

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228443312>

Finite Size Scaling in Quantum Mechanics

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · NOVEMBER 1998

Impact Factor: 2.69 · DOI: 10.1021/jp9820572

CITATIONS

15

READS

5

2 AUTHORS, INCLUDING:



Sabre Kais

Purdue University- USA; QEERI - Qatar and S...

231 PUBLICATIONS 2,318 CITATIONS

SEE PROFILE

Chapter 6

Finite Size Scaling in Quantum Mechanics

Sabre Kais[†] and Pablo Serra[‡]

[†]*Department of Chemistry, Purdue University, West Lafayette, IN 47907*

[‡]*Facultad de Matemática, Astronomía y Física,
Universidad Nacional de Córdoba - Ciudad Universitaria - 5000 Córdoba -
Argentina*

e-mail: kais@purdue.edu, serra@famaf.unc.edu.ar

ABSTRACT

We present the finite-size scaling approach for the calculations of the critical parameters for quantum systems. As an example of how this approach can be used we calculate critical conditions for stable dipole-bound anions. The approach is general and can be used to calculate critical parameters for any given quantum system.

6.1 Introduction

The existence of phase transitions is associated with singularities of the free energy. These singularities occur only in the thermodynamic limit[1, 2]. In statistical mechanics, the finite size scaling method provides a systematic way to extrapolate information obtained from a finite system to the thermodynamic limit[3, 4, 5, 6]. Recently, 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[7, 8]. These new transitions are tuned by parameters in the Hamiltonian.

In quantum mechanics, we have shown that the finite size corresponds not to the spatial dimension, as in statistical mechanics, but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given

Hamiltonian and calculate the quantum critical parameters[9, 10]. This method is efficient and very accurate for estimating the critical screening length for one-electron screened Coulomb potentials[9], the critical nuclear charges for two-electron atoms[11, 12], three-electron atoms[13] and simple diatomic molecules[14]. For three-body Coulomb systems with charges (Q, q, Q) and masses (M, m, M) , full numerical results, using finite size scaling method, with an arbitrary mass ratio $0 \leq \kappa = (1 + \frac{m}{M})^{-1} \leq 1$ show that there exists a transition curve $\lambda_c(\kappa)$ through which all systems undergo a first-order phase transition from stable to unstable. This approach lead to a new proposed classification of the three-body Coulomb systems: molecule-like systems and atom-like systems[15].

In the next section we will introduce the finite size scaling approach for quantum systems followed by an example of how this approach can be used to calculate critical conditions for stable dipole-bound anions. The approach is general and can be used to calculate critical parameters for any given quantum system.

6.2 Finite Size Scaling in Quantum Mechanics

In order to apply the finite size scaling to quantum mechanics problems we will consider the following Hamiltonian[16]

$$\mathcal{H} = \mathcal{H}_0 + V_\lambda . \quad (6.1)$$

where \mathcal{H}_0 is λ -independent 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. Without loss of generality, we will assume that the Hamiltonian, Eq. (6.1), has a bound state E_λ for $\lambda > \lambda_c$ which becomes equal to zero at $\lambda = \lambda_c$. As in statistical mechanics, we can define some critical exponents related to the asymptotic behavior of different quantities near the critical point. In particular, for the energy we can define the critical exponent α as

$$E_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^\alpha \quad (6.2)$$

For general potentials of the form $V_\lambda = \lambda \overline{V}$, Simon[17] showed that the critical exponent α is equal to one if and only if $\mathcal{H}(\lambda_c)$ has a normalizable eigenfunction with eigenvalue equal to zero. The existence or absence of a bound state at the critical point is related to the type of the singularity in the energy. Using statistical mechanics terminology, we can associate “first order phase transitions” with the existence of a normalizable eigenfunction at the critical point. The absence of such a function could be related to “continuous phase transitions”[9, 10].

In order to obtain the value of λ_c from studying the eigenvalues of a finite-size Hamiltonian matrix one has to define a sequence of pseudo-critical parameters, $\lambda^{(N)}$.

Although there is no unique recipe to define such a sequence, one can use the first order method which can be applied if the threshold energy is known [11, 18], or the phenomenological renormalization [19, 5] method, where the sequence of the pseudo-critical values of λ can be calculated by knowing the first and the second lowest eigenvalues of the \mathcal{H} -matrix for two different orders, N and N' [11, 12, 13]. In this chapter we will introduce a direct approach which is closely related to the variational method in quantum calculations.

