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Methods for locating periodic orbits in highly unstable systems☆

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Abstract

The multishooting method for solving 2-point boundary value problems is applied to locate highly unstable periodic orbits in molecular systems. Results are presented for ozone, and it is shown that periodic orbits which have previously been associated with the recurrences of the time autocorrelation function in the photodissociation of ozone, originate from saddle–node bifurcations.

1. Introduction

The study of vibrationally highly excited molecules has always been a challenge to spectroscopists. Significant progress has been made in the last years with the advances of new experimental techniques, such as stimulated emission pumping spectroscopy [1], and the development of theories to extract the dynamics of the molecules from the spectrum [2].

Among the theoretical methods classical and semiclassical mechanics have played an important role. Classical mechanics not only offer the frame for an insight into nuclear motion in vibrationally highly excited molecules, but also, they are the only available theories which provide the computational means to carry out dynamic calculations in polyatomic molecules.

In highly energized molecules the nonlinear coupling of all degrees of freedom affects the dynamic processes such as isomerizations and reactions. Therefore, potential energy surfaces valid all over nuclear configuration space are needed. The Murrell–Sorbie potential functions [3] have served this purpose for about 2 decades now. These are functions which are based on many body expansion terms and interpolate among known regions of the hypersurface and extrapolate to unknown ones. By construction they are nonlinear functions and suitable for studying vibrationally highly excited molecular species.

Previous work by us involved the use of Murrell–Sorbie potentials to study the spectroscopy and dynamics of HCN [4], SO_2 [5], C_2H_2 [6] and O_3 [7,8]. The purpose of these works was to investigate the nonlinear mechanical behaviour of the molecules and the correspondence between quantum and classical mechanics. The latter was achieved by locating stationary classical objects around which quantum mechanical wavefunctions are localized [9].

Starting from the stationary points of the potential energy surface (minima and saddle points) we find the *principal families* of periodic orbits which

☆ Dedicated to Professor John N. Murrell.

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originate from them. Then, we follow the evolution of the periodic orbits with the total energy and we locate new periodic orbits which bifurcate from the principal families. The results of the periodic orbit search are portrayed with bifurcation (or continuation) diagrams. Other classical objects which can attract the wavefunctions are tori, reduced dimension tori, and stable and unstable manifolds of the unstable periodic orbits [10]. This hierarchical approach offers a systematic way to unravel the structure of phase space, i.e. to find regular and chaotic regions in phase space.

It turns out, that periodic orbits are the most important objects to locate [11]. First, they reveal the structure of phase space at high energies where most of the phase space is chaotic. Regular trajectories or the least unstable regions are found by the stability analysis of periodic orbits, and that provides evidence for the localization of the wavefunctions of the energized molecule [12].

Second, periodic orbits offer the means for a semiclassical quantization in the chaotic regions of phase space by calculating the density of states through the Gutzwiller's trace formula [9]. This is the only available method for semiclassical quantization of chaotic trajectories.

The location of periodic orbits is not always an easy task. This is because of the high instability that some molecules show. A well known example is O_3 in the electronic excited state, $^1B_2$, in which the molecule is excited during its photodissociation [13]. In previous work a number of trajectories were located that returned close to their initial conditions, but because of the high instability it was not possible to close them accurately, and even more, to propagate these periodic orbits in energy [8,14,15].

The problem of finding periodic orbits may be seen as a *2-point boundary value problem*. The boundary conditions are the relations of closing the trajectory in phase space. There are two classes of numerical methods for solving in general 2-point boundary value problems [16]. The first is the *shooting methods* in which the 2-point boundary value problem is converted to an *initial value* one. Choosing an initial value for the trajectory we integrate the equations of motion and check the discrepancy in the boundary conditions. By varying the initial conditions or some free parameters we successively approach the trajectory which satisfies the boundary conditions.

The second class is the *relaxation methods*. In these methods the differential equations are replaced with difference equations by choosing an appropriate mesh of points for the variables. Then, starting with an approximate solution we try to bring it into successively closer agreement with the finite difference equations, and with the boundary conditions. Relaxation methods are recommended for unstable systems [16].

