Notes on relative equilibria of isosceles molecules in classical approximation

Damaris McKinley∗  Daniel Paşca† Cristina Stoica‡

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Abstract We study a classical model of isosceles triatomic “A-B-A” molecules. The atoms, considered mass points, interact mutually via a generic repulsive-attractive binary potential. First we show that the steady states, or relative equilibria (RE), corresponding to rotations about the molecule symmetry axis may be determined qualitatively assuming the knowledge of 1) the shape of the binary interaction potential, 2) the equilibrium diatomic distances (i.e., the equilibrium bond length) of the A-A and A-B molecules, and 3) the distance at which the RE of the diatomic A-A molecule ceases to exist. No analytic expression for the interaction potentials is needed. Second we determine the stability of the isosceles RE modulo rotations using geometric mechanics methods and using Lennard-Jones diatomic potentials. As a by-product, we verify the qualitative results on RE existence and bifurcation. For isosceles RE we employ the Reduced Energy-Momentum method presented in [J.E. Marsden, Lectures in Mechanics, Cambridge University Press, 1992], whereas for linear (trivial isosceles) RE we introduce the Symplectic Slice method, a technique based on the findings in the paper [R.M. Roberts, T. Schmah and C. Stoica, Relative equilibria for systems with configurations space isotropy, J. Geom. Phys., 56, 762, (2006)].

Keywords: classical approximation, isosceles triatomic molecules, relative equilibria, bifurcations, Reduced Energy Momentum, Symplectic Slice method

1 Introduction

In molecular dynamics, classical approximations are used in order to reduce the computational effort required when using the corresponding quantum-based models. These approximations consist in modeling the atoms in the realm of classical mechanics as mass points that interact mutually via a repulsive-attractive potential. The latter is either determined experimentally and tabulated consequently, or it is described via a functional relation with parameters fitted experimentally.

A functional relation expressing the atomic repulsive-attractive interaction is the 12-6 Lennard-Jones potential [Lennard-Jones (1881)]. Its parameters are derived from “second-virial” or “viscosity coefficients” [Bird & al. (1967)], providing a particularly accurate model for neutral atoms and molecules, as well as noble gas atoms. However, the use of the powers 12 and 6 in the potential is due to a computational convenience [Brush (1970)]. For instance, the power of the repulsive inverse of the distance term is slightly different from one gas to another, taking values in between 12 and 13. Thus a qualitative analysis of an atomic model within the framework of classical mechanics need not be restricted to the 12-6 potential, but rather to a repulsive-attractive binary interaction given by some generic graphical representation.

As discussed in the physical-chemistry literature [Pavlichenkov & al. (1988), Kozin & al. (1999), Kozin & al. (2000)], rotating steady states about stationary axes during which the “shape” of a molecule

∗Wilfrid Laurier University, 75 Univ. Av. West, Waterloo, N2L 3C5, Ontario, Canada. Email: damaris.duma@gmail.com
†Department of Mathematics and Informatics, University of Oradea, University Street 1, 410087, Oradea, Romania. Email: dpasca@uoradea.ro
‡Wilfrid Laurier University, 75 Univ. Av. West, Waterloo, N2L 3C5, Ontario, Canada. Email: cstoica@wlu.ca
Figure 1: The model of an isosceles molecules considered here is given by a three-degrees of freedom system with coordinates are \( r, z \) and the angle \( \theta \). The molecule is rotated about the \( Oz \) axis and (by symmetry) it maintains its isosceles shape at all time.

does not change can be used to explain and predict features of quantum spectra. In classical mechanics, such states are called relative equilibria (RE). A detailed study of triatomic molecules’ RE can be found in [Kozin & al. (1999), Kozin & al. (2000)]; in these papers the authors use experimentally determined potentials. Also, criteria of bifurcations of RE from equilibria are determined in [Montaldi & al. (1999)].

Here we consider RE of “A-B-A”-type molecules in classical approximation. Such molecules are formed by three atoms that form an isosceles triangle, with two identical \( A \) atoms located at the vertices of the triangle’s base, and the third \( B \) atom at the third vertex (see Figure 1). We show that the isosceles RE and their bifurcations may be determined qualitatively when no analytical expression of the repulsive-attractive molecular diatomic potentials is available. The necessary and sufficient information required consists of three parameters: the equilibrium diatomic distances of the \( A-A \) and \( A-B \) molecules and diatomic distance at which the RE of the \( A-A \) molecule ceases to exist (see Proposition 4.1). Further, we determine the isosceles RE stability in the full phase-space using geometric methods, in particular the Reduced Energy Momentum (REM) method of Marsden and co-workers [Marsden (1992)] and the Symplectic Slice method based on the findings in [Roberts & al. (2006)]. We implement these on some numerical examples using Lennard-Jones-type potentials, which also verify the qualitative results on the RE existence and bifurcations.