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 . In the present approach, the finite size corresponds not to the spatial dimension, as in statistical mechanics, but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. For a given complete orthonormal λ -independent basis set $\{\Phi_n\}$, the ground state eigenfunction has the following expansion

$$\Psi_\lambda = \sum_n a_n(\lambda) \Phi_n \quad (6.3)$$

where n represents the set of quantum numbers. In order to approximate the different quantities, we have to truncate the series, Eq. (6.3) at order N . Then the Hamiltonian is replaced by $M(N) \times M(N)$ 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 N th-order approximation for the energies are given by the eigenvalues $\{\Lambda_i^{(N)}\}$ of the matrix $\mathcal{H}^{(N)}$. The corresponding eigenfunctions are given by

$$\Psi_\lambda^{(N)} = \sum_n^{M(N)} a_n^{(N)}(\lambda) \Phi_n \quad (6.4)$$

where the coefficients $a_n^{(N)}$ are the components of the ground-state eigenvector. In this representation, the expectation value of any operator \mathcal{O} at order N is given by

$$\langle \mathcal{O} \rangle_\lambda^{(N)} = \sum_{n,m}^N a_n^{(N)}(\lambda)^* a_m^{(N)}(\lambda) \mathcal{O}_{n,m} \quad (6.5)$$

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

$$\langle \mathcal{O} \rangle_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^{\mu_{\mathcal{O}}}. \quad (6.6)$$

In statistical mechanics, the singularities in thermodynamic functions associated with a critical point occur only in the thermodynamic limit. In the variation approach singularities in the different mean values will occur only in the limit of infinite basis functions[16].

As in the finite size scaling ansatz in statistical mechanics [5, 20], we will assume that there exists a scaling function for the truncated magnitudes such that

$$\langle \mathcal{O} \rangle_\lambda^{(N)} \sim \langle \mathcal{O} \rangle_\lambda F_{\mathcal{O}}(N|\lambda - \lambda_c|^\nu) \quad (6.7)$$

with a different scaling function $F_{\mathcal{O}}$ for each different operator but with a unique scaling exponent ν .

Now we are in a position to obtain the critical parameters by defining the following function[16]

$$\Delta_{\mathcal{O}}(\lambda; N, N') = \frac{\ln \left(\langle \mathcal{O} \rangle_\lambda^{(N)} / \langle \mathcal{O} \rangle_\lambda^{(N')} \right)}{\ln(N' / N)} . \quad (6.8)$$

At the critical point, the mean value depends on N as a power law, $\langle \mathcal{O} \rangle \sim N^{-\mu_{\mathcal{O}}/\nu}$, thus one obtains an equation for the ratio of the critical exponents

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \frac{\mu_{\mathcal{O}}}{\nu} , \quad (6.9)$$

which is independent of the values of N and N' . Thus, for three different values N, N' and N'' the curves defined by Eq. (6.8) intersect at the critical point

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \Delta_{\mathcal{O}}(\lambda_c; N'', N) \quad (6.10)$$

In order to obtain the critical exponent α , which is associated with the energy, we can take $\mathcal{O} = \mathcal{H}$ in Eq. (6.9) with $\mu_{\mathcal{O}} = \alpha$,

$$\frac{\alpha}{\nu} = \Delta_{\mathcal{H}}(\lambda_c; N, N') . \quad (6.11)$$

and by using the Hellmann-Feynman theorem[21] we obtain,

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \frac{\partial \mathcal{H}}{\partial \lambda} \right\rangle_\lambda = \left\langle \frac{\partial V_\lambda}{\partial \lambda} \right\rangle_\lambda . \quad (6.12)$$

