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Stability, Continuity, and Symmetry of Variational Wave-Functions*

N. MOISEYEV AND J. KATRIEL

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

Abstracts

Interrelations between the local and the global aspects of the stability, continuity, and symmetry properties of variational wave-functions are discussed. The spherical limit of one-electron diatomic molecules and the Hartree–Fock approximation of the ground state of the two-electron atom are shown to exhibit the various concepts involved in an *ab initio*, yet sufficiently simple, manner.

On discute certaines relations entre les aspects locaux et globaux des propriétés de stabilité, de continuité et de symétrie de fonctions d'onde variationelles. A titre d'exemple on traite la limite sphérique des molécules diatomiques à un électron et l'approximation de Hartree–Fock dans l'état fondamental de l'atome à deux électrons.

Beziehungen zwischen den lokalen und globalen Aspekten der Stabilitäts-, Stetigkeits- und Symmetrieeigenschaften von Variationswellenfunktionen werden diskutiert. Die verschiedenen Begriffe werden mit zwei Beispielen illustriert: die sphärische Grenze zweiatomiger Moleküle mit einem Elektron und die Hartree–Fock-Näherung im Grundzustande des Zweielektronenatoms.

1. Introduction

The Euler–Lagrange equation derived from the variation principle is the Schröedinger equation, provided that the variation is allowed within the whole relevant Hilbert space. If, however, the space within which variations are allowed is restricted in some arbitrary manner, the resulting Euler–Lagrange equation turns out to be nonlinear. Consequently, the solutions obtain various nonphysical features. This is so unless the restricted subspace coincides with the natural subdivision of the complete Hilbert space induced by the symmetry properties of the Hamiltonian.

Let us denote by V the subspace within which variations are made and by U the subspace belonging to a particular symmetry species (irreducible representation) with respect to the Schröedinger group (i.e., the symmetry group of the Hamiltonian). V consists of all functions satisfying some shape restriction, such as being a single-determinant, spherically shaped, etc. One can perform either unrestricted variation within V or restricted variation within the intersection of V and U, $V \cap U$. If unrestricted variation is attempted, a broken symmetry solution, belonging to the relative complement of V with respect to U, $V \backslash U$, may result, which is lower in energy than the restricted solution within $V \cap U$. This is the situation referred to by Löwdin [1] as the symmetry dilemma.

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The symmetry adapted solution is the absolute minimum in $V \cap U$. If a lower energy, symmetry broken solution exists in V, the symmetry adapted solution, which satisfies the Euler–Lagrange equation, is in either a local minimum or in a saddle point within the variational space V. This has been shown in the context of the Hartree–Fock approximation by Delbrück [2], Roothaan [3], and Löwdin [4]. To show that the symmetry adapted absolute minimum is stationary with respect to symmetry breaking variations in the general case, we note that if Φ is symmetry adapted and $\delta\Phi$ is a symmetry breaking variation such that

$$\Phi \in U \quad \text{and} \quad \delta\Phi \in V \backslash U$$

then

$$\langle \Phi | \delta\Phi \rangle = 0 = \langle \Phi | H | \delta\Phi \rangle$$

hence

$$E(\Phi + \delta\Phi) = \frac{[E(\Phi) + \langle \delta\Phi | H | \delta\Phi \rangle]}{[1 + \langle \delta\Phi | \delta\Phi \rangle]}$$

so that

$$\left. \frac{\delta E}{\delta \Phi} \right|_{\delta\Phi = 0} = 0$$

The symmetry dilemma thus provides one example of the occurrence of multiple solutions of the variational problem [5], some of which correspond to local minima and the others to maxima or to saddle points [6].

Further complications arise if the solution is studied as a function of some physical parameter appearing in the Hamiltonian. The number of solutions of the variational problem, their local nature (i.e. minimum, maximum, or saddle point), as well as their global role (i.e. being the absolute minimum), may change in a manner which is necessarily discontinuous. A symmetry broken solution may become the absolute minimum in a manner involving a discontinuity in either the first derivative of the energy (first-order transition), in the second derivative (second-order transition), or in a higher derivative [7]. Discontinuities of this type are not by any means restricted to transitions between a symmetry adapted and a symmetry broken solution. Rather, they can occur between two symmetry adapted or between two symmetry broken solutions just as well. In this latter case the situation does not involve a symmetry dilemma but rather a continuity dilemma: The physically plausible requirement of having a solution which depends in a continuous manner on the parameters involved is in conflict with the requirement of choosing the absolute minimum as the actual approximate solution. The choice of either one of the two possible solutions may have far reaching consequences from the point of view of the quality of the description of the system under study.

