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Multicritical phenomena for the hydrogen molecule at the large-dimension limit

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Abstract

We show that symmetry breaking of the electronic structure configurations for the Hartree–Fock hydrogen molecule at the large-dimension limit can be described as standard phase transitions. The phase diagram in the internuclear distance–nuclear charge plane shows three different stable phases corresponding to different electronic structure configurations. This phase diagram is characterized by a bicritical point where the two continuous phase transition lines join a first order transition line.

1. Introduction

Dimensional scaling methods involve generalizing a problem to D-dimensional space and treating D as a free parameter. Typically, the limit $D \to \infty$ yields dramatic simplification in the analysis of a wide class of problems, and often an analytic solution can be obtained in that limit. Finite-D corrections then can be taken into account by introducing a systematic perturbation expansion in $1/D$ [1]. At the end of the calculations, one sets $D = 3$ to obtain the "real world" solution. Yaffe has shown that this expansion, not surprisingly, is semiclassical in nature, but distinct from the WKB theory [2]. Dimensional perturbation and scaling techniques have recently attracted considerable attention. Encouraging results have been obtained for a diverse class of problems. These range from quantum chromodynamics, nuclear physics, and critical phenomena to challenging problems in both quantum and statistical mechanics [3].

In the application of dimensional scaling to electronic structure, the limit $D \to \infty$ reduces to a semiclassical electrostatic problem in which the electrons assume fixed positions relative to the nuclei and to each other in the D-scaled space [1]. This configuration corresponds to the minimum of an effective potential which includes Coulomb interactions as well as centrifugal terms arising from the generalized D-dependent kinetic energy. Typically, in the large-D regime the electronic structure configuration undergoes symmetry breaking for certain ranges of nuclear charges [4] or molecular geometries [5]. The large-D limit is just a zeroth order approximation; finite-D corrections can then be taken into account by introducing a systematic perturbation expansion in $1/D$ for both bound [6] and unstable states [7].

Recently [8], we have shown that symmetry breaking of electronic structure configurations at the

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large-D limit is completely analogous to mean field theories of phase transitions and critical phenomena in statistical mechanics [9]. For N-electron atoms in weak magnetic and electric fields at the large-dimension limit, this analogy is shown by allowing the nuclear charge to play a role analogous to temperature in statistical mechanics [10]. For the exact solution of N-electron atoms at the large-dimension limit, the symmetry breaking is shown to be a first order phase transition. For the special case of two-electron atoms, the first order transition shows a triple point where three phases with different symmetry exist. Treatment of the Hartree–Fock solution reveals a different kind of symmetry breaking where a second order phase transitions exist for $N = 2$. The Hartree–Fock two-electron atoms in weak external electric field exhibit a critical point with mean field critical exponents ($\beta = \frac{1}{2}$, $\alpha = 0_{\rm dis}$, $\delta = 3$, and $\gamma = 1$) [8].

Symmetry breaking of the molecular electronic structure configurations at the large-dimension limit show similar phase transitions. For the hydrogen molecular ion the analogy to standard phase transitions was shown by allowing the inverse internuclear distance to play a role analogous to temperature in statistical mechanics. This system also exhibits a critical point, with the same mean field critical exponents [8].

In this Letter, we report the symmetry breaking and phase diagram for the Hartree–Fock hydrogen molecule at the large-D limit. Our calculations indicate that there are three stable phases, with two continuous phase transition lines joining a first order transition line at a bicritical point.

2. Hartree–Fock hydrogen molecule

The treatment of the hydrogen molecule in D-dimensional cylindrical coordinates is a straightforward generalization of the usual treatment at $D = 3$ [11]. The nuclei a and b are located on the z axis at $-R/2$ and $R/2$, respectively, with equal charges $Z_a = Z_b = Z/2$. The electrons are located at (ρ_1, z_1) and (ρ_2, z_2), with a dihedral angle ϕ specifying their relative azimuthal orientation about the molecular axis. In the Hartree–Fock approximation we set this angle at 90° [12]. The Born–Oppenheimer approximation is used to separate the electronic and nuclear motion, with the electronic energy $E_D(R)$ then parametrically dependent upon the internuclear distance R. The D-dimensional electronic Schrödinger equation in Hartree–Bohr atomic units is given by

