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Mean field phase diagrams for one-electron molecules

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Abstract. We describe a simple model for symmetry breaking of electronic structure configurations of one-electron systems. This model involves generalizing the problem to D-dimensional space and finding the solution at $D \to \infty$, a semiclassical limit which can be solved exactly. The large-D limit model reduces the problem to a variational calculation which is equivalent to mean-field theories of critical phenomena in statistical mechanics. We show that symmetry breaking of electronic structure configurations can be described as standard phase transitions. Rich phase diagrams with multicritical points are reported for both linear and planar one-electron systems.

1. Introduction

Large-dimension models and dimensional expansion schemes have proven their efficiency in dealing with a diverse class of fields ranging from nuclear physics, critical phenomena and particle physics to atomic and molecular physics [1, 2]. This method involves generalizing the problem to D-dimensional space and treating D as a free parameter. This large-D limit is a semiclassical approximation to $D = 3$, but distinct from the conventional WKB approximation [3]. The most important characteristics of the large-D limit are that it is simple, captures the main physics of the system, is applicable for a wide class of theories and is analytically solvable. In this paper, the large-D model will be used to describe symmetry breaking and phase transitions in electronic structure problems. In order to study critical phenomena and phase transitions one quite often has to rely on solvable models. For example, the Curie–Weiss Hamiltonian has been used in the magnetic phase transition theory [4]. This Hamiltonian model has an analytical solution not only for the simplest ferromagnetic model, but also for more complicated spin interactions such as spin-glasses and neural networks [5].

Recently [6], we have shown that symmetry breaking of electronic structure configurations at the large-D limit is completely analogous to the standard phase transitions and critical phenomena in statistical mechanics [7]. For N-electron atoms in weak magnetic and electric fields at the large-D limit, this analogy is shown by allowing the nuclear charge to play a role analogous to temperature in statistical mechanics [8]. The complete mapping can be represented with the following analogies:

- nuclear charge $Z \leftrightarrow$ temperature T;
- external electric field $\mathcal{E} \leftrightarrow$ ordering field h;
- ground-state energy $E_\infty(Z, \mathcal{E}) \leftrightarrow$ free energy $f(T, h)$;

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- asymmetry parameter $\eta \leftrightarrow$ order parameter m;
- 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 symmetry breaking and phase transitions of electronic structure configurations for atoms.

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 transition exists for $N = 2$. The Hartree–Fock two electron atoms in a weak external electric field exhibit a critical point with mean field critical exponents ($\beta = \frac{1}{2}$, $\alpha = 0_{\text{dis}}$, $\delta = 3$, 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. As for the N-electron atoms, to calculate the critical exponents we performed the following mapping [6]:

- inverse nuclear distance $\frac{1}{R} \leftrightarrow$ temperature T;
- difference between the nuclear charges $\Delta \leftrightarrow$ ordering field h;
- ground-state energy $E_\infty(R, \Delta) \leftrightarrow$ free energy $f(T, h)$;
- asymmetry parameter $\psi \equiv -\frac{\partial E_\infty(R,\Delta)}{\partial \Delta} \leftrightarrow$ order parameter $m \equiv -\frac{\partial f(T,h)}{\partial h}$;
- stability limit point $(R_c, \Delta = 0) \leftrightarrow$ critical point $(T_c, h = 0)$.

The hydrogen molecular ion exhibits a critical point with mean field critical exponents [6]. For the Hartree–Fock hydrogen molecule at the large-D limit [9] symmetry breaking of the electronic structure configurations was also 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 was characterized by a bicritical point where the two continuous phase transition lines join a first-order transition line.

In this paper, we present mean field phase diagrams for electronic configuration of general one-electron molecules. In section 2, we present details of the large-D model for general N-Coulomb centre problems. In section 3 we show that symmetry breaking of the electronic structure configurations for linear molecules leads to rich phase diagrams. Detailed calculations are presented for H_2^+ and H_3^{++} molecules. In section 4, symmetry breaking and phase transitions are generalized for one-electron planar molecules, detailed calculations are given for the H_3^{++} equilateral molecule and for the one-electron four atom molecule.