It is of considerable interest to examine these phenomena in the context of the Hartree–Fock scheme, which is the most commonly used approximation involving a shape restriction of the wave-function. This has been attempted by Koutecky

[8], Čižek and Paldus [9], Pople [10], Gregory [11], and many others, following essentially the pioneering work of Thouless [12] and Adams [13]. However, all these treatments have been carried out within the restrictions of some semiempirical model system. Therefore, one is probably justified in suspecting that at least certain aspects of the results may depend on the particular approximations made on top of using a Hartree–Fock type wave-function. Furthermore, most of these systems are too complicated to allow an exhaustive treatment.

The symmetry dilemma has been encountered in a physically very significant context in a study of hole states in O_2^+ by Bagus and Schaefer [14]. The situation encountered in that system is very closely related to the much simpler model consisting of the spherical limit of H_2^+ [15].* In the present contribution we extend the study of this model in a number of ways, so as to exhibit certain novel features of the general problem. In particular, we discuss the connection between local and global properties of solutions, which is shown to make the somewhat hopeless problem of obtaining the absolute minimum amenable to systematic study. We further show the existence of a continuity dilemma in the corresponding heteronuclear molecule, thus clearly exhibiting the existence of difficulties associated with multiple solutions not involving a breakdown of symmetry.

We then turn our attention to the Hartree–Fock problem for the ground state of the helium sequence, which exhibits many of the variational features discussed. Both the fundamental similarities and the somewhat superficial differences between the two systems discussed turn out to be of interest.

2. The Symmetry Dilemma in the Spherical Limit of H_2^+

The spherical limit of H_2^+ [16], i.e., the best spherically shaped wave-function of that system, has been shown in Part I to exhibit a symmetry dilemma associated with the existence of multiple minima, as well as instabilities (see also Ref. [17]). The spherical wave-function is $\psi(r; R, d)$, where r is the electronic distance from a point on the molecular axis at a distance d from the midpoint of the molecule, and R is the internuclear distance. It was shown by means of straightforward variational computations that for $R < 2.2$ a.u. the symmetry adapted solution, with $d = 0$, is the only extremum, but at $R \simeq 2.2$ a.u. a new local minimum emerges with $d \simeq 0.8$ a.u., along with a corresponding maximum. This broken symmetry minimum becomes the absolute minimum at $R \simeq 2.35$ a.u., as a consequence of which a discontinuity in the first derivative of the energy with respect to R occurs. Curves *a* and *c* in Figure 1 and the curve corresponding to H_2^+ in Figure 2 constitute a transparent and comprehensive presentation of the results, most of which were discussed in Part I.

It is of some interest that on representing the spherical wave-function in terms of a single optimized Gaussian one obtains a second-order transition, i.e., the broken symmetry *minima* bifurcate from the symmetry adapted one so that the symmetry breakdown is associated with a discontinuity in the second rather than

* Reference [15] represents an earlier work by one of the authors (J. K) on which the current study is based. It will hereafter be referred to as Part I.

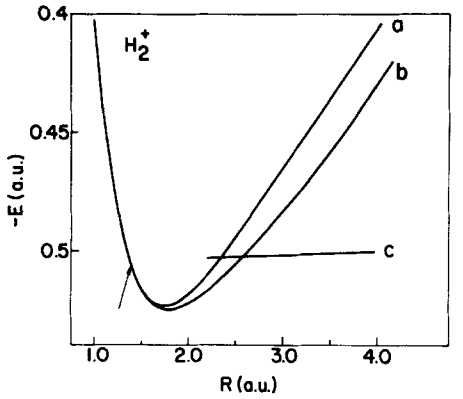

Figure 1. Energy *vs.* internuclear distance for the various spherical limit minima. (a) symmetry adapted ($d = 0$); (b) imaginary d; (c) real d.

