritical points in the complex $\lambda^N$-plane for the ground state of the Yukawa potential. As one increases the size of the basis set, the pairwise complex conjugated pseudocritical points converge to the real axis $\lambda_c = 0.839908$.

This approach is more computationally intensive than the straightforward finite size scaling method. While those calculations were done up to $N = 100$, the complex $\lambda$ analysis is performed up to $N = 11$, because the nonnumerical matrix becomes too difficult to diagonalize. However, it has some distinct advantages. Most notably, the data analysis is simplified significantly since the $\partial\mathscr{V}_\lambda/\partial\lambda$ operator and $\Delta_\mathscr{C}$ notation is no longer necessary.

Table 1
Results of the complex $\lambda$ analysis for the critical parameters of the Yukawa potential and two-electron atoms for ground state, $l = 0$

| $N$ | $\lambda_c^{(N)}$ For Yukawa potential | $\lambda_c^{(N)}$ For two-electron atoms |
|---|---|---|
| 2 | $1.074630 \pm 0.3446870i$ | $1.34477 \pm 0.2283220i$ |
| 3 | $1.046600 \pm 0.3213890i$ | $1.87989 \pm 0.2981270i$ |
| 4 | $0.964489 \pm 0.2106080i$ | $1.18676 \pm 0.0648140i$ |
| 5 | $0.948479 \pm 0.1876140i$ | $1.15630 \pm 0.0586431i$ |
| 6 | $0.924654 \pm 0.1523830i$ | $1.14841 \pm 0.0292630i$ |
| 7 | $0.915001 \pm 0.1361560i$ | $1.13704 \pm 0.0251776i$ |
| 8 | $0.904174 \pm 0.1188130i$ | $1.13142 \pm 0.0156169i$ |
| 9 | $0.897862 \pm 0.1076450i$ | $1.12578 \pm 0.0130579i$ |
| 10 | $0.891668 \pm 0.0971325i$ | $1.12212 \pm 0.0090999i$ |
| 11 | $0.887289 \pm 0.0892111i$ | $1.11882 \pm 0.0075290i$ |
| $\infty$ | 0.839908 | 1.09766 |

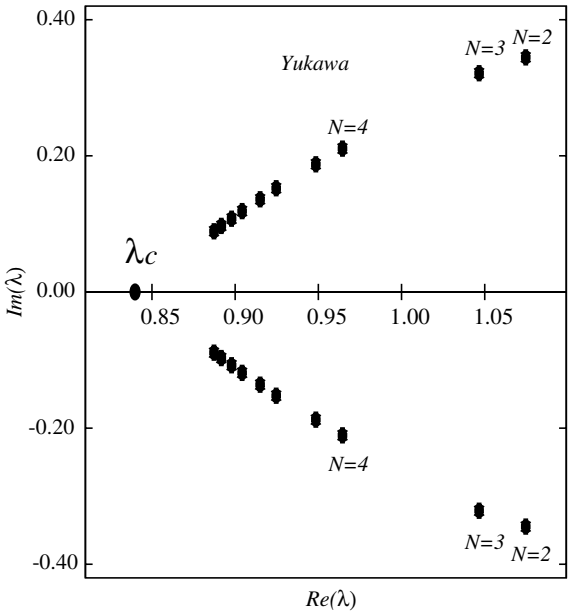


Fig. 2. Pseudocritical points in the complex $\lambda^N$-plane for the ground state of the Yukawa potential.

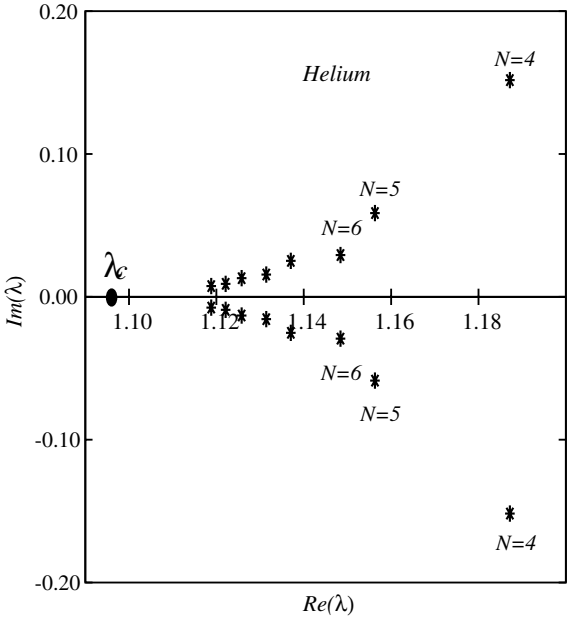


Fig. 3. Pseudocritical points in the complex $\lambda^N$-plane for the ground state of the two-electron atoms.