$$\left\{ -\frac{1}{2}\sum_{i=1}^{2}\left[\frac{1}{\rho_i^{D-2}}\frac{\partial}{\partial\rho_i}\left(\rho_i^{D-2}\frac{\partial}{\partial\rho_i}\right)+\frac{\partial^2}{\partial z_i^2}+\frac{\mathscr{L}_{D-2}^2}{\rho_i^2}\right] + V(\rho_1, \rho_2, z_1, z_2, \phi)\right\}\Psi = E_D(R)\Psi, \qquad (1)$$

where $\mathscr{L}_{D-2}^2$ is the D-dimensional generalized orbital angular momentum operator and $V(\rho_1, \rho_2, z_1, z_2, \phi)$ is the potential energy of the electron–nucleus and electron–electron interactions. By incorporating the square root of the Jacobian into the wavefunction via $\Psi \rightarrow J^{-1/2}\Phi$, one may separate the centrifugal energy from other kinetic terms and also render the volume element of the transformed wavefunction Φ independent of dimension. The centrifugal energy becomes singular in the limit $D \rightarrow \infty$, but this dimension dependence can be removed by scaling all coordinates by a factor with quadratic dependence on dimension. The scaling factor is chosen to give finite energies in the limit $D \rightarrow \infty$, while reducing to unity at $D = 3$. This results in units of $1/\kappa^2$ hartree for energy and κ^2 bohr radii for distances, where $\kappa = (D-1)/2$ [1].

The scaled effective Hamiltonian for the Hartree–Fock hydrogen molecule at the large-D limit is readily obtained from Eq. (1) [12]

$$\mathscr{H}_\infty = \sum_{i=1}^{2}\left[\frac{1}{2\rho_i^2} - \frac{Z}{2}\left(\frac{1}{r_{ai}}+\frac{1}{r_{bi}}\right)\right] + \frac{1}{\left[\rho_1^2+\rho_2^2+(z_1-z_2)^2\right]^{1/2}}, \qquad (2)$$

where Z is the total charge and r_{ai} and r_{bi} are the electron–nucleus distances:

$$r_{ai} = \sqrt{\rho_i^2 + (z_i + R/2)^2}\,,$$

$$r_{bi} = \sqrt{\rho_i^2 + (Z_i - R/2)^2}\,. \qquad (3)$$

Evaluating the ground state electronic energy for $D \to \infty$ reduces simply to determining the minimum of the scaled effective Hamiltonian $\mathscr{H}_\infty$. For finding this minimum and studying symmetry breaking of the different electronic structure configurations it is convenient to introduce spheroidal coordinates (λ_i, μ_i). These coordinates are related to the cylindrical coordinates by

$$\lambda_i = r_{ai} + r_{bi}, \quad \mu_i = r_{ai} - r_{bi},$$

$$\rho_i^2 = \frac{(\lambda_i^2 - R^2)(R^2 - \mu_i^2)}{4R^2}, \quad z_i = \frac{\lambda_i \mu_i}{2R},$$

$$i = 1, 2. \tag{4}$$

In these coordinates, the Hamiltonian takes the form

$$\mathscr{H}_\infty = \sum_{i=1}^{2} \left[\frac{2R^2}{(\lambda_i^2 - R^2)(R^2 - \mu_i^2)} - \frac{2Z\lambda_i}{\lambda_i^2 - \mu_i^2} \right] + \frac{2R}{\left[R^2(\lambda_1^2 + \mu_1^2 + \lambda_2^2 + \mu_2^2) - 2\lambda_1\lambda_2\mu_1\mu_2 - 2R^4\right]^{1/2}}. \tag{5}$$

The ground state energy is given by

$$E_\infty(R, Z) = \min_{\{\lambda_1, \mu_1, \lambda_2, \mu_2\}} \mathscr{H}_\infty. \tag{6}$$

This condition leads to four variational equations:

$$\frac{\partial \mathscr{H}_\infty}{\partial \lambda_i} = -\frac{4R^2\lambda_i}{(\lambda_i^2 - R^2)^2(R^2 - \mu_i^2)} + \frac{2(\lambda_i^2 + \mu_i^2)Z}{(\lambda_i^2 - \mu_i^2)^2} - \frac{2R(R^2\lambda_i - \mu_i\mu_j\lambda_j)}{\left[R^2(\lambda_1^2 + \mu_1^2 + \lambda_2^2 + \mu_2^2) - 2\lambda_1\lambda_2\mu_1\mu_2 - 2R^4\right]^{3/2}} = 0, \tag{7}$$

