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Application of efficient composite methods for computing with certainty periodic orbits in molecular systems

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Abstract

Recently, we have proposed a technique for the computation of periodic orbits in molecular systems, based on the characteristic bisection method [Vrahatis et al., Comput. Phys. Commun. 138 (2001) 53]. The main advantage of the characteristic bisection method is that it converges with certainty within a given starting rectangular region. In this paper we further improve this technique by applying, on a surface of section of a Poincaré map, an iterative scheme based on the composition of the characteristic bisection method with other more rapid root-finding methods such as Newton's or Broyden's methods. Thus, the composite schemes compute rapidly with certainty periodic orbits of molecular systems. By applying these methods to the LiNC/LiCN molecular system we obtain promising results. We have reproduced previous results using considerable less CPU time. Also, we have located and computed new asymmetric families of periodic orbits.

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Keywords: Characteristic bisection method; Newton's method; Broyden's method; Quasi-Newton methods; Molecular systems; Periodic orbits; Poincaré map

1. Introduction

In the study of the dynamics of molecular systems, the computation of periodic solutions is of fundamental importance. In general, the techniques used for the numerical computation of periodic solutions of the corresponding Hamilton's equations of motion are based on various corrector-like schemes. These schemes usually depend on solving systems of approximate equations involving the equations of motion and variation and thereupon the derivatives of the components of the periodic solution.

Recently, we have proposed a technique for the computation of periodic orbits in molecular systems, based on the characteristic bisection method [1]. To do this, we have applied the characteristic bisection method on a surface of section of a Poincaré map in order to compute a periodic orbit of a given pe-

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riod. The main advantage of the characteristic bisection method is that it converges with certainty within a given starting rectangular region. Also, we have further improved this technique by considering an iterative scheme based on the composition of the characteristic bisection method with Newton's method [2]. Based on this approach various composite methods can be created by composing characteristic bisection method with other root-finding methods, such as Broyden, nonlinear SOR or nonlinear Jacobi methods [3]. Here we study the application to the 2D LiNC/LiCN system of the combination of the characteristic bisection method with the widely used Newton's and Broyden's method. In general, Broyden's method behaves like Newton's method and when a periodic orbit has long period it computes it more rapidly, since it requires less number of integrations (function evaluations), than Newton's method. The great disadvantage of Broyden's method, as well as Newton's method, is that they depend strongly on good estimations of the starting values. We manage to overcome this problem by combining Newton's or Broyden's method with that of characteristic bisection. The composite scheme first utilizes the characteristic bisection method to locate a periodic solution within relatively large regions of initial conditions. Then, when the orbit is located within the desired accuracy (so that the conditions of convergence of Newton's or Broyden's method are satisfied) the method utilizes Newton or Broyden method to compute the periodic solution rapidly and accurately. In practice it is a heavy task to check the conditions under which the convergence of Newton's or Broyden's method is secured [3]. Thus, we apply the characteristic bisection method in order to locate a periodic solution within an arbitrary accuracy, say $\varepsilon = 10^{-2}$, and then to check whether the Newton's or Broyden's method converges with this approximation; otherwise we shift again to the characteristic bisection. The characteristic bisection requires one iteration in order to compute one binary digit of the solution. Specifically, it requires approximately $1/\log 2$ iterations in order to compute a decimal digit while, with a good starting value, Newton converges quadratically and Broyden superlinearly.

The composite approach is used in molecular systems with two degrees of freedom where the phase space is four-dimensional. If we consider the autonomous system of two degrees of freedom:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}), \tag{1}$$

we can reduce the four-dimensional phase space to a three-dimensional subspace by utilizing the integral of motion $\mathbf{F}(\mathbf{x}) = E$, for a particular value of the energy constant. So, we define a subspace of isoenergetic solutions. The final reduction to two dimensions is made with the criterion that one component of the solution must take up again the value it had for the periodic solution at $t = 0$.

The paper is organized as follows. In the next section we briefly exhibit Newton's and Broyden's method and we describe the composite approach. In Section 3 we apply them to the LiNC/LiCN system and we compare it with Newton's and Broyden's method. We finally end, in Section 4, with some concluding remarks.

