I. INTRODUCTION

A wide variety of physical systems exhibit phase transitions and critical phenomena such as liquid-gas, ferromagnetic-paramagnetic, fluid-superfluid, and conductor-superconductor transitions [1]. Phase transitions can be classified mainly as first-order and second-order phase transitions. First-order phase transitions are generally defined to be those that involve a nonzero latent heat and radical change of the structure of the material at the transition points. Second-order phase transitions are continuous phase changes where the properties of the system do not change discontinuously at the critical point, but at least one of their rates of change does [2].

Yaffe [3] 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 semiclassical Hamiltonian such that the resulting dynamics agrees with the large-dimension quantum dynamics. One should emphasize that the large-D limit is a semiclassical approximation to $D=3$ completely different from the conventional WKB approximation [3]. In the application of dimensional scaling to electronic structure, the limit $D \rightarrow \infty$ reduces to a semiclassical electrostatic problem in which the electrons are assumed to have fixed positions relative to the nuclei and to each other in the $D$-scaled space [4]. 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 [5] or molecular geometries [6].

Recently [7], we have shown that symmetry breaking of electronic-structure configurations at the large-dimension limit for Hartree-Fock (HF) two-electron atoms and the two-Coulomb center problems is completely analogous to standard phase transitions. This analogy was shown by allowing the nuclear charge for atoms and the inverse internuclear distance for the two-Coulomb problem to play a role analogous to temperature in statistical mechanics. These systems exhibit critical points with mean field critical exponents. In this paper we will use the large-dimension limit model for the general $N$-electron atom to study symmetry breaking of electronic-structure configurations leading to ionization. This model is simple, has an analytical solution for highly symmetric configurations [8], and yet contains a great deal of information about the "real" atom. This model of the atom is just the zeroth-order approximation and can be improved upon by a systematic perturbation expansion in $1/D$ [9].

The general outline of this paper is as follows. In Sec. II, we present detailed calculations for Hartree-Fock two-electron atoms in external weak electric and magnetic fields. We show that the symmetry breaking of the symmetric configuration exhibits critical points with mean field critical exponents ($\beta=\frac{1}{2}$, $\alpha=0$, $\delta=3$, and $\gamma=1$). These results are generalized to the Hartree-Fock $N$-electron atoms in weak electric and magnetic field in Sec. III. Section IV describes symmetry breaking leading to ionization for the general exact $N$-electron atoms including correlations. Finally, we discuss corresponding states of $N$-electron atoms and ways to improve this zeroth-order model.

II. HARTREE-FOCK TWO-ELECTRON ATOMS

In the HF approximation at the $D \rightarrow \infty$ limit, the dimensional-scaled effective Hamiltonian for the two-electron atom in an external weak electric field $E$ can be written as [10]

$$\hat{H}_e = \frac{1}{2} \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) - Z \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} + \frac{1}{(\rho_1 + \rho_2)^2} \right) - E(\rho_1 - \rho_2),$$

(1)

where $\rho_1$ and $\rho_2$ are the electron-nucleus radii, and $Z$ is the nuclear charge.
nuclear charge. The direction of the electric field was chosen in order to preserve the symmetry of the effective Hamiltonian

$$\mathcal{H}_0(Z, \mathcal{E}, \rho_1, \rho_2) = \mathcal{H}_0(Z, -\mathcal{E}, \rho_2, \rho_1).$$

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

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

This condition yields the equations

$$-\frac{1}{\rho_i} + \frac{Z - \rho_i}{\rho_i^2 (\rho_1^2 + \rho_2^2)^{3/2}} = \sigma_i \mathcal{E},$$

$$i = 1, 2, \quad \sigma_1 = 1, \quad \sigma_2 = -1.$$  

In the absence of an external electric field, $\mathcal{E} = 0$, Herschbach and co-workers [11] have found that these equations have a symmetric solution with the two electrons equidistant from the nucleus, with $\rho_1 = \rho_2 = \rho = 2^{3/2}/(2^{3/2} - 1)$. This symmetric solution represents a minimum in the region where all the eigenvalues of the Hessian matrix are positive, $Z \geq Z_c = \sqrt{2}$, and the ground-state energy is given by

$$E_\infty(Z) = \left( \frac{2^{3/2}}{2} \right)^2.$$  

For values of $Z$ smaller than $Z_c$, the solutions of the variational equations (4) become unsymmetric with one electron much closer to the nucleus than the other ($\rho_1 \neq \rho_2$). In order to describe this symmetry breaking, it is convenient to introduce new variables ($\rho, \eta$) of the form

$$\rho_1 = \rho, \quad \rho_2 = (1 - \eta) \rho,$$

where $\eta \neq 0$ measures the deviation from the symmetric solution. In these new variables, the electric field $\mathcal{E}$ can be written as a function of $Z$ and $\eta$,