Both techniques have been applied to locate periodic orbits in molecular systems or model potentials. The shooting methods, which are also known as Newton methods, are the most popular [17]. There are several variants of it resulting from fixing the total energy or the period of the periodic orbit, using or not a Poincaré surface of section, and using analytical second derivatives of the Hamiltonian or numerically estimating the gradient in the Newton–Raphson method by integrating neighbouring trajectories. The *Monodromy Method* of Baranger and coworkers [18–20] is a technique which is classified in the relaxation methods.

An extension of the shooting techniques which tries to incorporate the benefits of the relaxation technique is the *multishooting method* [21–26]. In this case the 1-point initial value problem is converted to $(m-1)$ initial value problems by choosing m nodes in the independent variable. We do not take a finite difference representation of the equations of motion, but instead, we integrate $(m-1)$ trajectories and by varying their $(m-1)$ initial conditions we approach a smooth trajectory which satisfies the boundary conditions.

In this article we present the multishooting method, and show that it is quite robust in locating periodic orbits of high instability such as in the case of ozone. The article is structured as follows. In section 2 we develop the multishooting method in some detail for the case of finding periodic orbits in multidimensional molecular systems (Hamiltonian systems), in section 3 we present the results of the application of the method to ozone, and in section 4 we summarize the conclusions and point out further work.

2. The shooting methods and the 2-point boundary value problems

2.1. The 2-point boundary value problem

If $q_1, q_2, \ldots, q_N$ are the generalized coordinates of a dynamic system of N degrees of freedom and $p_1, p_2, \ldots p_N$ are their conjugate momenta, we define the column vector

$$\vec{x} = (\vec{q}, \vec{p})^{+} \tag{1}$$

where + denotes the transpose matrix. Using $\vec{x}$ we can write Hamilton equations in the form

$$\frac{\mathrm{d}\vec{x}(t)}{\mathrm{d}t} = \dot{\vec{x}}(t) = J\nabla H[\vec{x}(t)] \qquad (0 \le t \le T) \tag{2}$$

where H is the Hamiltonian function, and J is the symplectic matrix

$$J = \begin{pmatrix} 0_N & I_N \\ -I_N & 0_N \end{pmatrix} \tag{3}$$

0_N and I_N are the zero and unit $N \times N$ matrices respectively. $J\nabla H(\vec{x})$ is a vector field, and J satisfies the relations,

$$J^{-1} = -J \quad \text{and} \quad J^2 = -I_{2N} \tag{4}$$

If $\vec{x}(0)$ denotes the initial conditions of a trajectory at time $t_1 = 0$, then this trajectory is periodic if it returns to its initial point in phase space after the time $t_2 = T$ (period)

$$\vec{x}(T) - \vec{x}(0) = 0 \tag{5}$$

Thus, to find periodic solutions it is necessary to solve Eq. (2) subject to the 2-point boundary condition, Eq. (5).

2.2. The initial value problem

The above boundary value problem is converted to an *initial value problem* by considering the initial values of the coordinates and momenta $\vec{s}$

$$\vec{x}(0) = \vec{s} \tag{6}$$

as independent variables in the nonlinear functions

$$\vec{B}(\vec{s}) = \vec{x}(T;\vec{s}) - \vec{s} \tag{7}$$

We denote the roots of Eq. (7) as $\vec{s}_*$, i.e.

$$\vec{B}(\vec{s}_*) = 0 \tag{8}$$

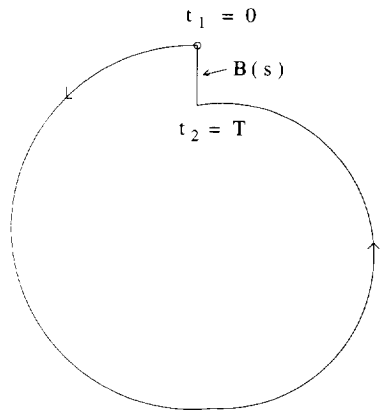

Fig. 1. A schematic representation of the simple shooting method for locating periodic orbits. By changing the initial conditions $\vec{s}$ with a Newton–Raphson method, we try to make the function B equal to zero.

Thus, if $\vec{s}$ is a nearby value to the solution $\vec{s}_*$ we can compute the functions $\vec{B}(\vec{s})$ by integrating Hamilton equations for the period T. By appropriately modifying the initial values $\vec{s}$ we hope to converge to the solution, i.e. $\vec{s} \to \vec{s}_*$ and $B \to 0$. The idea is illustrated in Fig. 1.

