Critical Phenomena for Electronic Structure at the Large-Dimension Limit

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We show that the symmetry breaking of the electronic structure configurations at the large-D limit is completely analogous to the standard phase transitions and critical phenomena in statistical mechanics. Electronic structure at the large-D limit exhibits critical points with mean field critical exponents ($\beta = \frac{1}{2}$, $\alpha = 0_{\rm dis}$, $\delta = 3$, and $\gamma = 1$). The complete mapping is presented for the Hartree-Fock two-electron atom in weak electric field and the two Coulomb center problems. [S0031-9007(96)00621-7]

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Large-D expansions were originally developed for specific theories in the fields of nuclear physics, critical phenomena, and particle physics [1]. They subsequently found wide use in other areas such as atomic and molecular physics [2] and quantum optics. This method involves generalizing the problem to D-dimensional space and treating D as a free parameter. Typically, the limit $D \rightarrow \infty$ 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 can then be taken into account by introducing a systematic perturbation expansion in $1/D$. In atomic and molecular physics, dimensional scaling offers promising new computational procedures for the study of a variety of physical problems [2]. Among recent applications of dimensional scaling are the large order dimensional perturbation expansion [3], including complex dimensional scaling for resonances and unstable states [4], correlated electronic structure models for atoms and solids based on the sub-Hamiltonian [5], and dimensional renormalization for atoms [6] and simple diatomic molecules [7].

Yaffe has shown that if a quantum theory satisfies certain assumptions then it is possible to find a set of generalized coherent states which can be used to obtain a classical Hamiltonian such that the resulting dynamics agrees with the large-D quantum dynamics [8]. In the application of dimensional scaling to electronic structure, the limit $D \rightarrow \infty$ reduces to a classical electrostatic problem in which the electrons assumed fixed positions relative to the nuclei and to each other in the D-scaled space. This configuration corresponds to the minimum of an effective potential which includes Coulomb interactions as well as centrifugal terms arising from the generalized D-dependence kinetic energy. Typically, in the large-D regime the electronic structure configuration undergoes symmetry breaking for certain ranges of nuclear charges or geometries and thus acquires multiple minima. Breaking the total symmetrical configuration and tunneling among different minima, which is akin to resonance among valence bond structures, are completely analogous to phase transitions and critical phenomena in statistical mechanics [9].

One important aspect of critical phenomena is the characterization of the critical points by the critical exponents [10]. In mean field theories all systems have the same critical exponents independent of the model systems or the details of the forces. In this Letter we show that electronic structure of atoms and molecules at the large-D limit exhibit critical phenomena with mean field critical exponents ($\beta = \frac{1}{2}$, $\alpha = 0_{\rm dis}$, $\delta = 3$, and $\gamma = 1$). This analogy is shown by allowing the nuclear charge for atoms and the inverse internuclear distance for molecules to play the role of temperature as in the standard phase transition. For simplicity we present here the detailed calculations for two-electron atom and two Coulomb center problems at the large-D limit. More complete and general results for N-electron atoms will be given elsewhere [11].

The effective Hamiltonian at the large dimension limit can be obtained from the D-dimensional Hamiltonian by a simple scaling transformation; κ^2 Bohr radii for distance and $1/\kappa^2$ hartree for energy, where $\kappa = \frac{1}{2}(D - 1)$. In the rescaled D-dimensional Schrödinger equation, $1/\kappa^2$ multiplies all kinetic terms associated with the internal motions. Thus as $\kappa \rightarrow \infty$, the kinetic term vanishes and the wave function becomes δ function located at the minimum of the effective potential [2]. In the Hartree-Fock approximation at the $D \rightarrow \infty$ limit, the dimensional-scaled effective Hamiltonian for a two-electron atom in an external weak electric field $\mathcal{E}$ can be written as [12]

$$\mathcal{H}_\infty = \frac{1}{2}\left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2}\right) - Z\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{(\rho_1^2 + \rho_2^2)^{1/2}} - \mathcal{E}(\rho_1 - \rho_2), \qquad (1)$$

where ρ_1 and ρ_2 are the electron-nucleus radii, and Z is the nuclear charge. The direction of the electric field was chosen in order to preserve the symmetry of the effective Hamiltonian

$$\mathcal{H}_\infty(Z, \mathcal{E}; \rho_1, \rho_2) = \mathcal{H}_\infty(Z, -\mathcal{E}; \rho_2, \rho_1).$$