$$\frac{\partial \mathscr{H}_\infty}{\partial \mu_i} = -\frac{4r^2\mu_i}{(\lambda_i^2 - R^2)(R^2 - \mu_i^2)^2} + \frac{4\lambda_i\mu_i Z}{(\lambda_i^2 - \mu_i^2)^2} - \frac{2R(R^2\mu_i - \lambda_i\lambda_j\mu_j)}{\left[R^2(\lambda_1^2 + \mu_1^2 + \lambda_2^2 + \mu_2^2) - 2\lambda_1\lambda_2\mu_1\mu_2 - 2R^4\right]^{3/2}} = 0, \tag{8}$$

where $i = 1, 2$; $j = 1, 2$, $j \neq i$. The minimum condition of Eq. (6) implies that, for a given solution of Eqs. (7) and (8), all the eigenvalues of the 4×4 Hessian matrix must be positive.

3. Symmetry breaking

For fixed total charge $Z = 2$, corresponding to the hydrogen molecule, the potential energy surface has a single minimum for small internuclear distance R while for large R the surface splits into two minima. The symmetry breaking which splits the single minimum in the united atom limit into the symmetric double minima in the separated atom limit occurs at a critical internuclear distance. Herschbach and co-workers [5] have investigated the symmetry breaking of electronic structure for the H_2 molecule at the large-D limit. They have found that at $R = 0$, the effective potential has a single minimum located at $z_1 = z_2 = 0$. The minimum begins to split into two minima antisymmetric in z when R reaches the inner critical point at $R^- = 0.9111$ and then split further into two more minima, symmetric in z, when R reaches the outer value $R^+ = 1.9136$. It is interesting to note that the antisymmetric solution in z is always the global minimum for all values of R. The two antisymmetric wells correspond to covalent structures while the two symmetric wells correspond to ionic structures, with both electrons on one or the other nucleus. That is, the effective potential exhibits the familiar chemical concept of resonance among valence bond structures, $H^-H^+ \leftrightarrow H{:}H \leftrightarrow H^+H^-$. Loeser and co-workers [12] have found similar results for symmetry breaking of the Hartree–Fock H_2 molecule at the large-D limit.

In this study, we will concentrate on symmetry breaking and the phase diagram of the Hartree–Fock H_2-like molecules with charge Z and internuclear distance R. This approximation has fewer variational parameters than the exact solution and qualitatively exhibits a similar phase diagram.

Symmetry breaking configurations can be determined by studying the stability of the different solutions of the variational equations, Eqs. (7) and (8), as a function of both the nuclear charge Z and the internuclear distance R. An extensive analytical and numerical study shows that there are only three different solutions corresponding to a global minimum in the region $R \geqslant 0$ and $Z \geqslant 1$.

One possible solution of Eqs. (7) and (8) is the symmetric solution with $\lambda_1 = \lambda_2 = \lambda$ and $\mu_1 = \mu_2 = 0$. This solution corresponds to the symmetric electronic structure configuration where the two elec-

trons are located in the symmetry plane $z = 0$, at equal distances from the two nuclei. The symmetric solution of Eq. (7) gives λ implicitly in terms of R and Z:

$$Z(R, \lambda) = \frac{\left[(\lambda^2 - R^2)^{1/2} + 2^{5/2}\right]\lambda^3}{(\lambda^2 - R^2)^2}. \tag{9}$$

This solution is a minimum in the region where all the eigenvalues of the Hessian matrix are positive. In this case, the two smallest eigenvalues of the Hessian matrix are given by

$$\Lambda_1^{(\mathrm{sym})} = \frac{4(R^2 + 3\lambda^2)}{(\lambda^2 - R^2)^3} - \frac{4Z}{\lambda^3} - \frac{1}{2^{1/2}(\lambda^2 - R^2)^{3/2}}, \tag{10}$$

$$\Lambda_2^{(\mathrm{sym})} = \frac{4}{R^2(\lambda^2 - R^2)} - \frac{4Z}{\lambda^3} - \frac{\lambda^2 + R^2}{2^{1/2}R^2(\lambda^2 - R^2)^{3/2}}. \tag{11}$$

The stability limits are given by the condition $\Lambda_i^{(\mathrm{sym})} = 0$ and Eq. (9). These equations give two cubic polynomials where their roots are the stability limit lines of the symmetric solution. Both eigenvalues are equal to zero at the point (R_{bc}, Z_{bc})

$$R_{bc} = 1, \quad Z_{bc} = 81/64 \approx 1.2656; \tag{12}$$

as we will show later, this point has the characteristics of a multicritical point.