While the existence of isosceles RE is qualitatively determined using three parameters only, establishing RE stability require additional “second order” parameters that lead to cumbersome qualitative classifications diagrams, beyond our scope. For example, one needs to know the dissociation distance, that is the distance at which the diatomic potential changes its concavity. Thus we chose to calculate the RE stability assuming the knowledge the inter-atomic \( A-A \) and \( A-B \) potentials.

Recall that the stability of an equilibrium calculated on an invariant manifold of a ODE does not imply stability in the full phase space; in our case, stability within the isosceles invariant manifold may be lost in directions that breaks the symmetry of the triangle. Thus we must consider the molecule as a 6 degree of freedom mechanical system (using Jacobi coordinates) with spatial rotational symmetry and apply appropriate stability methods that ignore the neutral symmetry directions. N-body systems with spatial rotational symmetry stability involve the moment of inertia tensor at the RE configuration, represented by a \( 3 \times 3 \) matrix and its inverse. For isosceles RE the inertia matrix is non-singular, and in this case we employ the phase-space splitting of the Reduced Energy-Momentum (REM) method of Marsden and co-authors [Marsden (1992)]. For linear RE, the inertia matrix is singular (having a zero eigenvalue), and thus the splittings of the REM method are not applicable. In this case we introduce the Symplectic Slice method, based on the theoretical work in [Roberts & al. (2006)] (but also see [Lawson & al. (2011)]).
Practically, we apply a change of coordinates that re-organises the dynamics as a coupled system of a rigid-body-like system (corresponding to the invertible part of the locked inertia tensor I) and a simple mechanical system of type "kinetic+ potential". Note that while the theory was formulated previously, to our knowledge, it is the first time the Symplectic Slice method is implemented on a concrete example. Future work will extend its use to more complex systems.

We verify our qualitative findings in RE existence and bifurcation and calculate stability numerically using Lennard-Jones-type binary potentials [Lennard-Jones (1881)]. For interactions between atoms of different species we adopt the Lorentz-Berthelot rule ([Lorentz (1881), Berthelot (1889), Kirchner & al. (2012)]), a rule that assumes the knowledge of the coefficients of identical atoms. We consider examples in the cases when the outer atoms have greater, equal and smaller mass then the central atom; we call these models $D_2H$, $H_3$ and $H_2D$, respectively. For each case we present the RE Energy-Momentum (EM) diagram.

The paper is organized as follows: first we define binary interactions qualitatively and provide a generic picture of the RE of diatomic molecules in classical approximation. In Section 3 we introduce isosceles triatomic molecules and determine the RE equations. In Section 4 we establish criteria for the existence and bifurcations of the RE. In Section 5 we describe the REM and the Symplectic Slice methods. In the next Section we consider specific Lennard-Jones-type binary potentials and calculate numerically the EM diagrams. We end with Conclusions.

2 A generic model for molecular interactions

Classical approximations of molecules consist in $N$-body problems with mutual binary interaction given by a repulsive-attractive smooth potential as in Figure 2. The atoms are idealized mass points, and the interatomic potential is either determined directly from experiments, or is described via a functional relation (for example, a 12-6 Lennard-Jones potential) with parameters fitted experimentally.

**Definition 2.1** A generic binary molecular potential is a function $U : (0, \infty) \rightarrow \mathbb{R}$ such that

1. $\lim_{r \to 0^+} U(r) = \infty$ (the atoms repel when close);

2. the function $U$ has a unique minimum, and no other critical point (the atoms attract each other at medium range, displaying a unique stable equilibrium position);

3. $\lim_{r \to \infty} U(r) = 0$ (at long range the interaction vanishes);

4. $U(r)$ is $o(r^2)$ (the binary long-range interaction decays faster than the centrifugal forces).
Definition 2.2 A molecule in classical approximation consists of \( N \) mass points interacting mutually via a generic binary molecular potential.

Figure 3: The amended potential \( U_c(r) \) for various values of \( c \). The black curve corresponds to \( c = 0 \) (color online).

Consider the classical approximation of a molecule formed by two atoms \( A \) and \( B \) of mass \( m_A \) and \( m_B \), respectively. The molecule is rotated with constant angular velocity about an axis perpendicular to the centre of mass of the \( AB \) system. The rotating steady states, or relative equilibria (RE), are the states where the (inter-atomic) attractive and centrifugal forces are balanced. The distance between the atoms at a RE is determined as a critical point of the amended (or reduced, or effective) potential

\[
U_c(r) := \frac{c^2}{mr^2} + U(r),
\]

where \( c \) denotes the angular momentum and \( m \) is the relative mass \( m = m_A m_B / (m_A + m_B) \).