2. Large D-model

The Born–Oppenheimer approximation is used to separate the electronic and nuclear motions. The electronic energy is then parametrically dependent upon the internuclear distances. The D-dimensional electronic Hamiltonian for one-electron molecules is given by

$$\mathcal{H}_D = -\tfrac{1}{2}\nabla_D^2 + V(\boldsymbol{x}) \tag{1}$$

where $\boldsymbol{x} = (x_1, x_2, \ldots, x_D)$, and $V(\boldsymbol{x})$ is the N-Coulomb centres potential

$$V(\boldsymbol{x}) = -\sum_{i=1}^{N} \frac{Z_i}{|\boldsymbol{x}_i - \boldsymbol{x}|} \tag{2}$$

where Z_i and $\boldsymbol{x}_i$ are the charge and the position of the ith nucleus. In the Born–Oppenheimer approximation, the positions of the nuclei are fixed at certain points in space. These points define a subspace of dimension $d \leqslant N$. The Coulomb potential of equation (2) can be written as

$$V(\boldsymbol{x}) = V(x_1, \ldots, x_d, \rho) \tag{3}$$

where $(x_1, \ldots, x_d)$ are the coordinates of the d-dimensional space defined by the positions of the N-nuclei and ρ is the distance of the electron to this hyperplane, $\rho^2 = x_{d+1}^2 + \cdots + x_D^2$.

In these hypercylindric coordinates, the Laplacian operator is given by

$$\nabla^2 = \sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} + \frac{1}{\rho^{D-d-1}} \frac{\partial}{\partial \rho} \left(\rho^{D-d-1} \frac{\partial}{\partial \rho} \right) - \frac{\mathcal{L}_{D-d-1}^2}{\rho^2} \tag{4}$$

where $\mathcal{L}_k^2$ is the total squared angular momentum operator in a $(k+1)$-dimensional space.

The Schrödinger equation is separable by writing the wavefunction as

$$\Psi(\boldsymbol{x}) = \psi(x_1, \ldots, x_d, \rho) \mathcal{Y}_{D-d-1}(\Omega) \tag{5}$$

where $\mathcal{Y}_{D-d-1}(\Omega)$ is the hyperspherical harmonic, which is an eigenfunction of the generalized angular momentum operator [10]

$$\mathcal{L}_{D-d-1}^2 \mathcal{Y}_{D-d-1}(\Omega) = \Lambda \mathcal{Y}_{D-d-1}(\Omega) \tag{6}$$

and ψ obeys the equation

$$\left\{ -\frac{1}{2} \left[\sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} + \frac{1}{\rho^{D-d-1}} \frac{\partial}{\partial \rho} \left(\rho^{D-d-1} \frac{\partial}{\partial \rho} \right) \right] + \frac{\Lambda}{\rho^2} + V \right\} \psi = \mathcal{E} \psi. \tag{7}$$

By incorporating the square root of the Jacobian into the wavefunction via

$$\psi(x_1, \ldots, x_d, \rho) = \rho^{-(D-d-1)/2} \Phi(x_1, \ldots, x_d, \rho). \tag{8}$$

Equation (7) can be transformed to a simpler form where the centrifugal energy separates out from other kinetic terms. The resulting Hamiltonian has the following form

$$\left\{ -\frac{1}{2} \left[\sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial \rho^2} - \frac{(D-d-1)(D-d-3)}{4\rho^2} \right] + \frac{\Lambda}{\rho^2} + V \right\} \Phi = \mathcal{E} \Phi. \tag{9}$$

For the ground-state, the eigenvalue of the angular momentum is equal to zero for all dimensions, therefore equation (9) reduces to

$$\left\{ -\frac{1}{2} \left[\sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial \rho^2} - \frac{(D-d-1)(D-d-3)}{4\rho^2} \right] + V \right\} \Phi_0 = \mathcal{E}_0 \Phi_0. \tag{10}$$

The centrifugal term contains a quadratic dependence on the dimension and thus becomes singular in the limit $D \to \infty$. The dimension dependence can be removed by scaling all the coordinates by a factor with quadratic dependence on dimension. The scaling factor is chosen to give a finite energy in the limit $D \to \infty$ while reducing to unity for $D = 3$. Therefore, distances are given in units of κ^2 Bohr radii and $1/\kappa^2$ Hartree for the energy, with $\kappa = (D-1)/2$. The rescaled Schrödinger equation takes the form

$$\left\{ -\frac{1}{2\kappa^2} \left[\sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial \rho^2} - \frac{(D-d-1)(D-d-3)}{\rho^2} \right] + V \right\} \Phi_0 = \mathcal{E}_0 \Phi_0. \tag{11}$$

