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Finite size scaling for critical parameters of simple diatomic molecules

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We use the finite size scaling method to study the critical points, points of non-analyticity, of the ground state energy as a function of the coupling parameters in the Hamiltonian. In this approach, the finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given molecular Hamiltonian. To illustrate this approach, we give detailed calculations for systems of one electron and two nuclear centres, $Z^+e^-Z^+$. Within the Born–Oppenheimer approximation, there is no critical point, but without the approximation the system exhibits a critical point at $Z = Z_c = 1.228\,279$ when the nuclear charge, Z, varies. We show also that the dissociation occurs in a first-order phase transition and calculate the various related critical exponents. The possibility of generalizing this approach to larger molecular systems using Gaussian basis sets is discussed.

1. Introduction

The calculations of critical parameters for stability of atomic and molecular systems, such as particle masses, nuclear charges and external fields, is a research area of increasing interest. This increasing interest is motivated by the following [1]: recent experimental searches for the smallest stable multiply charged anions in the gas phase [2–4]; finding limits on the stability of positive molecular ions [5–7], and experimental and theoretical work on systems in external electric and magnetic fields [8, 9]. For example, Rost *et al.* [8] presented the first experimental observation of the control of the dissociation energy of a polyatomic molecule with an external magnetic field. They observed that the NO_2 photodissociation threshold is linearly lowered with magnetic field strength. So, estimating the critical field for breaking molecular bonds is of great value.

Moreover, by calculating the critical nuclear charges, the minimum charge necessary to bind N electrons, one can explain and predict the stability of atomic anions. Morgan and co-workers [10] concluded that the critical charge obeys the following inequality, $N - 2 \le Z_c \le N - 1$. Our numerical results [11], as well as the *ab initio* results of Hogreve [12] and that of Davidson and co-workers [13] for atoms up to $N = 18$, confirmed this inequality, and showed that at most, only one electron can be added to a free atom in the gas phase.

Recently with Serra [1] we have found that one can describe stability of atomic ions and symmetry breaking of electronic structure configurations as quantum phase transitions and critical phenomena. Quantum phase transitions can take place when some parameter in the Hamiltonian of the system is varied. We identify any point of non-analyticity in the ground state energy as a critical point. The non-analyticity could be either the limiting case of an avoided level crossing or an actual level crossing [14]. For the Hamiltonian of N-electron atoms, this parameter was taken to be the reciprocal nuclear charge. As the nuclear charge reaches a critical point, the quantum ground state changes its character from being bound to being degenerate or absorbed by a continuum. For two- [15] and three-electron atoms [16], we have used the finite size scaling method to obtain the critical nuclear charges. The finite size scaling method was formulated in statistical mechanics to extrapolate information obtained from a finite system to the thermodynamic limit [17, 18]. In quantum mechanics, the finite size corresponds to the number of elements in a complete basis set used to expand the exact wave function for a given Hamiltonian [19].

Molecular systems are challenging from the critical phenomenon point of view. In this paper, we present the finite size scaling calculations to obtain critical parameters for simple molecular systems. As an example we give detailed calculations for the critical parameters for H_2^+-like molecules without making use of the Born–Oppenheimer approximation. The system exhibits a critical point and dissociates through a first-order phase transition.

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2. Scaled quantum Hamiltonian

In this section, the general Hamiltonian for A charged point particles under Coulomb interactions is represented, in Cartesian coordinates, by

$$\mathbf{H} = \sum_{i}^{A} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i<j}^{A} \frac{Q_i Q_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \tag{1}$$

where $\mathbf{P}_i$, $\mathbf{R}_i = [X_i, Y_i, Z_i]$, M_i and Q_i are the momentum operator, column-vector coordinates, mass, and charge of particle i respectively. Atomic units (au) are used unless otherwise specified.

After separation of the translational motion [20] of the centre-of-mass (CM) $M_0 = \sum_i^A M_i$ through

$$\begin{pmatrix} \mathbf{r}_0 \\ \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_a \end{pmatrix} = \begin{pmatrix} \frac{M_1}{M_0} & \frac{M_2}{M_0} & \frac{M_3}{M_0} & \cdots & \frac{M_A}{M_0} \\ -1 & 1 & 0 & \cdots & 0 \\ -1 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & 0 & 0 & \cdots & 1 \end{pmatrix} \begin{pmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \\ \mathbf{R}_3 \\ \vdots \\ \mathbf{R}_A \end{pmatrix} \tag{2}$$

and

$$\begin{pmatrix} \mathbf{p}_0 \\ \mathbf{p}_1 \\ \mathbf{p}_2 \\ \vdots \\ \mathbf{p}_a \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & \cdots & 1 \\ -\frac{M_2}{M_0} & -\left(\frac{M_2}{M_0} - 1\right) & -\frac{M_2}{M_0} & \cdots & -\frac{M_2}{M_0} \\ -\frac{M_3}{M_0} & -\frac{M_3}{M_0} & -\left(\frac{M_3}{M_0} - 1\right) & \cdots & -\frac{M_3}{M_0} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -\frac{M_A}{M_0} & -\frac{M_A}{M_0} & -\frac{M_A}{M_0} & \cdots & -\left(\frac{M_A}{M_0} - 1\right) \end{pmatrix} \begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \\ \mathbf{P}_3 \\ \vdots \\ \mathbf{P}_A \end{pmatrix}, \tag{3}$$