In Figure 3 we sketch a plot of the augmented potential for various momentum values. The relative equilibria (RE) are found as the critical points of \( U_c(r) \). At momentum zero (black curve), apart from the equilibrium configuration (at bottom of the well), a fictitious equilibrium is located at \( r = \infty \).

For small non-zero momenta (brown curves) there are two RE: one stable (minimum), emerging from the equilibrium at the bottom of the well, and one unstable (maximum), emerging from the fictitious equilibrium at infinity. As the momentum increases, at critical value \( c_0 \), the two RE merge and cease to exist at a cusp. The red and pink curves correspond to \( c_0 \) and a value \( c > c_0 \), respectively.

Figure 4 depicts a energy-momentum (EM) diagram. Each point represents a RE in coordinates given by angular momentum against total energy. At zero momentum we have the equilibrium configuration (the minimum of the potential) and a fictitious RE at infinity.

3 Isosceles three point-mass systems

Consider a triatomic molecule of type A-B-A as a classical three point-mass problem with binary repulsive-attractive interaction. We set up the dynamics in Jacobi coordinates coordinates \((r, s)\), with \( r \) is the relative vector between the two A atoms, and \( s \) is the vector between the centre of mass (and also midpoint) of the A atoms system and the B atom. The configuration of the atoms is \( Q := (\mathbb{R}^6 \setminus \{\text{collisions}\}) \) and the dynamics is given by the Lagrangian system with \( L : TQ \to \mathbb{R} \),

\[
L(r, s, \dot{r}, \dot{s}) = \frac{M_1}{2} \dot{r}^2 + \frac{M_2}{2} \dot{s}^2 - V(r, s)
\]
with \( \mathbf{r} = (r_x, r_y, r_z) \), \( \mathbf{s} = (s_x, s_y, s_z) \),

\[
V(\mathbf{r}, \mathbf{s}) = V_{AA}(|\mathbf{r}|) + V_{AB}(|\mathbf{s} + (1/2)\mathbf{r}|) + V_{AB}(|\mathbf{s} - (1/2)\mathbf{r}|)
\]

(2)

\( M_1 = m_A/2 \) and \( M_2 = (2m_A m_B)/(2m_A + m_B) \), and \( V_{AA} \) and \( V_{AB} \) the potentials between two A atoms, and A and B atoms, respectively.

Given that two of the mass points are equal, one can prove that motions with the three atoms in an isosceles shape at all times form a 6 dimensional invariant submanifold of the flow in the full 12 dimensional phase-space. Let the configuration space of the isosceles sub-system be described by the coordinates \((r_x, r_y, s_z)\).

Passing to cylindrical coordinates \((r_x, r_y, s_z) \rightarrow (r, \theta, z)\) and using Legendre transform, we obtain the Hamiltonian formulation of the isosceles problem, with a Hamiltonian given by

\[
H(r, \theta, z, p_r, p_\theta, p_z) := \frac{1}{m_A} \left( p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{2m_A + m_B}{2m_A m_B} p_z^2 + F(r) + 2G \left( \sqrt{\frac{r^2}{4} + z^2} \right)
\]

(3)

where we denote \( F := V_{AA}, \ G := V_{AB} \). From the general theory or by direct verification, we have that the conservation of the energy of the system, and also, the conservation of angular momentum \( \dot{p}(t) = \text{const.} =: c \). Substituting the latter into (3) we obtain the reduced Hamiltonian

\[
H_{\text{red}}(r, z, p_r, p_z; c) = \frac{1}{m_A} p_r^2 + \frac{2m_A + m_B}{4m_A m_B} p_z^2 + \frac{c^2}{m_A r^2} + F(r) + 2G \left( \sqrt{\frac{r^2}{4} + z^2} \right).
\]

(4)

Thus the dynamics is reduced to a two-degrees of freedom Hamiltonian system parametrized by the angular momenta \( c \). The equations of motion are

\[
\dot{r} = \frac{2}{m_A} p_r, \quad \dot{p}_r = \frac{2c^2}{m_A r^3} - F'(r) - G' \left( \sqrt{\frac{r^2}{4} + z^2} \right) \frac{r}{2\sqrt{\frac{r^2}{4} + z^2}},
\]

