

ARTICLES

On the crossing of electronic energy levels of diatomic molecules at the large- D limit

Qicun Shi

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Sabre Kais

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 and The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

Françoise Remacle

Département de Chimie, B6, Université Liège, B4000 Liège, Belgium

R. D. Levine

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

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Analytical and numerical results are presented for the intersection of electronic energies of the same space symmetry for electrons in the field of two Coulomb centers in D -dimensions. We discuss why such crossings are allowed and may be less “exceptional” than one could think because even for a diatomic molecule there is more than one parameter in the electronic Hamiltonian. For a one electron diatomic molecule at the large- D limit, the electronic energies are shown analytically to diverge quadratically from the point of their intersection. The one electron two Coulomb centers problem allows a separation of variables even when the charges on the two centers are not equal. The case of two electrons, where their Coulombic repulsion precludes an exact symmetry, is therefore treated in the large- D limit. It is then found that, in addition to the quadratic intersection, there is also a curve crossing where the energies diverge linearly. © 2001 American Institute of Physics. [DOI: 10.1063/1.1372181]

I. INTRODUCTION

Intersections of potential energy surfaces of polyatomic molecules are receiving much current attention^{1,2} because of the increasing evidence for their role in the dynamics of ultrafast intramolecular electronic state changing processes.³ For diatomic molecules (or for atom–atom collisions, see, e.g., Ref. 4) one often appeals to the “noncrossing” rule of von Neumann and Wigner.⁵ This rule is taken to imply that an intersection of electronic potential energy curves, of the same symmetry is not to be expected. The rigor of the rule is stated differently by different authors, varying from “cannot cross” (Ref. 6, p. 295) to the usually quoted “highly improbable circumstances” down to “exceptional.”^{7,8} A careful summary of the situation is provided in Sec. II B of Ref. 1.

In this paper we discuss the crossing of electronic potential energy curves of the same symmetry. We do not claim that the mathematical discussion of von Neumann and Wigner⁵ is at fault. We do claim that the application of a mathematical result to a physical situation must take into consideration the assumptions made in the background to the mathematical discussion. We will provide both a general argument and detailed proofs specific to the cases of one and two electrons that crossing is possible. Our discussion for the case of one electron is a generalization of the results of Gershtein and Krivchenkov.⁹ Other key references for the case

of the one electron diatomics are Power,¹⁰ and Hatton.¹¹

Beyond the one electron case, a proof that the crossing of electronic potential energy curves, of the same symmetry, is possible requires changing one of the assumptions made by von Neumann and Wigner.⁵ Specifically, we allow more than one parameter in the Hamiltonian. This, unlike von Neumann and Wigner⁵ who only discussed variations in the interatomic distance R . As a function of two (or more) parameters, crossing is possible. In a two parameter plane, the crossing is generally allowed along a curve. If these parameters are R and, say, Z , the crossing occurs at different values of R for different values of Z . It is then a matter of semantics if one wants to call such crossings “exceptional.” For us, they are not exceptional because our interest in the problem of electronic isomerism¹² arose in response to the experimental ability to continuously tune parameters in the Hamiltonian.¹³

Over the years there have been a number of papers questioning the noncrossing rule. Mathematically, the present results are in the spirit of the point made by Teller.^{14,15} He noted that in a polyatomic molecule there are two (or more) interatomic distances than can be independently varied and so potential energy surfaces can cross. We could easily adopt Teller’s (quite simple, see Ref. 14) mathematics to our case but we would then be subjected to a criticism by Hatton *et al.*¹¹ that we are working in a finite dimensional Hilbert

space. Other questions have been well dealt with by Longuet-Higgins⁷ and by Mead.⁸ The one reference to the earlier literature that should perhaps be made is that our conclusions seem to go in the opposite direction to that of Naqvi and Byers Brown,¹⁶ who sought to extend the non crossing rule from diatomic molecules to polyatomics.

Our motivation for examining this problem is the search for quantum phase transitions¹⁷ due to electronic state changes.¹² The language of phase transitions will therefore be also employed. Specifically, a first-order transition is one where the energies diverge linearly from the crossing point. In a second order, also called “continuous,” transition the two energies merge smoothly and so diverge quadratically from the crossing. The plot of the energies in a two parameter plane will then be referred to as a phase diagram. The stable phase is the one of lowest energy. An intersection of two electronic states which is second order, a continuous phase transition, is actually not so unexpected. For such an intersection what was the lower energy state changes smoothly into a higher energy state and vice versa. In other words, the character of the lower energy state switches as one goes through the intersection.

In our earlier work,¹² we investigated the symmetry breaking and electronic structure phase diagrams for two-center molecules with one and two electrons at the large- D limit. For one electron the phase diagram, in the internuclear distance R -nuclear charge Z plane, has two different stable phases. One corresponding to the electron at equidistance from the two nuclei and the other has the electron localized on one nucleus. The transition from one phase to the other is a continuous phase transition, the energies of the two phases merge continuously as we cross the boundary. For two electrons with two equal charge centers, the phase diagram shows three different stable phases corresponding to different electronic structure configurations. In addition to continuous phase transitions, there is also a line of a first-order phase transition. This line is the line where the global minimum is degenerate with two different phases having the same energy.

In this paper, we examine the familiar noncrossing rule for electrons of diatomics in the large- D limit. Background technical comments are made in Sec. II. Section III demonstrates the separability of the (nonrelativistic) Schrödinger equation for one electron in the field of two Coulomb centers of different charges in the familiar $D=3$ case. Numerical results for energy crossings for H_2^+ and for HHe^{+2} systems are provided. In Sec. IV, we generalize the proof of the possibility of intersection of terms of the same symmetry for electrons in the field of two Coulomb centers to D -dimensions. Section V, shows that for a one electron diatomic molecule at the large- D limit the intersection between the two stable phases is of a Renner-Teller-type; the energies diverge quadratically from their intersection. In the presence of interelectronic repulsion there is no known exact symmetry. Section VI presents a perturbation expansions in order to classify the different types of intersections for two electron diatomics. We show that in addition to Renner-Teller intersections, there is also a curve crossing, a Jahn-Teller inter-

section, where the energies linearly diverge from the crossing point.