Now, let us demonstrate this analogy for calculating the critical parameters for two-electron atoms. In our previous studies, we have shown that near the critical charge for two-electron atoms, the minimum charge necessary to bind two electrons, can be modeled by the following Hamiltonian [31],

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{\lambda}{r}(1 - e^{-\delta r}), \tag{13}$$

where $\lambda = \frac{1}{Z}$, $Z$ is the nuclear charge and $\delta$ is determined by the following equation:

$$\delta = \frac{\delta_0(\lambda - \gamma_1) - \delta_1(\lambda - \gamma_0)}{\gamma_0 - \gamma_1}. \tag{14}$$

Here $(\delta_0,\gamma_0)$ and $(\delta_1,\gamma_1)$ are parameters corresponding to the neutral atom and its isoelectronic negative ion respectively. For Helium-like atom, $\delta_0 = 1.066$, $\gamma_0 = 0.5$, $\delta_1 = 0.881$, and $\gamma_1 = 1.0$. Choosing the same complete basis set as in the previous example, Eq. (2), we can obtained a similar formula for the Hamiltonian matrix elements,

$$\begin{aligned} H_{a,b} = & -\frac{1}{2\sqrt{(a+1)(a+2)(b+1)(b+2)}} \\ & \times \left\{ \frac{1}{4}\frac{\Gamma(a+3)}{a!}\delta(a,b) + \frac{2\lambda}{\delta}\sum_{i=0}^{a}\sum_{j=0}^{b} f_a^{(2)}(i) f_b^{(2)}(i) \right. \\ & \times \frac{(i+j+1)!}{2^{(i+j+2)}} - \left(\frac{2\lambda}{\delta} - \frac{2}{\delta} + b + 1\right)\frac{\Gamma(\min(a,b)+3)}{2\min(a,b)!} \\ & - b\frac{\Gamma(\min(a,b)+3)}{6\min(a,b)!}(2[a+b-2\min(a,b)+1] \\ & + (a+b+1)) + (b+2)\frac{\Gamma(\min(a,b-1)+3)}{6\min(a,b-1)!} \\ & \left. \times (2[a+b-1-2\min(a,b-1)+1] + (a+b)) \right\}. \end{aligned} \tag{15}$$

Solving the characteristic equation, which is a polynomial in $E$, gives an analytic eigenvalues. The values of $\lambda_c^{(N)}$ are found by numerically equating $E_i^{(N)}(\lambda) = E_j^{(N)}(\lambda)$, for $\lambda$ with all combinations of $i$ and $j$ where $i \neq j$ and $i,j \leqslant N$. The results are given in Table 1. As in the previous case, Fig. 3 shows the pairwise complex conjugated pseudocritical points in the complex $\lambda^N$-plane for the ground state of the two-electron atoms. As one increases the size of the basis set, the pairwise complex conjugated pseudocritical points converge to the real axis $\lambda_c = 1.09766$. When $\lambda < \lambda_c = 1.09766$ the nuclear charge is large enough to bind two electrons, and this situation remains until the system reaches a critical point $\lambda_c$, the minimum charge necessary to bind two electrons. For $\lambda > \lambda_c$, one of the electrons jumps to infinity with zero kinetic energy.

In summary, we have established a complete analogy between the application of finite size scaling, based on the number of particles, in thermodynamic phase transitions and quantum finite size scaling, based on the number of basis functions, in quantum phase transitions in systems with variable Hamiltonian parameters. We have shown rigorously that singularities in the ground state energy occur only in the infinite complete basis set limit in an analogy with Yang and Lee theorem in classical statistical mechanics. Moreover, this method is general and might be used to analyze quantum critical phenomena in many physical systems such as nuclei, atoms, molecules, quantum dots, clusters, and solids.

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