the Hamiltonian becomes

$$\mathbf{H} = \sum_{i=0}^{a} \frac{\mathbf{p}_i^2}{2\mu_i} + \frac{1}{2M_1} \sum_{1=i\neq j}^{a} \mathbf{p}_i \cdot \mathbf{p}_j + \sum_{0=i<j}^{a} \frac{Q_{i+1} Q_{j+1}}{r_{ij}}, \tag{4}$$

where $a = A - 1$; the μ_i are the reduced masses with $\mu_0 = M_0$ and $\mu_i = (M_1 M_{i+1})/(M_1 + M_{i+1})$; $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{R}_{i+1} - \mathbf{R}_{j+1}|$ and $r_i = |\mathbf{r}_i| = |\mathbf{R}_{i+1} - \mathbf{R}_1|$; $(\mathbf{r_0})$ is the CM vector, and $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_a)$ are the vectors of internal coordinates of particle $2, 3, \ldots, A$ respectively, and $(\mathbf{p}_0, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_a)$ are their corresponding momenta. It is interesting to note that equations (2) and (3), for the separation of the translational degrees of freedom, do not change the representation of the Coulomb potentials.

Now, an explicit form of the coulombic interactions V for a quantum system including B electrons and C positive charged centres (protons) may be written as

$$V = \sum_{0=i<j}^{b} \frac{1}{r_{ij}} - \sum_{i=0}^{b} \sum_{k=b+1}^{a} \frac{Z_k}{r_{ik}} + \sum_{b+1=k<l}^{a} \frac{Z_k Z_l}{r_{kl}}, \tag{5}$$

where the indices i, j are for electrons and k, l for protons with $b = B - 1$ and $a = A - 1 = B + C - 1$. The potential V in equation (5) includes electron–electron repulsive terms, electron–proton attractive terms and proton–proton repulsive terms.

The Z^2-scaled Hamiltonian, if we consider the internal motion only, is given by

$$H = \sum_{i=1}^{a} \frac{\mathbf{p}_i^2}{2\mu_i} + \frac{1}{2M_1} \sum_{0=i\neq j}^{a} \mathbf{p}_i \cdot \mathbf{p}_j + \sum_{0=i<j}^{b} \frac{1}{Zr_{ij}} - \sum_{i=0}^{b} \sum_{k=b+1}^{a} \frac{Z_k}{Zr_{ik}} + \sum_{b+1=k<l}^{a} \frac{Z_k Z_l}{Zr_{kl}}. \tag{6}$$

For atoms, $C = 1$ and $a = b + 1$, the last term in equation (6) drops out, and we may choose $Z = Z_{b+1}$ and then introduce $\lambda = 1/Z$ to put the Hamiltonian in the general form [21]

$$H = \sum_{i=1}^{a} \frac{\mathbf{p}_i^2}{2\mu_i} + \frac{1}{2M_1} \sum_{0=i\neq j}^{a} \mathbf{p}_i \cdot \mathbf{p}_j - \sum_{i=0}^{b} \frac{1}{r_{ib+1}} + \lambda \sum_{i<j}^{b} \frac{1}{r_{ij}}. \tag{7}$$

Equation (7) is a Z^2-scaled non-adiabatic Hamiltonian for a quantum system with one proton and B electrons. Assuming an infinite mass approximation for the proton, one recovers the atomic Hamiltonians used in the finite size scaling calculations [15, 16].

Generally, we should choose $\lambda = 1/Z$ to maintain a linear operator for a multi-electron and multi-proton system, where the λ-dependent part includes both repulsive and attractive terms. However, for one-electron system, $B = 1$, $b = 0$ and $a = C$, the Z^2-scaled Hamiltonian becomes

$$H = \sum_{i=1}^{a} \frac{\mathbf{p}_i^2}{2\mu_i} + \frac{1}{2M_1} \sum_{0=i\neq j}^{a} \mathbf{p}_i \cdot \mathbf{p}_j - \sum_{k=1}^{a} \frac{Z_k}{Zr_{0k}} + \sum_{1=k<l}^{a} \frac{Z_k Z_l}{Zr_{kl}}, \tag{8}$$

where the electron–electron term drops out compared to equation (6) but H is still a function of Z and $\{Z_k\}$. In the special case of equal charged centres, we may choose $\lambda = Z = Z_k$ and the simplified Hamiltonian reads

$$H = \sum_{i=1}^{a} \frac{\mathbf{p}_i^2}{2\mu_i} + \frac{1}{2M_1} \sum_{0=i\neq j}^{a} \mathbf{p}_i \cdot \mathbf{p}_j - \sum_{k=1}^{a} \frac{1}{r_{0k}} + \lambda \sum_{1=k<l}^{a} \frac{1}{r_{kl}}, \tag{9}$$

Therefore, the Hamiltonian of simple molecular systems can be represented as

$$\mathcal{H}(\lambda) = \mathcal{H}_0 + \mathcal{V}_\lambda, \tag{10}$$

where $\mathcal{H}_0$ is λ independent and $\mathcal{V}_\lambda$ is the λ-dependent part. This Hamiltonian has the correct general form for the application of the finite size scaling method to determine the critical value of the parameter λ [15, 16].

3. Finite size scaling theory

We have shown that the finite size scaling method is very efficient and accurate for the calculations of the critical parameters of the few-body Schrödinger equation [19]. The finite size scaling method was formulated in classical statistical mechanics to extrapolate information obtained from a finite system to the thermodynamic limit [17, 18]. In quantum mechanics, 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 [1].