At the $D \to \infty$ limit, the kinetic terms vanish and the wavefunction becomes a δ-function. The effective Hamiltonian at this limit is given by

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} + V(x_1, \ldots, x_d, \rho). \tag{12}$$

Hence for $D \to \infty$, the electronic structure becomes rigid and the ground-state energy is found simply from the global minimum of the effective Hamiltonian

$$\mathcal{E}_\infty(\{Z_i\}, \{\boldsymbol{x}_i\}) = \min_{\{x_1,\ldots,x_d,\rho\}} \mathcal{H}_\infty(\{Z_i\}, \{\boldsymbol{x}_i\}; x_1, \ldots, x_d, \rho). \tag{13}$$

In this paper, we would like to draw the analogy between the study of symmetry breaking and stability of the solutions of the variational equations (13) for the ground-state energy of one-electron molecules with the traditional variational mean-field theory of critical phenomena. This analogy was established between the ground-state energy $\mathcal{E}_\infty$ and the variational mean-field free energy for the two-Coulomb centre problems [6], the N-electron atoms [8] and the hydrogen molecule [9]. For these systems, the internuclear distance and the nuclear charges play an analogous role to thermodynamic fields in statistical mechanics. Symmetry breaking of the electronic structure configurations of the ground-state energy as a function of these fields can be interpreted as phase transitions. In this work, we will study phase transitions for both linear and planar one-electron molecules.

3. Linear molecules

The simplest one-electron system is the $d = 0$ case, which corresponds to the hydrogen-like atoms. The large-D Hamiltonian for one electron in the field of a nuclear charge Z located at the origin is given by

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \frac{Z}{\rho}. \tag{14}$$

The minimum of this effective Hamiltonian is located at $\rho_{\min} = \frac{1}{Z}$, and the energy is simply given by $E_\infty = -\frac{1}{2}Z^2$ [11].

This simple example has a trivial phase diagram because there is no true free parameter in the effective Hamiltonian. By scaling the distance with the nuclear charge the rescaled Hamiltonian has the nuclear charge as a global scaling factor [3].

In order to have nontrivial phase diagrams, we must study Hamiltonians with free parameters, where symmetry breaking configurations are the global minimum of equation (13) for some values of the free parameters.

The first nontrivial examples are systems in one dimension, $d = 1$. In particular, we will examine the two and three-atom collinear molecules. The general effective Hamiltonian for three-Coulomb centre problems can be written as

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} - \frac{Z_c}{r_c} \tag{15}$$

where the nuclei of charges Z_a, Z_b and Z_c are located on the x-axis at $\boldsymbol{x}_a, \boldsymbol{x}_b$ and $\boldsymbol{x}_c$ respectively and the electron-nuclear distances are given by, r_a, r_b and r_c.

In statistical mechanics models it is necessary to put the field conjugated to the order parameter equal to zero in order to examine symmetry breaking and phase transitions. A non-zero field will destroy the phase transition. In our previous study of symmetry breaking of electronic structure configurations we have shown [6] that it is necessary to identify an order parameter and an effective conjugated field that must be equal to zero in order to get phase transitions.

For linear molecules, the symmetric configuration corresponds to the one where the electron coordinates $(x_1, \ldots, x_d)$ corresponds to the geometric centre of the molecule. This configuration is equivalent to the high temperature phase in the traditional phase transition theory. The nonsymmetric phases correspond to configurations where the electron is located out of the geometric centre of the molecule. This simple picture gives us a clear way to choose an order parameter. Taking the geometric centre as the centre of coordinates, the order parameter can be defined as the (normalized) coordinates of the electron in the d-dimensional hyperplane $\vec{\Psi} \propto (x_1, \ldots, x_d)$. The vectorial character of the order parameter is necessary in order to identify the different (equivalent) nonsymmetric phases. In [6] we have shown that the asymmetry in the nuclear charges for the two-atom molecules plays an equivalent role of the external field in magnetic phase transitions. The same condition is valid for the linear three-atom molecules, therefore we will take a symmetric configuration of nuclear charges located on the x-axis at $x = -a$, $x = 0$ and $x = a$ respectively. Because the Hamiltonian scales with the nuclear charge, we can arbitrarily choose one nuclear charge to be equal to one. Then for nuclear charges $Z_a = Z_c = 1$ and $Z_b = Z$ the effective Hamiltonian is given by

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \frac{1}{r_-} - \frac{Z}{r} - \frac{1}{r_+} \tag{16}$$

where $r^2 = x^2 + \rho^2$ and $r_\pm^2 = (x \mp a)^2 + \rho^2$.