2. Composite schemes for computing periodic orbits of molecular systems

Suppose that $\mathbf{F} = (f_1, f_2, \ldots, f_n) : \overline{\mathcal{D}} \subset \mathbb{R}^n \to \mathbb{R}^n$ is a Fréchet-differentiable function on the closure of the domain $\mathcal{D}$ and $\mathbf{x}^*$ a solution of the nonlinear system of equations:

$$\mathbf{F}(\mathbf{x}) = \mathbf{\Theta}^n \equiv (0, 0, \ldots, 0), \tag{2}$$

within the interior of $\mathcal{D}$. A well known and widely used approach for the computation of roots of system (2) is Newton's method. Given an initial guess $\mathbf{x}_0$, Newton's method computes a sequence of points $\{\mathbf{x}_k\}_{k=0}^{\infty}$ which approximates the solution $\mathbf{x}^*$ of the nonlinear system (2) as follows:

For $k = 0, 1, \ldots$ until convergence **do**:
  Solve $\mathbf{F}'(\mathbf{x}_k)\mathbf{s}_k = -\mathbf{F}(\mathbf{x}_k)$ for $\mathbf{s}_k$
  Set $\mathbf{x}_{k+1} = \mathbf{x}_k + \mathbf{s}_k$

where $\mathbf{F}'(\mathbf{x}_k)$ defines the Jacobian matrix of $\mathbf{F}$ at $\mathbf{x}_k$. Under some suitable assumptions, Newton's method converges to a solution of (2) quadratically [3]. The quadratic convergence of Newton's method is attractive. However, the method depends on a good initial approximation and it requires in general $(n^2 + n)$ func-

tion evaluations per iteration besides the solution of an $(n \times n)$ linear system.

Quasi-Newton methods were developed to save computational effort of individual iterations while maintaining some convergence properties of Newton's method. They maintain approximations of $\mathbf{x}^*$ and the Jacobian at the solution $\mathbf{F}'(\mathbf{x}^*)$ as the iteration progresses. If $\mathbf{x}_k$ and $\mathbf{B}_k$ are the current approximate solution and Jacobian, then after the computation of $\mathbf{x}_{k+1}$, $\mathbf{B}_k$ is *updated* to form $\mathbf{B}_{k+1}$. The construction of $\mathbf{B}_{k+1}$ determines the quasi-Newton method. Given an initial guess $\mathbf{x}_0$, this method computes a sequence of points $\{\mathbf{x}_k\}_{k=0}^{\infty}$, obtained by solving the following *quasi-Newton* or *secant* equation:

$$\mathbf{B}_{k+1}(\mathbf{x}_{k+1} - \mathbf{x}_k) = \mathbf{F}(\mathbf{x}_{k+1}) - \mathbf{F}(\mathbf{x}_k).$$

The advantages of quasi-Newton methods is that they require only n function evaluations for each iteration. Hence, if a good preconditioner (initial approximation to $\mathbf{F}'(\mathbf{x}^*)$) can be found, these methods have an advantage in terms of function evaluation cost over Newton's method. In most quasi-Newton methods derivatives are not computed at every iteration. On the other hand, the local rate of convergence turns out to be superlinear instead of quadratic for most of these methods.

The most frequently used approximation to the Jacobian has been proposed by Broyden. This method is locally superlinearly convergent and therefore is a very powerful alternative to Newton's method. Broyden's algorithm for solving (2) has the following general form: Given an initial guess $\mathbf{x}_0$ and a nonsingular matrix $\mathbf{B}_0$, this method computes a sequence of steps $\mathbf{s}_k$ obtained as follows:

For $k = 0, 1, \ldots$ until convergence **do**:

Solve $\mathbf{B}_k\mathbf{s}_k = -\mathbf{F}(\mathbf{x}_k)$ for $\mathbf{s}_k$

Set $\mathbf{x}_{k+1} = \mathbf{x}_k + \mathbf{s}_k$

Set $\mathbf{z}_k = \mathbf{F}(\mathbf{x}_{k+1}) - \mathbf{F}(\mathbf{x}_k)$

Set $\mathbf{B}_{k+1} = \mathbf{B}_k + \dfrac{(\mathbf{z}_k - \mathbf{B}_k\mathbf{s}_k)\mathbf{s}_k^{\top}}{\mathbf{s}_k^{\top}\mathbf{s}_k}$.

Broyden's method is very popular in practice for two main reasons: first, it generally requires fewer function evaluations than a finite difference Newton's method and second, it can be implemented in ways that require only $O(n^2)$ arithmetic operations per iteration.