The large-D limit ground state energy is then given by

$$E_\infty(Z, \mathcal{E}) = \min_{\{\rho_1, \rho_2\}} \mathcal{H}_\infty. \qquad (2)$$

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This condition yields the equations

$$-\frac{1}{\rho_i^3}+\frac{Z}{\rho_i^2}-\frac{\rho_i}{(\rho_1^2+\rho_2^2)^{3/2}}=\sigma_i\mathcal{E},$$
$$i=1,2,\quad \sigma_1=1,\quad \sigma_2=-1. \tag{3}$$

In the absence of an external field $\mathcal{E}=0$, Herschbach and co-workers [13] have found that these equations have a symmetrical solution with the two electrons equidistant from the nucleus, with $\rho_1=\rho_2=\rho=2^{3/2}/(2^{3/2}Z-1)$. This symmetrical solution represents a single minimum in the region where all the eigenvalues of the Hessian matrix are positive, $Z\geq Z_c=\sqrt{2}$. For smaller Z, this symmetry is broken. When $Z<Z_c$ or $\mathcal{E}\neq 0$, the solutions of the variational equations (3) become unsymmetrical with one electron much closer to the nucleus than the other ($\rho_1\neq\rho_2$). Introducing new variables (ρ,η)

$$\rho_1=\rho,\qquad \rho_2=(1-\eta)\rho, \tag{4}$$

where $\eta\neq 0$ measures the deviation from the symmetrical solution, the electric field $\mathcal{E}$ can be written as a function of Z and η,

$$\mathcal{E}(Z,\eta)=-\frac{1}{\rho^3}+\frac{Z}{\rho^2}-\frac{1}{\rho^2[2(1-\eta)+\eta^2]^{3/2}}, \tag{5}$$

where

$$\frac{1}{\rho}=\frac{(1-\eta)[2(1-\eta)+\eta^2]}{(1-\eta)^3+1}\times\left[Z-\frac{(2-\eta)(1-\eta)^2}{[2(1-\eta)+\eta^2]^{5/2}}\right]. \tag{6}$$

For $\mathcal{E}=0$, the asymmetry parameter η is given by

$$\eta(Z,\mathcal{E}=0)=\frac{(Z_c+Z)^{1/2}[Z-(Z_c^2-Z^2)^{1/2}]}{Z^2-1}\times(Z_c-Z)^{1/2}. \tag{7}$$

By studying the eigenvalues of the Hessian matrix, we have found that this solution is a minimum of the effective potential for the range $1\leq Z\leq Z_c$.

Now a complete mapping between this problem and critical phenomena in statistical mechanics is readily feasible with the following analogies: (i) nuclear charge $Z\leftrightarrow$ temperature T, (ii) external electric field $\mathcal{E}\leftrightarrow$ ordering field h, (iii) ground state energy $E_\infty(Z,\mathcal{E})\leftrightarrow$ free energy $f(T,h)$, (iv) asymmetry parameter $\eta\leftrightarrow$ order parameter m, and (v) stability limit point $(Z_c,\mathcal{E}=0)\leftrightarrow$ critical point $(T_c,h=0)$.

Using this scheme, we can define the critical exponents (β, α, δ, and γ) for the electronic structure of the two-electron atom in the following way:

$$\begin{aligned}\eta(Z,\mathcal{E}=0)&\sim(-\Delta Z)^{\beta},\quad \Delta Z\to 0^-\\ E_\infty(Z,\mathcal{E}=0)&\sim|\Delta Z|^{2-\alpha},\quad \Delta Z\to 0\\ \mathcal{E}(Z_c,\eta)&\sim\eta^{\delta}sg(\eta),\quad \eta\to 0\\ \frac{\partial\eta}{\partial\mathcal{E}}\Big|_{\mathcal{E}=0}&\sim|\Delta Z|^{-\gamma},\quad \Delta Z\to 0,\end{aligned} \tag{8}$$

where $\Delta Z\equiv Z-Z_c$.

