Finite Size Scaling In Quantum Mechanics

Sabre Kais

Department of Chemistry, Purdue University West Lafayette, IN 47907

ABSTRACT

We present the finite size scaling method for studying the critical behavior of a quantum Hamiltonian $\mathcal{H}(\lambda_1, \cdots, \lambda_k)$ as a function of a set of parameters $\{\lambda_i\}$. In this context, critical means the values of $\{\lambda_i\}$ for which a bound state energy is non-analytic. 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 a given Hamiltonian.

Finite size scaling, quantum phase transitions, stability of atomic and molecular systems.

1 Introduction

In statistical mechanics, the finite-size scaling method gives a way to extrapolate information obtained from a finite system to the thermodynamic limit. In the present 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[1]. In this method, we assume that the two lowest eigenvalues of the quantum Hamiltonian can be taken as the leading eigenvalues of a transfer matrix of a classical pseudo-system. Using finite-size scaling arguments, the phenomenological renormalization equation was used to obtain the critical properties of the classical pseudo-system and therefore of the quantum system[2]. By searching for a fixed point of the phenomenological renormalization equation, the critical charge for two-electron atoms is found to be $Z_c \simeq 0.911$, which is in complete agreement with previous calculations[1]. The fact that this critical charge is below $Z = 1$ explains why H^- is a stable negative ion. For the three-electron atoms, the critical nuclear charge for the ground state was found to be $Z_c \simeq 2.08$, which explains why the He^- is an unstable ion[3].

2 Finite Size Scaling in Quantum Mechanics

In quantum mechanics, when using variation methods, one encounters the finite size problem in studying the critical behavior of a quantum Hamiltonian $\mathcal{H}(\lambda_1, \cdots, \lambda_k)$ 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 non-analytic. This critical point is the point where a bound state energy becomes absorbed or degenerate with a continuum. Here 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[4].

In order to apply the finite size scaling method to quantum mechanics problems, let us consider the following Hamiltonian of the form $\mathcal{H} = \mathcal{H}_0 + V_\lambda$, 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 as the value of λ varies. In quantum calculations, the variation method is widely used to approximate the solution of the Schrödinger equation. To obtain exact results, one should expand the exact wave function in a complete basis set and take the number of basis functions to infinity. In practice, one truncates this expansion at some order N. For a given complete orthonormal λ-independent basis set $\{\Phi_n\}$, the ground state eigenfunction has the following expansion $\Psi_\lambda = \sum_n a_n(\lambda)\Phi_n$, where n represents the 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 a $M(N) \times M(N)$ matrix $\mathcal{H}^{(N)}$, with $M(N)$ being the number of elements in the truncated basis set at order N. Using the standard linear variation method, the Nth-order approximation for the expectation value of any operator $\mathcal{O}$ at order N is given by

$$\langle \mathcal{O} \rangle_\lambda^{(N)} = \sum_{n,m}^{N} a_n(\lambda)^* \, a_m(\lambda) \, \mathcal{O}_{n,m} \qquad (1)$$

where $\mathcal{O}_{n,m}$ are the matrix elements of $\mathcal{O}$ in the basis set $\{\Phi_n\}$. In general, the mean value $\langle \mathcal{O} \rangle$ is not analytical at $\lambda = \lambda_c$, and we can define a critical exponent, $\mu_\mathcal{O}$, by the relation

$$\langle \mathcal{O} \rangle_\lambda \underset{\lambda \to \lambda_c^+}{\sim} (\lambda - \lambda_c)^{\mu_\mathcal{O}} \qquad (2)$$

In statistical mechanics, the singularities in thermodynamic functions associated with a critical point occur only in the thermodynamic limit. In quantum mechanics using the variation approach, singularities in the different mean values will occur only in the limit of infinite

basis functions.

As in the finite size scaling method ansatz in statistical mechanics, we are now in a position to obtain the critical parameters by defining the following function[4]

$$\Delta_{\mathcal{O}}(\lambda; N, N') \;=\; \frac{\ln\left(\langle\mathcal{O}\rangle_{\lambda}^{(N)} \;/\; \langle\mathcal{O}\rangle_{\lambda}^{(N')}\right)}{\ln\left(N' \,/\, N\right)} \;. \qquad (3)$$

Thus, for three different values N, N' and N'' the curves defined by Eq. (3) intersect at the critical point[2]

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') \;=\; \Delta_{\mathcal{O}}(\lambda_c; N'', N) \qquad (4)$$

In order to obtain the critical exponent α, which is associated with the energy, we can take $\mathcal{O} = \mathcal{H}$. The equations are valid only in the asymptotic limit $N \to \infty$, but with a finite basis set, unique values of λ_c and the critical exponents can be obtained as a succession of values as a function of N, N' and N''. The extrapolated values of the critical parameters can be obtain using the algorithm of Bulirsch and Stoer[2].