To compute the periodic solutions of a Hamilton's equations of motion we must solve the nonlinear equations:

$$\begin{aligned} x(x_0, \dot{x}_0) &= x_0, \\ \dot{x}(x_0, \dot{x}_0) &= \dot{x}_0, \end{aligned} \tag{3}$$

where $(x_0, \dot{x}_0)$ are the initial guesses of an orbit at $t_0 = 0$, on the surface of section of the Poincaré map for a certain value of the energy constant E (see Section 3). The above system can be solved by Newton's method [2]. Thus, if the above periodicity conditions are not satisfied, we have to consider corrections δx_0 and $\delta\dot{x}_0$ by using Newton's method such that:

$$\begin{aligned} x(x_0 + \delta x_0, \dot{x}_0 + \delta\dot{x}_0) &= x_0 + \delta x_0, \\ \dot{x}(x_0 + \delta x_0, \dot{x}_0 + \delta\dot{x}_0) &= \dot{x}_0 + \delta\dot{x}_0, \end{aligned}$$

and, by expanding to first-order terms in the corrections, we obtain the following corrector system:

$$\begin{aligned} \left(\frac{\partial x}{\partial x_0} - 1\right)\delta x_0 + \frac{\partial x}{\partial \dot{x}_0}\delta\dot{x}_0 &= x_0 - x, \\ \frac{\partial \dot{x}}{\partial x_0}\delta x_0 + \left(\frac{\partial \dot{x}}{\partial \dot{x}_0} - 1\right)\delta\dot{x}_0 &= \dot{x}_0 - \dot{x}. \end{aligned}$$

The derivatives involved here refer to isoenergetic variations in accordance with the definition of the mapping of the Poincaré surface of section into itself. Then we write the above corrector system in the form:

$$\begin{aligned} (a-1)\delta x_0 + b\delta\dot{x}_0 &= x_0 - x, \\ c\delta x_0 + (d-1)\delta\dot{x}_0 &= \dot{x}_0 - \dot{x}, \end{aligned}$$

where $a = \partial x/\partial x_0$, $b = \partial x/\partial \dot{x}_0$, $c = \partial \dot{x}/\partial x_0$ and $d = \partial \dot{x}/\partial \dot{x}_0$ are the isoenergetic stability indices of the mapping [4]. The stability indices a, b, c and d can be obtained with additional integrations by using the following formula:

$$f'(x) \cong \frac{f(x+\varepsilon) - f(x)}{\varepsilon}.$$

The value of ε is chosen to be $\varepsilon = |x|\sqrt{\text{eps}}$, where eps is the relative machine precision. In our case the above formula becomes:

$$\begin{aligned} a &\cong \frac{x(x_0 + \varepsilon, \dot{x}_0) - x(x_0, \dot{x}_0)}{\varepsilon}, \\ b &\cong \frac{x(x_0, \dot{x}_0 + \varepsilon) - x(x_0, \dot{x}_0)}{\varepsilon}, \\ c &\cong \frac{\dot{x}(x_0 + \varepsilon, \dot{x}_0) - \dot{x}(x_0, \dot{x}_0)}{\varepsilon}, \end{aligned}$$

$$d \cong \frac{\dot{x}(x_0, \dot{x}_0 + \varepsilon) - \dot{x}(x_0, \dot{x}_0)}{\varepsilon}.$$

The corrector is applied successively until the periodicity conditions are satisfied with the desired accuracy.

An alternative way to solve system (3) for the accurate computation of periodic solutions of the equations of motion of a molecular system is to use Broyden's method. Thus, we have to apply successively the previous mentioned algorithm of Broyden's method until the periodicity conditions (3) are fulfilled.

As already mentioned, the great disadvantage of Broyden's method, as well as Newton's method is that they depend strongly on good estimations of the starting values. To overcome this problem our approach utilizes the characteristic bisection method in order to locate with certainty a periodic orbit.

Next, we will briefly discuss the characteristic bisection method. This method is based on the characteristic polyhedra which define a domain in phase space where the topological degree is not zero. It is well known that if we have a function $\mathbf{F}$, which is continuous in an open and bounded domain $\mathcal{D}$ and the *topological degree of* $\mathbf{F}$ *at* $\mathbf{0}$ *relative to* $\mathcal{D}$, denoted by $\deg[\mathbf{F}, \Pi^n, \mathbf{0}]$, is not equal to zero, then there is at least one solution of the system $\mathbf{F}(\mathbf{x}) = \mathbf{0}$ within $\mathcal{D}$. This criterion can be used, in combination with the construction of a suitable n-polyhedron, called the *characteristic polyhedron*, for the calculation of a solution contained in this region. This is done as follows. Let $\mathcal{M}_n$ be the $2^n \times n$ matrix whose rows are formed by all possible combinations of -1 and 1. Consider now an oriented n-polyhedron Π^n, with vertices $\mathbf{V}_k$, $k = 1, \ldots, 2^n$. If the $2^n \times n$ *matrix of signs associated with* $\mathbf{F}$ *and* Π^n, $\mathcal{S}(\mathbf{F}; \Pi^n)$, whose entries are the vectors

$$\operatorname{sgn}\mathbf{F}(\mathbf{V}_k) = \big(\operatorname{sgn} f_1(\mathbf{V}_k), \operatorname{sgn} f_2(\mathbf{V}_k), \ldots, \operatorname{sgn} f_n(\mathbf{V}_k)\big), \quad (4)$$