The expression for the electric field, Eq. (5), has the following asymptotic expansion near the critical point:

$$\mathcal{E}(\Delta Z,\eta)=\frac{9}{16}\Delta Z\eta+\frac{9}{32}\Delta Z\eta^2+\frac{9}{64\sqrt{2}}\eta^3+O(\Delta Z^2\eta,\eta^4). \tag{9}$$

From this expression and Eqs. (3) and (8), it is straightforward to obtain the critical exponents

$$\beta=\frac{1}{2},\quad \alpha=0_{\rm dis},\quad \delta=3,\quad \gamma=1. \tag{10}$$

The results of the asymmetry parameter η as a function of nuclear charge at $\mathcal{E}=0$ and as a function of the external field for different values of the nuclear charge are shown in Figs. 1(a) and 1(b). The behavior of the asymmetry parameter (order) shown in these figures is completely analogous to figures representing the behavior of magnetization as a function of the temperature in mean field theory.

Analogous symmetry breaking effects appear at the large-D limit for molecules when either the nuclear charges or the internuclear distances are varied [14]. As an example we consider the one electron two-center

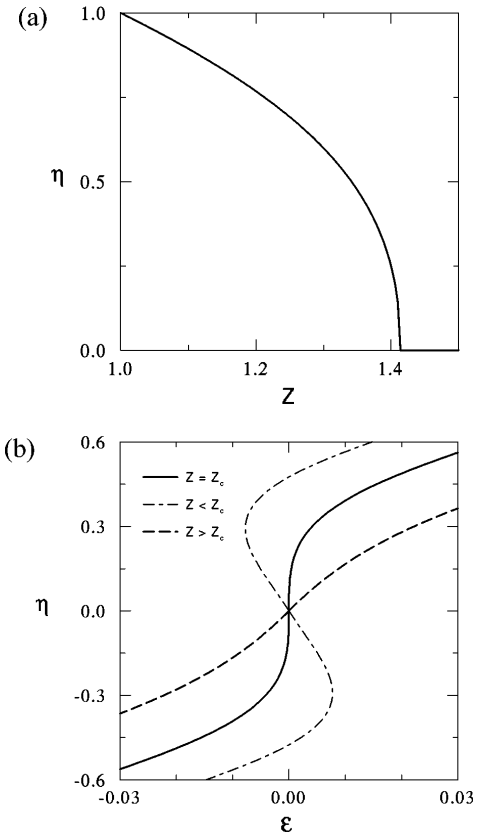

FIG. 1. (a) The asymmetry parameter η as a function of the nuclear charge Z for the two-electron atom. (b) The asymmetry parameter η as a function of the external electric field $\mathcal{E}$ for three different values of Z: $Z+Z_c=\sqrt{2}$; $Z=1.35<Z_c$; $Z=1.5>Z_c$.

Coulomb systems. The treatment of these systems at the large-D limit parallels the previous treatment for atoms. The nuclei A and B are located on the z axis at $z = -R/2$ and $z = +R/2$ with nuclear charges Z_A and Z_B, respectively; the electron is located at (ρ, z), where ρ is the distance from the z axis.

In the Born-Oppenheimer approximation, the electronic energy $E(R, \Delta)$ is then parametrically dependent upon the internuclear distance R and the difference between the nuclear charges, $\Delta = (Z_B - Z_A)/2$. The scaled effective Hamiltonian at the large-D limit is given by [14]

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \frac{1-\Delta}{r_a} - \frac{1+\Delta}{r_b}, \tag{11}$$

where r_a, r_b are the electron-nuclear distances.