For this case, the variational equations, equation (13), takes the simple form

$$\frac{\partial \mathcal{H}_\infty}{\partial x} = \frac{x+a}{r_-^3} + \frac{Zx}{r^3} + \frac{x-a}{r_+^3} = 0 \tag{17}$$

$$\frac{\partial \mathcal{H}_\infty}{\partial \rho} = -\frac{1}{\rho^3} + \rho\left[\frac{1}{r_-^3} + \frac{Z}{r^3} + \frac{1}{r_+^3}\right] = 0. \tag{18}$$

In the following subsections 3.1 and 3.2 we will study symmetry breaking and phase transitions for the limiting case $Z = 0$, which corresponds to the H_2^+ molecule and the three-atom collinear molecule, H_3^{++}.

3.1. H_2^+ molecule

For $Z = 0$, the Hamiltonian in equation (16) reduces to the homonuclear two-atom molecule studied in [6]. In this case, equations (17) and (18) take the form

$$\frac{\partial \mathcal{H}_\infty}{\partial x} = \frac{x+a}{r_-^3} + \frac{x-a}{r_+^3} = 0 \tag{19}$$

$$\frac{\partial \mathcal{H}_\infty}{\partial \rho} = -\frac{1}{\rho^3} + \rho\left[\frac{1}{r_-^3} + \frac{1}{r_+^3}\right] = 0. \tag{20}$$

The symmetric electronic configuration is given by the solution of equations (19) and (20) with $x = 0$. In this case, from equation (20) we obtain that ρ_s is a positive root of the polynomial

$$4\rho^8 - (\rho^2 + a^2)^3 = 0. \tag{21}$$

The stability limit of this solution is given by the value of the internuclear distance $2a$ where the smallest eigenvalue of the Hessian matrix is equal to zero. This condition yields (see appendix)

$$a_c = \frac{3\sqrt{3}}{8} \qquad \rho_c = \frac{3}{4}\sqrt{\frac{3}{2}}. \tag{22}$$

We have found numerically that there is only one stable solution in the region $a > a_c$ for the nonsymmetric solutions with $x \neq 0$. This point (a_c, ρ_c) has the characteristics of a critical point. By allowing the internuclear distance to play the role of temperature, it is possible to define the critical exponents α and β. In this case, the exponents have the classical values, $\alpha = 0_{\text{dis}}$ and $\beta = \frac{1}{2}$. For heteronuclear diatomic molecules, the difference between the nuclear charges plays the same role of an external magnetic field as in the Curie–Weiss mean field theory of magnetism. Then, it is possible to define the 'magnetic' critical exponents γ and δ, which also in this case have mean field values $\gamma = 1$ and $\delta = 3$ [6].

3.2. H_3^{++} molecule

We next consider the one-electron three collinear hydrogen atoms with the Hamiltonian given by equation (16). Equation (17) has a symmetric solution with $x = 0$, and in this case equation (18) gives the following equation for ρ_s

$$\frac{1}{\rho_s^4} = \frac{2}{(a^2 + \rho_s^2)^{3/2}} + \frac{Z}{\rho_s^3}. \tag{23}$$