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

where

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

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

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

and the energy is given by

$$E_\infty(Z, \mathcal{E} = 0) = \frac{1}{(1 - \eta) \rho} \left[ \frac{2(1 - \eta) + \eta^2}{2(1 - \eta) \rho} \right]^{3/2} - \frac{3(1 - \eta) + \eta^2}{[2(1 - \eta) + \eta^2]^{3/2}}.$$  

By studying the eigenvalues of the Hessian matrix, we have found that this solution is a minimum of the effective potential for the range $1 \leq Z \leq Z_c$. We now turn to the question of how to describe the system near the critical point. To answer this question, 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 $m$, (v) stability limit point $(Z_c, \mathcal{E} = 0) \leftrightarrow$ critical point $(T_c, h = 0)$.

Using the above scheme, we can define the critical exponents ($\beta$, $\gamma$, $\delta$, $\alpha$, and $\eta$) for the electronic structure of the two-electron atom in the following way:

$$\eta(Z, \mathcal{E} = 0) \sim (-\Delta Z)^\beta, \quad \Delta Z \to 0^-,$$

$$E_\infty(Z, \mathcal{E} = 0) \sim |\Delta Z|^{2 - \alpha}, \quad \Delta Z \to 0,$$

$$|\partial \mathcal{E}(Z_c, \eta)| \sim |\Delta Z|^{-\gamma}, \quad \Delta Z \to 0,$$

where $\Delta Z = Z - Z_c$. These critical exponents describe the nature of the singularities in the above quantities at the critical charge $Z_c$. To calculate these critical exponents we start with the asymptotic expression for the electric field near the critical point, we obtain from Eqs. (7) and (8)

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

From this expression and Eqs. (3) and (11), it is straightforward to obtain the critical exponents. The critical exponent $\beta$ determines the rate of vanishing of the order parameter, which is the asymmetry parameter $\eta$, in the absence of external electric fields. For $\mathcal{E} = 0$, we obtain from Eq. (12)

$$0 = \frac{9}{16} \Delta Z + \frac{9}{64 \sqrt{2}} \eta^2 + O(\Delta Z, \eta, \eta^3).$$  

This condition gives $\eta \sim 2^{5/4} (-\Delta Z)^{1/2}$ when $\Delta Z \to 0^-$. Comparing this result with the above definition of the critical exponent $\beta$, Eq. (11), gives $\beta = \frac{7}{4}$. The $\alpha$ exponent gives the rate of divergence of the second derivative of the energy with respect to the nuclear charge, which is analogous to the divergence of the heat capacity near the critical temperature. From Eqs. (5) and (10) we obtained

$$\frac{\partial^2 E_\infty(Z, \mathcal{E} = 0)}{\partial Z^2} \bigg|_{Z = Z_c} = \begin{cases} \frac{7}{4}, & \Delta Z \to 0^- \\ -2, & \Delta Z \to 0^+ \end{cases}.$$  

This quantity has a discontinuity at $Z = Z_c$, and therefore $\alpha = 0_{\text{dis}}$. The subindex discontinuity, dis, is necessary in order to distinguish this case from other known systems where the divergence is logarithmic with $\alpha = 0$ as in the two-
dimensional Ising model. At the critical charge, the external field varies with the $\delta$ power of the asymmetry parameter $\eta$. For $\Delta Z = 0$, Eq. (12) gives $\mathcal{E} \sim (9/64\sqrt{2}) \eta^3$. Thus the response to a small electric field is highly nonlinear with $\delta = 3$. Finally, in standard phase transition, the exponent $\gamma$ determines the rate of divergence of the susceptibility, or more generally, the divergence of rate of change of the field with the order parameter. From Eq. (12) we obtain

$$\frac{\partial \mathcal{E}}{\partial \eta} \bigg|_{\mathcal{E}=0} = \begin{cases} \frac{9}{16} \Delta Z + \frac{27}{64\sqrt{2}} \eta^2 = \frac{18}{16} (-\Delta Z), & \Delta Z \to 0^- \\ \frac{9}{16} \Delta Z, & \Delta Z \to 0^+ \end{cases}$$

and therefore $\gamma = 1$. The values obtained for these critical exponents are known as classical or mean-field critical exponents with

$$\beta = \frac{1}{2}, \quad \alpha = 0, \quad \delta = 3, \quad \gamma = 1. \quad (16)$$

Only two of the four are independent because of the two relations between them known as Rushbrooke’s and Griffiths’ laws [2].

$$\alpha + 2\beta + \gamma = 2, \quad \alpha + \beta(\delta + 1) = 2. \quad (17)$$

The results of the asymmetry parameter $\eta$ 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 and 2. These curves of the asymmetry parameter shown in these figures are completely analogous to curves representing the behavior of magnetization as a function of the temperature in mean field models of ferromagnetic systems [2].