The difference between the nuclear charges, Δ, plays the same role as the external electric field for the two-electron atoms with

$$\mathcal{H}_\infty(r_a, r_b; \Delta) = \mathcal{H}_\infty(r_b, r_a; -\Delta). \tag{12}$$

As with the two-electron atom, evaluating the electronic energy for $D \to \infty$ reduces simply to determining the minimum of the effective potential. For finding this minimum, it is convenient to introduce spheroidal coordinates $\lambda = (r_a + r_b)/R$ and $\mu = (r_a - r_b)/R$ which are related to the cylindrical coordinates by $z = R\lambda\mu/2$ and $\rho^2 = R^2(\lambda^2 - 1)(1 - \mu^2)/4$. In these coordinates,

$$E_\infty(R, \Delta) = \min_{\{\lambda,\mu\}} \mathcal{H}_\infty. \tag{13}$$

This equation leads to the two variational equations $\partial\mathcal{H}_\infty/\partial\lambda = 0$ and $\partial\mathcal{H}_\infty/\partial\mu = 0$.

Herschbach and co-workers [14] studied the symmetrical problem with $\Delta = 0$ and have found that the symmetrical solution exists for $\mu = 0$, where the electron is equidistant from the two nuclei ($r_a = r_b$). For small R, this solution corresponds to a minimum while for large R it corresponds to a saddle point. 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 the critical internuclear distance $R_c = 3\sqrt{3}/4$ and $\lambda_c = \sqrt{3}$. For $R > R_c$, or $\Delta \neq 0$, it is necessary to consider the nonsymmetrical solutions in order to describe the phase transition. From the variational equations, $\partial\mathcal{H}_\infty/\partial\lambda = 0$ and $\partial\mathcal{H}_\infty/\partial\mu = 0$, we obtained

$$\Delta = \frac{\mu\{\lambda^2[\lambda^2 + 3(\mu^2 - 1)] - \mu^2\}}{\lambda\{\lambda^2 - \mu^2[\mu^2 + 3(\lambda^2 - 1)]\}} \tag{14}$$

and

$$\frac{1}{R} = \frac{(\lambda^2 - 1)^2(\mu^2 - 1)^2}{\lambda\{\lambda^2 - \mu^2[\mu^2 + 3(\lambda^2 - 1)]\}}. \tag{15}$$

For $\Delta = 0$ and $\mu \neq 0$, this solution is a minimum for $R > R_c$.

As for the two-electron atom, to calculate the critical exponents we perform the following mapping: (i) inverse nuclear distance $\frac{1}{R} \leftrightarrow$ temperature T, (ii) difference between the nuclear charges $\Delta \leftrightarrow$ ordering field h, (iii) ground state energy $E_\infty(R, \Delta) \leftrightarrow$ free energy $f(T, h)$, (iv) asymmetry parameter $\psi \equiv -\partial E_\infty(R, \Delta)/\partial\Delta \leftrightarrow$ order parameter $m \equiv -\partial f(T, h)/\partial h$, and (v) stability limit point $(R_c, \Delta = 0) \leftrightarrow$ critical point $(T_c, h = 0)$.

To obtain the critical exponents, the asymptotic expansion of Eqs. (14) and (15) around the critical point gives

$$\begin{aligned}\Delta = &\left[2 - \frac{(\lambda - \lambda_c)}{\sqrt{3}} + \frac{(\lambda - \lambda_c)^2}{3}\right](\lambda - \lambda_c)\mu \\ &+ \left[\frac{8}{\sqrt{3}} + 10(\lambda - \lambda_c)\right]\mu^3 \\ &+ O\big(\mu(\lambda - \lambda_c)^4, \mu^3(\lambda - \lambda_c)^2, \mu^5\big),\end{aligned} \tag{16}$$

$$\begin{aligned}\epsilon = &\sqrt{3}(\lambda - \lambda_c) - \frac{(\lambda - \lambda_c)^3}{3\sqrt{3}} + \frac{2}{\sqrt{3}}(\lambda - \lambda_c)\mu^2 \\ &+ O\big((\lambda - \lambda_c)^4, \mu^2(\lambda - \lambda_c)^2, \mu^4\big),\end{aligned} \tag{17}$$

where ϵ plays the role of the reduced temperature

$$\epsilon \equiv \frac{1/R - 1/R_c}{1/R_c}.$$

The critical exponents are now defined as

$$\begin{aligned}\psi(\epsilon, \Delta = 0) &\sim (-\epsilon)^\beta, \quad \epsilon \to 0^-, \\ E_\infty(\epsilon, \Delta = 0) &\sim |\,\epsilon\,|^{2-\alpha}, \quad \epsilon \to 0, \\ \Delta(\epsilon = 0, \psi) &\sim \psi^\delta sg(\psi), \quad \psi \to 0, \\ \frac{\partial\psi}{\partial\Delta}\Big|_{\Delta=0} &\sim |\,\epsilon|^{-\gamma}, \quad \epsilon \to 0.\end{aligned} \tag{18}$$