2.3. The Newton–Raphson iterative method

The common procedure for finding the roots of Eq. (8) is the Newton–Raphson method. This is an iterative scheme and at each iteration, k, we update the initial conditions of the orbit

$$\vec{s}_{k+1} = \vec{s}_k + \Delta\vec{s}_k \tag{9}$$

The corrections $\Delta\vec{s}_k$ are obtained by expanding Eq. (7) in a Taylor series up to the first order

$$\vec{B}(\vec{s}_{k+1}) \approx \vec{B}(\vec{s}_k) + \frac{\partial \vec{B}}{\partial \vec{s}_k}\Delta\vec{s}_k = 0$$

$$\vec{B}(\vec{s}_k) + \left[\frac{\partial \vec{x}_k(T;\vec{s})}{\partial \vec{s}_k} - I_{2N}\right]\Delta\vec{s}_k = 0 \tag{10}$$

where at the kth iteration

$$\vec{B}(\vec{s}_k) = \vec{x}_k(T;\vec{s}) - \vec{s}_k \tag{11}$$

The matrix

$$Z_k(T) = \frac{\partial \vec{x}_k(T;\vec{s})}{\partial \vec{s}_k} \tag{12}$$

is the *Fundamental Matrix* which is evaluated by integrating the *variational equations*

$$\dot{\vec{\zeta}}(t) = A(t)\vec{\zeta}(t) \quad (0 \le t \le T) \tag{13}$$

where the second derivatives of the Hamiltonian with respect to coordinates and momenta are needed

$$A(t) = J\partial^2 H[\vec{x}(t)] \tag{14}$$

These equations calculate the linearized part of the difference of two initially neighbouring trajectories in time, $\vec{\zeta} = \vec{x} - \vec{x}'$. The Fundamental Matrix is also a solution of the variational equations

$$\dot{Z}(t) = A(t)Z(t) \tag{15}$$

Thus, to complete the kth iteration in the Newton Raphson method we first integrate for time T the differential equations

$$\begin{aligned} \dot{\vec{x}}_k(t) &= J\nabla H[\vec{x}_k(t)] \\ \dot{Z}_k(t) &= A_k(t)Z_k(t) \end{aligned} \tag{16}$$

with initial conditions

$$\begin{aligned} \vec{x}_k(0) &= \vec{s}_k \\ Z_k(0) &= I_{2N} \end{aligned} \tag{17}$$

Then, we solve the linear algebraic equations

$$[Z_k(T) - I_{2N}]\Delta\vec{s}_k = -\vec{B}(\vec{s}_k) \tag{18}$$

in order to find the initial conditions for the $(k+1)$th iteration (Eq. (9)).

For a periodic orbit the Fundamental Matrix at time $t = T$ is called *Monodromy Matrix*, $M = Z(T)$. The eigenvalues of the Monodromy Matrix are used for the stability analysis of the periodic orbit. Details can be found in Ref. [12].

2.4. The underrelaxed Newton–Raphson method

Quite often the Newton-Raphson method diverges, although, when it converges it does that quadratically. Sometimes problems of divergence are cured by scaling the corrections with a parameter λ_k

$$\vec{s}_{k+1} = \vec{s}_k + \lambda_k \Delta\vec{s}_k \tag{19}$$

where $0 \le \lambda_k \le 1$, and $\lambda_k \to 1$ as $\vec{s}_k \to \vec{s}_*$. Several schemes for selecting λ_k have been proposed [22]. A simple one is

$$\lambda_k = \frac{\lambda_{\min}}{\max(\lambda_{\min}, \|\Delta\vec{s}_k\|)} \tag{20}$$

$\lambda_{\min}$ is an input minimum value for the parameter, and $\|\ \|$ denotes the norm of the vector. For convergence criteria we use the norms

$$\|\vec{B}(\vec{s}_k)\| = \left[\sum_{i=1}^{2N} B_i(\vec{s}_k)^2\right]^{1/2} < d_1 \tag{21}$$

and

$$\|\Delta(\vec{s}_k)\| = \left[\sum_{i=1}^{2N} \Delta s_{i(k)}^2\right]^{1/2} < d_2 \tag{22}$$

The linear system of Eq. (18), $\Delta\vec{s}_k$, may be solved by several algorithms; (i) LU-decomposition methods, (ii) Singular Value Decomposition (SVD), and (iii) iterative methods such as the conjugate gradient, variable metric, and quasi-Newton methods [16].