(5)

\[
\dot{z} = \frac{2m_A + m_B}{2m_A m_B} p_z, \quad \dot{p}_z = -2G' \left( \sqrt{\frac{r^2}{4} + z^2} \right) \frac{z}{\sqrt{\frac{r^2}{4} + z^2}}.
\]

(6)

The RE are determined as the equilibria of \( H_{\text{red}} \). Note that the equilibria of the un-reduced Hamiltonian (3) correspond to RE with zero angular momentum. The RE have \( p_r = p_z = 0 \) and their coordinates
are found by solving the system

\[ \frac{2c^2}{m_A r^3} - F'(r) - G' \left( \sqrt{\frac{r^2}{4} + z^2} \right) \frac{r}{2\sqrt{\frac{r^2}{4} + z^2}} = 0, \]

(7)

\[ 2G' \left( \sqrt{\frac{r^2}{4} + z^2} \right) \frac{z}{\sqrt{\frac{r^2}{4} + z^2}} = 0. \]

(8)

To simplify the presentation, we call RE the solutions of the algebraic system (7) - (8).

**Remark 3.1** Since the mass parameter \( m_B \) does not appear in the system (7) - (8) the RE do not depend on the mass \( m_B \). (Physically, this is because \( m_B \) does not add to the rotational inertia of the system.)

### 4 Relative equilibria

We distinguish 2 classes of RE (modulo the sign of \( c \)): 1) **linear** RE, that is solutions with \( z = 0 \). In this case the atoms form a rigid steadily rotating segment; and 2) **isosceles** RE, that is solutions with \( z \neq 0 \). In this case the atoms form a rigid steadily rotating isosceles triangle. Without losing generality, we consider \( c > 0 \).

Recall that the potential \( F \) describes the attractive-repulsive interaction between the identical \( A \) atoms, whereas \( G \) describes the attractive-repulsive interaction between the \( A \) and \( B \) atoms. Let the equilibrium diatomic distances be \( r^F_e \) and \( r^G_e \) for the potentials \( F \) and \( G \), respectively.

#### 4.1 Linear RE (\( z = 0 \))

Let \( c \) be fixed. From system (7) - (8) and using that \( z = 0 \), we have that linear RE are solutions of \( \frac{2c^2}{m_A r^3} = F'(r) + G' \left( \frac{r}{2} \right) \). We determine these by counting of the number of intersections of the curves \( \frac{2c^2}{m_A r^3} \) and \( F'(r) + G' \left( \frac{r}{2} \right) \); each intersection of these curves corresponds to a root of the given equation.

**Equilibria (\( c = 0 \))** We solve

\[ F'(r) + G' \left( \frac{r}{2} \right) = 0 \]

(9)

Given the shape of \( F(r) \) and \( G(r) \) (see Figure 2), this equation can have one, two or three roots. Assuming that the function \( F(r) + G' \left( \frac{r}{2} \right) \) behaves as a potential described by Definition 2.1, we consider that any three atoms in a classical interaction display a unique linear equilibrium configuration and so Equation (9) has a unique solution.

**Relative Equilibria (\( c \neq 0 \))** Since the sum \( F(r) + G' \left( \frac{r}{2} \right) \) is a generic molecular potential, linear RE are determined in the same manner as for a diatomic molecule (see Section 2).

#### 4.2 Isosceles RE (\( z \neq 0 \))

For \( z \neq 0 \) the system (7) - (8) becomes

\[ \frac{2c^2}{m_A r^3} - F'(r) = 0 \]

(10)

\[ G' \left( \sqrt{\frac{r^2}{4} + z^2} \right) = 0 \]

(11)
Figure 5: The RE of the diatomic molecule formed by the identical A atoms are determined as intersections of \( y(r) = F'(r) \) (in black) with curves \( y(r) = c^2/(mr^3) \) for various values of the angular momentum \( c \) (color online). Let \( c_{0,F} \) be the critical momentum value above which such RE disappear. For a fixed \( c \in (0, c_{0,F}) \), we plot the curve \( y(r) = c^2/(mr^3) \) (in red) and denote by \( r_{0,1} \) and \( r_{0,2} \) the corresponding RE. At \( c = c_{0,F} \) we have the curve \( y(r) = c_{0,F}^2/(mr^3) \) (in blue) and denote \( l = r(c_{0,F}) \) the corresponding RE distance.

**Equilibria** \((c = 0)\) In this case Equation (10) reduces to \( F'(r) = 0 \), which is solved by \( r = r_e^F \). Then using Equation (11), and the fact that \( G'(r_e^G) = 0 \), we obtain

\[
\sqrt{\frac{(r_e^F)^2}{4} + z^2} = r_e^G.
\]

Provided \( r_e^F \leq 2r_e^G \) it follows that there are two isosceles equilibria located at \( \left(r_e^F, \pm \sqrt{(r_e^G)^2 - \left(\frac{(r_e^F)^2}{4}\right)}\right) \) that degenerate to a linear RE when \( r_e^F = 2r_e^G \).