is identical to $\mathcal{M}_n$, possibly after some permutations of these rows, then Π_n is called the *characteristic polyhedron relative to* $\mathbf{F}$. Furthermore, if $\mathbf{F}$ is continuous, then, under some suitable assumptions on the boundary of Π^n,

$$\deg[\mathbf{F}, \Pi^n, \mathbf{0}] = \sum_{\mathbf{X} \in \mathbf{F}^{-1}(\mathbf{0}) \cap \mathring{\Pi}^n} \operatorname{sgn}\det \mathbf{F}'(\mathbf{X}) = \pm 1 \neq 0, \quad (5)$$

which implies the existence of a periodic orbit within the interior $\mathring{\Pi}^n$ of Π^n. The generalized bisection method simply amounts to constructing another refined characteristic polyhedron, by bisecting a known one, say Π^n, in order to calculate the solution with the desired solution. We compute the midpoint $\mathbf{M}$ of an one-simplex, e.g., $\langle \mathbf{V}_i, \mathbf{V}_j \rangle$, which is one edge of Π^n. Then we obtain another characteristic polyhedron, Π^n_*, by comparing the sign of $\mathbf{F}(\mathbf{M})$ with that of $\mathbf{F}(\mathbf{V}_i)$ and $\mathbf{F}(\mathbf{V}_j)$ and substituting $\mathbf{M}$ for that vertex for which the signs are identical. Then we continue with another edge. This method is very useful in cases where the period of the periodic orbit is very high and especially when the orbit is unstable, since it always converges within the initial specified region [5,6]. This method computes a specific periodic orbit with certainty but its convergence is not as rapid as that of Newton's or Broyden's method.

With the proposed approach we improve the computational speed of the characteristic bisection method by combining it with Broyden's or Newton's method. First, the method utilizes the characteristic bisection method (by constructing a characteristic polyhedron around a region where a point of the desired periodic solution is expected to exist) and locates the periodic solution with a predetermined accuracy ε, typically $\varepsilon \leqslant 10^{-2}$. Then we utilize the obtained estimate of the orbit as a starting value for Newton's or Broyden's method. If, after one iteration of Newton's or Broyden's method, a better approximation is not accomplished we apply again characteristic bisection utilizing the final characteristic polyhedron obtained by the previous application of the characteristic bisection, in order to achieve a superior estimate, say $\varepsilon \leqslant 10^{-3}$. Then we reapply Newton's or Broyden's method and we continue the same procedure until the solution is determined with the desired accuracy.

3. Results

We apply these methods to the LiNC/LiCN molecular system to locate periodic orbits. We utilize the same potential energy surface used in the study by Prosmiti et al. [7] and Vrahatis et al. [1]. This is a Hartree–Fock electronic potential computed by Essers et al. [8]. The same potential was used in all quantum mechanical calculations for the two-dimen-

sional vibrational problem with fixed the CN^- bond. The Hamiltonian is expressed in Jacobi coordinates, (R, θ), where R is the distance of Li^+ from the center of mass of CN^-, and θ is the angle between R and the bond length of CN^-, r, which is fixed at $2.186a_o$.

The Hamiltonian has the form:

$$H = \frac{P_R^2}{2\mu_1} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R,\theta), \qquad (6)$$

where $\mu_1^{-1} = m_{\mathrm{Li}}^{-1} + (m_{\mathrm{C}} + m_{\mathrm{N}})^{-1}$, $\mu_2^{-1} = m_{\mathrm{C}}^{-1} + m_{\mathrm{N}}^{-1}$ are the reduced masses, and $m_{\mathrm{C}}, m_{\mathrm{N}}$, and m_{Li} are the atomic masses.

The potential surface, $V(R,\theta)$, has two minima with linear geometries: the absolute minimum is for LiNC at ($R = 4.3487a_o$, $\theta = \pi$), and the relative minimum is for LiCN at ($R = 4.7947a_o$, $\theta = 0$) with energy 2281 cm^{-1} above the LiNC minimum. The barrier of isomerization between these two minima is at 3455.5 cm^{-1} and with the geometry ($R = 4.2197a_o$, $\theta = 0.91799$). Also, there is a plateau in the LiNC at 1207 cm^{-1} well above the absolute minimum, and with geometry ($R = 3.65a_o$, $\theta = 1.92$).

To produce the surface of section of the problem, we take successive sections of an orbit with the straight line $\theta = \pi$, along the positive direction of the flow ($P_\theta > 0$). Therefore, the initial conditions are (R, π, P_R, P_θ) where the value of P_θ is computed using the equation of energy for a given value of E. Each section is depicted as a point in the (R, P_R) plane. Thus, a periodic orbit which intersects the R-axis $2p$ times will be represented in the (R, P_R) plane by p points.