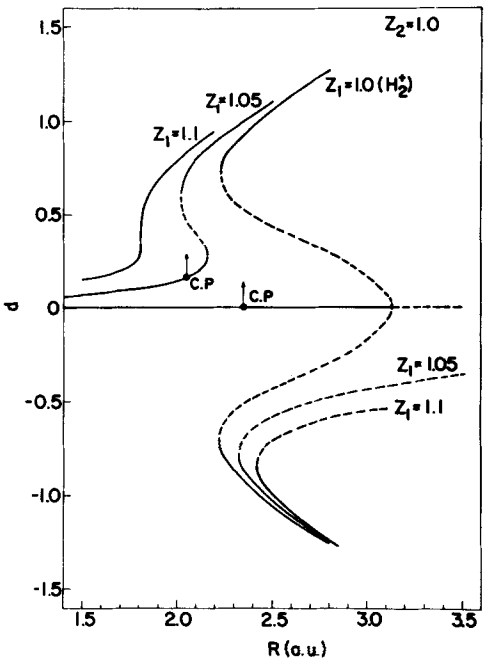

Figure 2. d *vs.* internuclear distance for the energy extrema of the homo- and heteronuclear molecules: (———) local minimum; (– – – –) local maximum. Positive d corresponds to the expansion center being nearer to Z_1. C.P. denotes the first-order transition point.

first derivative of the energy with respect to the internuclear distance. A very similar result is obtained on using a single Slater function [18].

The problem we encounter in the first place is a global one; in order to detect a first-order transition, such as the one described, in a straightforward manner, one has to investigate the global properties of the energy surface. However, the

observation of a bifurcation of broken symmetry extrema from the symmetry adapted one, at $R \simeq 3.1$ *a.u.* (Fig. 2), in some sense reduces the problem to a local one. This follows from the fact that a smooth curve connects the bifurcation point with the broken symmetry minima. The appearance of the broken symmetry local minima is in this way shown to be related to the local behaviour of the symmetry adapted solution and therefore predictable from a study of the local properties of the latter. The possible emergence of a pair of symmetry broken extrema (a minimum and a maximum) which remain forever unconnected with the symmetry adapted extremum cannot be excluded in general, though this is not the case in the example here studied. The existence of an instability in the symmetry adapted solution is, therefore, a sufficient but not a necessary condition for the existence of a symmetry broken solution.

In the neighborhood of the symmetry adapted solution one can write

$$E = E_0 + \tfrac{1}{2}E_1 d^2 + \tfrac{1}{24}E_2 d^4 + \cdots \tag{1}$$

having explicitly taken advantage of E being an even function of d, which follows from the symmetry property $E(d) = E(-d)$. Hence

$$\frac{\partial E}{\partial d} = E_1 d + \frac{1}{6}E_2 d^3 + \cdots$$

and

$$\frac{\partial^2 E}{\partial d^2} = E_1 + \frac{1}{2}E_2 d^2 + \cdots$$

The symmetry adapted solution becomes unstable at the point at which $\left.\frac{\partial^2 E}{\partial d^2}\right|_{d=0}$ vanishes, prior to becoming negative. This is, of course, the point determined by the condition $E_1 = 0$.

The bifurcation of symmetry broken solutions from the symmetry adapted one implies the existence of extrema with small but nonzero d, satisfying the equation $\partial E/\partial d = 0$. For small d one can neglect all terms beyond the second in the expression for $\partial E/\partial d$, obtaining $d = \pm\sqrt{-6E_1/E_2}$. Hence, at the value of R corresponding to $E_1 = 0$, at which the symmetry adapted solution becomes locally unstable, broken symmetry solutions bifurcate from the symmetry adapted one. This point can be obtained from the properties of the symmetry adapted solution only. However, it provides an upper bound for the physically more relevant one which corresponds to the global instability; in a second-(or higher)-order transition the two types of instability coincide, and in a first-order transition the global instability occurs prior to the local one, i.e., a symmetry broken solution becomes the absolute minimum before the symmetry adapted one becomes a local maximum. In the case in which the broken symmetry solutions remain forever unconnected with the symmetry adapted one a global instability may occur at some finite value of the parameter corresponding to R of the present example,

though a local instability never occurs. The occurrence of a local instability cannot precede that of the global one, but does not necessarily follow it.