**Relative Equilibria** \((c \neq 0)\) We observe that the real solutions of the Equation (10) are in fact the critical points of the amended potential

\[
F_c(r) := \frac{c^2}{m_A r^2} + F(r)
\]

associated to the diatomic molecule formed by the A atoms. Thus isosceles RE exist only for momenta \( c \) that allow the existence of RE for the diatomic A-A molecule. We denote by \( c_{0,F} \) the critical momentum value above which the diatomic A-A RE disappear, and by \( l \) the corresponding inter-atomic distance, i.e. \( l := r(c_{0,F}) \) (see Figure 5). For \( 0 < c \leq c_{0,F} \), let the solutions of Equation (10) be \( r_{0,1}(c) \) and \( r_{0,2}(c) \). We have \( r_e^F < r_{0,1}(c) \leq l \leq r_{0,2}(c) \). Note that \( \lim_{c \to 0} r_{0,1}(c) = r_e^F \), \( \lim_{c \to 0} r_{0,2}(c) = \infty \), and \( \lim_{c \to c_{0,F}} r_{0,1}(c) = \lim_{c \to c_{0,F}} r_{0,2}(c) = l \). Equation (11) becomes

\[
z^2 = \left(r_e^G\right)^2 - \frac{r_{0,1}^2(c)}{4}
\]

and it accepts real solutions only if

\[
r_{0,1}(c) \leq 2r_e^G \text{ or } r_{0,2}(c) \leq 2r_e^G.
\]
We are able now to distinguish:
1. If $2r_e^G \leq r_e^F$, then there are no solutions.
2. If $r_e^F < 2r_e^G$ then consider the momentum value $c_{1,s}$ for which $2r_e^G$ is a RE for a diatomic molecule formed by the identical atoms, that is, $c_{1,s}$ is the momentum value for which

$$F'(2r_e^G) = \frac{2c_{1,s}^2}{m_A(2r_e^G)^3}.$$  \hspace{1cm} (15)

We have the following subcases:
(a) If $2r_e^G < l$ then for $c \in (0,c_{1,s})$ we have one RE family with

$$z_{1,2} = \pm \sqrt{(r_e^G)^2 - \frac{(r_{0,1}(c))^2}{4}}.$$  \hspace{1cm} (16)

This family ceases to exist at $c = c_{1,s}$ where it meets a linear family.
(b) If $l < 2r_e^G$ then
   (i) for $c \in (0,c_{1,s})$ we have one RE family with

   $$z_{1,2} = \pm \sqrt{(r_e^G)^2 - \frac{(r_{0,1}(c))^2}{4}};$$  \hspace{1cm} (17)

   (ii) at $c = c_{1,s}$, a second family “$z_{3,4}$” of spatial RE branches from a linear RE;
   (iii) for $c \in (c_{1,s},c_{0,F})$ we have two RE families with

   $$z_{1,2} = \pm \sqrt{(r_e^G)^2 - \frac{(r_{0,1}(c))^2}{4}}, \quad z_{3,4} = \pm \sqrt{(r_e^G)^2 - \frac{(r_{0,2}(c))^2}{4}};$$  \hspace{1cm} (18)

   (iv) at $c = c_{0,F}$, the isosceles families “$z_{1,2}$” and “$z_{3,4}$” join. No isosceles RE exist for $c > c_{0,F}$.

We summarize our findings in:

**Proposition 4.1** Let $r_e^F$ be the equilibrium distance of the diatomic molecule formed by the identical $A$ atoms and with potential $F$ and let $r_e^G$ be the equilibrium distance of the diatomic molecule formed by the non-identical atoms $A$ and $B$ with potential $G$. Further, let $c_{0,F}$ be the threshold value of the momentum where the two RE families of the diatomic $A$-$A$ molecule merge and disappear, and denote by $l$ the corresponding distance between the atoms; in other words, let $l := r(c_{0,F})$. Then we have the following:

1. If $2r_e^G \leq r_e^F$ then there are no isosceles RE.
2. If $r_e^F < 2r_e^G$, let us denote by $c_{1,s}$ the momentum value for which $2r_e^G$ is a RE for a diatomic molecule formed by the identical atoms and with potential $F$. Then we distinguish:
   (a) If $2r_e^G \leq l$, then there is one isosceles family of RE parametrized by $c \in (0,c_{1,s})$. This family emerges from the isosceles equilibrium and at $c = c_{1,s}$ it joins a linear family of RE.
   (b) If $l < 2r_e^G$ then:
      i. For values $c \in (0,c_{1,s})$ there is one isosceles family of RE which emerges from the isosceles equilibrium.
      ii. At $c = c_{1,s}$ there is a bifurcation. A second isosceles RE family occurs and the two isosceles families of RE co-exist for $c \in (c_{1,s},c_{0,F})$; they merge at $c = c_{0,F}$.
      iii. For $c > c_{0,F}$, no isosceles RE exist.