2.5. The multishooting method

The idea of multishooting is to combine shooting and relaxation techniques. Let us assume that we divide the period T into $(m-1)$ time intervals, while first for convenience we introduce a new scaled time $\tau = t/T (0 \le \tau \le 1)$,

$$0 = \tau_1 < \tau_2 < \cdots < \tau_{m-1} < \tau_m = 1 \tag{23}$$

Thus, for the simple shooting method $m = 2$.

From now on we drop the index for the iterations k, and we use the index j to denote the nodes in the periodic orbit. If the initial conditions of the trajectory at each node j is $\vec{s}_j$ at time τ_j, and the final value of the trajectory at time τ_{j+1} is denoted by $\vec{x}(\tau_{j+1}; \vec{s}_j)$, then $(m-2)$ *continuity conditions* should be satisfied (for an illustration see Fig. 2)

$$\begin{aligned} &\vec{C}_j(\vec{s}_j, \vec{s}_{j-1}) = \vec{x}(\tau_{j+1}; \vec{s}_j) - \vec{s}_{j-1} = 0 \\ &j = 1, 2, \cdots, m-2 \end{aligned} \tag{24}$$

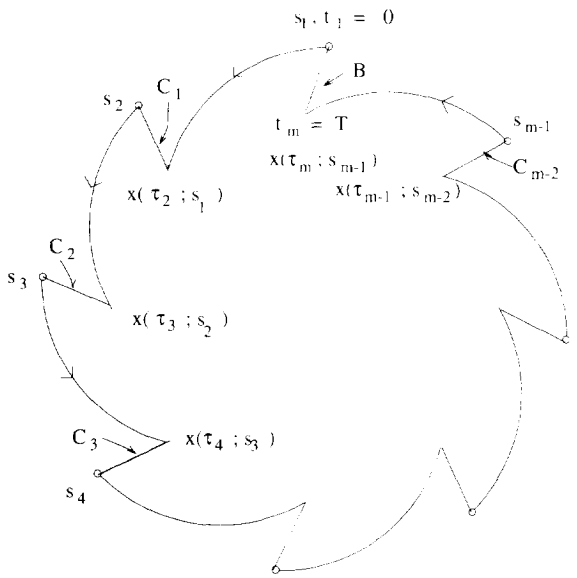

Fig. 2. A schematic representation of the multishooting method for locating periodic orbits. Through Newton–Raphson iterations we try to produce a smooth orbit which satisfies the periodic boundary conditions.

together with the boundary conditions

$$\vec{B}(\vec{s}_{m-1},\vec{s}_1)=\vec{x}(\tau_m;\vec{s}_{m-1})-\vec{s}_1=0 \tag{25}$$

Now we have to solve $(m-1)$ initial value problems, and for that we follow the linearized Newton–Raphson method of the previous sections

$$\vec{C}_j(\vec{s}_j,\vec{s}_{j+1})+\frac{\partial\vec{C}}{\partial\vec{s}_j}\Delta\vec{s}_j+\frac{\partial\vec{C}}{\partial\vec{s}_{j-1}}\Delta\vec{s}_{j-1}=0 \tag{26}$$

which become

$$\vec{C}_j(\vec{s}_j,\vec{s}_{j+1})+Z_j(\tau_{j-1})\Delta\vec{s}_j-\Delta\vec{s}_{j-1}=0$$
$$1\le j\le m-2 \tag{27}$$

Using the boundary conditions (Eqs (25)) we get

$$\vec{B}(\vec{s}_{m-1},\vec{s}_1)+Z_{m-1}(\tau_m)\Delta\vec{s}_{m-1}-\Delta\vec{s}_1=0 \tag{28}$$

where,

$$Z_j(\tau_{j+1})=\frac{\partial\vec{x}(\tau_{j-1};\vec{s}_j)}{\partial\vec{s}_j} \tag{29}$$