II. ON THE INTERSECTION OF ELECTRONIC TERMS OF THE SAME SYMMETRY FOR DIATOMIC MOLECULES

For diatomic molecules, Wigner and Neumann⁵ have shown that electron terms of different symmetries can intersect as a function of the internuclear distance R . However, the intersection of terms of the same symmetry is exceptional. The derivation of this theorem presented, for example in Landau and Lifshitz,¹⁸ is as follows. Assume that at a certain distance R_0 between the two nuclei, the Hamiltonian $\hat{H}(R_0)$ has nearly equal eigenvalues E_1^0 and E_2^0 , corresponding to eigenfunctions Ψ_1^0 and Ψ_2^0 . At R close to R_0 , the Hamiltonian can be written as

$$\hat{H}(R_0 + \delta R) = \hat{H}(R_0) + \left. \frac{\partial \hat{H}}{\partial R} \right|_{R=R_0} \delta R. \quad (1)$$

The difference between the eigenvalues of the energy at the point R can be obtained by first order perturbation approximation¹⁸

$$\{(E_1^0 - E_2^0 + V_{11} - V_{22})^2 + 4V_{12}^2\}^{1/2}, \quad (2)$$

where the matrix elements V_{ij} of the operator $\hat{V} = (\partial \hat{H} / \partial R)|_{R=R_0} \delta R$ are taken over the wave functions Ψ_1^0 and Ψ_2^0 .

For the energy intersections to take place, the expression in Eq. (2) must vanish. Since it is the sum of two squares, both positive numbers must vanish simultaneously,

$$E_1^0 - E_2^0 + V_{11} - V_{22} = 0, \quad (3)$$

$$V_{12} = 0. \quad (4)$$

The matrix element V_{12} can vanish identically when the two terms are of different symmetry. Otherwise, the two Eqs. (3) and (4) must be simultaneously satisfied and there is only one arbitrary parameter, the magnitude δR . There are at least three questions about this proof. (i) Are Eqs. (3) and (4) two independent conditions? Gershtein and Krivchenkov⁹ were the first (that we know) to demonstrate that the considerations above do not exclude crossing for the case of one electron in the field of two Coulomb centers at $D=3$. Below we generalize this result to an arbitrary number of dimensions. (ii) Is the proof equally valid for more than one parameter that can be varied? We will provide both analytical and numerical results showing that crossing is possible. (iii) The derivation of the conditions (3) and (4) is only to first order. What is the result for higher orders? It is here that the notion of first and second order transitions is introduced.

III. THE SEPARATION OF VARIABLES FOR THE ONE ELECTRON PROBLEM

To set the stage for the discussion of arbitrary D -dimensions, we first re-examine the one electron in the field of two Coulomb centers problem at $D=3$. Eventually we will regard the charges on the two centers as parameters

of the Hamiltonian and so we demonstrate the separation of variables for the general case when the charges on the two centers need not be equal.

Following the work of Hunter and Pritchard¹⁹ the wave function $\Psi(\xi, \eta, \phi)$ can be written as a product of three separate independent wave functions in prolate spheroidal coordinates,²⁰

$$\Psi(\xi, \eta, \phi, R, Z_1, Z_2) = X(\xi, R, Z_1, Z_2)Y(\eta, R, Z_1, Z_2)K_m(\phi), \quad (5)$$

where $K_m(\phi)$ is the eigenfunction of the total angular momentum operator L^2 with eigenvalues $m(m+1)$. Thus, from the Schrödinger equation we get two independent one-dimensional equations as a function of elliptic coordinates ξ and η . The functions X and Y can be expanded in the associated Legendre polynomials,¹⁹

$$X(\xi, R, Z_1, Z_2) = (\xi^2 - 1)^{m/2} (\xi + 1)^t e^{-p\xi} \times \sum_{i=0}^{\infty} g_i(R, Z_1, Z_2) \left(\frac{\xi - 1}{\xi + 1} \right)^i, \quad (6)$$

$$Y(\eta, R, Z_1, Z_2) = \sum_{i=0}^{\infty} f_i(R, Z_1, Z_2) P_{m+i}^m(\eta), \quad (7)$$

where $t = [R(1+q)/2p] - m - 1$, m is the magnetic quantum number, $q = Z_1/Z_2$ and $p^2 = -(R^2/4)(E - (q/R))$. Putting the expansions into the two elliptic equations, we obtain a set of difference equations which are represented in the following matrix forms:

$$\mathbf{G} \cdot \mathbf{g} = -A_g \mathbf{g}, \quad (8)$$

$$\mathbf{F} \cdot \mathbf{f} = +A_f \mathbf{f}, \quad (9)$$

where \mathbf{g} and \mathbf{f} are the column vectors $g_i(R, Z_1, Z_2)$ and $f_i(R, Z_1, Z_2)$, respectively, the matrix elements of \mathbf{G} and \mathbf{F} are given in Ref. 19 and A_g, A_f are the separation constants. Given R, Z_1 , and Z_2 the problem is to find a value of E such that eigenvalue A of $-\mathbf{G}$ is the same as an eigenvalue A of \mathbf{F} . The solution was found numerically by iteration using the known R, E, Z_1, Z_2 as input. The iteration process was then repeated until the difference of energy between two continual loops was smaller 1.0×10^{-9} and that for the separation constant 1.0×10^{-8} .

In Fig. 1 we show the lowest potential energy curves, $E_3(R)$, for the H_2^+ system. Note the crossings of terms of the same symmetry such as $3d\sigma_g$ and $2s\sigma_g$ (left) and $4f\sigma$ and $4d\sigma$ (right). These numerical results are in complete agreement with previous calculations.²¹

For the case of unequal charges, $Z_1=1$ and $Z_2=2$ (HHe^{+2} system), Figs. 2 and 3 give energy curves $E_3(R)$ as a function of the internuclear distance R . Note that the ground state energy is unstable, the curve is completely repulsive as shown in the small window in Fig. 2. Curves of the same symmetry can cross as shown in this figure, for example, the crossing between $2s\sigma$ and $3d\sigma$ (left) and $4f\sigma$ and $4d\sigma$ (right). Figure 3 shows similar crossings of terms with the same spatial symmetry such as $5g\sigma$ with $5f\sigma$ (left) and $6h\sigma$ and $6g\sigma$ (right). These numerical results confirm the previous calculations and show that the von Neumann–