Finally, we consider the effect of a uniform magnetic field on the symmetry breaking and phase transitions of the Hartree-Fock (HF) two-electron atoms. In the presence of a uniform external magnetic field $B$, the Hamiltonian is given by [10]

$$\mathcal{H}(Z,B) = \frac{1}{2} \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) - Z \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) + \frac{1}{(\rho_1 + \rho_2)^2}$$

$$+ \frac{B^2}{2}(\rho_1^2 + \rho_2^2)$$

and the variational equations are

$$- \frac{1}{\rho_1} + \frac{Z}{\rho_1} - \frac{\rho_1}{(\rho_1 + \rho_2)^2} + B^2 = 0, \quad i = 1, 2 \quad (19)$$

as in the zero-field case. We have a symmetric solution with $\rho_1 = \rho_2 = \rho$, given by

$$\rho \left( Z - \frac{1}{2} \right) + B^2 \rho^4 = 1. \quad (20)$$

The smallest eigenvalue of the Hessian matrix equal to zero gives the stability limit

$$\lambda = \frac{\partial^2 \mathcal{H}_c}{\partial \rho_1^2} - \frac{\partial^2 \mathcal{H}_c}{\partial \rho_1 \partial \rho_2} \bigg|_{\rho_1 = \rho_2 = \rho} = \frac{1}{\rho^3} \left[ 3 \rho - 2Z - \frac{1}{2} \right] + B^2 = 0. \quad (21)$$

Equations (20) and (21) at the stability limit give the value of the magnetic field as a function of the nuclear charge for the symmetric solution

$$B_{\text{sym}}(Z) = \frac{3}{16} Z [3Z(\sqrt{2} - Z)]^{1/2}. \quad (22)$$

With a nonzero magnetic field, the symmetry will be broken and we should consider the nonsymmetric solutions of Eqs. (19). Again, with $\eta$ measuring the deviation from the symmetric solution, we obtained the two equations

$$\frac{1}{\rho} = \left[ 3(1 - \eta) + \eta^2 \right] (1 - \eta)Z \quad (23)$$

and

FIG. 1. The asymmetry parameter $\eta$ as a function of the nuclear charge $Z$ for the Hartree-Fock two-electron atom.

FIG. 2. The asymmetry parameter $\eta$ as a function of the external electric field $\mathcal{E}$ for the Hartree-Fock-two-electron atom for three different values of $Z$: $Z = Z_c = \sqrt{2}$; $Z = 1.35 < Z_c$; $Z = 1.5 > Z_c$. 
FIG. 3. Phase diagram for the Hartree-Fock two-electron atom in an external magnetic field.

\[
\frac{1}{2(1 - \eta + \eta^2)} \left[ \frac{Z}{2 - \eta} - \frac{1}{2(1 - \eta + \eta^2)} \right] + B^2 = 0.
\]  

(24)

The stability limit of this solution is the same as the one given by Eq. (22). Therefore, in the external magnetic field the value of the critical charge will change with the magnetic field but not the order of the phase transition. The phase diagram for two-electron atoms in an external magnetic field is shown in Fig. 3. We note that at \( Z = 1 \) and critical field \( B_c = \frac{1}{\pi} [3(\sqrt{2} - 1)]^{1/2} \approx 0.209 \), the electron energies converge to a quadratic potential. With higher fields, \( B > B_c \), there is only a single phase, which is the symmetric phase.

III. HARTREE-FOCK N-ELECTRON ATOMS

In this section, we would like to generalize the previous results of symmetry breaking and phase transitions of the HF two-electron atoms in weak magnetic and electric fields to the general case of HF \( N \)-electron atoms. The dimensionless scaled effective Hamiltonian for HF \( N \)-electron atoms at the large-\( D \) limit can be obtained by the constraint that the interelectron angles become fixed at 90° [10].

\[
\mathcal{H}_c = \frac{1}{2} \sum_{i=1}^{N} \frac{1}{\rho_i} - \sum_{i=1}^{N} \frac{1}{\rho_i} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left( \frac{1}{\rho_i^2 + \rho_j^2} \right)^{1/2},
\]

(25)

where \( \rho_i \) are the electron-nucleus radii, and \( Z \) is the nuclear charge.