Eqs. (27) and (28) are written in a matrix form of dimension $2N(m-1)\times 2N(m-1)$

$$\begin{bmatrix} Z_1 & -I_{2N} & 0 & \cdots & 0 & 0\\ 0 & Z_2 & -I_{2N} & \cdots & 0 & 0\\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots\\ 0 & 0 & 0 & \cdots & Z_{m-2} & -I_{2N}\\ -I_{2N} & 0 & 0 & \cdots & 0 & Z_{m-1}\end{bmatrix}\times\begin{bmatrix}\Delta\vec{s}_1\\ \Delta\vec{s}_2\\ \cdots\\ \Delta\vec{s}_{m-2}\\ \Delta\vec{s}_{m-1}\end{bmatrix}=-\begin{bmatrix}\vec{C}_1\\ \vec{C}_2\\ \cdots\\ \vec{C}_{m-2}\\ \vec{B}\end{bmatrix} \tag{30}$$

The above system of linear equations is solved by invoking the so called *condensing algorithm* [23]

$$\Delta\vec{s}_1=-E^{-1}\vec{u} \tag{31}$$

$$\Delta\vec{s}_{j-1}=Z_j\Delta\vec{s}_j+\vec{C}_j \qquad j=1,2,\cdots,m-2 \tag{32}$$

where

$$E=Z_{m-1}Z_{m-2}\cdots Z_2Z_1-I_{2N}$$
$$\vec{u}=\vec{B}+Z_{m-1}\{\vec{C}_{m-2}+Z_{m-2}[\vec{C}_{m-3}+Z_{m-3}(\vec{C}_{m-4}+\cdots+Z_2\vec{C}_1)\cdots]\} \tag{33}$$

2.6. Implementation

The $(m-1)$ Fundamental Matrices required in the multishooting method may be evaluated either from numerically obtained derivatives or analytically. The first requires the integration of $2N(m-1)$ neighboring trajectories, and the derivatives are then computed by finite differences. In the case that the analytic second derivatives of the Hamiltonian are available, we integrate Hamilton and the variational equations, Eqs. (16) and (17). After converging to the periodic orbit we can have an estimate of the Monodromy Matrix from the product of matrices.

$$M=Z_{m-1}Z_{m-2}\cdots Z_2Z_1 \tag{34}$$

The theory of stability analysis of the periodic orbits in three or more degrees of freedom systems has been described elsewhere [12].

Sometimes it is desirable to bring all periodic orbits onto a common Poincaré surface of section. The Henon method [27] is not suitable for highly unstable systems. Then, it is more convenient to increase the boundary conditions by fixing one coordinate (momentum), i.e.

$$x_l - \xi = 0 \tag{35}$$

and to consider that the period of the periodic orbit satisfies the trivial differential equation [25]

$$\dot{T} = 0 \tag{36}$$

Thus, a $(2N+1)$ dimensional boundary value problem must be solved.

In the continuation of a family of periodic orbits we found it useful to vary the period as a parameter, and for that we use predictor–corrector algorithms with trivial or secant predictors [28].

3. Results

The multishooting algorithm has been tested for ozone. Hay et al. [29] and Sheppard and Walker [30] (SW) used ab initio and empirical data to fit an analytical function of Murrell–Sorbie type [3] for the excited electronic state of ozone ($^1B_2$), and calculated the absorption spectrum using the Gaussian wave packet method, and the classical Wigner method, respectively [31].

The main topographical characteristics of the potential surface are the saddle located at $R_1 = R_2 = 2.73$ a.u., $\sigma = 109.5$ and with energy of -3.91 eV, and a minimum of 1.2 eV below the dissociation limit of ozone, -4.196 eV; the zero energy is defined when the three atoms are infinitely separated in the excited state, $2O(^3P) + O(^1D)$.

The main characteristics of the absorption spectrum of ozone is a broad peak, the Hartley band, with a weak structure on the top, which consists of small peaks separated by approximately 250 cm^{-1} [13]. Several papers have been published to explain this structure of ozone, using classical [7,15,30] or quantum mechanics [32–34]. Johnson and Kinsey [15], and Farantos and Taylor [7] located a number of trajectories which were closed to a limited accuracy. From the periods of these trajectories a connection with the recurrence times extracted from the time autocorrelation function was made. However, the instability of phase space was so high that it was difficult to locate these periodic orbits accurately with the simple shooting algorithms available to use at that time.

Later, the author of the present article studied the time evolution of wave packets on the SW potential function by solving the time dependent Schrödinger equation in two dimensions, the symmetric and antisymmetric stretch modes, and freezing the bend mode [8]. In this study we found new periodic orbits to emanate above the saddle point of the potential, and it was conjectured that they should originate from *saddle–node bifurcations*.