In Part I the Hellmann–Feynman theorem has been applied to the system under investigation in an essentially qualitative manner, in order to establish the asymptotic behaviour of the solutions at small and large internuclear distances. We now extend this application to quantitatively study the intermediate range of internuclear distances, which will enable the detection of the bifurcation point. From the Hellmann–Feynman theorem applied in the manner mentioned,

$$\frac{\partial E}{\partial d} = 4\pi\left[\frac{1}{R_-^2}\cdot\int_0^{R-}|\psi(r)|^2 r^2\,dr - \frac{1}{R_+^2}\cdot\int_0^{R+}|\psi(r)|^2\cdot r^2\,dr\right] \tag{2}$$

where $R_\pm = R/2 \pm d$, and the dependence of ψ on R and d has been suppressed. Expanding in powers of d, one obtains for the leading coefficient

$$E_1 = \frac{64\pi}{R^3}\left[2\cdot\int_0^{R/2}|\psi_0(r)|^2 r^2\,dr - (R/2)^3\cdot|\psi_0(R/2)|^2\right] \tag{3}$$

where $\psi_0(r)$ corresponds to $d = 0$. The value of R for which $E_1 = 0$ is graphically obtained in Figure 3, resulting in $R^* = 3.12$ *a.u.* as the bifurcation point. The values of E_1 computed from Eq. (3) agree with the values of $\partial^2 E/\partial d^2|_{d=0}$ evaluated numerically in Part I.

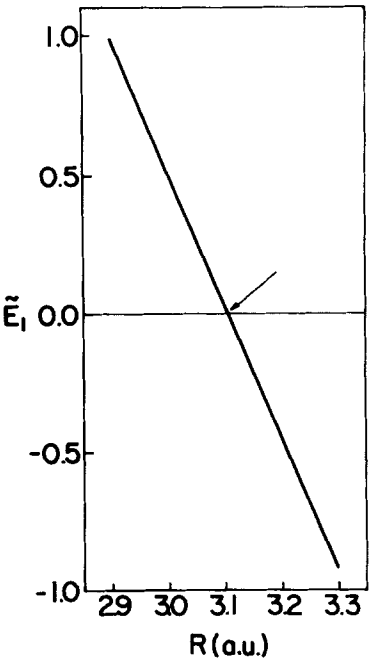

Figure 3. $\tilde{E}_1 = \frac{R^3}{64\pi}E_1$ *vs.* R for H_2^+.

Further insight into the nature of this result can be gained by noting that it can also be obtained in the context of (first-order) perturbation theory. This is done by writing the symmetry adapted and symmetry broken spherical limit Hamiltonians

$$\mathscr{H}_0 = -\frac{1}{2}\nabla_r^2 - \frac{2}{\max(r, R/2)} \tag{4}$$

and

$$\mathscr{H} = -\frac{1}{2}\nabla_r^2 - \frac{1}{\max(r, R_+)} - \frac{1}{\max(r, R_-)} \tag{5}$$

from which $V \equiv \mathscr{H} - \mathscr{H}_o$ is obtained (Fig. 4). The first-order correction to the energy is straightforwardly shown to be equal to E_1 in Eq. (3). However, Figure 4

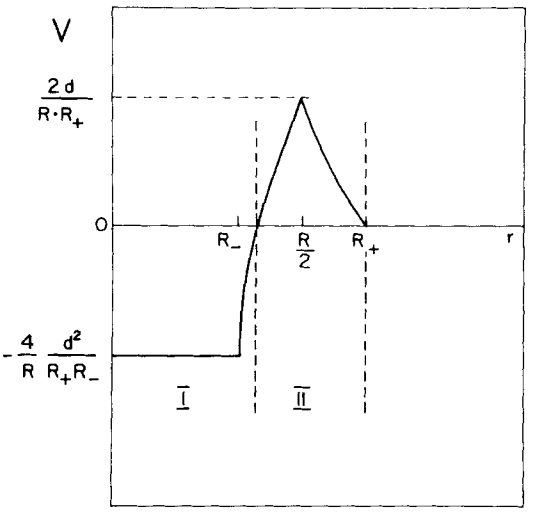

Figure 4. The symmetry breaking perturbation of the H_2^+ spherical limit Hamiltonian: (I) destabilizing region of the symmetry adapted solution; (II) stabilizing region.