As in the atomic studies, for a given Hamiltonian, $\mathcal{H}(\lambda)$, we have to choose a complete orthonormal λ-independent basis set $\{\Phi_n\}$. In this case, the eigenfunction of $\mathcal{H}(\lambda)$ has the following expansion

$$\Psi(\lambda) = \sum_n c_n \Phi_n, \tag{11}$$

where the sum is over all adequate sets of indices which characterize the commutation of all symmetry operations with the Hamiltonian. To calculate the different quantities, we have to truncate the infinite series expansion, equation (11), at order N. For the Hamiltonian $\mathcal{H}(\lambda)$, we project equation (10) to the finite basis set and obtain a $M(N) \times M(N)$ Hamiltonian matrix, where $M(N)$ is the expansion length.

Using standard diagonalization procedures, an approximate energy series can be obtained at order N for negative and positive eigenvalues $\{\Lambda_i^{(N)}\}$. The lowest eigenvalue corresponds to the ground state as a function of the parameter λ at order N,

$$E_0^{(N)}(\lambda) = \min_i \{\Lambda_i^{(N)}\}. \tag{12}$$

The corresponding eigenvector is the projection of the eigenfunction onto the finite basis set $\{\Phi_n\}$ which is given by

$$\Psi_0^{(N)}(\lambda) = \sum_n^{M(N)} c_n^{(N)}(\lambda)\Phi_n. \tag{13}$$

In this representation, the expectation value of any operator $\mathcal{O}$ at order N is given by

$$\langle \mathcal{O} \rangle^N(\lambda) = \sum_{n,m}^{M(N)} c_n^{(N)}(\lambda) c_m^{(N)}(\lambda) \mathcal{O}_{n,m}, \tag{14}$$

where $\mathcal{O}_{n,m}$ is the matrix elements of $\mathcal{O}$ in the basis set $\{\Phi_n\}$.

Generally, the mean value of the operator $\mathcal{O}$ is not analytic at $\lambda = \lambda_c$ and can be written as

$$\langle \mathcal{O} \rangle(\lambda) \underset{\lambda \to \lambda_c}{\sim} (\lambda - \lambda_c)^{\mu_{\mathcal{O}}}, \tag{15}$$

where $\mu_{\mathcal{O}}$ is the corresponding exponent.

The finite size scaling hypothesis assumes the existence of a scaling function such that [18]

$$\langle \mathcal{O} \rangle^{(N)}(\lambda) \sim \langle \mathcal{O} \rangle(\lambda) F_{\mathcal{O}}(N/\xi_\infty(\lambda)), \tag{16}$$

where $\xi_\infty(\lambda)$ is the correlation length in the infinite system. Equation (16) should be valid for different dynamical quantities. In particular, it is correct for the correlation length itself which is singular at $\lambda = \lambda_c$

$$\xi^{(N)}(\lambda) \sim N \phi_\xi(N^{1/\nu} \mid \lambda - \lambda_c \mid). \tag{17}$$

Here $\phi(x)$ is an analytic function and ν is the critical exponent for the singularity of the correlation length.

Once λ approaches λ_c for a large but finite system, $\phi(x)$ approaches a constant. Hence the finite size scaling intrinsically gives for finite systems of sizes N and N'

$$\frac{\xi^{(N)}(\lambda)}{N} = \frac{\xi^{(N')}(\lambda)}{N'}. \tag{18}$$

This equation was originally developed by Nightingale [22] as a realization of an approximate renormalization group transformation of the infinite system [23].

In order to obtain an explicit expression of the correlation length, we utilize the following mapping: first, a d-dimensional quantum system is equivalent to a $d+1$-dimension classical system [14, 24]; and second, the transfer matrix of a classical system is non-negative, as is its leading eigenvalue [23]. Hence we may take the two eigenvalues of the quantum Hamiltonian $\mathcal{H}(\lambda)$ as those of the transfer matrix for the corresponding classical pseudo system. This mapping allows us to approximately define the correlation length of a finite quantum system as [15]

$$\xi^{(N)}(\lambda) = -\frac{1}{\log\left(E_1^{(N)}(\lambda)/E_0^{(N)}(\lambda)\right)}, \tag{19}$$

where $E_0^{(N)}(\lambda)$ is given by equation (12) and $E_1^{(N)}(\lambda)$ is the second lowest eigenvalue.

4. One electron diatomic systems

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 [25–28]. However, we have shown [29], 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 non-analyticity in the energy). But, without making use of the Born–Oppenheimer approximation the H_2^+-like system exhibits a critical point. In this section, we introduce the basis sets we used and the calculations of the critical parameters using the finite size scaling approach.

4.1. *Basis set*

As an example, we choose H_2^+-like systems to show the critical phenomena and phase transitions of simple molecules. Equation (9) is used with $\lambda = Z$, $a = C = 2$, $\mu = M/(1 + M)$ and $M = 1836.152\,701$ au.

The ground state eigenfunction is expanded in the following basis set [30] $\Phi_{(n,m,l)}$,

$$\Phi_{(n,m,l)}(r_1, r_2, r_{12}) = N_0 \phi_n(x) \phi_m(y) \phi_l(z), \qquad (20)$$

where N_0 is the normalization coefficient and $\phi_n(x)$ is given in terms of Laguerre polynomials $L_n(x)$,

$$\phi_n(x) = L_n(x) \exp(-x/2). \qquad (21)$$

The coordinates x, y, z are expressed in the following perimetric coordinates [31]

$$\begin{aligned} x &= \frac{\theta}{k_x}(r_1 + r_2 - r_{12}), \\ y &= \frac{\theta}{k_y}(-r_1 + r_2 + r_{12}), \\ z &= \frac{\theta}{k_z}(r_1 - r_2 + r_{12}). \end{aligned} \qquad (22)$$

Here we choose $k_x = 1 = k_y/2 = k_z/2$ and adopt the definition of Pekeris [31]. θ is an adjustable parameter which will be given in the following subsection.