Choosing a value for the energy E and keeping this value fixed we integrate numerically the equations of motion to compute successively the intersection points with the surface of section. Such a surface of section is plotted in Fig. 1 for several initial conditions with arbitrarily chosen value of energy $E = 0.008201$ Hartree.

First, we are going to look for initial conditions of periodic orbits of period p of the LiNC/LiCN system that intersect the surface of section at a finite number of points p. Then, for the above surface of section and the specific surfaces of section shown in Vrahatis et al. [1], we apply and compare the methods described previous for the computation of the periodic orbits.

Our experience is that the characteristic bisection method always converges to the periodic solution

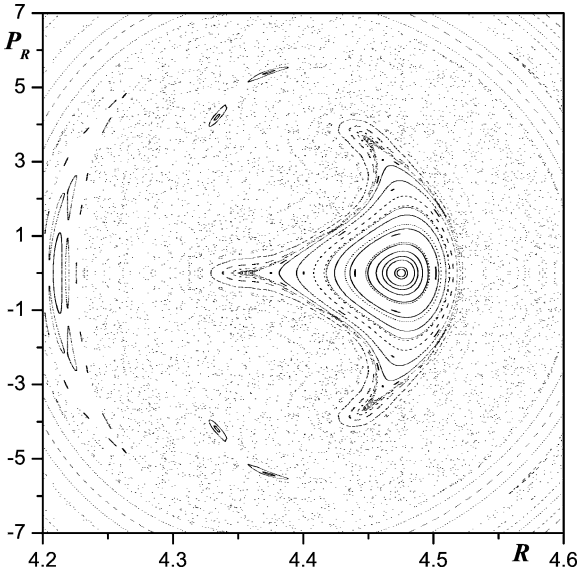

Fig. 1. Surface of section points of LiNC/LiCN system with energy constant $E = 0.008201$ Hartree.

within any region that does not contain orbits whose period is a submultiple of the period of the desired periodic orbit. So, the characteristic bisection method has large regions of initial guesses to locate and compute a periodic orbit and converges in either case of stable and unstable periodic orbits, independently of the initial guess and the multiplicity.

Contrary to the above, Newton's and Broyden's methods behave quite differently. In particular, the higher the period, the smaller the regions of convergence are. Also, in general, the stability properties of a periodic orbit affect the convergence of these two methods. Thus, an unstable periodic orbit has smaller basins of convergence than the respective stable periodic orbit. So, for periodic orbits of high period, especially for unstable high period periodic orbits, it turns out that these two methods need an initial guess lying within a very small distance from the solution [9].

In Fig. 2(a)–(b) we see the phenomenon of the sensitivity of the initial guesses which occurs in the case of Newton's and Broyden's method. An initial guess which lies near a specific periodic point may cause convergence to another point which does not lie in the neighborhood of this initial guess.

To tackle this disadvantage of Newton's or Broyden's method we utilize the characteristic bisection, within relatively large regions of initial conditions, to

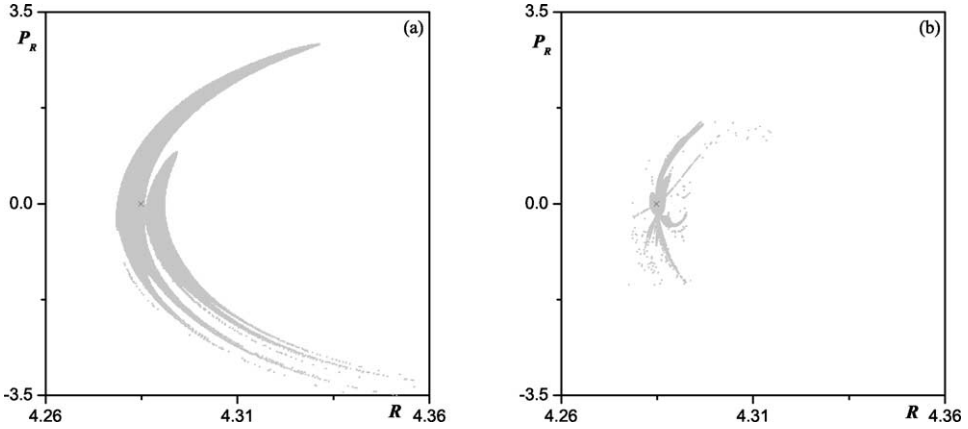

Fig. 2. Basins of convergence of Newton's and Broyden's method for the 1-period stable periodic point $(4.28484649, 0)$ with energy $E = 0.005695$ Hartree. The exact position of the periodic point is marked by $\times$. (a) Basins of convergence of Newton's method and (b) basins of convergence of Broyden's method, for the same 1-period stable periodic point.

locate a fixed point with a predetermined accuracy, sufficient for the location to be used as an initial guess so that the convergence conditions of Newton's as well as Broyden's method are satisfied, as explained in Section 2. By using Broyden's method instead of Newton's, we succeed to avoid the computation of the derivatives involved in Newton's method. So, we reduce the computational cost for the determination of a periodic point since Broyden does not need any additional integrations to compute this.