This equation has two simple particular limits. The hydrogen-like atom limit, with nuclear charge equal to $2 + Z$ for $a \to 0$. At this limit, the solution is stable for all values of Z. The other limit, $Z \to 0$, corresponds to the H_2^+ molecule. As we have shown in the previous subsection, the solution at this limit is stable for $a \leqslant 3\sqrt{\frac{3}{8}}$. In order to obtain the stability lines as a function of Z and a for this system, we have to calculate the Hessian matrix. For this collinear three atoms system, the off-diagonal terms $\partial^2\mathcal{H}_\infty/\partial x \partial\rho|_{\text{sym}}$ are equal to zero (see appendix) and the eigenvalues are given by

$$\lambda_1 = \left.\frac{\partial^2\mathcal{H}_\infty}{\partial x^2}\right|_{\text{sym}} = \frac{2}{(a^2 + \rho_s^2)^{3/2}}\left(1 - \frac{3a^2}{a^2 + \rho_s^2}\right) + \frac{Z}{\rho_s^3} \tag{24}$$

$$\lambda_2 = \left.\frac{\partial^2\mathcal{H}_\infty}{\partial \rho_s^2}\right|_{\text{sym}} = \frac{3 - 2Z\rho_s}{\rho_s^4} + \frac{2}{(a^2 + \rho_s^2)^{3/2}}\left(1 - \frac{3\rho_s^2}{a^2 + \rho_s^2}\right). \tag{25}$$

We have found numerically that $\lambda_2 > 0$ in the region where $\lambda_1 \leqslant 0$. Therefore, the stability line of the symmetric phase is given by the condition $\lambda_1(a, Z) = 0$.

The analysis of nonsymmetric solutions shows that the stability lines of both symmetric and nonsymmetric configurations are coincident for small values of Z. The transition between different electronic configurations has the characteristic of a continuous phase transition. However, there exists a point in the (a, Z) plane where the stability lines split leading to a coexistence zone where both solutions are minimum of the Hamiltonian equation (16). As in the usual variational mean field calculations, a Maxwell construction gives the phase-order transition line. In our case, the first-order phase transition line $Z_1(a)$ is given by the line where the global minimum of the energy degenerates

$$\mathcal{H}_\infty(Z_1(a), a; x = 0, \rho_s) = \mathcal{H}_\infty(Z_1(a), a; x_{ns}, \rho_{ns}). \tag{26}$$

The special point where the first-order line meets with the second-order line has particular critical properties, and is called a tricritical point [12]. This point was calculated as the point where the symmetric solution degenerates, with $(a_{tc} \simeq 0.967\,26, Z_{tc} \simeq 0.326\,07)$. The phase diagram including stability lines is shown in figure 1. The first-order phase transition line is asymptotic to the line $Z = 1$ for $a \to \infty$, because in this limit the electron always remains close to the central nucleus if $Z > 1$.

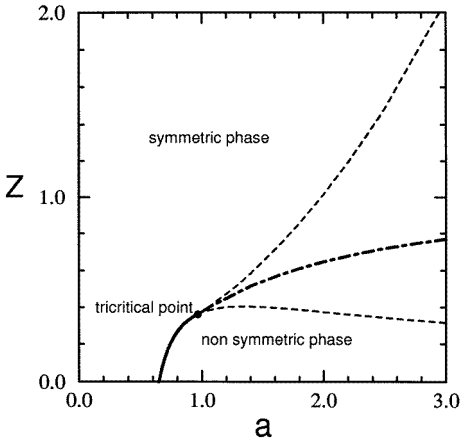

Figure 1. Phase diagram with a tricritical point for the linear three-atoms molecule in the (a, Z) plane. The full lines represent second-order phase transitions while the chain line is a first-order phase transition line. The broken lines are the stability limits of the phases. The region between these lines is the coexistence zone.

4. Planar molecules

In this section, we will study N-atom molecules with nuclear charges localized in a plane. As discussed above, we will be looking for symmetric atomic configurations, but now in a two-dimensional array. The molecules will be defined as fixed charges on the vertices of a regular N-polygon, and the electronic configuration will be studied as a function of the nuclear charges and the radii of the polygon. For some values of N a symmetric solution exists even for nonregular polygons (for example a symmetric solution exists for all even values of N and different distances to the geometric centre for even and odd nuclei).

It is convenient to write the Hamiltonian equation (12) for a N-atom regular molecule in the following form

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \sum_{j=0}^{N-1} \frac{Z_j}{r_j} \tag{27}$$

where $r_j^2 = (x - x_j)^2 + (y - y_j)^2 + \rho^2$ is the square distance of the electron to the jth nucleus. The subindex j takes the values from zero to $N - 1$ in order to write a simple expression for the nuclear position

$$x_j = a\,\mathrm{Re}(U_j) \qquad y_j = a\,\mathrm{Im}(U_j) \qquad j = 0, \ldots, N-1 \tag{28}$$

where a is the radius of the polygon and $U_j = \exp(2\pi \mathrm{i} j/N)$ are the N roots of the unity.