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 $M(N)$. For example, $M(N) = 946$, $20\,336$ at $N = 20$, 60 respectively. The symmetric matrix is represented in a sparse row-wise format [32] and then reordered [33] before triangularizations. The Lanczos method [34] of block-renormalization procedure was employed.

4.2. *Calculations*

We chose $\theta = \theta_t = 1.5$ in equation (22) for the H_2^+-like systems. Our calculations over $1 < \theta < 10$ show that θ_t accelerates the convergence of the ratio of the two lowest eigenvalues and thus the series $\{\lambda^{(N)}\}$ converges to the critical point λ_c. This procedure is different from the technique of minimization to obtain the leading eigenvalue. In fact, over all possible λ, θ and N the minimization leads to a stable ground state corresponding to $\lambda = Z = 1$, which is far from the critical point. The minimization produces the first and second eigenvalues for H_2^+, $-0.597\,139\,063\,119$ au and $-0.587\,155\,679\,091$ au at $N = 63$ and $\theta = \theta_m = 8.9$, which might compare with the results of $-0.597\,139\,063\,123$ au at $N = 70$ and $-0.587\,155\,679\,212$ au at $N = 74$ by Grémaud *et al.* [30] with $\theta = \theta_m = 9.5$.

In the following sections, we will give the numerical results for the critical point and the related critical exponents. The present results cover the range $7 \leq N \leq 60$ with a numerical accuracy better than 1.0×10^{-4} with a λ-mesh interval of 5×10^{-5}.

4.3. *Critical point*

For the ground state of H_2^+-like molecules, the critical point λ_c of $\mathcal{H}(\lambda)$ may be defined as a point at which the bound state energy $E(\lambda)$ is degenerate or absorbed at the first threshold E_0^{th},

$$E_0^{\text{th}} - E_0^{(N)}(\lambda) \underset{\lambda \to \lambda_c^-}{\sim} (\lambda_c - \lambda)^{\alpha}, \qquad (23)$$

Here α is the energy critical exponent and $E_0^{\text{th}} = -0.499\,727\,84$ au is the ground state energy of the atomic hydrogen in the finite mass calculations. Figure 1 shows the ground state energy $E_0^{(N)}(\lambda)$ as a function of $\lambda = Z$ for different values of N, $31 \leq N \leq 60$ at $\theta = \theta_t = 1.5$.

One method to obtain the critical value λ_c is to equate the energy with the known threshold,

$$E_0^{(N)}(\lambda) = E_0^{\text{th}}. \qquad (24)$$

This equation gives a series $\{\lambda^{(N)}\}$ which is analogous to the series obtained in the first-order method used in classical statistical mechanics [1]. As we have done in previous works, we employ the extrapolation arithmetic of Bulirsch and Stoer [35, 36]. The final extrapolated

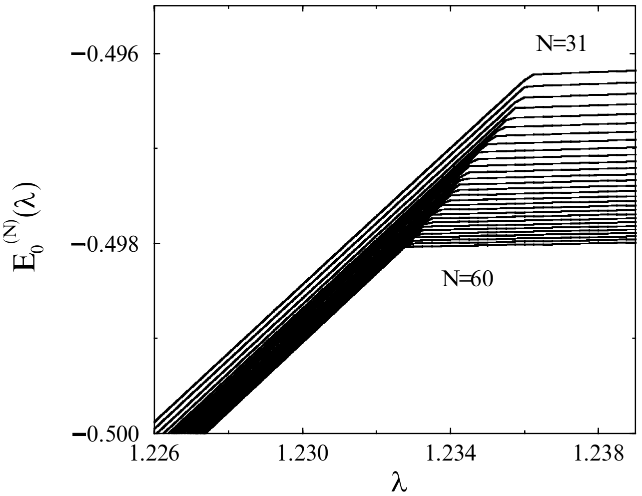

Figure 1. The ground state energy, $E_0^{(N)}(\lambda)$, for the H_2^+-like molecules as a function of λ $(= Z)$ at $\theta_t = 1.5$ for $N = 31, 32, \ldots, 60$.

Table 1. The critical parameters λ_c $(= Z_c)$, α, ν and $\langle \mathbf{r}_{12} \rangle_c$ for H_2^+-like molecules.

Method	Value	Error
	λ_c	
Equation (24)	1.228 21	±0.000 05
Equation (25)	1.228 279	±0.000 001
Equation (26)	1.228 6	±0.000 5
[37]	1.237 0[a]	
[37]	1.207 3[b]	
	α	
Equation (28)	1.000	±0.005
	ν	
Equation (31)	0.3	±0.2
	$\langle \mathbf{r}_{12} \rangle_c$	
Equation (24)	2.78	±0.02
Equation (25)	2.765 41	±0.000 01

[a] Reciprocal of 0.8084 [37].
[b] Reciprocal of 0.8283 [37].

value is listed in table 1 together with the error which mainly comes from the interpolation on an equally spaced λ-mesh of an interval 5×10^{-5}.