The large-\( D \) limit ground-state energy is given by

\[
E_c(N,Z) = \min_{\{\rho_i\}} \mathcal{H}_c.
\]

(26)

This condition yields the set of equations

\[
-\frac{1}{\rho_i} + \frac{Z}{\rho_i} - \rho_i \sum_{j \neq i} \frac{1}{(\rho_i^2 + \rho_j^2)^{1/2}} = 0, \quad i = 1, 2, \ldots, N.
\]

(27)

As in two-electron atoms, these equations have a symmetric solution with the \( N \) electrons equidistant from the nucleus, with \( \rho_1 = \rho = 2^{3/2}(2^{3/2}Z - N + 1) \). This symmetric solution represents a minimum in the region where all the eigenvalues of the Hessian matrix are positive, \( Z \approx Z_c(N) = (N - 2)/2^{3/2} \), and the energy is given by

\[
E^{sm}(N,Z) = -\frac{N}{2} \left( Z - \frac{N - 1}{2^{3/2}} \right)^2.
\]

(28)

For \( N \)-electron atoms, the symmetry is broken in a different way than in the special case of \( N = 2 \). In general, the phase transition does not coincide with the stability limit of the symmetric phase point \( Z_s(N) \). For \( N \neq 2 \) we found a region with two or more stable solutions of the variational equations. This indicates that there are several local minima corresponding to different electronic configurations. This phenomenon is completely equivalent to phase coexistence in mean field theories of first-order phase transitions, where the first-order phase transition line appears when the global minimum degenerates.

For small values of \( N \), solutions with lower symmetry appear by the removal of one electron to a much larger distance leaving a core of \( N - 1 \) equivalent electrons with

\[
\rho_1 = \rho_2 = \cdots = \rho_{N-1} = \rho, \quad \rho_N = (1 + \eta) \rho.
\]

(29)

This solution, which we will refer to as phase \( A_1 \), is stable for small values of \( Z \), but there is a coexistence region with the symmetric solution where both are minima of the variational equations. For a fixed value of \( N \), the first-order phase transition point \( Z_1 \) is given by the condition

\[
E^{sm}(N,Z_1) = E^{(A_1)}(N,Z_1),
\]

(30)

where \( E^{(A_1)}(N,Z) \) is the energy in the phase \( A_1 \).

Equation (29) gives two electronic configurations for \( \eta > 0 \) and \( \eta < 0 \) with different values of energy \( E^{(A_1)}_\infty \) and \( E^{(A_1)}_\infty \), respectively. For \( N > 2 \) the global minimum corresponds to \( E^{(A_1)}_\infty \), while for \( N < 2 \), \( E^{(A_1)}_\infty \) is the global mini-
For neutral atoms the symmetric solution is the global minimum. Since there is no shell structure, the mechanism of symmetry breaking involves the removal of one electron to complete ionization at the limit \( Z \to N - 1 \). At this value of \( Z \), the system again makes a transition to the nonsymmetric phase \( A_1 \) configuration, but with \( N - 1 \) electrons. A phase diagram with stability lines is shown in Fig. 7.

For \( N_1 < N < N_2 = 27.45 \) the nonsymmetric phases \( A_m \) are not the global minimum for \( m > 1 \). At \( N = N_2 \), the global minimum for neutral atoms jumps to the nonsymmetric \( m = 2 \) electronic configurations. This change in the electronic configuration for neutral atoms might be regarded as a kind of “shell structure” (which is not the ordinary shell structure at \( D = 3 \)) for the HF \( N \)-electron atom at the large-\( D \) limit.

Now, we turn to the effect of an external electric field on the symmetry breaking and phase transitions for the general case of \( N \)-electron atoms. The effective Hamiltonian for \( N \)-electron atoms in a weak external electric field takes the form

\[
E^{(A_1)}_\infty(N,Z_B) = E^{(B)}(N,Z_B).
\]
For $N \neq 2$, the phase transition between symmetric to nonsymmetric $A_1$ configuration is not continuous and the system has a different response to the external field in comparison with the continuous transition at $N=2$. In Fig. 8 we show the energy versus the external electric field for $N=3$ over the first-order phase transition line $Z_1=2.405$. In this case, the energy presents the typical behavior of the free energy in mean-field theories of first-order phase transitions.