The variational equations (13) for this problem are

$$\begin{aligned}
\frac{\partial \mathcal{H}_\infty}{\partial x} &= \sum_{j=0}^{N-1} \frac{(x - x_j) Z_j}{r_j^3} = 0 \\
\frac{\partial \mathcal{H}_\infty}{\partial y} &= \sum_{j=0}^{N-1} \frac{(y - y_j) Z_j}{r_j^3} = 0 \\
\frac{\partial \mathcal{H}_\infty}{\partial \rho} &= -\frac{1}{\rho^3} + \rho \sum_{j=0}^{N-1} \frac{Z_j}{r_j^3} = 0.
\end{aligned} \tag{29}$$

We are interested in nuclear charge configurations that give a symmetric solution $x_s = 0$, $y_s = 0$ for equations (29). This symmetric configuration corresponds to the electron located at the centre of the regular polygon with $r_j^2 = a^2 + \rho_s^2 \forall j$. For this phase, the variational equations (29) take the simple form

$$\begin{aligned} &\sum_{j=0}^{N-1} x_j Z_j = 0 \\ &\sum_{j=0}^{N-1} y_j Z_j = 0 \\ &-\frac{1}{\rho^3} + \frac{\rho}{(\rho^2 + a^2)^{3/2}} \sum_{j=0}^{N-1} Z_j = 0. \end{aligned} \tag{30}$$

Because of the well known property of the roots of the unity $\sum_{j=0}^{N-1} U_j = 0$, the homonuclear molecules always give a symmetrical solution. In order to obtain heteronuclear molecules with symmetric electronic configuration, we note that for the N roots of the equation $U^N = -1$ also holds $\sum_{j=0}^{N-1} U_j = 0$. Then an alternating charge configuration $Z_{2k} = Z_{\text{even}}$; $Z_{2k+1} = Z_{\text{odd}}$ will have a symmetric solution if $N = 4k$, with k a positive integer. It is interesting to note that the scaling freedom implies that we can choose an irregular polygon with two different distances of the nuclear charges to the centre, one for the 'odd' and another one for the 'even' atoms. In the following subsections, we will present the solutions for two systems; the equilateral homonuclear H_3^{++} molecule, and the four-atom molecule, which is the smallest molecule with $N = 4k$.

4.1. H_3^{++} equilateral molecule

The H_3^{++} equilateral molecule has a symmetric configuration with the electron coordinates $(x = 0, y = 0, \rho_s)$ only for the homonuclear case $Z = 1$. From equations (13), ρ_s is a positive root of the polynomial

$$9\rho^8 - (\tfrac{4}{3}a^2 + \rho^2)^3 = 0. \tag{31}$$

By studying the eigenvalues of the Hessian matrix (see appendix) for this solution, we have found that it is stable for $a \leqslant a_s = 3/\sqrt{2}$. A nonsymmetric solution with the electron near one of the nuclei exist for $a > 1$. Therefore it defines a coexistence zone where both configurations correspond to the minimum of the energy. The equal energy condition gives for the first-order phase transition point the value $a_1 \simeq 1.09$.

4.2. Four-atom molecules

For the four-atom molecules, the symmetry breaking phenomenon occurs if the nuclei are fixed on the vertices of a square with two alternating charges. The Hamiltonian in this case can be written as

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \frac{1}{r_1} - \frac{1}{r_2} - Z\left(\frac{1}{r_3} + \frac{1}{r_4}\right) \tag{32}$$

where the electron-nuclear distances are given by

$$\begin{aligned} r_1^2 &= (x + a)^2 + y^2 + \rho^2 \qquad & r_2^2 &= (x - a)^2 + y^2 + \rho^2 \\ r_3^2 &= x^2 + (y + a)^2 + \rho^2 \qquad & r_4^2 &= x^2 + (y - a)^2 + \rho^2. \end{aligned}$$