In order to check the extrapolation arithmetic and get a more accurate value for the critical point λ_c, we combined the minimization procedure with the first threshold method to produce another series $\{\lambda^{(N)}\}$

$$E_0^{(N)}(\lambda)\,|_{\theta=\theta_o^{(N)}} = E_0^{\mathrm{th}}, \qquad (25)$$

where $\theta_o^{(N)}$ is the optimal value obtained from the energy minimization. This is a procedure to approach the first threshold through a continuous stable state of the $\mathcal{H}(\lambda)$ system. The series $\{\lambda^{(N)}\}$ and the corresponding $\theta_o^{(N)}$ are shown in figure 2. Here the optimization accuracy is 1.0×10^{-8} and $\lambda_c = 1.228\,279$. The value of λ_c, along with the upper and lower boundary values of the variational approximations of Rebane [37], are listed for comparison in table 1.

Using the finite size scaling equation directly we can obtain the fixed point by putting equation (19) into equation (18) to obtain,

$$\left(\frac{E_1^{(N)}(\lambda)}{E_0^{(N)}(\lambda)}\right)^N = \left(\frac{E_1^{(N')}(\lambda)}{E_0^{(N')}(\lambda)}\right)^{N'}. \qquad (26)$$

Figure 3 shows the curves $E_1^{(N)}(\lambda)/E_0^{(N)}(\lambda)$ as a function of λ for $N = 31$ up to $N = 60$. In virtue of this behaviour, we expect that the first derivative of the energy as a function of λ develops a step-like discontinuity at λ_c as shown in figure 4. The crossing points between two different sizes N and $N+1$ give another series for $\{\lambda^{(N)}\}$. Figure 5 shows the oscillatory behaviour of the crossing points as a function of the size N. This behaviour makes the extrapolation arithmetic a difficult task. However, the pseudo-convergent points stay between 1.226 and 1.232 at $N > 30$ as presented in figure 5. By systematically increasing the order N, one can reach a reasonable critical point $\lambda_c = 1.2286$ with an error listed in table 1. Here λ_c and the error are estimated using the final minimum and maximum values and their difference over $48 < N < 60$. This value is in agreement with the previous estimate of λ_c.

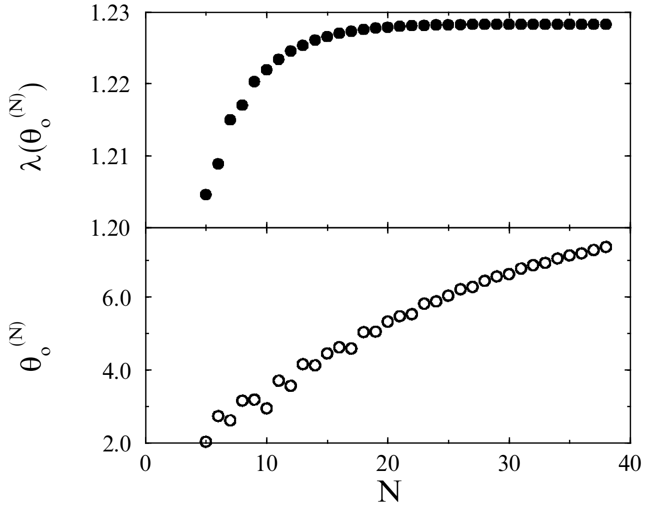

Figure 2. The $\{\lambda^{(N)}\}$ series (upper) determined by equation (25), and the optimal $\theta_o^{(N)}$ (lower) as a function of the order of the expansion N.

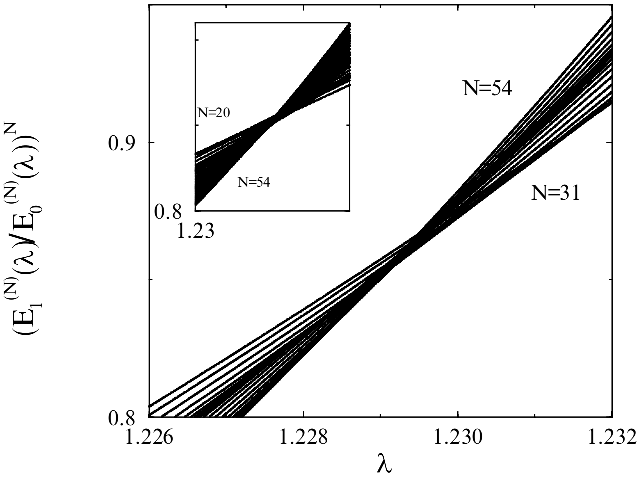

Figure 3. The ratio between the ground state energy and the second lowest eigenvalue raised to a power N as a function of λ $(= Z)$ at $\theta_t = 1.5$ for $N = 31, 32, \ldots, 60$.

4.4. *Critical exponents*

For a given operator, equation (15) defines its non-analytic properties by giving the critical point and the

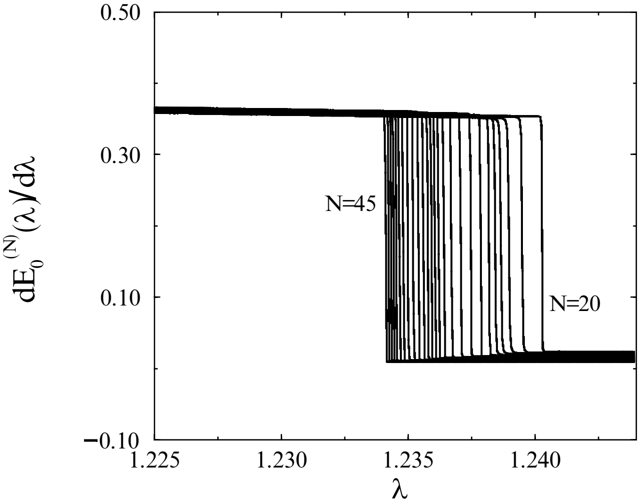

Figure 4. First derivative of the ground state energy as a function of $\lambda\ (=Z)$ at $\theta_t = 1.5$ for $N = 20, 21, \ldots, 45$.