For two-electron atoms, $\lim_{Z \to Z_c} \eta = 0$ and therefore $\eta$ is a good order parameter to measure the asymmetry of the electronic configuration. Because $\eta$ is a real parameter, which goes to infinity as $Z \to N-1$, it is convenient to define a new order parameter for the general $N$-electron atom as

$$\eta = \frac{\rho_N - \rho_1}{\rho_2} = \begin{cases} \eta, & \eta < 0 \\ \frac{\eta}{1 + \eta}, & \eta > 0 \end{cases},$$

where $\rho_{2}$ is the maximum between $\rho_1$ and $\rho_N$.

In Fig. 9 curves of $\psi$ versus $\epsilon$ over the phase transition line is shown for different values of $N$. Note that only at $N=2$, where both nonsymmetric $A_1$ configurations are equivalent, is the curve symmetric with respect to $\epsilon$.

### IV. $N$-ELECTRON ATOMS

For the exact solution of the $N$-electron atom at the $D \to \infty$ limit, the dimensional-scaled effective Hamiltonian can be written as [8]

---

**FIG. 8.** Energy versus electric field in the Hartree-Fock approximation for $N=3$ and $Z=Z_1=2.405$.

**FIG. 9.** Order parameter versus external electric field for different values of $N$ in the Hartree-Fock approximation, over the first-order line: $(N=2, Z=Z_c=\sqrt{3})$, $(N=3, Z=Z_1=2.405)$, and $(N=4, Z=Z_1=3.457)$. Only the curve $N=2$ is symmetric with respect to $\epsilon$.

**FIG. 10.** Phase diagram in the $Z-N$ plane for small values of $Z$. Dashed lines represent first-order phase transitions. The line between the nonsymmetric phases ends at a triple point.
\[
\mathcal{H}_N = \frac{1}{2} \sum_{i=1}^{N} \frac{1}{r_i^2} - 2 \sum_{i=1}^{N} \rho_i - Z \sum_{j=1}^{N} \frac{1}{r_j} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{(r_i^2 + r_j^2 - 2 \rho_i \rho_j \gamma_{ij})^{3/2}}.
\]

Here, \(\rho_i\) are the electron-nucleus radii, \(Z\) is the nuclear charge, \(\gamma_{ij}\) are the cosines of the angle between electrons \(i\) and \(j\), \(\Gamma_N\) is the Grammian determinant \([\gamma_{ij}]\) for all \(N\) electrons, and \(\Gamma_N^i\) is the Grammian determinant for all but the \(i\)th electron.

The \(N(N-1)/2\) angles \([\gamma_{ij}]\) are new variational parameters along with the \(N\) radii \(\{\rho_i\}\). The large-\(D\) limit ground-state energy is given by the minimum of the effective Hamiltonian,

\[
E_p(N,Z) = \min_{\{\rho_i, \gamma_{ij}\}} \mathcal{H}_N.
\]

This condition yields the radial equations

\[
\frac{\partial \mathcal{H}_N}{\partial \rho_i} = -\frac{\Gamma_N^i}{\Gamma_N} \frac{1}{r_i^2} - \frac{Z}{r_i^2} - \sum_{j=1}^{N} \frac{\rho_i - \rho_j \gamma_{ij}}{(r_i^2 + r_j^2 - 2 \rho_i \rho_j \gamma_{ij})^{3/2}} = 0
\]

for \(i=1,2,\ldots,N\). The angular extremum conditions give the equations

\[
\frac{\partial \mathcal{H}_N}{\partial \gamma_{ij}} = \frac{1}{2} \sum_{k=1}^{N} \frac{1}{\Gamma_N^i \Gamma_N^j} \left( \Gamma_N^k \frac{\partial \Gamma_N^i}{\partial \gamma_{ij}} - \Gamma_N^k \frac{\partial \Gamma_N^j}{\partial \gamma_{ij}} \right) \frac{1}{r_k} + \frac{\rho_i \rho_j}{(r_i^2 + r_j^2 - 2 \rho_i \rho_j \gamma_{ij})^{3/2}} = 0
\]

Solving these equations gives a closed form expression for the ground-state energy of the total symmetric configuration

\[
E_p^{\text{sym}}(N,Z) = -\frac{N[1+(N-1)\gamma]^2[1+(2N-3)\gamma+(N-1)(N-2)\gamma^2]Z^2}{2(1-\gamma)},
\]

where \(\gamma(N,Z)\) is the largest negative root of the equation

\[
Z = -\frac{(1-\gamma)^{1/2}}{2^{3/2}[2+(N-2)\gamma]^{1/2}}.
\]

As in the HF \(N\)-electron atoms, we define new variables \((\eta,\mu)\) to describe the motion which breaks the total symmetric configuration and allows us to study the transitions to the nonsymmetric phase \(A_1\) electronic configurations

\[
\rho_1 = \cdots = \rho_{N-1} = \rho, \quad \rho_N = (1+\eta)\rho, \quad \gamma_{ij} = \gamma, \quad i,j < N, \quad \gamma_{i,N} = \mu.
\]

The Grammian determinant and its derivates can be calculated analytically for this phase (see the Appendix).