Taking $\mathcal{O} = \partial V_\lambda / \partial \lambda$ in Eq. (6.9) gives an equation for $(\alpha - 1)/\nu$, that together with Eq. (6.11) give the exponents α and ν . Now, we can define the following function

$$\Gamma_\alpha(\lambda; N, N') = \frac{\Delta_{\mathcal{H}}(\lambda; N, N')}{\Delta_{\mathcal{H}}(\lambda; N, N') - \Delta_{\partial V_\lambda / \partial \lambda}(\lambda; N, N')} \quad (6.13)$$

which is also independent of the values of N and N' at the critical point $\lambda = \lambda_c$ and gives the critical exponent α ,

$$\alpha = \Gamma_\alpha(\lambda_c; N, N') \quad (6.14)$$

From Eq. (6.11) the critical exponent ν is readily given by

$$\nu = \frac{\alpha}{\Delta_{\mathcal{H}}(\lambda_c; N, N')} . \quad (6.15)$$

The finite size scaling equations are valid only as an asymptotic expressions, $N \rightarrow \infty$, but with finite basis set unique values of λ_c, α and ν can be obtained as a succession of values as a function of N, N' and N'' . The relation between N, N' and N'' was extensively studied in finite size scaling in statistical mechanics[5], and it is known that the fastest convergence is obtained when the difference between these numbers is as small as possible. In previous work[9, 10], we took $\Delta N = 1$, and when there are parity effects we used $\Delta N = 2$. In order to obtain the extrapolated values for $\lambda^{(N)}, \alpha^{(N)}$ and $\nu^{(N)}$ at $N \rightarrow \infty$ we used the algorithm of Bulirsch and Stoer[22] with $N' = N + \Delta N$ and $N'' = N - \Delta N$.

6.3 Applications

Finite size scaling method have been used to calculate critical parameters for atomic and molecular systems[9]. Here as an example we will apply this approach to obtain the critical conditions for stable dipole-bound anions[25]. Dipole-bound anions are unstable relative to autodetachment unless the dipole moment strength exceeds a certain critical value. This interesting problem has a long history with a number of methods having been used to obtain the critical value of the dipole moment [26, 27, 28, 29, 30, 31, 32].

The Hamiltonian, in atomic units, for an electron in a two-center Coulomb potential with a charge $+Z$ at $\vec{r} = 0$ and a charge $-Z$ localized along the z -axis is given by

$$\mathcal{H}(Z; R; \vec{x}) = -\frac{1}{2}\nabla^2 - Z \left(\frac{1}{r} - \frac{1}{|\vec{r} - R\hat{k}|} \right) , \quad (6.16)$$

where R is the distance between the fixed charges and \hat{k} is a unitary vector in the z -direction.

After scaling the Hamiltonian has only one free parameter, the electric dipole moment $\mu = ZR$,

$$\mathcal{H}(Z; R; \vec{x}) = Z^2 \mathcal{H}(1; \mu; Z\vec{x}) = \frac{1}{R^2} \mathcal{H}(\mu; 1; \vec{x}/R) . \quad (6.17)$$

In order to apply the finite size scaling method one has to introduce an appropriate basis set. Since the potential has a cylindrical symmetry, the ground state wave function in spherical coordinates can be written as

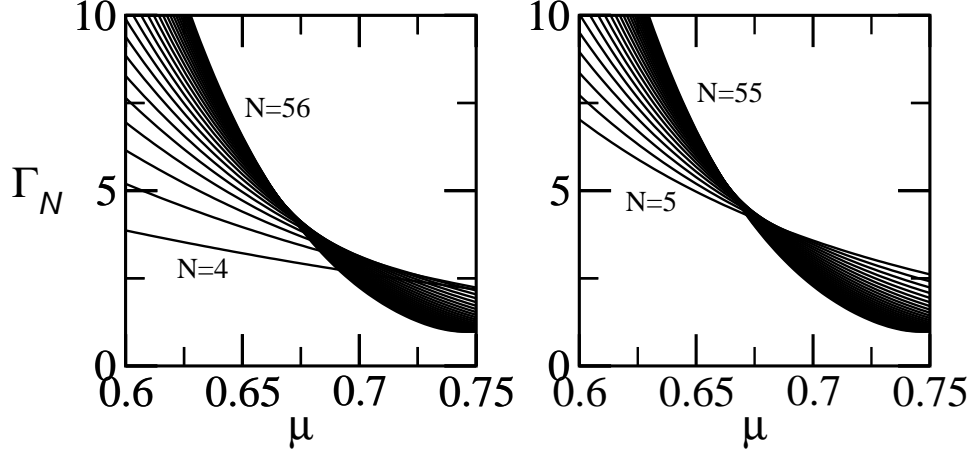


Figure 6.1: $\Gamma(\beta = 0.01; \mu)$ as a function of μ for the ground state energy of the electric dipole potential for even values of $N = 4, \dots, 56$ and for odd values of $N = 5, \dots, 55$.

$$\Psi_0(\vec{r}) = \Psi_0(r, \theta). \quad (6.18)$$

This ground-state wave function could be expanded in a complete spherical basis-set using spherical harmonics with $m = 0$. We use a (non-orthogonal) Slater basis-set of the form[25]

$$\Phi_{n,l}(\vec{r}) = \left[\frac{\beta^{2n+3}}{(2n+2)!} \right]^{1/2} e^{-\beta r/2} r^n Y_l^0(\theta, \phi) \quad ; \quad n = 0, 1, \dots \quad ; \quad l = 0, \dots, n, \quad (6.19)$$

where β is a variational parameter used to optimize the numerical results.