indicates the way in which the symmetry adapted solution becomes locally unstable. The existence of a region in V which contributes to stabilizing the symmetry adapted extremum as well as a region which destabilizes it, is a helpful hint with respect to the occurrence and location of the bifurcation point.

The main practical significance of this result is that the symmetry adapted solution does contain enough information concerning the existence of a broken symmetry solution, even in the case of a first-order transition, corresponding to a global instability.

It is tempting to explore the possibility that allowing the parameter d to vary in the complex plane may lead to some deeper insight into the nature of the

transitions involved. The energy for complex-valued d has been evaluated employing a technique discussed by Allison, Handy, and Boys [19]. The symmetry adapted wave-function ($d_C = d_R + id_I = 0$) is the only minimum of the energy for $R < 1.4$, but at $R \simeq 1.4$ a second-order transition to a new broken symmetry solution with imaginary d occurs (Fig. 1). No extrema were observed for complex-valued d, i.e., either the real or the imaginary part of d turned out to vanish at the extrema. One should note that, whereas for real d the wave-function is real, for imaginary d the wave-function is complex, i.e., contains both a real and an imaginary nonvanishing term. This implies that the nonexistence of complex d extrema cannot be accounted for in terms of Brändas' theorem [20]. In the range $1.4 < R < 2.6$ the imaginary d solution is the absolute minimum, but at $R = 2.6$ a first-order transition to the real d broken symmetry solution occurs.

3. The Heteronuclear Molecule: A Continuity Dilemma

The variational computations for HeH^{++} presented in Part I exhibit no discontinuity in the energy as a function of the internuclear distance. This result, which was also obtained by Horak and Siskova [18] in a closely related context, seems to suggest that the discontinuity is a consequence of the symmetry breakdown, which can occur in the homonuclear system only. However, the qualitative behavior suggested for an infinitesimal heteronuclear molecule by inspection of the H_2^+ extrema (Fig. 2) is at variance with this conclusion. The results for H_2^+ imply that if one of the nuclear charges is slightly enlarged multiple solutions of the variational problem should still exist over a certain range of internuclear distances. Consequently, for the heteronuclear molecule one can still observe a transition from one local minimum to another. The energy curve, corresponding to the absolute minimum, will not be smooth in spite of the fact that no symmetry breakdown is involved. On the other hand, in the case of a second-order transition even an infinitesimal shift from the symmetrical system results in a smooth dependence of the solution on R.

The results in Figure 2 exhibit the discontinuity in the case of the heteronuclear molecule and its relation to the homonuclear one. The difference between the homonuclear and heteronuclear cases is essentially in the non-existence of the branching (bifurcation) point in the latter case. However, the discontinuity is shown to be independent of the symmetry breakdown; the symmetry dilemma is thus a special case of the continuity dilemma. Whereas the existence of a discontinuity associated with a breakdown of symmetry can in many cases be anticipated on physical grounds, it is much more difficult to detect the existence of a discontinuity within the symmetry adapted or symmetry broken space.

The results in Figure 2 clarify the fact that in HeH^{++} a completely smooth behavior is observed. They do, however, indicate that discontinuities in single-center expansions may be observed in real heteronuclear (as well as homonuclear) molecules. For the single Slater [18] or Gaussian computation, for which the homonuclear molecule exhibits a second-order transition, a discontinuity is neither expected nor observed in the heteronuclear case. This is, of course, a consequence of the order of the transition, rather than of the loss of symmetry.