**Remark 4.2 (Three identical atoms)** If the three atoms are identical, then $F(r) = G(r)$, and so $r_e^F = r_e^G$. In particular, $r_e^F < 2r_e^G = 2r_e^F$ and so Case 2. of the Proposition above applies.
5 Stability

We now present two geometric methods appropriate for computing stability of the isosceles and linear RE, respectively, modulo spatial rotations. These methods will be employed on the numerical examples in the next section.

Broadly speaking, the symmetry reduced Hamiltonian of a mechanical system with rotational symmetry takes the form “kinetic plus reduced potential”. A RE is stable modulo rotations if the Hessian matrix $D^2V_{\text{amended}}(r_e, z_e; c)$ of the amended potential is positive definite. This test is in fact a specialization of the non-linear (Lyapunov) stability test to mechanical systems with symmetry. The positive definiteness of the amended potential $D^2V_c(r_e, z_e; c)$ insures that the Hessian of the reduced Hamiltonian $D^2H_{\text{red}}$ is also positive definite and so $(r_e, z_e; c)$ corresponds to a local minimum of the energy. If $D^2V_c(r_e, z_e; c)$ is not positive definite, then one proceeds to the spectral analysis of the linearization of the vector field. In the canonical Hamiltonian context, linear stability is guaranteed if the linearization matrix is semi-simple and all its eigenvalues have zero real part. Linear stability does not ensure stability, but only the existence of the local normal modes (simple harmonic motions) near RE. However, linear instability predicts instability.

In the present stability calculations we employ two methods: for the isosceles RE, we use the splitting of the phase space of the REM method (see [Marsden (1992)]), whereas for the linear RE we introduce the Symplectic Slice method, that is a method with theoretical justification in [Roberts & al. (2006)] (also, see [Lawson & al. (2011)]). We sketch below the application of these methods to our class of RE.

5.1 The REM method for isosceles RE

Using the notation from Section 3, the dynamics of a three mass point system is given by the $SO(3)$-invariant Hamiltonian

$$H(r, s, p_r, p_s) = \frac{p_r^2}{2M_1} + \frac{p_s^2}{2M_2} + V(r, s).$$

where $(p_r, p_s) \in \mathbb{R}^3 \times \mathbb{R}^3$ are the generalized momenta corresponding to the coordinates $(r, s)$. We denote the Lie algebra and co-Lie algebra of $SO(3)$ by $so(3)$ and $so^*(3)$. The (angular) momentum map corresponding to the action of $SO(3)$ on the phase space is $J : T^*Q \to so^*(3)$, $J(r, s, p_r, p_s) = r \times p_r + s \times p_s.$

Consider a RE with angular velocity $\xi_e \in so(3)$, angular momentum $\mu_e \in so^*(3)$, and base-point $q_e = (r_e, s_e)$. The REM method uses the augmented Hamiltonian

$$H_\xi(r, s, p_r, p_s) := H(r, s, p_r, p_s) - \langle J(r, s, p_r, p_s), \xi \rangle, \quad \xi \in so(3)$$

as a Lyapunov function on an appropriate splitting of the co-tangent bundle phase-space variations that has the additional property of bringing the linearized equations of motion into a normal form. The stability computation is reduced to a test of positive definiteness of the second variation $\delta^2V_{\mu_e}$ at $q_e$ of the amended potential

$$V_{\mu_e}(r, s) := V(r, s) + \frac{1}{2} \langle \mu_e, \Pi^{-1}(r, s) \mu_e \rangle$$