As for the two-electron atom, we obtain the same critical behavior as shown in Figs. 2(a) and 2(b), with the same mean field critical exponents.

In analogy with the mean field theory of magnetism [9], we show that the deviation from the symmetrical configurations at the large-D limit is zero for all values of $Z > Z_c$. At the critical charge Z_c, symmetry breaking occurs and the value of the asymmetry parameter η increases as Z decreases to below the critical point $Z < Z_c$. Under these conditions, one electron begins moving away from both the nucleus and the other electron. In the limit $Z \to 1$ the electron is no longer bound to the atom. The two symmetry breaking phases represent either of the two electrons escaping the nucleus.

The same behavior is found in the two-center Coulomb problem for the dissociation process, where we have a symmetrical configuration for $R < R_c$ with $\Delta = 0$. At $R = R_c$ the symmetry breaking occurs and we have two symmetrical phases with the electron localized on one or the other nucleus, which is akin to resonance among valence bond structures [15]. When $R > R_c$, the value of the asymmetry parameter increases, and as a result one obtains the atomic dissociation limit as $R \to \infty$.

It is straightforward to generalize these results to more complex electronic structure problems where rich

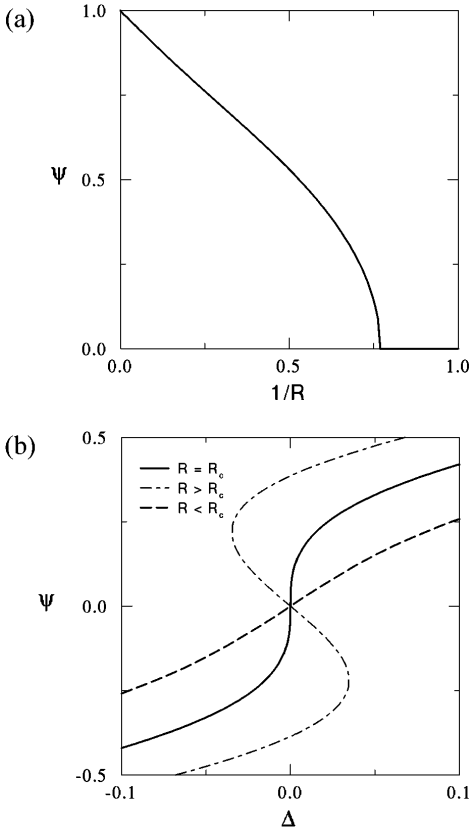

FIG. 2. (a) The asymmetry parameter μ as a function of the inverse internuclear distance $1/R$ for the two-center Coulomb problem. (b) The asymmetry parameter μ as a function of the difference in nuclear charge Δ for three different values of the internuclear distance R: $R = R_c = 3\sqrt{3}/4$; $R = 2 > R_c$; $R = 1 < R_c$.

phase diagrams appear [11]. The mapping between electronic structure at the large-D limit and the mean field theory of phase transitions invites applications of other powerful statistical mechanical techniques such as the renormalization group method to electronic structure of atoms and molecules [16].

According to the hypothesis of the universality of the critical exponents [17], only two quantities determine the critical behavior of most systems: the dimensionality of space and the dimensionality of the order parameter. All systems that have the same values of these two quantities are said to be members of the same universality class [18]. According to variational calculations at the large-D limit, we obtained classical critical exponents for the symmetry breaking of electronic structure configurations leading to ionization and dissociation. Research is underway to examine the underlying structure of phase transitions and the universality class at $D = 3$.

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