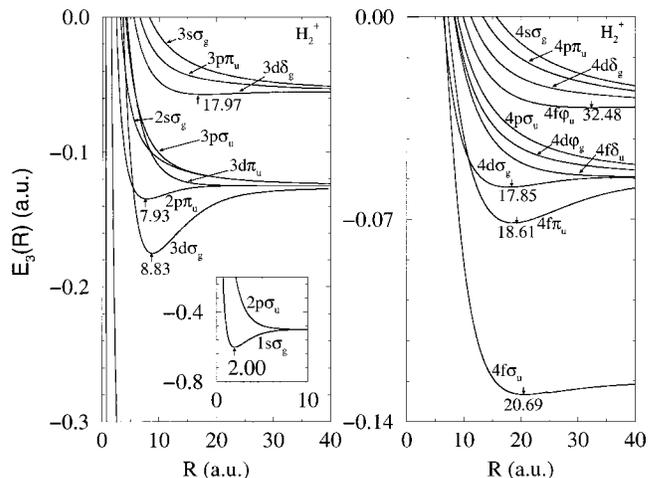


FIG. 1. Total energy curves for H_2^+ , $E_3(R)$, at $D=3$ as a function of the internuclear separation R . Note for example the intersection between $3d\sigma_g$ and $2s\sigma_g$ (left) and $4f\sigma_u$ and $4d\sigma_g$ (right).

Wigner conclusion on the rarity of crossing of terms of the same symmetry is not valid for one electron in the field of two stationary Coulomb centers of charges Z_1 and Z_2 . One can argue that the sheer fact that there is a separation of variables implies that there are additional symmetries.²² This is the point made by Hatton²³ and Power.¹⁰ The present results are consistent with their conclusions and, as will be shown analytically in Sec. V, this means that the crossing is of the second order.

IV. INTERSECTION OF ELECTRONIC TERMS OF THE SAME SYMMETRY FOR ONE ELECTRON IN THE FIELD OF TWO COULOMB CENTERS IN D -DIMENSIONS

We begin with the Schrödinger equation for an one-electron molecule with the two Coulomb centers Z_1 and Z_2 located on the \hat{z} axis of a D -dimensional space at $-R/2$ and $+R/2$, respectively.²⁴ The Hamiltonian can be separated in

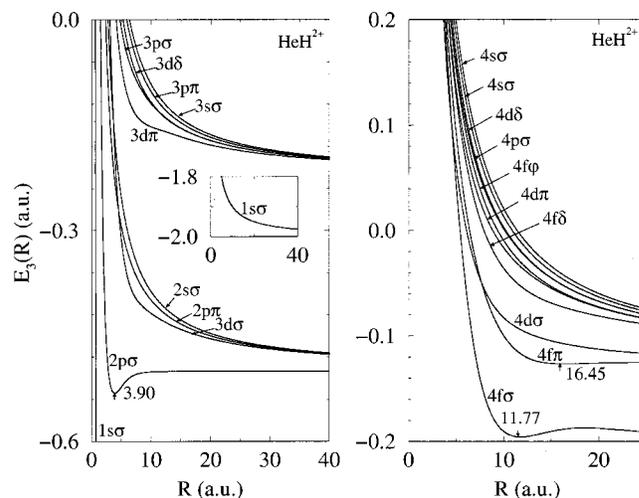


FIG. 2. Total energy curves for HHe^{+2} , $E_3(R)$, at $D=3$ as a function of the internuclear separation R . Note for example the intersection between $3d\sigma$ and $2s\sigma$ (left) and between $4f\sigma$ and $4d\sigma$ (right).

D -dimensional prolate spheroidal coordinates. In this coordinate system, the distance between the electron and either of the charges r_i ($i=1,2$) and the hyper-radius ρ are given by

$$\xi = \frac{r_1 + r_2}{R}, \quad \eta = \frac{r_1 - r_2}{R}, \quad \rho^2 = \frac{R^2}{2} (\xi^2 - 1)(1 - \eta^2), \quad (10)$$

where R is the distance between the two charges. With the coordinate system defined above the D -dimensional Hamiltonian in atomic units takes the form,²⁵

$$\hat{H} = -\frac{1}{2} \left\{ \frac{1}{\alpha \rho^{D-1}} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \left(\rho^{D-1} \frac{\partial}{\partial \xi} \right) + (1 - \eta^2) \frac{\partial}{\partial \eta} \left(\rho^{D-1} \frac{\partial}{\partial \eta} \right) \right] - \frac{\mathbf{L}_{D-2}^2}{\rho^2} \right\} - \frac{R((Z_1 + Z_2)\xi + (-Z_1 + Z_2)\eta)}{2\alpha} + \frac{Z_1 Z_2}{R}, \quad (11)$$

where $\alpha = (R^2/4)(\xi^2 - \eta^2)$ and \mathbf{L}_{D-2}^2 is the projection of the generalized orbital angular momentum operator \mathbf{L}_{D-1}^2 onto the internuclear axis with an eigenvalues $|m|(|m| + D - 3)$. Here the quantum number $|m| = 0, 1, 2, \dots, l$ for $\sigma, \pi, \delta, \dots$ electronic terms.

Now, the the solution $\Psi(\xi, \eta, \Omega_{D-2})$ of the Schrödinger equation can be written as a product of three independent solutions $\Psi(\xi, \eta, \Omega_{D-2}) = X(\xi)Y(\eta)K(\Omega_{D-2})$. The function $K(\Omega_{D-2})$ is the eigenfunction of the generalized orbital angular momentum operator \mathbf{L}_{D-2}^2 and the other two functions, in elliptic coordinates, satisfy

$$\frac{1}{(\xi^2 - 1)^{(D-3)/2}} \frac{\partial}{\partial \xi} (\xi^2 - 1)^{(D-1)/2} \frac{\partial X}{\partial \xi} + \left\{ R(Z_1 + Z_2)\xi - \frac{|m|(|m| + D - 3)}{\xi^2 - 1} - p^2 \xi^2 + A \right\} X = 0, \quad (12)$$