4. Instabilities in the Hartree–Fock Solution for Two-Electron Atoms

The unrestricted Hartree–Fock (UHF) wave-function of the ground state of the helium sequence

$$\psi_{\mathrm{UHF}} = \chi(1) \cdot \eta(2) \tag{6}$$

is certainly associated with a lower energy than the restricted Hartree–Fock (RHF) one

$$\psi_{\mathrm{RHF}} = \phi(1) \cdot \phi(2) \tag{7}$$

at least at the low nuclear charge end of the isoelectronic sequence. The transition from the RHF wave-function to the UHF one involves a breakdown of symmetry and should, therefore, occur discontinuously. Whereas the mere existence of a discontinuity can be inferred almost *a priori*, its nature and location can be determined only by direct computation.

The existence of a first-order transition involving the RHF local minimum becoming the absolute minimum while the UHF solution is still locally stable has been observed by Kaplan and Kleiner [21] in a computation employing a minimal basis set of STO's. However, expressing the inner and outer orbitals in terms of two sets, each of N primitive ($1s$) even-tempered STO's, which differ by a scaling parameter β, we have observed a second-order transition for $N > 1$. This is indicated in Figure 5 by the energy having a discontinuity in the second rather than

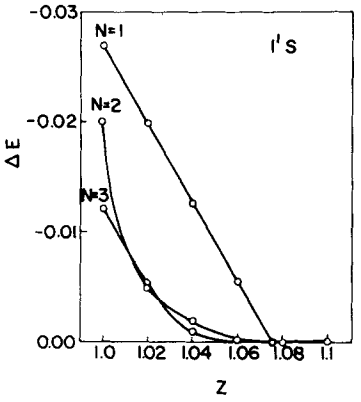

Figure 5. The energy difference between the UHF and RHF approximations in the ground state of the helium sequence, for different basis sizes.

first derivative, and in Figure 6 by the variational parameter β exhibiting a discontinuity on the first derivative rather than in the parameter itself. The nature of the transition was confirmed by the fact that no local UHF minimum was detected beyond the transition point. In the present example the nature of the transition changes from first- to second-order on enlarging the basis set, whereas a change from a second- to a first-order transition has been observed for the spherical approximation to H_2^+.

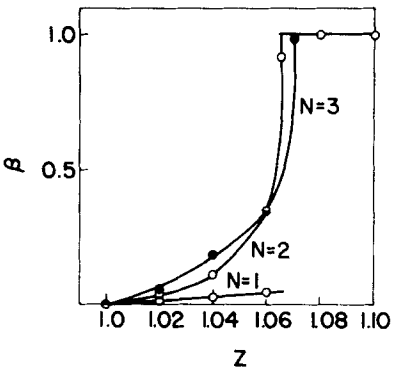

Figure 6. Behavior of the relative scale parameter of the inner and outer orbitals in the UHF approximation for the ground state of the helium sequence.

The manner in which the outer electron becomes unbound on decreasing the nuclear charge has attracted some attention over the past few years [22, 23]. The RHF solution penetrates the continuum at $Z \simeq 1.03$ but remains locally stable and normalizable even below $Z = 1$. The exact solution is known to be bound at $Z = 1(H^-)$, and the critical binding value of the nuclear charge has been estimated to be $Z_c \sim 0.894$ [22]. However, the UHF energy touches the continuum in a tangential manner at $Z = 1$, below which the UHF wave-function is not even locally bound. This fact is of straightforward relevance to Stillinger's discussion of the existence of bound states in the continuum, specifically his "counterargument" [24, 25].

The symmetry property violated by the UHF solution is, of course, the electronic permutational symmetry. Consider now a two-particle Hamiltonian without permutational symmetry, such as

$$\mathcal{H} = -\left(\frac{1}{2}\nabla_1^2 + \frac{Zq_1}{r_1}\right) - \left(\frac{1}{2}\nabla_2^2 + \frac{Zq_2}{r_2}\right) + \frac{q_1 \cdot q_2}{r_{12}} \tag{8}$$

If the transition involved in the permutation-symmetric case ($q_1 = q_2 = 1$) is of second order, one should expect an altogether smooth behavior for $q_1 \neq q_2$. This is, however, not the case if the transition is of first order, in which case a discontinuous behavior is expected for the lowest (UHF) solution for the nonsymmetric system as well, at least in some neighborhood of the symmetric system.