As a saddle–node bifurcation we describe the simultaneous genesis of a pair of periodic orbits, one stable and one unstable, at some particular point in phase space without the existence of a parent family of periodic orbits. Because of the high instability of ozone it was not possible before to close these periodic orbits accurately nor to continue them in energy, and thus, to confirm that the periodic orbits found originate from saddle–node bifurcations. Now, we test the multishooting technique in such a highly unstable system. The SW potential function is employed.

In Fig. 3 we show representative periodic orbits of the two families that we have studied. These periodic orbits are symmetric with respect to the line $(R_1 = R_2)$ on which the momenta of the periodic orbit are not zero, but $P_1 = -P_2$. The studied periodic orbits cross over the symmetry axis and they should not be confused with periodic orbits that do not intersect this axis and remain in one half of the potential function.

Ten orbits of each family are plotted to show their evolution with energy. The increase in the bond lengths R_1 and R_2 is followed by an increase in total energy. We name the two families *sym-1* (Fig. 3a), and *sym-AB* (Fig. 3b) from the title "Arrow and Bow" which was given in our previous article [8]. The periods of the periodic orbits vary between (27.9–29.9) and (19.55–22.04) time units (the time is consistent with the energy in eV and distances in bohrs) for the *sym-1* and *sym-AB* families, respectively.

In Fig. 4 we show a projection of the bifurcation diagram. Bifurcation or continuation diagrams are

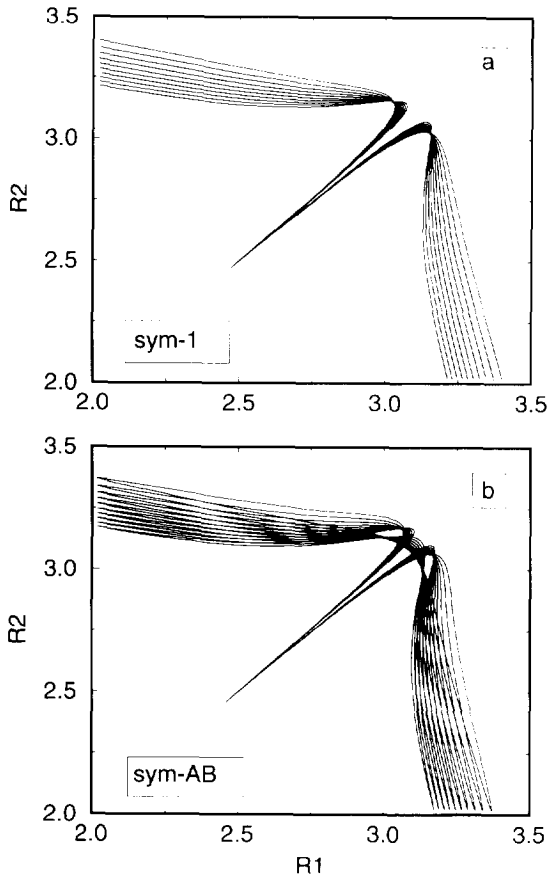

Fig. 3. Representative periodic orbits spanning an energy range of (−3.33, −3.30) and (−3.27, −3.10) eV for the *sym-1* and *sym-AB* families respectively. Distances in atomic units.