Loeser [8] obtained the totally symmetric solution when the effective Hamiltonian is completely symmetric in each set, \(\rho_i = \rho\) and \(\gamma_{ij} = \gamma\). Under this assumption, the Grammian determinant and its derivative takes the simple form (see the Appendix)

\[
\Gamma_N = [1+(N-1)\gamma](1-\gamma)^{N-1},
\]

\[
\frac{\partial \Gamma_N}{\partial \gamma_{ij}}\bigg|_{\text{sym}} = -2\gamma(1-\gamma)^{N-2}.
\]

Using these results, the radial, Eq. (40), and the angular, Eq. (41), become

\[
-\frac{1+(N-2)\gamma}{(1-\gamma)(1+(N-1)\gamma)} + \frac{Z}{2^{3/2}(1-\gamma)^{1/2}} = 0,
\]

\[
\frac{2+(N-2)\gamma}{[1+(N-1)\gamma]^{1/2}} \frac{\gamma}{(1-\gamma)^{1/2}} + \frac{Z}{2^{3/2}(1-\gamma)^{1/2}} = 0.
\]

Solving these equations gives a closed form expression for the ground-state energy of the total symmetric configuration

\[
\Gamma_N = (1-\gamma)^{N-2}[1+(N-2)\gamma-(N-1)\mu^2],
\]

\[
\frac{\partial \Gamma_N}{\partial \gamma_{ij}}\bigg|_{1} = \begin{cases} -2(1-\gamma)^{N-2}(\gamma-\mu^2), & i,j < N; j = N \end{cases},
\]

Substituting these expressions into Eqs. (40) and (41) gives four coupled nonlinear equations for the variational parameters \((\rho, \eta, \gamma, \mu)\) which have to be solved numerically. The phase diagram for small values of \(Z\) is qualitatively similar to the phase diagram obtained in the Hartree-Fock approximation. However, for the exact solution, the symmetry breaking of the electronic configuration is always a first-order phase transition. Therefore, the critical point at \(N=2\) in the HF approximation is now replaced by a triple point, as shown in Fig. 10.

For two-electron atoms there is only one interelectronic angle, so the equations take a much simpler form and some results can be obtained analytically. The Hessian matrix can be calculated for both phases, the stability limit of the sym-
metric configuration is given analytically with \(Z = 3^{1/4}(2 + \sqrt{3})/4 \approx 1.2279\) and \(\gamma = 1 - 2/\sqrt{3} \approx -0.1547\). For the nonsymmetric phase \(A_1\) configuration, the stability limit is given by \(Z \approx 1.2352\) and \(\gamma \approx -0.118\). For the first-order point, given by

\[
E_{\text{sym}}(N=2,Z_1) = E_{\text{sym}}^{(A_1)}(N=2,Z_1),
\]

we obtain \(Z_1(N=2) = 1.2334\). Figure 11 shows \(Z\) as a function of the order parameter \(\psi\) defined by Eq. (37) for both Hartree-Fock and the exact two-electron atoms. The different behavior at \(\psi = 0\) explains the change of the order of the phase transition.

The symmetric configuration corresponds to the global minimum for small values of \(N\). The value of \(N\) for which the symmetric solution no longer is the global minimum, \(N_{1/2}\), is defined by the condition \(Z_1(N_{1/2}) = 13.403\). For greater values of \(N\) \((N > N_{1/2})\) it is necessary to consider new nonsymmetric configurations. The nonsymmetric phase \(A_2\) electronic configuration is defined by

\[
\rho_i = \cdots \rho_{N-2} = \rho, \quad \rho_{N-1} = \rho_N = (1 + \eta)\rho,
\]

\[
\gamma_{i,j} = \gamma, \quad i, j < N - 1, \quad \gamma_{i,N-1} = \gamma_{i,N} = \mu, \quad i < N - 1, \quad \gamma_{N-1,N} = \omega.
\]