We call the composition of the characteristic bisection method CHABIS with Newton's method CHABISNEWT. Also, we call the composition of CHABIS with Broyden's method CHABISBR. In Table 1 we exhibit the results obtained with CHABISNEWT and CHABISBR and we compare them with the corresponding results obtained by CHABIS, Newton's and Broyden's methods. To compute the fixed points of Table 1 using CHABIS, we start with a box surrounding the periodic point $(x, \dot{x})$ of period p and refine this box until the desired periodic point is found with accuracy $\varepsilon \leqslant 10^{-8}$. Next, we have taken the same starting boxes and used the centers of these boxes as initial guesses for Newton's and Broyden's method and computed the corresponding fixed points. We note that, for these starting values, Newton's and Broyden's method have a rapid convergence to the specific fixed points but in many cases, and in particular for high period unstable points, these two methods do not converge. With CHABISNEWT we have computed all the periodic points as CHABIS has done but, at the same time, the convergence is more rapid. Finally, with our approach CHABISBR we have computed all the periodic points as CHABIS and CHABISNEWT have done, but we have simultaneously achieved to reduce the computational speed even more than CHABISNEWT.

Of course with other starting points "closer" to a fixed point of a periodic orbit Newton's and Broyden's methods converge. To study how "close" is close enough we have computed the radii of the basins of convergence of these methods to a fixed point. By radius of convergence of a method we define the radius of the largest ball, centered at the specific fixed point such that, for every starting value within it, the corresponding method converges to this point. The computed radii of convergence of Newton's (r_1) and Broyden's (r_2) method of the corresponding fixed points of Table 1 are exhibited in Table 2.

We have also found and calculated new asymmetric families of periodic orbits of LiNC up to energies of 4500 cm^{-1} by using CHABISBR. In Fig. 3 we exhibit the projection of these families in the (E, R) plane. In the continuation scheme the angle coordinate θ is kept equal to π. The new five families of simple asymmetric periodic orbits are labeled with the letter A and the new four families of asymmetric periodic orbits of multiplicity two are labeled with the letter D. Finally, we use the letter C to label the new family of symmetric periodic orbits of multiplicity

Table 1
Fixed points of periodic orbits of period p on the Poincaré surface of section for LiNC/LiCN system and their stability (ST) (S stable, U unstable); CPU time t in seconds (integral part) on a Personal Computer (Pentium III, Xeon at 550 MHz) required for their computation within accuracy $\varepsilon \leqslant 10^{-8}$ by applying the method of CHABIS (t_1), Newton (t_2), Broyden (t_3), CHABISNEWT (t_4) and CHABISBR (t_5); nc indicates non-convergence

p (ST)	Energy	Fixed point (R, P_R)	t_1	t_2	t_3	t_4	t_5
1 (S)	0.008201	(4.47521677, 0.00000000)	5	1	2	2	1
1 (U)	0.008201	(4.34824545, 4.84782024)	5	2	2	1	1
1 (S)	0.008201	(4.21116624, 0.00000000)	6	2	1	2	2
1 (S)	0.005695	(4.28484649, 0.00000000)	6	2	1	2	1
2 (S)	0.008201	(4.33367177, 4.19316634)	7	2	2	3	3
2 (S)	0.008201	(4.37375814, 5.41185767)	12	3	3	4	4
3 (S)	0.011390	(4.21309824, 0.00000000)	16	5	5	5	5
3 (U)	0.008825	(4.40329072, 0.00000000)	19	4	5	4	6
5 (S)	0.008201	(4.21884243, 0.00000000)	21	nc	nc	12	10
5 (U)	0.008201	(4.20471948, 0.00000000)	19	nc	nc	13	11
6 (S)	0.009112	(4.54083980, 0.12064771)	25	7	7	8	7
6 (U)	0.009112	(4.54019427, 0.00000000)	28	9	nc	11	9
7 (S)	0.009112	(4.56843550, 0.00000000)	35	11	10	17	14
7 (U)	0.009112	(4.45804429, 0.00000000)	38	nc	nc	15	14
8 (S)	0.009112	(4.18234538, −1.19641052)	59	16	16	29	28
8 (U)	0.009112	(4.17264206, 0.00000000)	78	nc	nc	33	27
9 (S)	0.009112	(4.56516170, 0.00000000)	57	11	9	19	11
9 (U)	0.009112	(4.46528109, 0.00000000)	65	nc	nc	23	18
10 (S)	0.011390	(4.51232428, 0.00000000)	67	19	17	18	16
10 (U)	0.011390	(4.49147743, 1.84209780)	84	nc	nc	35	32
11 (S)	0.007973	(4.52112213, 0.00000000)	76	15	nc	43	20
11 (U)	0.007973	(4.34305487, 0.00000000)	72	nc	nc	28	28
13 (S)	0.009112	(4.18891990, 0.00000000)	92	nc	23	42	25
13 (U)	0.009112	(4.17193325, 0.00000000)	98	56	nc	52	20
15 (S)	0.009112	(4.57472227, 0.00000000)	82	18	18	38	33
15 (U)	0.009112	(4.57628775, 0.00000000)	106	nc	nc	43	35
28 (S)	0.008825	(4.52039403, −2.55562870)	190	nc	nc	75	72
28 (U)	0.008825	(4.52306399, −2.33238052)	198	nc	nc	93	74