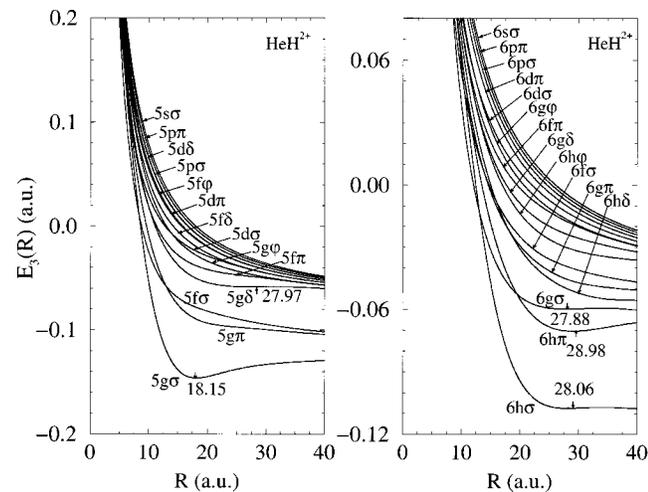


FIG. 3. Total energy curves for HeH^{2+} , $E_3(R)$, at $D=3$ as a function of the internuclear separation R . Note for example the intersection between $5g\sigma$ and $5f\sigma$ (left) and between $6h\sigma$ and $6g\sigma$ (right).

$$\frac{1}{(1 - \eta^2)^{(D-3)/2}} \frac{\partial}{\partial \eta} (\eta^2 - 1)^{(D-1)/2} \frac{\partial Y}{\partial \eta} + \left\{ R(Z_2 - Z_1)\eta - \frac{|m|(|m| + D - 3)}{1 - \eta^2} + p^2 \eta^2 - A \right\} Y = 0, \quad (13)$$

where $p^2 = -(R^2/2)(E - (Z_1 Z_2/R))$ and A is a separation constant. The equations can be solved numerically for a given R, Z_1, Z_2 , and D as described in the previous section and given in Ref. 25.

Gershtein and Krivchenkov⁹ demonstrated that the possibility of crossing of terms of the same symmetry for one electron in the field of two Coulomb centers at $D=3$. Now we are in a position to generalize their proof to D -dimensions.

For the Hamiltonian in Eq. (11), the perturbed operator \hat{V} can be written as

$$\hat{V} = \frac{\partial \hat{H}}{\partial R} \delta R = \left\{ -\frac{2}{R} \hat{H} + \frac{Z_1 Z_2}{R^2} - \frac{1}{R} \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) \right\} \delta R \quad (14)$$

and the nondiagonal matrix element V_{12} has the same form as the one at $D=3$ except that the integral is taken over a D -dimensional volume element $d\tau$,

$$V_{12} = -\frac{\delta R}{R} \int \Psi_1^{0*} \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) \Psi_2^0 d\tau \equiv -\frac{\delta R}{R} \left\langle \frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right\rangle_{12}, \quad (15)$$

where $d\tau = J d\xi d\eta d\theta_1 d\theta_2 \dots d\theta_{D-2}$, and J is the Jacobian factor.²⁵ By integrating over Ω_{D-2} we remove the $D-2$ dimensional angular parts and obtain for the matrix element of

$$\left\langle \frac{1}{r_1} \right\rangle_{12} = N \left[\int_1^\infty X_1 X_2 d\xi \int_{-1}^{+1} Y_1 Y_2 d\eta - \int_1^\infty X_1 X_2 d\xi \int_{-1}^{+1} Y_1 \eta Y_2 d\eta \right], \quad (16)$$

where the integral of the angular parts and the constants are factored into N .

On the other hand, it follows from Eqs. (12)–(13),

$$(A_1 - A_2) \int_1^\infty X_1 X_2 d\xi = (p_1^2 - p_2^2) \int_1^\infty X_1 \xi^2 X_2 d\xi, \quad (17)$$

$$(A_1 - A_2) \int_{-1}^{+1} Y_1 Y_2 d\eta = (p_1^2 - p_2^2) \int_{-1}^{+1} Y_1 \eta^2 Y_2 d\eta. \quad (18)$$

The separation constant A is the eigenvalue of Eqs. (12) and (13) for a given p, R, Z_1 , and Z_2 . For the nondegenerate eigenvalue spectrum, from the one-dimensional equation (12) or (13), we have $A_1 \neq A_2$, A_1 , and A_2 are the values of the separation constant for the states 1 and 2. But if $A_1 = A_2$, the two states have different (generalized) symmetry and therefore we obtain

$$\left\langle \frac{1}{r_1} \right\rangle_{12} = N_1 \left(\frac{E_1^0 - E_2^0}{A_1 - A_2} \right), \quad (19)$$

and

$$\left\langle \frac{1}{r_2} \right\rangle_{12} = N_2 \left(\frac{E_1^0 - E_2^0}{A_1 - A_2} \right), \quad (20)$$

with $N_1 = N_1(R, Z_1, Z_2)$ and $N_2 = N_2(R, Z_1, Z_2)$. Putting Eqs. (19)–(20) into Eq. (15) the matrix element V_{12} becomes

$$V_{12} = - \frac{Z_1 N_1 + Z_2 N_2}{R(A_1 - A_2)} \cdot (E_1^0 - E_2^0) \cdot \delta R. \quad (21)$$

Generally $Z_1 N_1 + Z_2 N_2 \neq 0$. No matter what the values of m_1, m_2, Z_1, Z_2 are, as long as $R \rightarrow R_0$ and $E_1^0 \rightarrow E_2^0, V_{12} \rightarrow 0$ and consequently terms of the same space symmetry but different generalized symmetry can intersect at any given dimension D . This proof generalizes the one given by Gershstein and Krivchenkov for $D = 3$.⁹

As an extension of the treatment using only one variable R for fixed Z_1 and Z_2 , we can consider the case of two variables, taking R and $Z_1 = Z$ for fixed $q = Z_1/Z_2$. For two parameters, the intersection occurs along curves when the symmetries of the terms are different and at points when they are the same. For the two neighboring points (R_0, Z_0) and $(R_0 + \delta R, Z_0 + \delta Z)$, the perturbation operator \hat{V} is

$$\hat{V} = \left(\frac{\partial \hat{H}}{\partial R} \delta R + \frac{\partial \hat{H}}{\partial Z} \delta Z \right) \Bigg|_{R=R_0, Z=Z_0} \quad (22)$$

and the nondiagonal matrix element becomes

$$V_{12} = - \left(\frac{1}{R} \delta R + \frac{1}{Z} \delta Z \right) \left\langle \frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right\rangle, \quad (23)$$

where $Z_1 = Z$ and $Z_2 = Z/q$. Thus, V_{12} vanishes simultaneously with $E_1^0 - E_2^0$ as we have shown before and in addition whenever $\delta R/R = -(\delta Z/Z)$.