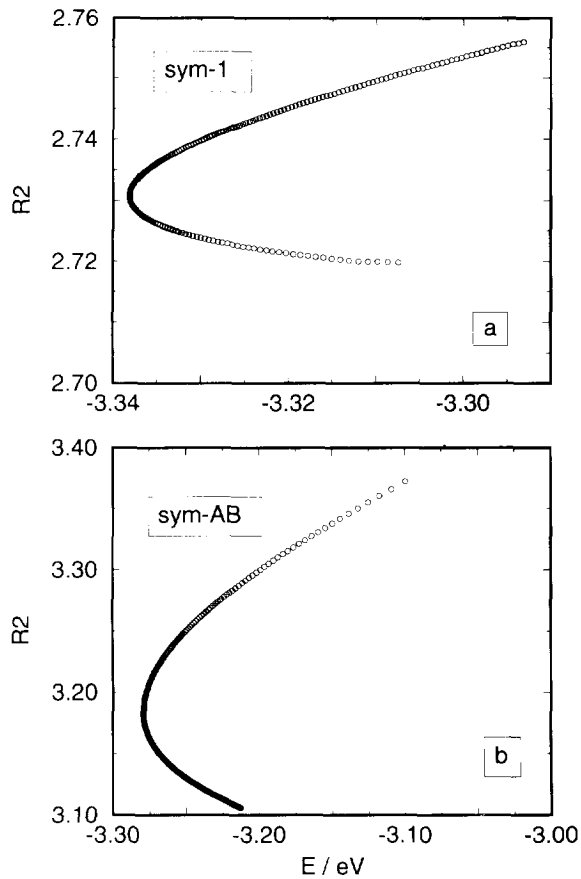

Fig. 4. Bifurcation diagrams for the two families of periodic orbits studied. The range for which the periodic orbits remain stable is so small that it does not appear on the scale of the graph. Distances in atomic units.

generally called plots of the initial conditions of the periodic orbits which are located by varying one parameter of the system. In Fig. 4 the bond length R_2 is plotted as a function of the total energy E. In Hamiltonian systems the total energy or the period of periodic orbits are common varying parameters.

The two pairs of periodic orbits are generated at −3.338148 eV (*sym-1*) and −3.27897 eV (*sym-AB*). Several criteria which distinguish a saddle–node bifurcation from bifurcations of parent families have been proposed [17,25,35]. For conservative Hamiltonian systems we have found that at the point of generation of the two branches (i) the eigenvalues of the Monodromy Matrix are all equal to unit, (ii) all the eigenvectors are parallel or antiparallel, (iii) topological reasons (conservation of the Poincaré index) require the simultaneous generation of one stable and one unstable periodic orbit, and (iv) the period in one branch increases with the total energy and in the other branch decreases. As energy increases the stable orbit may turn to unstable and vice versa.

Examining the variation of the periods of periodic orbits with the energy (Fig. 5) we find that in the unstable branch the period increases and in the other it decreases. Similar behaviour was found in other molecular systems which have a barrier separating two minima [5,12]. It was conjectured that the emanation of saddle–node bifurcations above the saddle of the potential is a general phenomenon [12].

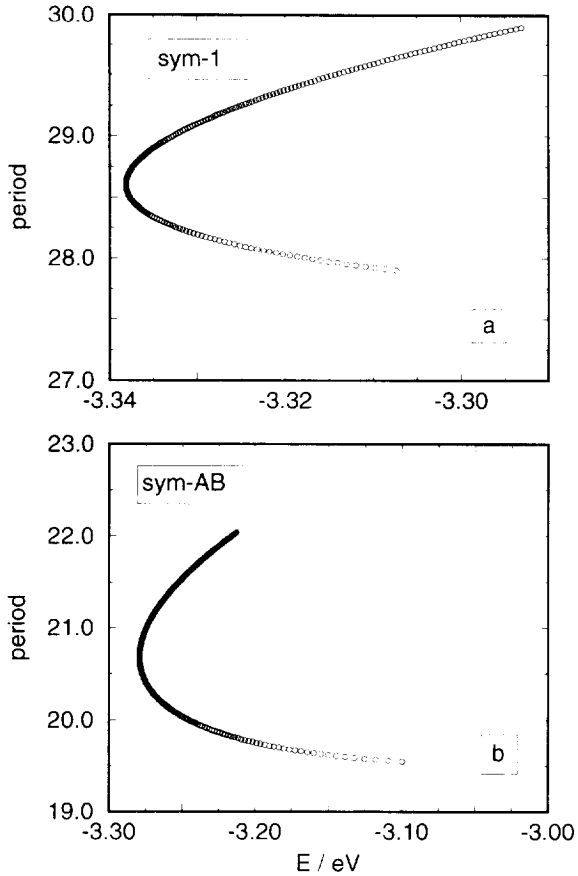

Fig. 5. Variation of the period of periodic orbits of the two families with the total energy. We can see that in one branch the period increases and in the other decreases with the energy. This is one characteristic of the saddle–node bifurcations.