The variational equations (13) reduces to

$$\frac{\partial \mathcal{H}_\infty}{\partial x} = \frac{x+a}{r_1^3} + \frac{x-a}{r_2^3} + Zx\left(\frac{1}{r_3^3} + \frac{1}{r_4^3}\right) = 0 \tag{33}$$

$$\frac{\partial \mathcal{H}_\infty}{\partial y} = y\left(\frac{1}{r_1^3} + \frac{1}{r_2^3}\right) + \frac{Z(y+a)}{r_3^3} + \frac{Z(y-a)}{r_4^3} = 0 \tag{34}$$

$$\frac{\partial \mathcal{H}_\infty}{\partial \rho} = -\frac{1}{\rho^3} + \rho\left[\frac{1}{r_1^3} + \frac{1}{r_2^3} + \frac{Z}{r_3^3} + \frac{Z}{r_4^3}\right] = 0 \tag{35}$$

as in the previous cases, the symmetric solution $x = 0$, $y = 0$ gives ρ_s as a positive root of the polynomial

$$4(1+Z)^2\rho^8 - (\rho^2 + a^2)^3 = 0. \tag{36}$$

Since the off-diagonal terms of the Hessian matrix are equal to zero, the eigenvalues of the Hessian matrix are given by

$$\lambda_1 = \left.\frac{\partial^2 \mathcal{H}_\infty}{\partial x^2}\right|_{\text{sym}} = \frac{2}{r_a^3}\left(1 + Z - \frac{3a^2}{r_a^2}\right) \tag{37}$$

$$\lambda_2 = \left.\frac{\partial^2 \mathcal{H}_\infty}{\partial y^2}\right|_{\text{sym}} = \frac{2}{r_a^3}\left(1 + Z - \frac{3Za^2}{r_a^2}\right) \tag{38}$$

$$\lambda_3 = \left.\frac{\partial^2 \mathcal{H}_\infty}{\partial \rho_s^2}\right|_{\text{sym}} = \frac{3}{\rho_s^4} + \frac{2(1+Z)}{r_a^3}\left(1 - \frac{3\rho_s^2}{r_a^2}\right) \tag{39}$$

where $r_a^2 = a^2 + \rho_s^2$.

The stability limit of the symmetrical solution is given by

$$\lambda_1 = 0 \Rightarrow a_1(Z) = \frac{3}{2(2-Z)^2}\sqrt{\frac{3}{1+Z}} \tag{40}$$

$$\lambda_2 = 0 \Rightarrow a_2(Z) = \frac{3}{2(2Z+1)^2}\sqrt{\frac{3Z^3}{1+Z}} \tag{41}$$

and $\lambda_3 > 0$ in the region where $\lambda_1 \geqslant 0$; $\lambda_2 \geqslant 0$.

We have found two different nonsymmetric solutions for equations (33)–(35), related by the symmetry of the system. A nonsymmetric phase A, given by $x_A \neq 0$, $y_A = 0$, $\rho_A \neq 0$ and a nonsymmetric phase B, given by $x_B = 0$, $y_B \neq 0$ and $\rho_B \neq 0$.

For the phase A, $y_A = 0$ is a trivial solution of equation (34), and we have to solve equations (33)–(35) for x_A and ρ_A. Because $\partial^2\mathcal{H}_\infty/\partial y\partial x = \partial^2\mathcal{H}_\infty/\partial y\partial\rho = 0$ for this electronic configuration, the Hessian matrix reduces to 1×1 and 2×2 matrices. By studying these eigenvalues, we have found that there is a tricritical point located on the line $a_1(Z)$ where the stability lines of the symmetric and nonsymmetric A phases split.

Because of the symmetry of the system, studying the nonsymmetric phase B is essentially the same as phase A. We have to use the transformation $Z \to 1/Z; a \to Za$ to go from one nonsymmetric phase to the other. Therefore, the symmetric–nonsymmetric phase B transition line also presents a tricritical point. Both first-order phase lines meet at the triple point $a_{tp} \simeq 1.53$, $Z_{tp} = 1$. The $Z = 1$ line, where the four nuclear charges have the same values, is a first-order line between both non symmetrical phases for $a \geqslant a_{tp}$. The numerical values of the tricritical points are

$$a_{tc}^A \simeq 1.0701 \qquad Z_{tc}^A \simeq .6193$$
$$a_{tc}^B \simeq 0.6627 \qquad Z_{tc}^B \simeq 1.6147.$$

The phase diagram in the (a, Z) plane is shown in figure 2.