The analytic considerations are sufficient to show that crossing is possible but they do not show how the terms diverge from the crossing point. Going to a higher order in perturbation theory will require a numerical approach. Therefore, in the next section we go to the large- D limit in order to obtain explicit analytic results. It then turns out that the condition $\delta R/R = -(\delta Z/Z)$ gives an equation for the line along which a continuous phase transition occurs (see Fig. 4 and also Ref. 12). Specifically, the symmetry breaking which splits the single minimum in the united atom limit into a double minimum in the separated atoms limit occurs along a critical line $Z_c = (3\sqrt{3}/4)(1/R)$.¹²

V. CROSSINGS OF ENERGY LEVELS FOR ONE ELECTRON IN THE FIELD OF TWO COULOMB CENTERS AT THE LARGE- D LIMIT

In the large- D limit the energy and geometry are found simply by minimization of an effective potential.²⁵ In our previous numerical calculations,¹² we have found that there are different electronic configurations at the large- D limit for

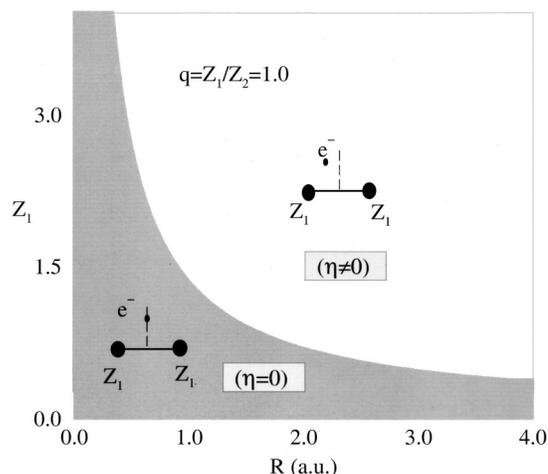


FIG. 4. Phase diagram in the $(R-Z_1)$ plane for one electron in the field of two equal charge centers $q = Z_1/Z_2 = 1$ at the large- D limit. The two different phases with $\eta = 0$ and with $\eta \neq 0$ are shown.

diatomics, which shows the possible stable structures of electronic isomers. This means that there are intersections at finite R and Z .

With the transformation $\Psi \rightarrow \rho^{[(D-1)/2]} \Phi$, the Hamiltonian in Eq. (5) becomes

$$H_D = - \frac{1}{2\alpha} \left((\xi^2 - 1) \frac{\partial^2}{\partial \xi^2} + (1 - \eta^2) \frac{\partial^2}{\partial \eta^2} \right) + \frac{\Lambda^2 - 1}{2\rho^2} - \frac{R((Z_1 + Z_2)\xi + (-Z_1 + Z_2)\eta)}{2\alpha} + \frac{Z_1 Z_2}{R}, \quad (24)$$

where $\Lambda = (|m| + [(D-3)/2])$. The large- D effective Hamiltonian H_∞ is readily obtained at $D \rightarrow \infty$ after the scaling transformation $r \rightarrow fr$ and $fH_D(R) \rightarrow H_D(R)$ with $f = (\Lambda^2 - 1)$,

$$H_\infty = \frac{2}{R^2(\xi^2 - 1)(1 - \eta^2)} - \frac{2Z_1}{R(\xi + \eta)} - \frac{2Z_2}{R(\xi - \eta)} + \frac{Z_1 Z_2}{R}, \quad (25)$$

in which the energy is given in units of $1/\kappa^2$ ($\kappa = (D-2)/2$) hartree and distance κ^2 in bohr radii. Therefore, evaluating the ground state electronic energy reduces to determining the minimum of the effective Hamiltonian function with respect to η and ξ in Eq. (25) for fixed parameters R, Z_1 , and Z_2 .

We have numerically shown¹² that there are two electronic geometrical configurations for one electron in the field of two equal Coulomb charge centers ($Z_1 = Z_2$), one is η -symmetrical ($\eta = 0$), and another η -nonsymmetrical ($\eta \neq 0$) as shown in Fig. 4. The transition from one phase to the other is a continuous phase transition. This means that as we move across the phase plane, the energies of the two isomers merge continuously as we cross the boundary.

To better understand the transitions and to be able to generalize it to the case of two electron molecules, we apply perturbation theory near the phase boundary. With the scaled elliptic coordinates for one-electron molecules with two cen-

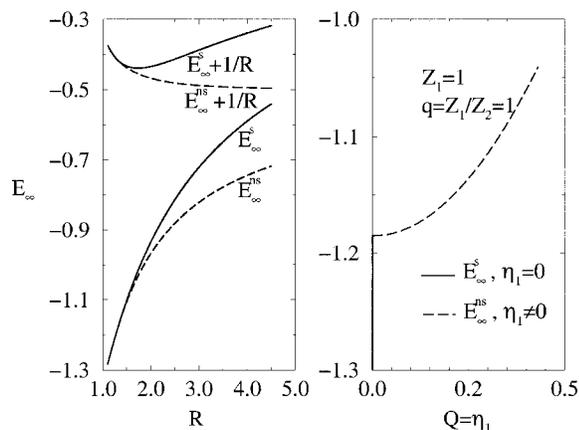


FIG. 5. The degenerate energy crossing of one-electron in the field of two equal charge centers, $Z_1 = Z_2 = Z = 1$, as a function of internuclear distance R (left) and the degenerate quadratic crossing as a function of generalized coordinate $Q = \eta_1$ (right).

ters $Z_1 = Z_2 = Z$, the optimized energy at the large- D limit for the symmetrical configuration ($\eta = 0$) is given by

$$E_{\infty}^s(\xi_1, \eta_1 = 0) = \frac{2}{R^2(\xi_1^2 - 1)} - \frac{4Z}{R\xi_1} + \frac{Z^2}{R}, \quad (26)$$

and the nonsymmetrical configuration ($\eta \neq 0$) has the form,

$$E_{\infty}^{ns}(\xi_2, \eta_2) = \frac{2}{R^2(\xi_2^2 - 1)(1 - \eta_2^2)} - \frac{4Z\xi_2}{R(\xi_2^2 - \eta_2^2)} + \frac{Z^2}{R}. \quad (27)$$

In Eqs. (26) and (27) we add to the elliptical coordinates ξ and η the indexes 1 and 2 in order to distinguish between the two phases.