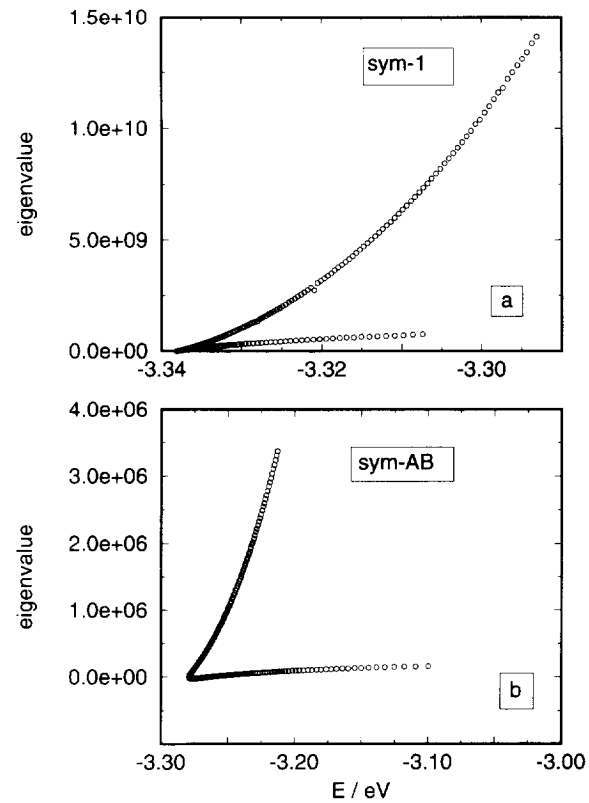

Fig. 6. The largest real eigenvalue of the Monodromy Matrix with the energy.

It was a surprise for us to see that the stable branch in the saddle–node bifurcations changes to unstable in an energy interval of less than 10^{-6} eV, and that the stability parameter in increases tremendously. In Fig. 6 we plot the largest eigenvalue of the Monodromy Matrix with the energy. We can see that the eigenvalues in one branch increase by orders of magnitude, but in the other the increment is a few hundreds of thousands. For the *sym-AB* family the eigenvalues become negative, then return to the unit complex circle and finally become positive again. During these transitions an infinite number of periodic orbits are generated.

With this behaviour of periodic orbits it is not surprising that our previous effort to locate them failed. The new programs based on the multishooting algorithms seem capable of dealing with such highly unstable systems. Difficulties were encountered in the continuation step, something which was cured by varying the number of nodes m. The values of m that we have used are between 8 and 100. Also, for the much more unstable family, the *sym-1*, it was necessary to employ integrators suitable for stiff differential equations, such as the backward differentiation formulas [16]. Finally, in some cases it was difficult to obtain the accuracy the two unit eigenvalues of the Monodromy Matrix. We believe that this problem will be cured if quadruple arithmetic precision is used. Nevertheless, in all cases the double precision code converged to the periodic orbit with a precision of less than $d_1, d_2 = 10^{-6}$, Eqs. (21) and (22).

4. Discussion and conclusions

In Newton methods for locating periodic orbits the starting point is important. Bad selection leads to deviation in the iterative procedure. This is especially demanded in extended chaotic regions of phase space where there may exist stable periodic orbits with small islands of stability around them.

Initial conditions close to periodic orbits can be obtained either by following the theorems of Weinstein and Moser [36,37], or by using simulation techniques. The first method allows us to locate periodic orbits which emanate from the stationary points of the potential function, the *principal families*. From these, during the continuation step, we can locate the bifurcating families of periodic orbits.

In the simulation methods we integrate trajectories, usually choosing them with a Monte Carlo method, and from their plots or Poincaré surfaces of sections we try to locate trajectories which return to their initial point to some limited accuracy. Graphical techniques are useful for systems with a small number of degrees of freedom. For larger systems the method of *Local Lyapunov Exponents* (LLE) proposed by Pollak and coworkers [38–40] seems very promising. With this method regions of phase space where the LLE is small are traced, and therefore, good initial conditions for locating the periodic orbits are obtained.

The multishooting method also tries to cure problems of bad initial guesses. By optimizing the initial conditions of $(m-1)$ trajectories we make a better sampling of phase space. In our application we have chosen equidistant nodes, $\tau_i = (i-1)/(m-1)$, $i = 1, \ldots, m$, however this is not necessary. Methods for selecting appropriately the nodes in the multishooting method have to be investigated.

We consider the case of ozone as a difficult test for algorithms which find periodic orbits in multidimensional highly unstable molecular systems. With the multishooting method we did locate and continue two important families of periodic orbits and showed that they originate from saddle–node bifurcations. We have also tested the multishooting method in other systems for which we encountered difficulties in the past and got satisfactory results. We currently use the multishooting method for acetylene.

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