3 Applications

3.1 Stability of N-electron atoms

To carry out the finite size scaling procedure, one has to choose a convenient basis set to obtain the two lowest eigenvalues and eigenvectors of the finite Hamiltonian matrix. For two-electron atoms, we choose the following basis set functions[1]

$$\begin{aligned}\Phi_{ijk,\ell}(\vec{x}_1, \vec{x}_2) \;&=\; \frac{1}{\sqrt{2}}\left(r_1^i\, r_2^j\, e^{-(\gamma r_1 + \delta r_2)} + \right. \\ &\quad \left. r_1^j\, r_2^i\, e^{-(\delta r_1 + \gamma r_2)}\right) \\ &\quad r_{12}^k \;\; F_\ell(\theta_{12}, \mathbf{\Omega}) \qquad (5)\end{aligned}$$

where γ and δ are variational parameters, r_{12} is the interelectronic distance and $F_\ell(\theta_{12}, \mathbf{\Omega})$is a suitable function of the angle between the positions of the two electrons θ_{12} and the Euler angles $\mathbf{\Omega} = (\vartheta, \phi, \psi)$. This function F_ℓ is different for each orbital-block of the Hamiltonian. For the ground state $F_0(\theta_{12}, \mathbf{\Omega}) = 1$ and $F_1(\theta_{12}, \mathbf{\Omega}) = \sin(\theta_{12})\cos(\vartheta)$ for the $2p^2\ {}^3P$ state. These basis sets are complete for each ℓ-subspace. The complete wave function is then a linear combination of these terms multiplied by variational coefficients determined by matrix diagonalization.

By diagonalizing the finite Hamiltonian matrix, one can obtain the lowest two energy eigenvalues as a function of the order of the truncated basis set, $E_0^{(N)}$ and $E_1^{(N)}$. Using equation (3), one can look for the fixed point of equation (4) by taking the ratio of these two eigenvalues raised to a power N as a function of λ. Figure (1) shows the crossing points, which are the fixed points of equations (4), for $N = 6, 7, 8, \ldots, 13$. The values of the fixed points as a function of N can be extrapolated to the limit $N \to \infty$ by using the Bulirsch and Stoer algorithm [2]. The extrapolated value is $\lambda_c = 1.0976 \pm 0.0004$. This result is in excellent agreement with the best estimate of $\lambda_c = 1.09766079$[1]. The behavior of the ground state energy and its first and second derivatives resemble the behavior of the free energy at a first order phase transition. For $\lambda < \lambda_c$ the nuclear charge is large enough to bind two electrons, and this situation remains until the system reaches a critical point λ_c, which is the maximum value of λ for which the Hamiltonian has a bound state or the minimum charge necessary to bind two electrons. For $\lambda > \lambda_c$, one of the electrons jumps to infinity with zero kinetic energy. The fact that this critical charge is below $Z = 1$ explains why H^- is a stable negative ion.

For three-electron atoms, similar finite size scaling calculations were performed using Hylleraas-type functions[3],

$$\begin{aligned}\Psi_{ijklmn}(\vec{x}_1, \vec{x}_2, \vec{x}_3) \;&=\; CA(r_1^i\, r_2^j\, r_3^k r_{12}^l\, r_{23}^m\, r_{31}^n \\ &\quad e^{-\alpha(r_1+r_2)} e^{-\beta r_3}\chi_1) \qquad (6)\end{aligned}$$

where α and β are variational parameters, χ_1 is the spin function with spin angular moment 1/2, $\mathcal{C}$ a normalization constant and $\mathcal{A}$ the usual three-particle antisymmetrizer operator. For larger atoms, we introduce a simple effective interaction potential to calculate the critical nuclear charges[5]. This potential approximates both the short-range potential of a negative ion core with $Z = N - 1$ electrons and the partially screened long-range Coulomb potential for $Z \neq N - 1$. The critical charge can be found from the following equation

$$E_I(Z_c) \equiv E(N, Z_c) - E(N-1, Z_c) = 0, \qquad Z_c = 1/\lambda_c \qquad (7)$$

where E_I is the extrapolated ionization energy. Results for the critical charges[5], for atoms with $2 \leq N \leq 18$ are in good agreement (mostly within an accuracy of 0.01) with the ab initio multireference configuration interaction calculations [2]

Our computations of critical charges were extended to atoms up to N=86. Our goal here is to perform a systematic check of the stability of atomic dianions. In order to have a stable doubly negatively charged atomic ion one should require the surcharge, $S_e(N) \equiv N - Z_c(N) \geq 2$. We have found that the surcharge never exceeds two. The maximal surcharge, $S_e(86) = 1.48$, is found for the closed-shell configuration of element Rn and can be related to the peak of electron affinity of the element $N = 85$. The results of the surcharges clearly exclude the existence of any stable doubly negatively charged atomic ions in the gas phase and confirms the

previous speculations that at most, only one electron can be added to a free atom in the gas phase. The second extra electron is not bound by the singly charged negative ion because of the repulsive potential surrounding the isolated negative ion.