The ground state energy was calculated using the Ritz-variational method for non-orthogonal basis-set[21]. The Slater basis-set is truncated allowing a maximum value of n in Eq.(6.19) $n = 0, \dots, N$, with the restriction over $l = 0, \dots, n$, we obtain the size of the truncated Hamiltonian matrix to be $M(N) = (N+1)(N+2)/2$.

In order to calculate the Hamiltonian matrix, its eigenvalues and eigenvectors, we have to discuss two technical problem. First of all, the matrix elements are in general a summation of large numbers of alternate signs given a small number. Secondly, the basis-set is non-orthogonal. It is known that the standard Gram-Schmidt orthogonalization process is not good numerically[23] therefore we used a Cholesky decomposition to the overlap matrix in order to solve the eigenvalue problem. But the determinant of the overlap matrix goes dramatically to zero,

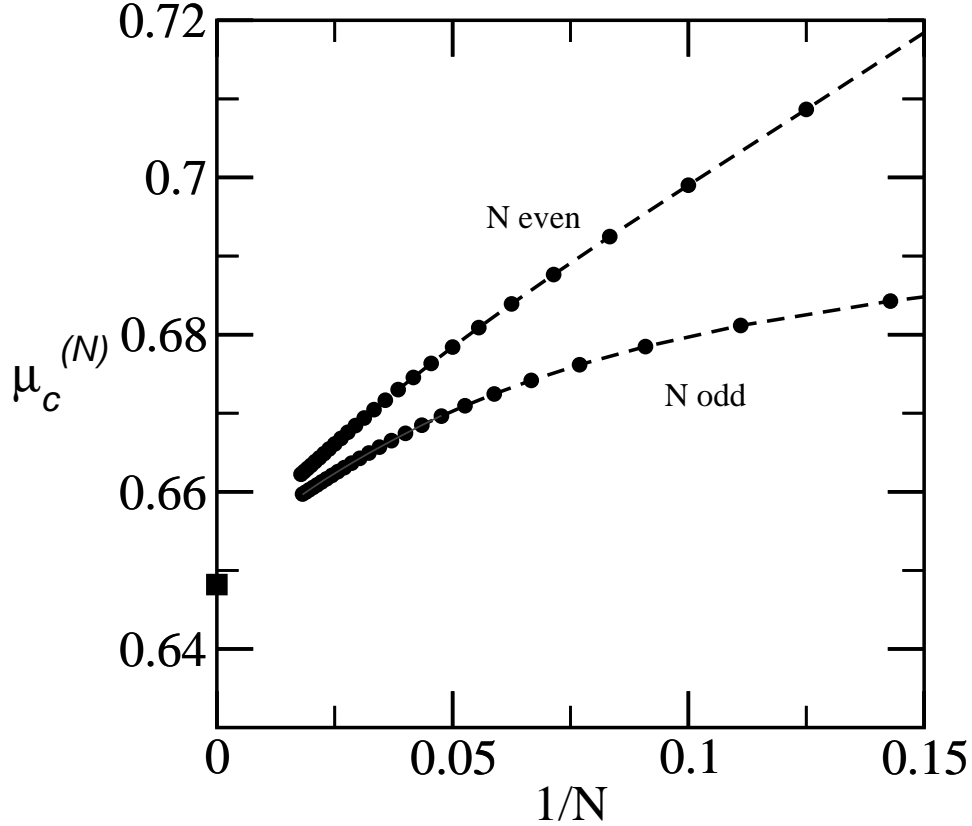


Figure 6.2: $\Gamma(\beta = 0.01; \mu)$ as a function of μ for the ground state energy of the electric dipole potential for even and odd values of $N = 7, \dots, 56$. The extrapolated value $\mu_c \simeq 0.648 a.u.$ is shown by a square.

and working with standard real(8) (16 digits) Fortran compilers the decomposition becomes numerically unstable for small values of $N \simeq 10$. In reference [25] we used quadruple precision (32 digits) to get the data for $N \leq 28$. In the present work we have used a multiprecision Fortran 90 code [24] with 150 digits to calculate the Hamiltonian matrix and the eigenvalues are calculated with standard real(8) codes. With this high precision we were able to calculate eigenvalues and eigenvectors up to $N = 58$, which means a Hamiltonian matrix of 1770×1770 .