For this solution, the Grammian determinant and its derivatives are given by (see the Appendix)

\[
\Gamma_N = (1 - \gamma)^{N-3}(1 - \omega)[1 - \omega + (N - 3) \gamma(1 - \omega) - 2(N - 2)\mu^2],
\]

\[
\frac{\partial \Gamma_N}{\partial \gamma_{i,j}} = \begin{cases} 
-2(1 - \gamma)^{N-4}(1 - \omega)[(1 + \omega)\gamma - 2\mu^2], & i, j < N - 1 \\
-2(1 - \omega)\mu(1 - \gamma)^{N-3}, & i < N - 1; \ j \geq N - 1 \\
-2(1 - \gamma)^{N-3}[1 + (N - 3)\gamma]\omega - (N - 2)\mu^2), & i = N - 1; \ j = N.
\end{cases}
\]

For neutral atoms at \(Z_e = 53\) the nonsymmetric phase \(A_2\) configuration has a lower energy than the nonsymmetric phase \(A_1\). We note that this “shell structure” appears for smaller values of \(N\) in the Hartree-Fock approximation compared with the exact solution. To study the symmetry breaking for large atoms requires a fair amount of labor because of the large number of variational parameters and the complexity of the Grammian determinant.

V. DISCUSSION

We established an analogy between mean-field theory of phase transitions and symmetry breaking of electronic structure configurations at the large-\(D\) limit. In this context, symmetry breaking solutions in both Hartree-Fock and exact solutions of \(N\)-electron atoms requires new interpretations. The mapping of this problem to standard phase transitions allows us to treat the nuclear charge in an analogous fashion as temperature in statistical mechanics. Therefore, the symmetric electronic configurations can be thought of as a high temperature phase. By “cooling” the system, new different ordered phases appear for certain values of the nuclear charges. For the Hartree-Fock solution, we have found a critical point at \((N_c = 2, Z_e = \sqrt{2})\) with mean field critical exponents. The exact solution has first order phase transitions with a triple point replacing the critical point found in the Hartree-Fock approximation.

Another characteristic of critical phenomena is the exist-
ence of the law of corresponding states. We note that from Eq. (28), the rescaled Hartree-Fock energy of the symmetric configuration does not depend on the value of \( N \) and can be written as

\[
E_s(N,Z) \rightarrow \frac{E_s(Z/Z_\infty)}{N^2Z_\infty^2},
\]

where \( Z_\infty \) defines the boundary line for ionization and is given by \( Z_\infty = N-1 \). The same scaling is valid, as an asymptotic law, for the exact solution. Figure 12 shows the corresponding states for the exact and HF \( N \)-electron atoms.

This symmetry breaking and phase transition offers a different point of view for looking at atomic and molecular processes such as ionization, electron affinity, dissociations, and related phenomena. The fact that one can formally treat electronic structure problems as thermodynamic systems gives the possibility of using powerful statistical mechanics techniques to treat large atomic and molecular systems [12].

Since the large-\( D \) limit is pseudoclassical, it does not exhibit shell structure, so some means to incorporate this is required. Loeser suggested a simple procedure which partitions the energy into shell contributions, scales each of these by a hydrogenic factor, and sums the successive shell ionization energies [8]. However, one can define a “pseudoshell structure” at the large-\( D \) limit. For the Hartree-Fock \( N \)-electron neutral atoms the symmetric solution is the global minimum for all values of \( N \) less than \( N_1 = 12.177 \). For values of \( N \) greater than \( N_1 \) the nonsymmetric phase \( A_1 \) is the global minimum. At \( N = N_2 \approx 27.45 \), the global minimum for neutral atoms jumps to the nonsymmetric \( m = 2 \) electronic configurations. For the exact solution of the \( N \)-electron neutral atoms the symmetric configuration corresponds to the global minimum for values of \( N \) less than \( N_1 = 13.403 \). For neutral atoms at \( N = 53 \) the nonsymmetric phase \( A_2 \) configuration has a lower energy than the nonsymmetric phase \( A_1 \). This change in the electronic configurations for neutral atoms at the large-\( D \) limit might be regarded as a kind of “pseudoshell structure” of variational nature. In order to examine the relation of this pseudoshell structure with the ordinary shell structure at \( D = 3 \), one still has to include higher order terms in the \( 1/D \) expansion.

Recently, Herschbach [13] suggested charge renormalization at the large-\( D \) limit, which involves finding an effective nuclear charge that renders the dimensionally scaled energy at the \( D \to \infty \) limit a good approximation to that for \( D = 3 \) with the actual nuclear charge \( Z \). The renormalized charge is readily evaluated by comparing the Hartree-Fock energy for \( D = 3 \) with its \( D \to \infty \) limit. Another procedure of charge renormalization is to determine an effective nuclear charge such that the Hartree-Fock results will be significantly closer to the exact energies by utilizing the large-\( D \) limit results. This procedure was proven to be useful for atoms [14] and simple diatomic molecules [15]. The study of critical phenomena presented in this paper might be useful in improving the different versions of charge renormalizations.