Proceeding from the fact of the nonexistence of gas phase atomic dianions, it is natural to ask under which conditions, if any, one could have stable atomic dianions. One possibility is to place these atoms in strong magnetic fields. Initial results for the critical magnetic field B_c, the minimum field necessary to obtain the surcharge $S_e = 2$, show that dianions with closed shell configurations such as O^{-2}, S^{-2}, Se^{-2}, Te^{-2}, and Po^{-2} became stable at about 1 to 2 a.u. (1 a.u. = 2.35 10^9 G). However, dianions with an external s-electron such as Ne^{-2}, Ar^{-2} and Kr^{-2} do not exist at any magnetic field strength.

3.2 Stability of small molecules

Molecular systems are challenging from the critical phenomenon point of view. Several investigators have performed calculations on the stability of H_2^+-like systems in the Born-Oppenheimer approximation. Critical charge parameters separating the regime of stable, metastable and unstable binding were calculated using ab initio methods. However, we have shown[6], using the finite size scaling approach that this critical charge is not a critical point (here a critical point, in the language of phase transitions, means a point of nonanalyticity in the energy). But, without making use of the Born-Oppenheimer approximation the H_2^+-like system does exhibit a critical point. In order to use finite size scaling we introduce the following basis set[6]

$$\begin{aligned} \Phi_{(n,m,l)}(r_1, r_2, r_{12}) &= N_0 \phi_n(x)\phi_m(y)\phi_l(z) \\ \phi_n(x) &= L_n(x)e^{-x/2} \end{aligned}$$

where N_0 is the normalization coefficient and $\phi_n(x)$ is given in terms of Laguerre polynomials $L_n(x)$. The coordinates (x, y, z) are expressed in perimetric coordinates[6]. Calculating the matrix elements of the Hamiltonian in this basis set gives a sparse, real, and symmetric $M(N) \times M(N)$ matrix of order N. By systematically increasing the order N we obtained the lowest two eigenvalues at different basis lengths $M(N)$. Using the finite size scaling equation we can obtain the fixed point[6]. The crossing points between two different sizes N and $N+1$ give a series for $\{\lambda^{(N)}\}$. By systematically increasing the order N, one can reach the critical point λ_c=1.2286. This result shows that for one-electron molecules, H_2^+ is the only stable system. Thus, systems like HeH^{+2}, He_2^{+3} etc. are all unstable. However, these systems might be stable in external fields. Exposure to electric and magnetic fields will lead to a dramatic variation of both the electronic structure and the dynamic processes of such systems. As an initial system, we studied the electronic stability of simple linear molecules in homogeneous stationary magnetic fields. The critical field is near $11 \times 10^9 G$ (4.7 a.u.) where the molecular potential energy curve begins to have a local minimum. The distance for bonding is near 1.95 a.u.

In order to apply the finite size scaling method for larger molecular systems, we have tested several types of Gaussian basis sets. Research is still underway to combine this method with the ab initio methods using Gaussian basis sets.

3.3 Search for stable multiply-charged anions in the gas phase

Small dianions such as O^{-2} or CO_3^{-2} are very common in solution and solid-state chemistry, but are unstable in the gas phase[7]. This instability is due to the strong Coulomb repulsion between the excess negative charges. Thus there is still an open question concerning the smallest molecule that can bind two or more excess electrons with both electronic, against electron detachment, and thermodynamic, against fragmentation, stability[7]. A number of multiply-charged anions with relatively large size, more than 10 atoms, have been observed in the gas phase. However, experimentally there are only a few stable small dianions[7], consisting of less than 10 atoms, including $C_n^{-2}(n = 7-9)$, $S_2O_6^{-2}$, and most recently found, four penta-atomic dianions, PtX_4^{-2} and PdX_4^{-2} (X=Cl and Br)[8]. Extensive theoretical works have been carried out on small gaseous multiply-charged anions. We used the finite size scaling method along with a model potential to investigate the stability of spherical molecular systems.

Initial results using WKB theory give an estimate of the lifetimes of the dianions as a function of their size. We estimate the transition from stable to metastable dianions to occur when the radius of the spherical molecule is about 6Å. This finding is consistence with the estimated repulsive Coulomb barrier from the photoelectron spectra of the citric acid doubly charged anion[9]. By choosing a convenient basis set for the finite size scaling procedure, research is underway to calculate the critical radius of the sphere, R_c, for stable dianions as a function of molecular parameters.

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