Finite size scaling calculations for spherically symmetric potentials show strong parity effects. We also find parity effects for the dipole potential, so Eq. (14) was used with $N' = N + 2$. In Fig. (6.1) we show the results of the finite size scaling

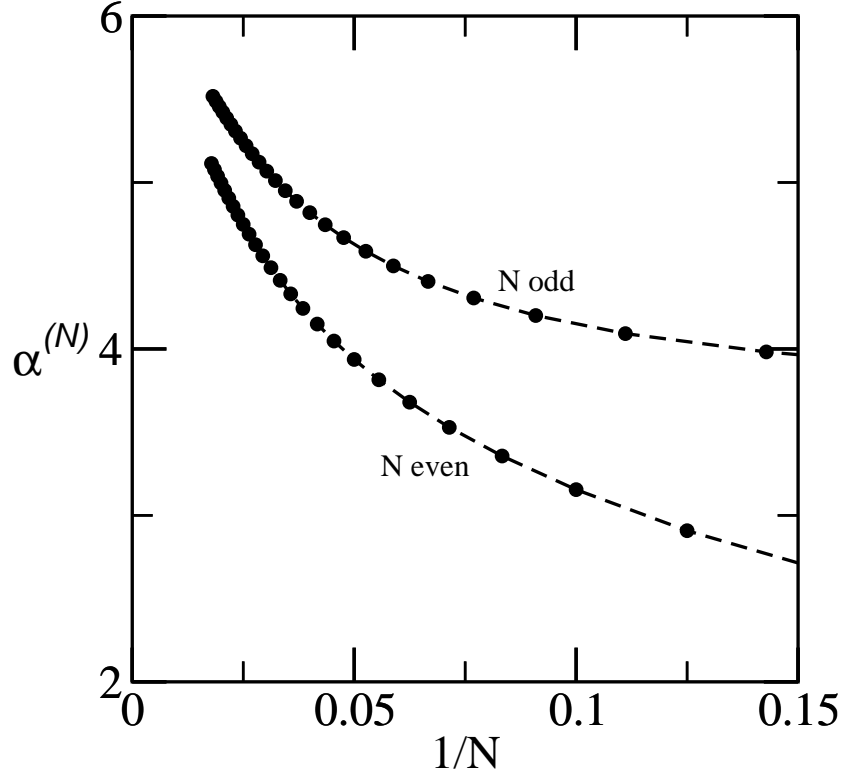


Figure 6.3: $\alpha^{(N)}(\beta = 0.01)$ as a function of $1/N$ for the ground state energy of the electric dipole potential for even and odd values of $N = 5, \dots, 56$.

calculations for even values of $N = 4, \dots, 56$ and for odd values of $N = 5, \dots, 55$. Plotting Γ_N as a function of μ for different values of N gives a family of curves with an intersection at μ_c . Since the intersection between two consecutive curves depends on the size of the basis set N , in Fig. (6.2) we show the extrapolation curves for the pseudo critical dipole moment $\mu_c^{(N)}(\beta = 0.01)$ as a function of $1/N$ for even and odd values of N . The scaling was done with $E(\mu; 1)$ and the extrapolated value is $\mu_c^{(ext)} \simeq 0.648 a.u.$. This value of the critical dipole is in a good agreement with results obtained using other methods[26, 27, 28].

An exact asymptotic analysis shows that the energy tends to zero exponentially as the dipole moment reaches the critical value [32]. That means it goes to zero faster than any power of $(\mu - \mu_c)$ and a value $\alpha = \infty$ is associated with the critical exponent [9]. In Fig. (6.3) we show the values of $\alpha^{(N)}$ obtained from Eq. (6.14). These data are compatible with value $\alpha = \infty$.

In summary, the finite size scaling method in quantum mechanics is simple accurate and can be used in a systematic way to estimate directly the critical parameters for any given quantum system.