restricted to a subspace of configuration variations. Briefly, the tangent to the configuration space at the RE allows a three-way splitting $T_{q_e}Q = \mathcal{M} \oplus \mathcal{V}_\text{RIG} \oplus \mathcal{V}_\text{INT}$. The subspace $\mathcal{M}$ contains variations along the symmetry group and the corresponding $[\delta^2V_{\mu_e}|_\mathcal{M}]$ matrix block is always zero. The subspace $\mathcal{V}_\text{RIG}$ contains rigid variations that, loosely speaking, do not affect the shape of the RE configuration which is perceived as a rigid body. The subspace $\mathcal{V}_\text{INT}$ is normal to $\mathcal{M} \oplus \mathcal{V}_\text{RIG}$ and is formed by internal variations which deform the RE configuration. The REM phase-space splittings are explained in detail in Section 2 of [Schmah & al. (2006)].
For isosceles RE, the variations along $M$ are given by infinitesimal rotations of the triangle along the symmetry axis; the variations along $V_{RIG}$ take the “rigid” RE triangle out of its plane; and the variations along $V_{INT}$ change the shape the RE triangle. Isosceles RE are of the form $q_e = (r_e, s_e)$, with $r_e = (0, r_e, 0)$ and $s_e = (0, 0, s_e)$, and with angular velocity $\xi_e = (0, 0, \xi_e) \in \mathbb{R}^3 \simeq so(3)$ and angular momentum $\mu_e = (0, 0, \mu_e) \in \mathbb{R}^3 \simeq so(3)^*$. The moment of inertia at a RE is

$$I(r_e, s_e) = \begin{bmatrix} M_1 r_e^2 + M_2 s_e^2 & 0 & 0 \\ 0 & M_2 s_e^2 & 0 \\ 0 & 0 & M_1 r_e^2 \end{bmatrix}. \quad (19)$$

It is clear that $I(r_e, s_e)$ becomes singular at linear configurations (where $s_e = 0$) and that in this case, one needs a modified method to calculate stability (treated in the next subsection).

Assuming $s_e \neq 0$, denoting $so(3)_{\frac{1}{2}} := \{ \omega \in so(3) | \omega = (\omega_x, \omega_y, 0) \}$ and using the REM block diagonalisation of $\delta^2 V_{\mu_e}|_{V_{INT}}$, after calculations, we have that an isosceles RE is Lyapunov stable if

1. the Arnold two-form $A_{\mu_e} : so(3)_{\frac{1}{2}} \times so(3)_{\frac{1}{2}} \to \mathbb{R}$, which has the matrix

$$[A_{\mu_e}] = \mu_e^2 [I^{-1}(r_e, s_e) - \lambda_e^{-1}I_3] = \mu_e^2 \begin{bmatrix} \frac{1}{M_2 s_e^2} - \frac{1}{M_1 r_e^2} & 0 \\ 0 & \frac{1}{M_1 r_e^2 + M_2 s_e^2} - \frac{1}{M_1 r_e^2} \end{bmatrix} \quad (20)$$

is positive definite, and

2. the second variation $\delta^2 V_{\mu_e}$ is positive definite on $V_{INT} = \{ (\delta r, \delta s) \in \mathbb{R}^3 \times \mathbb{R}^3 | \delta r_x = \delta s_x = 0, M_1 \delta r_x + M_2 \delta s + M_2 \delta s_y = 0 \}$. Choosing the parametrization $(\delta r, \delta s, \delta s_z) \in \mathbb{R}^3$ for $V_{INT}$, we calculate

$$\delta^2 V_{\mu_e}|_{V_{INT}} = \begin{bmatrix} V_{r_y r_y} & \alpha V_{r_y r_x} + V_{r_y s_y} & V_{r_y s_z} \\ \alpha V_{r_y r_x} + V_{r_y s_y} & 2\alpha V_{r_z s_y} + V_{r_y s_y} & \alpha V_{r_z s_x} + V_{s_y s_z} \\ \alpha V_{r_z s_x} + V_{s_y s_z} & \alpha V_{r_z s_x} + V_{s_y s_z} & V_{s_z s_z} \end{bmatrix} + (\xi_e)^2 \begin{bmatrix} M_1 & 0 & 0 \\ 0 & 4M_1 - M_2 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

where $\alpha := -\frac{M_2 s_e}{M_1 r_e}$.

From Condition 1. we deduce that the Arnold form is never positive definite, and so

**Remark 5.1** An isosceles RE rotating about its symmetry axis is never Lyapunov stable.

We then proceed to study linear stability and compute the eigenvalues of the linearization $L$ of the Hamiltonian vector-field $X_{H_{\xi_e}}$ at $(r_e, s_e)$. As known, for a canonical Hamiltonian system, if the matrix of $L$ is semi-simple and all its eigenvalues have zero real part, then the RE is linearly stable. We calculate

$$L = \begin{bmatrix} A & \circ & \circ \\ \circ & \circ & B^{-1}\delta^2 K_{\mu_e} \\ \circ & -B^{-1}\delta^2 V_{\mu_e}|_{V_{INT}} & \circ \end{bmatrix} \quad (21)$$