One striking aspect of critical phenomena is the hypothesis of the universality of the critical exponents [16]. According to this hypothesis, 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 [17]. Systems in the same universality class have the same critical exponents independent of the model systems or the details of the forces. To study the behavior of a given system near the critical point one has to rely on model calculations which are simple, capture the main physics of the problem, and belong to the same universality class. 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. Although we have focused upon symmetry breaking at the large-\( D \) limit, where multicritical phenomena appear for more complicated electronic structure problems [18], research is underway to examine phase transitions at \( D = 3 \) by including higher-order terms in \( 1/D \) expansion.

**ACKNOWLEDGMENTS**

The authors would like to thank Igal Szleifer, Aaron F. Stanton, and Richard E. Bleil for many useful discussions. One of the authors (P.S.) would like to acknowledge the partial financial support of the Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba–Argentina.

**APPENDIX**

In order to study the stability of the solutions at the large-\( D \) limit, we need to evaluate the Grammian determinant, \( \Gamma_{i,j} = \gamma_{i,j} \) with \( \gamma_{i,j} = 1 \), and the determinant of the Hessian matrix

\[
\delta^{2}H_{\approx} = \frac{\partial^{2}H_{\approx}}{\partial x_{i}\partial x_{j}},
\]

where \( \{x_{i}\} \) represent both the radial and angular coordinates where the determinant is evaluated for a particular solution. Actually, both matrices have a similar block structure. For example, the Hessian matrix of the nonsymmetric phase \( A_{m} \) electronic configuration for the \( N \)-electron HF atoms has the general form

\[
G = \begin{bmatrix}
ab,\ldots,b &=& c,\ldots,c \\
b,a,b,\ldots &=& c,\ldots,c \\
\vdots & & \\
b,b,\ldots,a &=& c,\ldots,c \\
c,\ldots,c &=& d,e,e,\ldots,e \\
\vdots & & \\
c,\ldots,c &=& e,e,\ldots,d \\
\end{bmatrix}.
\]

To calculate the determinant, we note that the vector \( \tilde{x} = (x_{1}, \ldots, x_{N-m}, 0, \ldots, 0) \) satisfies

\[
(G\tilde{x})_{i} = \begin{cases}
ax_{i} + b \sum_{j \neq i} x_{j}, & i \leq N-m \\
c \sum_{j} x_{j}, & i \geq N-m.
\end{cases}
\]
If we impose the condition $\Sigma_j x_j = 0$, then $\tilde{x}$ is an eigenvector with an eigenvalue $\lambda_1 = a - b$. But, there are $N - m - 1$ linear independent vectors that satisfy this condition, therefore $\lambda_1$ has the multiplicity $N - m - 1$. In the same way, we can define the vector $\tilde{y} = (0, \ldots, 0, y_{N-m}, \ldots, y_N)$ with $\Sigma_j y_j = 0$, which gives $\lambda_2 = d - e$ as an eigenvalue with multiplicity $m - 1$. The other two eigenvalues are calculated with two vectors orthogonal to $\{\tilde{x}, \tilde{y}\}; z_i = (1, \ldots, 1, \xi_1, \ldots, \xi_m)$ for $i = 1, 2$. The eigenvalue equation $G z_i = \lambda z_i$ gives

$$\lambda_\pm = \frac{1}{2} (a + d + (n - m - 1)b + (m - 1)e) \pm \sqrt{\left[(a - d + (n - m - 1)b - (m - 1)e)^2 - 4(N - m)c^2\right]^{1/2}}$$

and the determinant is given by the product of the eigenvalues $\det(G) = \lambda_1^{N-m-1} \lambda_2^{m-1} \lambda_+ \lambda_-$. (A5)

This expression is also useful for Grammian matrices. Setting the diagonal elements equal to 1, we obtain, for $m = 0$, the Grammian matrix for the symmetric solution, and, in general, from the $m$ Hessian matrix we obtain the $m - 1$ Grammian matrix. For more complicated electronic structure configurations, such as the nonsymmetric phase $B$, the matrices have a different structure, but it is still possible to use the same technique to calculate the determinants. General properties of the Grammian determinant and its derivatives are given in Ref. [19]. In particular, Eq. (A.6) of that reference,

$$\Gamma = \frac{1}{2} \sum_{j=i}^N \gamma_i, j \frac{\partial \Gamma}{\partial \gamma_{i,j}} = \Gamma^{(i)},$$

(A6)
gives us a linear system to obtain the derivates of the Grammian determinant for each particular solution.