The symmetry breaking solution of the variational equations can be obtained by defining

$$\lambda_1 = \lambda, \quad \lambda_2 = \alpha\lambda, \quad \mu_1 = \mu_2 = 0. \tag{13}$$

We will call this nonsymmetric electronic configuration phase A, which corresponds to both electrons in the symmetry plane $z = 0$, but with different distances from the molecular axis.

As in the symmetric phase, $\mu_i = 0$ is a trivial solution for Eqs. (8), which leaves us with only two equations to be solved. Eqs. (7) give

$$-\frac{2\lambda}{(\lambda^2 - R^2)^2} + \frac{Z}{\lambda^2} - \frac{\lambda}{\left[(1 + \alpha^2)\lambda^2 - 2R^2\right]^{3/2}} = 0, \tag{14}$$

$$-\frac{2\alpha\lambda}{(\alpha^2\lambda^2 - R^2)^2} + \frac{Z}{\alpha^2\lambda^2} - \frac{\alpha\lambda}{\left[(1 + \alpha^2)\lambda^2 - 2R^2\right]^{3/2}} = 0. \tag{15}$$

Another different nonsymmetric electronic configuration, referred to as phase B, is given by the condition

$$\lambda_1 = \lambda_2 = \lambda, \quad \mu_1 = \mu = -\mu_2. \tag{16}$$

In this phase, the electrons are not in the symmetry plane $z = 0$, but instead occupy symmetric positions with respect to this plane. This configuration corresponds to a covalent structure, with $r_{a1} = r_{b2}$ and $r_{b1} = r_{a2}$. The electron-dot representations of the three different phases; symmetric phase, phase A and phase B are shown in Fig. 1.

We have found two additional solutions to the variational Eqs. (7) and (8). One solution has $\lambda_1 = \lambda_2 = \lambda$ and $\mu_1 = \mu_2 = \mu$, which corresponds to ionic structures with both electrons on one or the other nucleus. The other solution is the total nonsymmetric solution with $\lambda_1 \neq \lambda_2$ and $\mu_1 \neq \mu_2$. These additional solutions correspond to local minima for certain values of R and Z, but never become the global minimum.

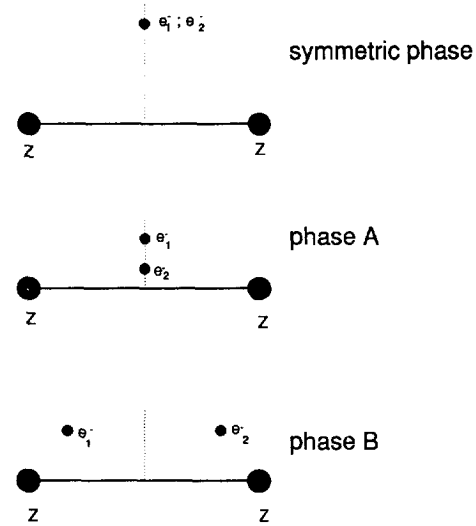


Fig. 1. Electron-dot representations of the three different stable phases corresponding to different electronic structure configurations: symmetric phase, phase A and phase B.

4. Phase diagram

As in the mean-field variational theory of phase transitions in statistical mechanics, the phase diagram is constructed by studying the stability of the different phases. If the stability limit of two different phases are coincident, then it corresponds to a second order phase transition. But if the stability lines are not coincident, a coexistence phase region appears, where two or more solutions correspond to local minima of the energy. A first order phase transition line is defined as the line where the global minimum is degenerate, with two different phases having the same energy.

Studying the eigenvalues of the Hessian matrix reveals the following: for $R \leqslant R_c$ the line $\Lambda_1^{sym} = 0$, which corresponds to the stability line of the nonsymmetric phase A, is a second order phase transition line. For $Z \geqslant Z_c$ the line $\Lambda_2^{sym} = 0$, which corresponds to the stability line of the nonsymmetric phase B, is also a second order phase transition line. The stability lines of the nonsymmetric phases for $R \geqslant R_c$ are not coincident. Therefore there is a first order phase transition line between the nonsymmetric phases A and B. The point where the first order transition line splits into two continuous phase transition lines is a multicritical point, in this case a bicritical point [13]. Finally, the line $Z = 1$ correspond to the ionization line in the symmetric phase A, where one of the electrons is at infinite distance. It is interesting to note that the total nonsymmetric solution for $Z = 1$ at $R = 3\sqrt{3}/4$, corresponding to the H_2^+ critical point [8], is localized in the zone where the phase B is the global minimum.