These expectations, analogous to those discussed with respect to the existence of discontinuities in the solution for the heteronuclear one-electron molecule, were examined for the relevant case, i.e. a minimal basis set of STO's. The wave-function studied is

$$\psi = e^{-\alpha r_1 - \beta r_2} \tag{9}$$

and the symmetry breaking parameter $\delta = (\alpha - \beta)/\sqrt{\alpha \cdot \beta}$ was defined. The results, shown in Figure 7, confirm the expected behavior. The two minima correspond to the smaller charge "electron" being the outer and the inner

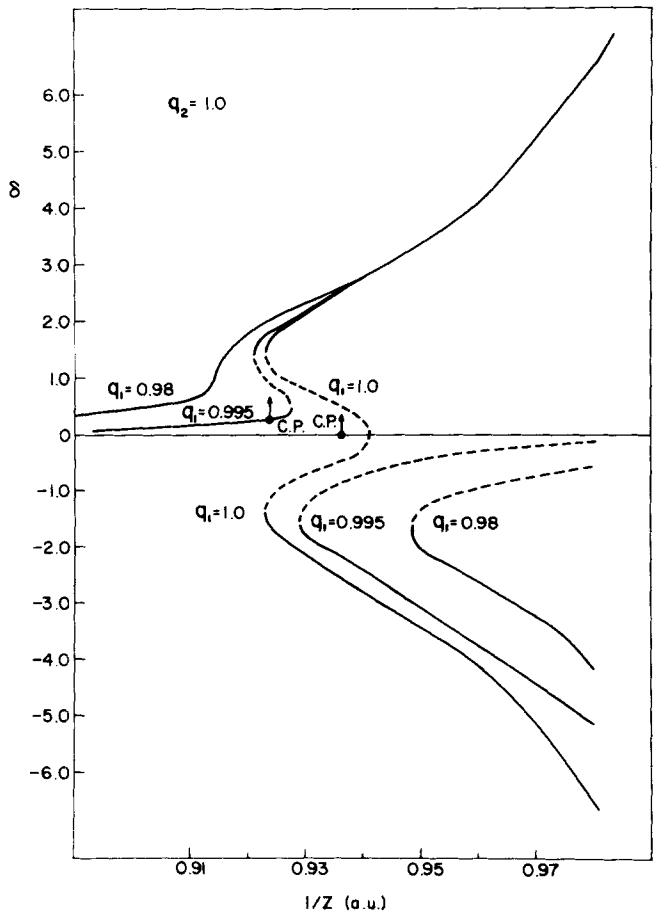

Figure 7. δ *vs.* $1/Z$ for the energy extrema of the "two-electron atom".

electron respectively. The value of Z at which the outer orbital fades into the continuum is, in the UHF level, equal to the charge of the inner electron, i.e., $Z = 1$ for the absolute minimum and $Z = 0.995$ for the higher energy local minimum.

5. Conclusions

The two main conclusions concern the role of symmetry and the local detectability of global discontinuities. The role of symmetry in a first- *vs.* higher-order transition (in a sense, in a global *vs.* local instability) is clearly exhibited by the heteronuclear molecule. The results suggest that in certain cases it may be advantageous to shift one's attention to the continuity properties of the solution with respect to some parameters appearing in the Hamiltonian.

The possibility of studying the occurrence of bifurcation points is a partial solution of the seemingly hopeless problem of detecting all the minima so as to

guarantee that the absolute minimum is actually obtained. This is a further advantage of studying the system over a wide enough range of the relevant physical parameters. It is not only the existence of additional, lower energy, solutions, but also the existence of an instability in a related system which may be a warning as well as a useful practical indication of the location of the additional solution sought.

These considerations are of immediate and straightforward relevance to the very many approaches based on a partitioning of the Hamiltonian in a non-symmetrical form in the context of perturbation theory. The success or failure of such an approach is intimately associated with the properties of the zero-order solution. If this zero-order solution is obtained in an approximate manner, one should allow for the possible occurrence of instabilities which do not involve a symmetry breakdown in the zero-order system investigated but are associated with such symmetry breaking instabilities in the higher symmetry system of actual interest.

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