two. Family C is bifurcated at 734.1 cm^{-1} with the D1 family. Also, there are interesting bifurcations of the simple symmetric families B3, B5, B10 and SNP1A, which have been calculated in [1], at 586.6, 1034.3, 1543.3 and 3123.7 cm^{-1}, respectively, which give rise to the asymmetric families A1, A2, A3 and A5, correspondingly.

The last case, where the families of the simple symmetric periodic orbits are bifurcated to simple planar non-symmetric families of periodic solutions, can be easily verified by the Hénon indices a_h, b_h, c_h and d_h. In each of these bifurcating points it holds that $a_h = 1$, $b_h = 0$ and $c_h \neq 0$. In Table 3 we give initial conditions for one periodic orbit of each new family and in Fig. 4 we show their shapes.

4. Concluding remarks

An efficient and effective approach for rapidly and accurately locating and computing with certainty stable or unstable periodic orbits of molecular systems to any desired accuracy and period has been described in this paper. We have applied this method to compute periodic orbits of the LiNC/LiCN molecular system.

These methods combine the advantages of the characteristic bisection CHABIS and Newton's or Broyden's method. First, the characteristic bisection, within relatively large regions of initial conditions, is utilized to locate with a predetermined accuracy a periodic orbit of a given multiplicity. The characteristic bisection method exploits the topological degree theory to construct a characteristic polyhedron for the localization of a periodic orbit without making any computation of the topological degree. Then, it subdivides this polyhedron in such a way that the value of the topological degree of an iterate of the mapping relative to this polyhedron is ± 1, by avoiding calculations concerning the topological degree. When the solution is located with a predetermined accuracy (2 to 4 decimal digits), sufficient for the convergence conditions of Broyden's or Newton's method to be satisfied, we proceed to employ Newton's or Broyden's method for the rapid computation of the periodic orbit.

The results of the proposed methods CHABISNEWT and CHABISBR, which are combinations of

Table 2
Radii of the basins of convergence of Newton's (r_1) and Broyden's (r_2) method of the corresponding fixed points of Table 1

p (ST)	r_1	r_2
1 (S)	0.084	0.087
1 (U)	0.015	0.0051
1 (S)	0.0073	0.0065
1 (S)	0.000061	0.0012
2 (S)	0.0046	0.0062
2 (S)	0.0089	0.0020
3 (S)	0.0024	0.0012
3 (U)	0.0084	0.00078
5 (S)	0.0013	0.000095
5 (U)	0.00012	0.000017
6 (S)	0.00076	0.00076
6 (U)	0.0017	0.00048
7 (S)	0.00092	0.00092
7 (U)	0.00031	0.000012
8 (S)	0.000049	0.00022
8 (U)	0.0000088	0.000099
9 (S)	0.00031	0.00041
9 (U)	0.000018	0.0000043
10 (S)	0.00019	0.00040
10 (U)	0.00026	0.00024
11 (S)	0.000029	0.00034
11 (U)	0.00095	0.00048
13 (S)	0.00015	0.00012
13 (U)	0.000025	0.0000034
15 (S)	0.00034	0.000076
15 (U)	0.000011	0.000019
28 (S)	0.00019	0.00045
28 (U)	0.00022	0.00012