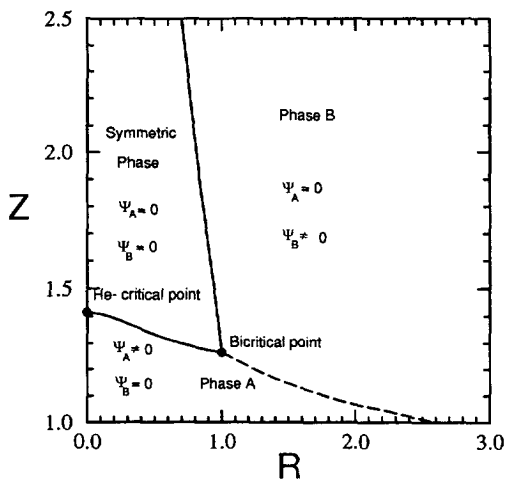


Fig. 2. Phase diagram in the $R-Z$ plane. The continuous lines represent second order phase transitions while the dashed line is a first order phase transition line. The bicritical point and the critical point which corresponds to the limiting case of the two-electron atom ($R = 0$) is also shown.

As in standard phase transitions, we can characterize a phase by an order parameter. The order parameter is nonzero only in the region of the phase diagram where the symmetry is broken. In the symmetric phase, the order parameter must be zero.

Phases A and B have different symmetry properties, and therefore must be characterized by different order parameters. The phase A is stable for small values of the nuclear charge Z and the internuclear distance R. The symmetry breaking occurs when both electrons move to the symmetry plane $z = 0$, giving an electronic structure configuration similar to the two-electron atom. In this phase the order parameter correspond to the united atom order parameter and is given by [8]

$$\Psi_A = (\lambda_1 - \lambda_2)/\lambda_> , \tag{17}$$

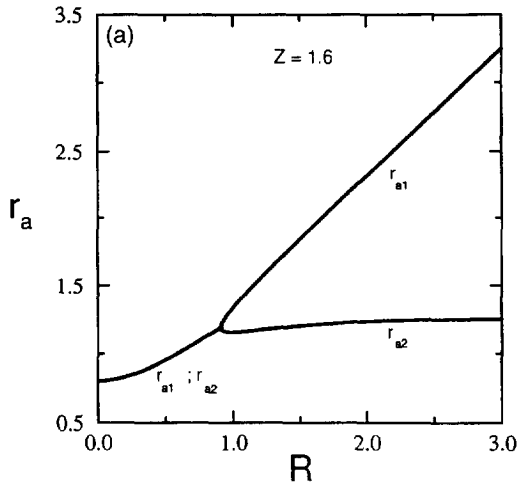
where $\lambda_> = \max(\lambda_1, \lambda_2)$.

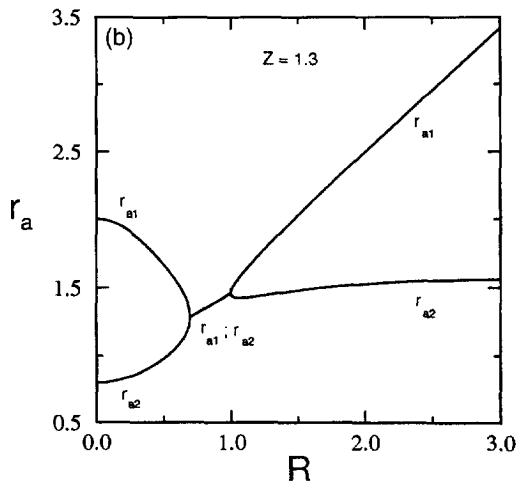
The phase B zone corresponds to larger values of R and the symmetry breaking leads to configurations where one electron near nucleus a and the other near nucleus b. In this phase $\Psi_A = 0$ and the order parameter corresponds to the separated atom limit. The order parameter for phase B is defined as