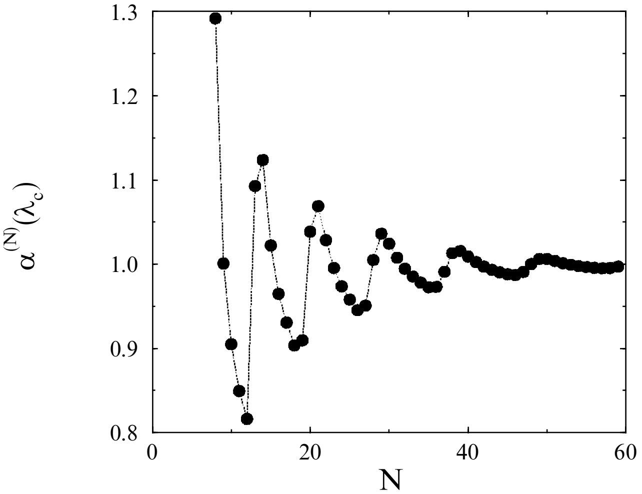

Figure 6. The $\{\alpha^{(N)}(\lambda_c = 1.228\,279)\}$ series as a function of N at $\theta_t = 1.5$.

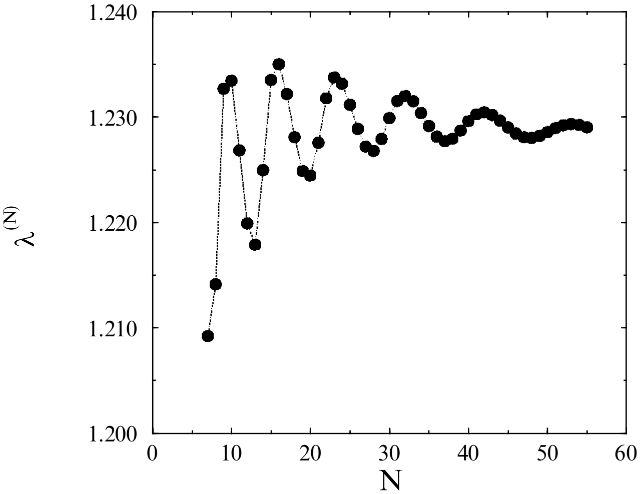

Figure 5. The $\{\lambda^{(N)}\}$ series, as determined by equation (26), as a function of N at $\theta_t = 1.5$.

related critical exponent. In particular, for the Hamiltonian operator $\mathcal{H}(\lambda)$, the energy exponent α is given by equation (23) while the correlation length $\xi^{(N)}$, which is singular at $\lambda = \lambda_c$, has the critical exponent ν, which is defined as

$$\xi(\lambda) \underset{\lambda \to \lambda_c}{\sim} (\lambda - \lambda_c)^{-\nu}. \tag{27}$$

For the exponent α, we start from the series $\{\alpha^{(N)}(\lambda)\}$ and follow the direct approach of finite size scaling for the Schrödinger equation [19] which gives,

$$\alpha^{(N)}(\lambda) = \Gamma(\lambda; N, N'), \tag{28}$$

where the function $\Gamma(\lambda; N, N')$ is given by

$$\Gamma(\lambda; N, N') = \frac{\Delta_{\mathcal{H}}(\lambda; N, N')}{\Delta_{\mathcal{H}}(\lambda; N, N') - \Delta_{\partial\mathcal{H}/\partial\lambda}(\lambda; N, N')}, \tag{29}$$

$N = N' + 1$, and Δ in this expression is defined as

$$\Delta_{\mathcal{O}}(\lambda; N, N') = \frac{\ln\left(\langle\mathcal{O}\rangle_\lambda^{(N)} \langle\mathcal{O}\rangle_\lambda^{(N')}\right)}{\ln(N'/N)}. \tag{30}$$

Using equations (28), (29) and (30), we obtain the series $\alpha^{(N)}(\lambda_c)$ shown in figure 6. From these data, we estimated the energy critical exponent to be $\alpha = 1.000 \pm 0.005$.

Now, after calculating the critical exponent α, the critical exponent $\{\nu^{(N)}(\lambda)\}$ is readily given by

$$\nu^{(N)}(\lambda) = \frac{\alpha^{(N)}(\lambda)}{\Delta_{\mathcal{H}(\lambda)}(\lambda; N, N')}. \tag{31}$$

The results of the calculations for the $\nu^{(N)}(\lambda)$ series are shown in figure 7. The data do not reach a limit at N up to 60, but it does show that the correlation exponent is smaller than one and decreases as N increases. We estimate the value using the final maximum and minimum points over $48 < N < 60$. This result, $\nu = 0.3 \pm 0.2$, is also listed in table 1.