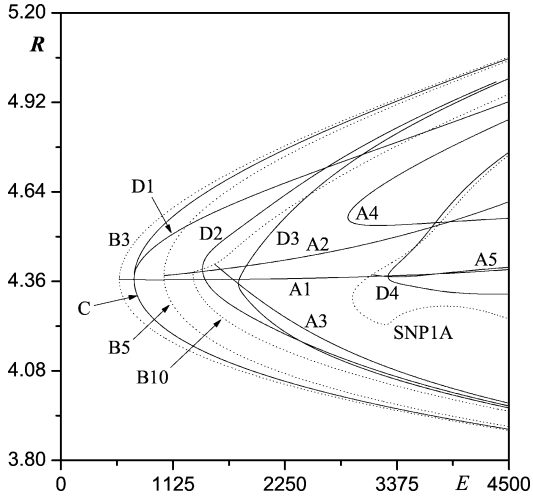

Fig. 3. Asymmetric families of periodic orbits of LiNC up to energies of 4500 cm^{-1} obtained by CHABISBR.

Table 3
Periodic orbits of the new families of Fig. 3. Energy in cm^{-1} and all other quantities in atomic units

	Energy	T	R	θ	P_R	P_θ	Stability
A1	3502.0512	13459.4768	4.37968863	π	16.71802999	13.19604842	U
A2	1500.5426	17163.2880	4.39385976	π	7.27521828	18.87724092	U
A3	3000.7020	18761.4398	4.12634545	π	6.84800571	25.69960607	U
A4	4001.0797	16720.2292	4.54831493	π	10.80062766	30.21398553	U
A5	4236.9813	16562.4712	4.39745746	π	−11.81388576	32.66516651	U
C	3735.6220	29027.1470	4.96812439	π	0.00000000	11.98587139	U
D1	4801.7266	29652.2010	4.95780000	π	10.37984114	11.62733606	U
D2	1790.3847	38828.7603	4.52610950	π	4.38825749	22.04351028	S
D3	1900.3088	36733.6409	4.42675814	π	6.59712042	23.18728330	S
D4	3780.9498	31595.9030	4.55147885	π	−2.38829884	36.16188228	U

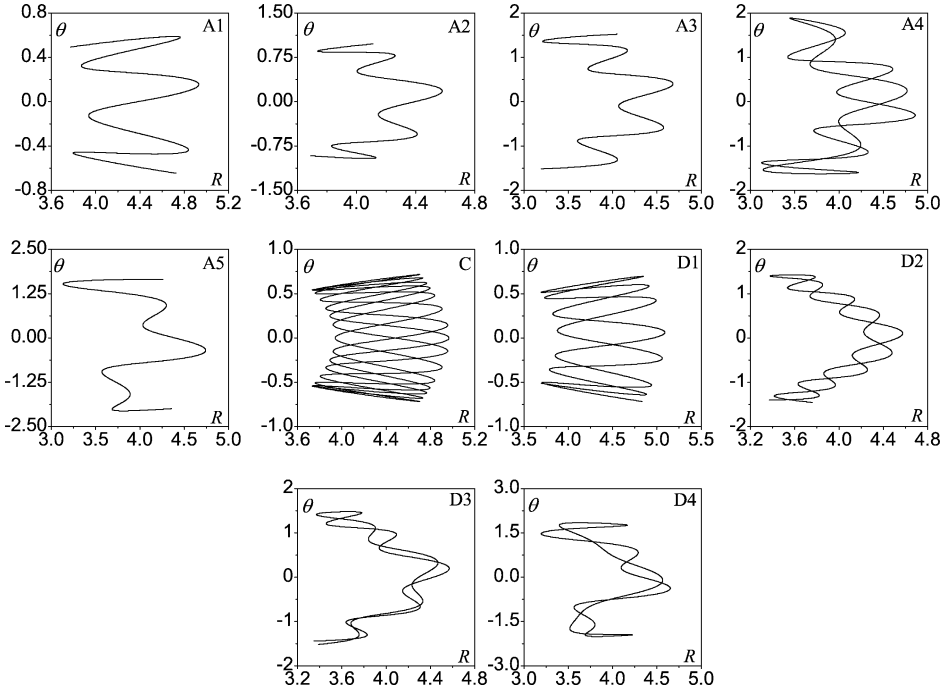

Fig. 4. Representative periodic orbits of the new families in the (R, θ) plane.

the characteristic bisection with Newton's and Broyden's methods, have been compared with those of CHABIS, Newton's and Broyden's method. We have found that CHABISBR method has computed the periodic orbits more rapidly than CHABISNEWT. This happens because Newton's method in CHABISNEWT needs more integrations. Our experience reveals that the proposed methods are very efficient and effective since they compute all the solutions with certainty and rapidly.

In a future correspondence we intend to extend our technique to higher dimensional systems which are of great interest in the field of molecular dynamics.

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