First of all one can see clearly that there is an intersection of the energy between the phase with $\eta = 0$ and the phase with $\eta \neq 0$, which is given by $E_{\infty}^{ns}|_{\eta_2=0} = E_{\infty}^s$. But in order to show what type of transition we have, it is convenient to introduce the generalized coordinates $Q_{\eta} = |(\eta_2 - \eta_1)/2|$ for η which is defined in the interval $[0, 1]$. With perturbation expansion of E_{∞}^{ns} in the vicinity of $(\eta_2 - \eta_1 \sim 0, \eta_1 = 0)$ we obtain

$$\begin{aligned} E_{\infty}^{ns}(\xi_2, \eta_2) - E_{\infty}^s(\xi_1) \\ = E_{\infty}^s(\xi_2) - E_{\infty}^s(\xi_1) + \left(\frac{2}{R^2(\xi_1^2 - 1)} - \frac{4Z}{R\xi_1^3} \right) (\eta_2 - \eta_1)^2 \\ + O((\eta_2 - \eta_1)^3), \end{aligned} \quad (28)$$

where the symbol $O(x^n, y^m)$ expresses the n th and m th order of variables x and y respectively. We note that the remaining terms are of order $(\eta_2 - \eta_1)^2$. It shows that as the parameter η varies from nonzero to zero the energy changes in a second-order phase transition. We designate this kind of energy crossing, or more accurately energy merging, as a Renner-Teller-type crossing. As an example, Fig. 5 gives the energy curve E_{∞} at $Z_1 = Z_2 = 1$ as a function of the internuclear distance R (left) and the generalized coordinate $Q = \eta_1$ (right) with $\eta_1 = 0$ for the symmetrical configuration and $\eta_1 \neq 0$ for the nonsymmetrical configuration. If Z_1 is not equal to Z_2 , we have only one phase for the one electron in

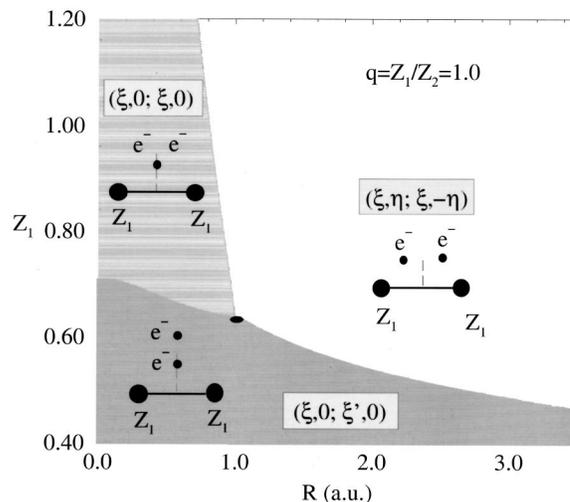


FIG. 6. Phase diagram in the $(R-Z_1)$ plane for two electrons in the field of two equal charge centers, $q = Z_1/Z_2 = 1$ at the large- D limit. There are continuous phase transitions between the phases $(\xi, 0; \xi, 0)$ and $(\xi, \eta; \xi, \eta)$ and between $(\xi, 0; \xi, 0)$ and $(\xi, 0; \xi', 0)$. But the transition between the phase $(\xi, 0; \xi', 0)$ and $(\xi, \eta; \xi, \eta)$ is a first-order phase transition. Here $(\xi, \eta; \xi', \eta')$ is a double elliptical coordinate representation.

the field of two Coulomb centers at the large- D limit. This phase corresponds to the electron localized on the higher charge center.

VI. CROSSING OF ENERGY LEVELS FOR TWO ELECTRONS IN THE FIELD OF TWO COULOMB CENTERS AT THE LARGE- D LIMIT

For diatomic molecules with two or more electrons one does not know of a method for the separation of variables. Algebraic methods do show that there is a useful and nearly exact symmetry^{26,27} but no exact dynamical symmetry is known. This case provides therefore a critical test case for the no crossing rule. We will indeed analytically demonstrate that in the large- D limit, there is a first order phase transition in addition to the second order transitions.

For the two-electron molecules with two equal charge centers, $Z_1 = Z_2 = Z$, our previous calculations have shown that there are three stable phases:^{12,28} the symmetric phase (s) with $(\xi, 0; \xi, 0)$, the antisymmetric phase (as) with $(\xi, \eta; \xi, -\eta)$, and the nonsymmetric phase (ns) with $(\xi, 0; \xi', 0)$ and $\xi \neq \xi'$ as shown in Fig. 6.

The optimized energy for the three stable phases in the $R-Z$ plane ($Z = Z_1, q = Z_1/Z_2 = 1$) are given by

$$E_{\infty}^s = \frac{\sqrt{2}}{R\sqrt{\xi_1^2 - 1}} + \frac{4}{R^2(\xi_1^2 - 1)} - \frac{8Z}{R\xi_1}, \quad (29)$$

$$\begin{aligned} E_{\infty}^{as} = & \frac{4}{R^2(\xi_2^2 - 1)(1 - \eta_2^2)} + \frac{\sqrt{2}}{R\sqrt{\eta_2^2 - 1 + \xi_2^2(\eta_2^2 + 1)}} \\ & - \frac{8\xi_2 Z}{(\xi_2^2 - \eta_2^2)R}, \end{aligned} \quad (30)$$

$$E_{\infty}^{ns} = \frac{2}{(-1 + \xi_3^2)R^2} + \frac{2}{(-1 + \xi_4^2)R^2} + \frac{2}{\sqrt{-2 + \xi_3^2 + \xi_4^2}R} - \frac{4(\xi_3 + \xi_4)Z}{\xi_3 \xi_4 R}. \quad (31)$$