In a molecular system as we have shown, there are three basic length scales involved: the correlation length $\xi(\lambda)$, the dimensionality N of the basis set space, and the microscopic length, i.e. the Bohr radius a_0 (= 1). The finite size scaling hypothesis assumes that, close to the critical point, the microscopic length drops out against the continuous increment of the correlation length. This is shown in figure 8, where the correlation length has a linear behaviour as a function of N at $\theta_t = 1.5$. Here we may relate the correlation length, defined in equation (19), to the energy interval. As N

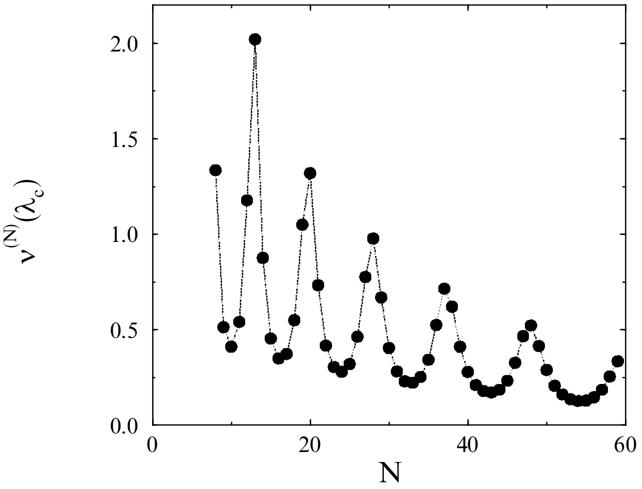

Figure 7. The $\{\nu^{(N)}(\lambda_c = 1.228\,279)\}$ series as a function of N at $\theta_t = 1.5$.

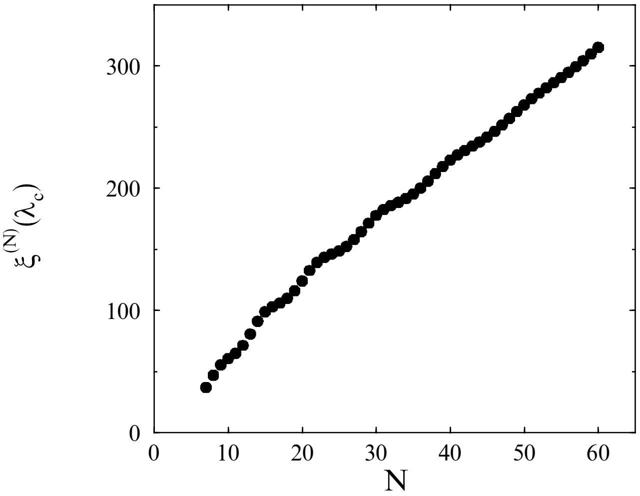

Figure 8. The correlation length $\xi^{(N)}(\lambda_c = 1.228\,279)$ as a function of order N at $\theta_t = 1.5$.

increases near the critical point, the lowest two eigenvalues satisfy an asymptote of the form

$$E_0^{(N)}(\lambda) \rightarrow E_1^{(N)}(\lambda). \tag{32}$$

If we define the energy interval $\Delta E_{10}^{(N)} = E_1^{(N)}(\lambda) - E_0^{(N)}(\lambda)$ and expand $\log(1 - \Delta E / \mid E_0 \mid)$ to first-order in $\Delta E / \mid E_0 \mid$, equation (19) gives

$$\xi^{(N)}(\lambda) = \frac{\mid E_0 \mid}{\Delta E_{10}^{(N)}(\lambda)}. \tag{33}$$

Under these considerations, $\xi^{(N)}(\lambda)$ can be mapped to the energy interval, or in the terminology of the field theory, the mass gap [24].

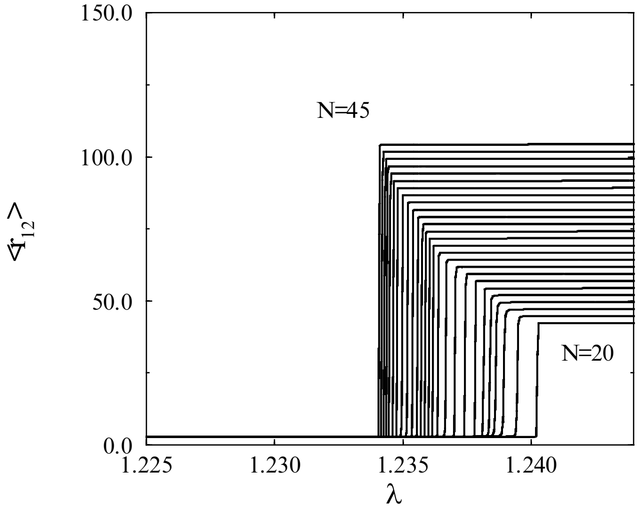

Figure 9. The expectation value of the distance between the two protons $\langle \mathbf{r}_{12} \rangle$ for the H_2^+-like molecules as a function of λ $(= Z)$ at $\theta_t = 1.5$ for $N = 20, 21, \ldots, 45$.

4.5. *Dissociation limit*

From the present calculations, the expectation value of the operator $\mathbf{r}_{12}$ may provide a direct physical picture about the thermodynamic stability and dissociation of H_2^+-like molecules. As shown in figure 9, there is a vertical jump of the mean value $\mathbf{r}_{12}$ at λ_c. At $\lambda \rightarrow \lambda_c^-$, equation (24) gives the mean value 2.78 au, which is in agreement with 2.765 41 au using equation (25). For $\lambda = 1$ (H_2^+ molecule) we estimated the mean value $\langle \mathbf{r}_{12} \rangle = 2.063\,9139$ au. The step-like discontinuity tells us about the behaviour of $\mathbf{r}_{12}$ close to the critical point. As $\lambda \rightarrow \lambda_c^-$

$$\langle \mathbf{r}_{12} \rangle \sim (\lambda - \lambda_c)^{-\tau}, \tag{34}$$

where the exponent τ should be zero.