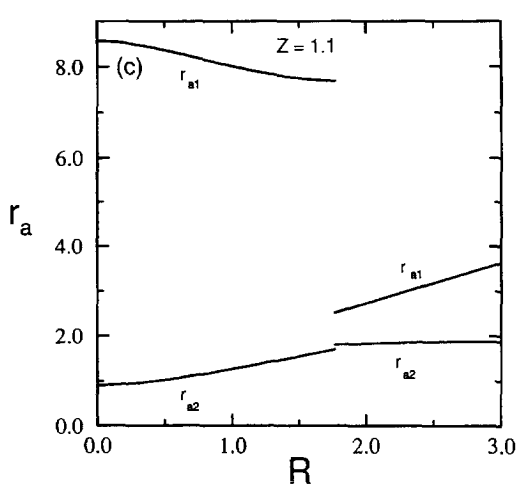
$$\Psi_B = (\mu_1 - \mu_2)/2R. \tag{18}$$

The phase diagram with the three different phases and the values of the order parameters in each phase is shown in Fig. 2. At the bicritical point the two order parameters go simultaneously to zero. Fig. 3 shows the variation with R of the coordinate r_a (r_b exhibits equivalent behavior) for both electrons at the global minimum of the effective potential for three different values of the total nuclear charge Z. In Fig. 3a, with $Z = 1.6 > Z_{bc}$, for $R < R_{bc}$ up to the

Fig. 3. Variation with R of the coordinate r_a for both electrons corresponding to the global minimum of the effective potential, for three values of the total nuclear charge: (a) $Z = 1.6$, (b) $Z = 1.3$, and (c) $Z = 1.1$.







symmetry breaking point $R_c(Z = 1.6)$, the effective potential has a single minimum corresponding to the symmetric electronic configuration. As R varies beyond this point, the minimum begins to split into two equivalent minima with the electron "1" ("2") near the nucleus "a" and electron "2" ("1") in a symmetric position near the nucleus "b". Fig. 3b shows the variation of r_a with R for an intermediate value of the nuclear charge, $Z = 1.3$. As R varies, two continuous transitions occur, from phase A to the symmetric phase to phase B. For $Z = 1.1$, the transition from phase A to phase B is a first order phase transition, with a discontinuous change in the electron–nuclear distance as shown in Fig. 3c.

5. Discussion

In the traditional area of critical phenomena, under simple circumstances, a phase transition is reached when the temperature approaches a special value, T_c, keeping the ordering field equal to zero. In many cases, with additional parameters, the transition point turns into a line or a surface. In this situation, some properties of the transition change abruptly along the transition line or surface. The points where these lines or surfaces join may have special critical proprieties, and are called multicritical points [13]. In this paper, we show that the symmetry breaking of electronic structure configurations of the Hartree–Fock hydrogen molecule at the large-D limit exhibit multicritical phenomena. The phase diagram was characterized by a bicritical point where the two continuous phase transition lines join a first order transition line.

For molecules at the large-D limt, the potential energy curves are purely repulsive, which occurs because the $D \to \infty$ limit lacks exchange, and higher order terms in a $1/D$ perturbation expansion are required to obtain chemical bonding in $D = 3$ molecules. Good approximations for bonding can be obtained by simply augmenting the large-D result with an exchange energy [14], by uniform scaling and interpolation procedures [12], or by charge renormalization methods [15]. Recently, Herschbach and co-workers [16] have found that the four one- and two-electron diatomic molecules (H_2^+, H_2, HHe^+

and He_2^{2+}) have similar scaled potential energy curves. The $D = 3$ potential energy can be derived from the large-D limit via

$$E_3(R) \approx E_\infty(R)/(1 - AR^2 e^{-aR}), \qquad (19)$$

where A and a are scaled parameters depending on the equilibrium distance and minimum energy values. It is interesting to note that this scaled factor depends only on the internuclear distance. Since in the construction of the phase diagram, the internuclear distance is not a variational parameter, we expect that the phase diagram at the large-D limit to be qualitatively similar to the $D = 3$ phase diagram. This study of phase transitions for the Hartree–Fock hydrogen molecule might shed a light on the origin of the corresponding-states correlation of intermolecular potential energy curves.

The analogy between electronic structure problems and the traditional ideas of phase transitions and critical phenomena offers a new point of view for looking at molecular processes such as ionization, dissociation and the formation of the chemical bond. Although we have focused upon symmetry breaking at the large-D limit, research is underway to examine this phase diagram at $D = 3$ by using a simple D-dimensional variational wavefunction and including higher order terms in $1/D$ expansion [17].

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