In order to analyze what type of transitions we have between pairs of the three different phases, we carry out the following perturbation expansion:

$$(E_{\infty}^{as}(\xi_2, \eta_2) - E_{\infty}^s(\xi_1))|_{\eta_2 \rightarrow 0, \xi_2 \rightarrow \xi_1} = \left(\frac{4(3\xi_1^2 + 1)}{R^2(\xi_1^2 - 1)^3} + \frac{(2\xi_1^2 + 1)}{2^{1/2}R(\xi_1^2 - 1)^{5/2}} - \frac{8Z}{R\xi_1^3} \right) (\xi_2 - \xi_1)^2 + \left(\frac{4}{(\xi_1^2 - 1)R^2} - \frac{1 + \xi_1^2}{\sqrt{2}(\xi_1^2 - 1)^{3/2}R} - \frac{8Z}{\xi_1^3 R} \right) \eta_2^2 + O((\xi_2 - \xi_1)^3, (\xi_2 - \xi_1)\eta_2^2), \quad (32)$$

where the generalized coordinates are $Q_{\eta} = [|\eta_2 - (-\eta_2)|/2] = |\eta_2|$ and $Q_{\xi} = |(\xi_2 - \xi_1)/\max(\xi_2, \xi_1)|$,

$$(E_{\infty}^{ns}(\xi_4, \xi_3) - E_{\infty}^s(\xi_1))|_{\xi_4 \rightarrow \xi_3, \xi_3 \rightarrow \xi_1} = \left(\frac{4(3\xi_1^2 + 1)}{R^2(\xi_1^2 - 1)^3} + \frac{(2\xi_1^2 + 1)}{2^{1/2}R(\xi_1^2 - 1)^{5/2}} - \frac{8Z}{R\xi_1^3} \right) (\xi_3 - \xi_1)^2 + \left(\frac{2 + 6\xi_1^2}{(\xi_1^2 - 1)^3 R^2} + \frac{2 + \xi_1^2}{4\sqrt{2}(\xi_1^2 - 1)^{5/2}R} - \frac{4Z}{\xi_1^3 R} \right) (\xi_4 - \xi_1)^2 + \frac{3\xi_1^2}{2\sqrt{2}(\xi_1^2 - 1)^{5/2}R} (\xi_3 - \xi_1)(\xi_4 - \xi_1) + O((\xi_4 - \xi_1)^3, (\xi_3 - \xi_1)^3, (\xi_4 - \xi_1)^2(\xi_3 - \xi_1), (\xi_4 - \xi_1)(\xi_3 - \xi_1)^2), \quad (33)$$

where the generalized coordinates are $Q_{\xi} = |(\xi_4 - \xi_3)/\max(\xi_4, \xi_3)|$ and $Q_{\xi'} = |(\xi_3 - \xi_1)/\max(\xi_3, \xi_1)|$. To consider transitions between E_{∞}^{ns} and E_{∞}^{as} we reconstruct a super-surface function,

$$E_{\infty}^{as+ns} = \frac{2}{(-1 + \xi_3^2)(1 - \eta_2^2)R^2} + \frac{2}{(-1 + \xi_4^2)(1 - \eta_2^2)R^2} + \frac{2}{\sqrt{-2 + \xi_3^2 + \xi_4^2 + 2\eta_2^2 + 2\xi_3\xi_4\eta_2^2}R} - \frac{4\xi_3 Z}{(\xi_3^2 - \eta_2^2)R} - \frac{4\xi_4 Z}{(\xi_4^2 - \eta_2^2)R} \quad (34)$$

with $E_{\infty}^{as+ns}|_{\eta_2 \rightarrow 0} = E_{\infty}^{ns}$ and $E_{\infty}^{as+ns}|_{\xi_4 \rightarrow \xi_2, \xi_3 \rightarrow \xi_2} = E_{\infty}^{as}$. $Q_{\xi} = |(\xi_4 - \xi_3)/\max(\xi_4, \xi_3)|$ is the generalized coordinate for E_{∞}^{as} and $Q_{\eta} = [|\eta_2 - (-\eta_2)|/2] = |\eta_2|$ for E_{∞}^{ns} . Referring to the supersurface, we try to expand Eq. (30) in terms of $(\eta_2)^n$ and Eq. (31) in terms of $(\xi_4 - \xi_3)^n$,

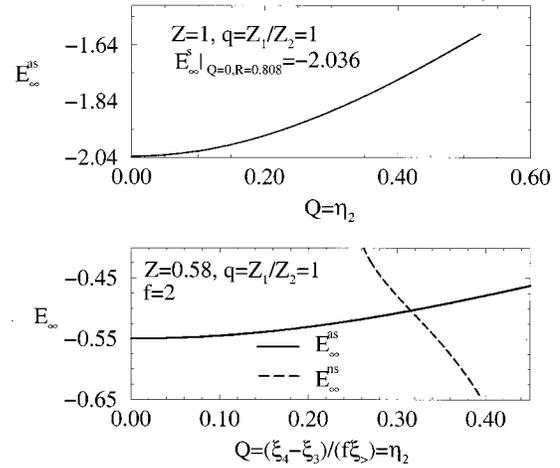


FIG. 7. Degenerate energy crossings for two electrons in the field of two equal charge centers, $q = Z_1/Z_2 = 1$ at the large- D limit. (Upper) The energy quadratic crossing as a function of the generalized coordinates $Q = \eta_2$ from the antisymmetrical configuration $(\xi, \eta; \xi, -\eta)$ in a double elliptic coordinate representation to the symmetrical configuration $(\xi, 0; \xi, 0)$. (Lower) The intersection of energy E_{∞}^{as} for antisymmetrical configuration and E_{∞}^{ns} for nonsymmetrical configuration at $Z_1 = 0.58 = Z_2$ as a function of the generalized coordinates $Q = (\xi_4 - \xi_3)/\xi_{\max}$ which is equal to η_2 , $Q = \eta_2$, if we introduce a factor f such that $Q = (\xi_4 - \xi_3)/[f \max(\xi_4, \xi_3)]$. This factor was found to be $f = 2$ for $E_{\infty}^{as}(R) = E_{\infty}^{ns}(R)$.

$$(E_{\infty}^{ns}(\xi_4, \xi_3) - E_{\infty}^{as}(\xi_2, \eta_2))|_{\eta_2 \rightarrow 0, \xi_4 \rightarrow \xi_3} = E_{\infty}^s(\xi_3) - E_{\infty}^s(\xi_2) + \left(-\frac{4\xi_3}{R^2(\xi_3^2 - 1)^2} - \frac{\xi_3}{\sqrt{2}R(\xi_3^2 - 1)^{3/2}} + \frac{4Z}{R\xi_3^2} \right) (\xi_4 - \xi_3) + O(\eta_2^2, (\xi_4 - \xi_3)^2). \quad (35)$$

Generally, $\xi_3 \neq \xi_2$. Equations (32) and (33) show continuous transitions, energy merging between symmetrical and antisymmetrical configurations, and symmetrical and nonsymmetrical configurations. But Eq. (35) indicates that there is a first-order transition between the antisymmetrical and nonsymmetrical configurations and it is of the Jahn-Teller-type.²⁹ As an example we show in Fig. 7, $E_{\infty}(R)$ for $Z = 1$ and $q = Z_1/Z_2 = 1$ for the energy merging (upper) and for the energy intersecting (lower).