From figure 9, we note that there are similarities and differences between helium-like atoms and H_2^+-like molecules. In previous studies of helium-like systems, based on an infinite mass assumption, we show that the electron at the critical point leaves the atom with zero kinetic energy in a first-order phase transition. This limit corresponds to the ionization of an electron as the nuclear charge varies.

For the H_2^+-like molecules, the two protons move in an electronic potential with a mass-polarization term. They move apart as λ approaches its critical point and the system approaches its dissociation limit through a first-order phase transition.

It is important to note that the present finite size scaling calculations indicate that for H_2^+-like molecules, one approaches the critical point through periodically attenuated vibrations in the λ_c vicinity, rather than simply a direct approach from above or below the critical point. We also notice that there is no ionization of the molecular system over the region of $1.0 \leq \lambda \leq 1.5$.

5. Conclusions and discussion

We present the finite size scaling calculations for the H_2^+-like molecules without making use of the Born–Oppenheimer approximation. As the nuclear charge varies, the system exhibits a critical point at $Z_c = 1.2283$ where the symmetry breaking occurs and the system dissociates into a proton and a hydrogen-like atom. This transition, from the H_2^+-like stable molecule to the dissociation phase, was shown to be a first-order phase transition. The first derivative of the ground state energy with respect to Z developed a step-like discontinuity at Z_c. By investigating the behaviour of internuclear distance $\langle \mathbf{r}_{12} \rangle$ as Z varies, one can see clearly from figure 9 that there is a step-like discontinuity at Z_c which tells us about the jump in $\langle \mathbf{r}_{12} \rangle$ and the dissociation of the H_2^+-like molecule. In comparison with the helium-like atoms, the critical point is the critical value of the nuclear charge Z_c for which the energy of a bound state becomes degenerate with the threshold. For $Z < Z_c = 0.911$ one of the electrons jumps to infinity, in a first-order phase transition, with zero kinetic energy [15].

Large molecular systems are challenging from the critical phenomenon point of view. In order to apply the finite size scaling method, one needs to have a complete basis set. The present basis set used for the finite size scaling calculations is built up on the perimetric coordinates which is only suitable for the three-body systems, and thus restricts its extension to treat larger molecules. Modern quantum chemistry computations are generally carried out using three types of basis sets: Slater orbitals, Gaussian orbitals and plane waves, the last being reserved primarily for extended systems in solid states. Each of these has their advantages and disadvantages. Evaluation of molecular integrals, four-centre integrals for example, are very difficult and time-consuming with Slater basis functions. These integrals are relatively easy to evaluate with Gaussian basis functions.

We have tested several types of Gaussian basis sets. The first one has the following general form

$$\Psi = (1 + \mathbf{P}_{12}) \sum_{m=1}^{M} \exp\left(-\alpha_m r_1^2 - \beta_m r_2^2 - \gamma_m r_{12}^2\right), \tag{35}$$

where M is the expansion length, $\mathbf{P}_{12}$ is the exchange operator and α_m, β_m and γ_m are the variational parameters. The finite size scaling results using this basis set were strongly dependent on the initial values of the variational parameters. Another two types of Gaussian basis sets which we used have the general form

$$\Psi = (1 + \mathbf{P}_{12}) \left(\sum_{m=1}^{M} \exp\left(-\alpha_m r_1^2 - \beta_m r_2^2 - \gamma_m r_{12}^2\right) \right) \times \sum_{k=0}^{N} C_{mk} r_{12}^{2k}, \tag{36}$$

where $k \leq N$, N is the order and M is expansion length for a set of given parameters $\{\alpha_m, \beta_m, \gamma_m\}$, and

$$\Psi = (1 + \mathbf{P}_{12}) \left(\sum_{m=1}^{M} \exp\left(-\alpha_m r_1^2 - \beta_m r_2^2 - \gamma_m r_{12}^2\right) \right) \times \sum_{i,j,k}^{N} C_{mijk} r_1^{2i} r_2^{2j} r_{12}^{2k}, \tag{37}$$

where $i + j + k \leq N$. These Gaussian basis sets are correlated and involve power law terms [20], which are equivalent to the power law terms used in the Laguerre polynomials in equation (21). Using equations (36) and (37) we have identified the first-order phase transition for the H_2^+-like system. Clearly this basis set will be suitable for larger diatomic molecules. The details of the calculations and the existence of problems in the finite size scaling studies on various kinds of Gaussian basis sets will be discussed elsewhere [38].

The present finite size scaling method provides a powerful tool to study molecular stability as a function of the coupling constants in the Hamiltonian. For atoms, the fact that for two-electron atoms the critical charge $Z_c \simeq 0.9110$ explains why the H^- is a stable negative ion while for three-electron atoms $Z_c \simeq 2.01$ and He^- is not stable. For one-electron molecular systems the fact that $Z_c \simeq 1.2283$ explains why H_2^+ is the only stable ion. Research is still underway to combine the finite size scaling with Gaussian basis functions to treat larger molecular systems and also to investigate the effect of external fields on the molecular stability and whether or not one can use this approach to selectively break chemical bonds in polyatomic molecules.

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