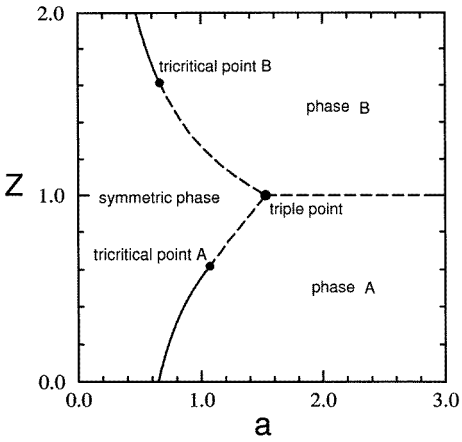

Figure 2. Phase diagram with triple and tricritical points for the four-atoms molecule in the (a, Z) plane. The full lines represent second-order phase transitions while the broken lines are first-order phase transition lines.

5. Conclusions

In this paper, we show that the large-D model for electronic structure problems is simple, exactly solvable and useful in describing symmetry breaking and phase transitions for electronic systems. This model can be improved upon by a systematic expansion in $1/D$. We have examined the analogy that recently has been established between mean-field theory of phase transitions and symmetry breaking of electronic structure configurations at the large-D limit. We have demonstrated the existence of critical points in both linear and planar molecules. Rich mean-field phase diagrams displaying multicritical points were obtained with a two-parameter 'free-energy' (ground-state) for three and four atom molecules. Work is underway to generalize this study to include the infinite linear chain of atoms and two- and three-dimensional lattices [13].

Appendix

In this appendix we will give the Hessian matrix for an arbitrary arrangement of the nuclear charges for $d = 2$ which will include all the cases that have been solved in this work.

For $d = 2$, the Hamiltonian for N-Coulomb centre problem at $D \to \infty$ is given by

$$\mathcal{H}_\infty = \frac{1}{2\rho^2} - \sum_{j=1}^{N} \frac{Z_j}{|\boldsymbol{x}_j - \boldsymbol{x}|}$$

where $\boldsymbol{x}_j = (x_j, y_j)$; $j = 1, \cdots, N$ are the positions of the nuclei in the (x, y) plane. The matrix elements of the Hessian are given by

$$h_{\alpha,\beta} = \left.\frac{\partial^2 \mathcal{H}_\infty}{\partial x_\alpha \partial x_\beta}\right|_{\text{solution}}.$$

Here, $x_\alpha, x_\beta, \alpha, \beta = 1, 2, 3$ are the coordinates of the electron $x_1 = x, x_2 = y$ and $x_3 = \rho$. The electron coordinates must be evaluated in a particular solution of the variational

equations (13). The second derivatives of the Hamiltonian are

$$\begin{aligned}
\frac{\partial^2 \mathcal{H}_\infty}{\partial x^2} &= \sum_{j=1}^{m} \frac{Z_j}{r_j^3}\left(1 - \frac{3(x-x_j)^2}{r_j^2}\right) \\
\frac{\partial^2 \mathcal{H}_\infty}{\partial y^2} &= \sum_{j=1}^{m} \frac{Z_j}{r_j^3}\left(1 - \frac{3(y-y_j)^2}{r_j^2}\right) \\
\frac{\partial^2 \mathcal{H}_\infty}{\partial \rho^2} &= \frac{3}{\rho^4} + \sum_{j=1}^{m} \frac{Z_j}{r_j^3}\left(1 - \frac{3\rho^2}{r_j^2}\right) \\
\frac{\partial^2 \mathcal{H}_\infty}{\partial x \partial y} &= -3\sum_{j=1}^{m} \frac{(x-x_j)(y-y_j)Z_j}{r_j^5} \\
\frac{\partial^2 \mathcal{H}_\infty}{\partial x \partial \rho} &= -3\rho\sum_{j=1}^{m} \frac{(x-x_j)Z_j}{r_j^5} \\
\frac{\partial^2 \mathcal{H}_\infty}{\partial y \partial \rho} &= -3\rho\sum_{j=1}^{m} \frac{(y-y_j)Z_j}{r_j^5}
\end{aligned} \tag{42}$$

where $r_j = |\boldsymbol{x} - \boldsymbol{x}_j|$.

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