For the case of unequal charges $q \neq 1$, we have shown in our previous study that the electronic phase diagram has only two different phases.¹² The covalent phase $(\xi, \eta; \xi', \eta')$, where $\xi \neq \xi'$, $\eta \neq \eta'$ and the ionic phase $(\xi, \eta; \xi, \eta)$. The phase diagram is characterized by a tricritical point where the first-order transition line meets with the second-order transition line. Thus in this case, we have continuous phase transition in one region and a first-order phase transition in another.

The energy of ionic phase can be expressed in the form,

$$E_{\infty}^{\text{ion}} = \frac{2}{R^2} \left(\frac{2}{(\xi_1^2 - 1)(1 - \eta_1^2)} + \frac{R}{\sqrt{2}\sqrt{(\xi_1^2 - 1)(1 - \eta_1^2)}} - \frac{2R(\eta_1(Z_2 - Z_1) + \xi_1(Z_2 + Z_1))}{\xi_1^2 - \eta_1^2} \right) \quad (36)$$

and the energy of the covalent phase takes the form,

$$E_{\infty}^{\text{cov}} = \frac{2}{(\xi_2^2 - 1)(1 - \eta_2^2)R^2} + \frac{2}{(\xi_3^2 - 1)(1 - \eta_3^2)R^2} + \frac{2}{\sqrt{-2 + \xi_2^2 + \xi_3^2 + \eta_2^2 - 2\xi_2\xi_3\eta_2\eta_3 + \eta_3^2}R} - \frac{2(\eta_2(Z_2 - Z_1) + \xi_2(Z_2 + Z_1))}{(\xi_2^2 - \eta_2^2)R} - \frac{2(\eta_3(Z_2 - Z_1) + \xi_3(Z_2 + Z_1))}{(\xi_3^2 - \eta_3^2)R}. \quad (37)$$

There is definitely energy crossing between the two phases because $E_{\infty}^{\text{cov}} = E_{\infty}^{\text{ion}}$ along the boundary line when $\xi_3 \rightarrow \xi_2$, $\xi_2 \rightarrow \xi_1$, $\eta_3 \rightarrow \eta_2$, $\eta_2 \rightarrow \eta_1$. Introducing the generalized coordinates $Q_{\xi} = |(\xi_3 - \xi_2)/\max(\xi_3, \xi_2)|$ and $Q_{\eta} = |(\eta_3 - \eta_2)/2|$, we can perform perturbation expansion of Eq. (37) in term of $(\xi_3 - \xi_2)^n$ and $(\eta_3 - \eta_2)^n$. The energy difference between the two phases is

$$E_{\infty}^{\text{cov}}(\xi_2, \eta_2; \xi_3, \eta_3) - E_{\infty}^{\text{ion}}(\xi_1, \eta_1) = E_{\infty}^{\text{ion}}(\xi_2, \eta_2) - E_{\infty}^{\text{ion}}(\xi_1, \eta_1) + \left(\frac{4\eta_2}{(\xi_2^2 - 1)(1 - \eta_2^2)^2 R^2} + \frac{(\xi_2^2 - 1)\eta_2}{\sqrt{2}((\xi_2^2 - 1)(1 - \eta_2^2))^{3/2} R} + \frac{2(\xi_2^2(Z_1 - Z_2) + \eta_2^2(Z_1 - Z_2) - 2\xi_2\eta_2(Z_2 + Z_1))}{(\xi_2^2 - \eta_2^2)^2 R} \right) (\eta_3 - \eta_2) + \left(\frac{-4\xi_2}{(\xi_2^2 - 1)^2(1 - \eta_2^2)R^2} + \frac{\xi_2(\eta_2^2 - 1)}{\sqrt{2}((\xi_2^2 - 1)(1 - \eta_2^2))^{3/2} R} + \frac{2(2\xi_2\eta_2(Z_2 - Z_1) + \xi_2^2(Z_2 + Z_1) + \eta_2^2(Z_2 + Z_1))}{(\xi_2^2 - \eta_2^2)^2 R} \right) \times (\xi_3 - \xi_2) + O((\xi_3 - \xi_2)^2, (\xi_3 - \xi_2)(\eta_3 - \eta_2), (\eta_3 - \eta_2)^2). \quad (38)$$

Usually $\xi_2 \neq \xi_1$ and $\eta_2 \neq \eta_1$. If both coefficients of the linear terms, $(\xi_3 - \xi_2)$ and $(\eta_3 - \eta_2)$ in Eq. (38) are zero the remaining terms are of order Q_{ξ}^2 , Q_{η}^2 or $\sqrt{Q_{\xi}Q_{\eta}}$. Thus, the energy transition will be of second-order. Otherwise we obtain a first-order transition as a function of Q_{ξ} , Q_{η} or both. This finding is consistent with our previous numerical results for the energy as a function of R and Z .¹²

VII. DISCUSSION

Quantum phase transitions and particularly so, first order transitions, are of current interest because they allow a molecular system to be used as a switching device. For this purpose, even a diatomic molecule can have more than one parameter in its Hamiltonian. Of course, for potential applications, the parameter to be varied must be under experimental control. The noncrossing rule seems to imply that such a

program will only succeed in exceptional cases. So it is of interest to know how rare is this exceptional behavior. In this paper we discussed what could be shown by analytical considerations for one and two electron systems. The results are summarized in Table I. There is still an important gap in the table but the bottommost entry gives us scope for hope: In the large- D limit, two electron systems, for which there is no known symmetry, exhibit a first-order phase transition.

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TABLE I. Phase transitions in diatomic molecules.

	$D=3$	D finite	$D \rightarrow \infty$
	one electron		
$Z_1 = Z_2$	no first-order	no first-order	no first-order yes second-order
$Z_1 \neq Z_2$	no first-order	no first-order	no transition only one phase
	two electron		
$Z_1 = Z_2$	a	a	both first and second-order
$Z_1 \neq Z_2$	a	a	

^aTo be determined.

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