Acknowledgements

We would like to thank Qicun Shi, Juan Pablo Neirotti, Alexie Sergeev, and Jiaxiang Wang for their contributions in applying finite size scaling for quantum systems. We would like also to acknowledge the financial support of the Office of Naval Research (N00014-97-1-0192), The National Science Foundation (NSF- 501 1393-0650) and The American Chemical Society (ACS PRF-37516-AC6). P. S. thanks CONICET and SECYTUNC for partial financial support.

Bibliography

- [1] C.N. Yang and T.D. Lee *Phys. Rev.* **87** 404 (1952).
- [2] T.D. Lee and C.N. yang *Phys. Rev.* **87** 410 (1952).
- [3] M. E. Fisher In *Critical Phenomena*, Proceedings of the 51st Enrico Fermi Summer School, Varenna, Italy, M. S. Green, ed. (Academic Press, New York 1971).
- [4] M. N. Barber *Finite-Size Scaling In Phase Transitions and Critical Phenomena* Ed. C. Domb and J. L. Lebowitz (Academic Press, New York 1983).
- [5] V. Privman ed. *Finite Size Scaling and Numerical Simulations of Statistical Systems*, (World Scientific, Singapore, 1990).
- [6] J.L. Cardy *Finite-Size Scaling*, (Elsevier Science Publishers, New York, 1988).
- [7] S. L. Sondhi, S. M. Girvin, J. P. Carini, D. Shahar *Rev. Mod. Phys.* **69** 315 (1997).
- [8] S. Sachdev *Quantum Phase Transitions* (Cambridge Univ. Press, New York 1999).
- [9] S. Kais, and P. Serra *Adv. Chem. Phys.* **125** 1 (2003).
- [10] S. Kais, and P. Serra *Int. Rev. Phys. Chem.* **19** 97 (2000).
- [11] J.P. Neirotti, P. Serra, and S. Kais *Phys. Rev. Lett.* **79** 3142 (1997).

- [12] J. P. Neirotti, P. Serra and S. Kais *J. Chem. Phys.* **108** 2765 (1998).
- [13] P. Serra, J. P. Neirotti, and S. Kais *Phys. Rev. Lett.* **80** 5293 (1998).
- [14] Q. Shi and S. Kais *Mol. Phys.* **98** 1485 (2000).
- [15] Q. Shi and S. Kais *Int. J. Quantum Chem.* **85** 307 (2001).
- [16] P. Serra, J. P. Neirotti, and S. Kais *Phys. Rev. A* **57** R1481 (1998).
- [17] B. Simon *J. Functional Analysis* **25** 338 (1977).
- [18] P. Serra and J. F. Stilck *Europhys Lett.* **17** 423 (1992); *Phys. Rev. E* **49** 1336 (1994).
- [19] M. P. Nightingale *Physica* **83A** 561 (1976).
- [20] B. Derrida and L. De Seze *J. Physique* **43** 475 (1982).
- [21] See for example in E. Merzbacher *Quantum Mechanics*, third edition (John Wiley, New York, **1998**).
- [22] R. Bulirsch and J. Stoer *Numer. Math.* **6** 413 (1964).
- [23] W.H. Press, S.A. Teukolsky, W.T. Vetterling and B.P. Flannery *Numerical Recipes in Fortran 77*, 2nd ed., Cambridge University Press, Cambridge (1996).
- [24] David H. Bailey *ACM Transactions on Mathematical Software* **21**, 379 (1995).
- [25] P. Serra and S. Kais *Chem. Phys. Lett.* **372** 205 (2003).
- [26] E. Fermi and E. Teller *Phys. Rev.* **72** 399 (1947).
- [27] J.E. Turner, V.E. Anderson and K. Fox *Phys. Rev.* **174**. 81 (1968).
- [28] J. Levy-Leblond *Phys. Rev.* **153** 1 (1967).
- [29] C. Sarasola, J.E. Fowler and J.M. Ugalde *J. Chem. Phys.* **110** 11717 (1999).
- [30] P. Skurski, M. Gutowski and J. Simons *J. Chem. Phys.* **110** 274 (1999).
- [31] F. Wang and K.D. Jordan *J. Chem. Phys.* **114** 10717 (2001).
- [32] D.I. Abramov and I.V. Komarov *Theor. Math. Phys.* **13** 209 (1972).