where

$$A = \begin{bmatrix} \frac{1}{M_2 s_e^2} - \frac{1}{M_1 r_e^2} & 0 \\ 0 & \frac{1}{M_1 r_e^2 + M_2 s_e^2} + \frac{1}{M_1 r_e^2} \end{bmatrix} \quad (22)$$
\[
B = \begin{bmatrix}
1 & 0 & -\frac{M_2 s_e^2}{M_1 r_e^2} & 0 \\
0 & 1 - \frac{M_2 s_e^2}{M_1 r_e^2} & 0 & \frac{M_1}{M_2} \\
0 & 0 & \frac{1}{M_1} & \frac{1}{M_2} \\
0 & 0 & 0 & 1
\end{bmatrix}
\quad\text{and}\quad
\delta^2 K_{\mu_e} = \begin{bmatrix}
\frac{1}{M_1} & 0 & 0 & 0 \\
0 & \frac{r_e^2}{M_1} & 0 & \frac{1}{M_2} \\
0 & 0 & 0 & \frac{1}{M_2}
\end{bmatrix}.
\]  

(23)

The eigenvalues of the block \(A\) are solutions of

\[
\lambda^2 - \frac{M_2 s_e^2 (M_1 r_e^2 - M_2 s_e^2)}{M_2 s_e^2 (M_1 r_e^2 + M_2 s_e^2) (M_1 r_e^2)^2} = 0.
\]  

(24)

We observe that for \(M_1 r_e^2 > M_2 s_e^2\) the real part of the eigenvalues differs from zero. We immediately deduce:

**Remark 5.2** A necessary condition for linear stability of an isosceles RE is that \(M_1 r_e^2 < M_2 s_e^2\), or equivalently, that the spin axis of the RE must be its shortest principal axis of inertia.

**Remark 5.3** From the calculations above, we deduce that linear RE may be (Lyapunov or linear) stable.

Finally, we need to calculate the eigenvalues of the remaining block

\[
\begin{bmatrix}
\mathbb{0} & B^{-1} \delta^2 K_{\mu_e} \\
-B^{-1} \delta^2 V_{\mu_e} & \mathbb{0}
\end{bmatrix}\bigg|_{V_{INT}}.
\]  

(25)

### 5.2 The Symplectic Slice method for linear RE

The stability of linear RE is determined using the theoretical findings in [Roberts & al. (2006)] and [Lawson & al. (2011)] that we briefly present below.

Let \(G\) be a Lie group, with Lie algebra \(\mathfrak{g}\), and consider a smooth left action of \(G\) on a finite-dimensional manifold \(Q\), written \((g, q) \mapsto g \cdot q\). For every \(\xi \in \mathfrak{g}\) and \(q \in Q\), the infinitesimal action of \(\xi\) on \(q\) is \(\xi \cdot q = \frac{d}{dt} \exp(t\xi) \cdot q\big|_{t=0}\). The isotropy subgroup of \(q \in Q\) is \(G_q := \{g \in G \mid g \cdot q = q\}\). For three-body \(SO(3)\)-symmetric problems, the action of \(SO(3)\) on the set of linear configurations has a non-trivial isotropy group given by a copy of \(SO(2)\). In our specific case, linear RE configurations \((r_e, s_e)\), \(r_e = (0, r_e, 0)\), \(s_e = (0, 0, 0)\), have isotropy group \(SO(2)\), the subgroup of rotations about the \(Oy\) axis.

The geometric framework for studying simple mechanical systems with configurations space (continuous) isotropy is given by degenerate parametrisations, called *slice coordinates*, for neighbourhoods of the isotropic points. The configuration space in the neighbourhood of an isotropic point is modeled as a twisted product, which is the base space of a principal bundle with fiber the isotropy group of the given point. Denote by \(\mathfrak{g}_{q_e}\) the isotropy Lie algebra of a point \(q_e\) and let \(\mathfrak{g}_{q_e}^\perp\) be a \(G_{q_e}\)-invariant complement of \(\mathfrak{g}_{q_e}\). The slice, \(S\), is a vector space normal to \(\mathfrak{g}_{q_e} \cdot q_e\); locally we have the identification \(Q \cong G \times S\) with \(q_e \cong (e, 0) \in G \times S\) (where \(e\) denotes the identity in \(G\)). Further, \(TQ \cong G \times \mathfrak{g}_{q_e}^\perp \times T^*S\), \(T^*Q \cong G \times (\mathfrak{g}_{q_e}^\perp)^* \times T^*S\), and the dynamics may be expressed in \(\mathfrak{g}_{q_e}^\perp \times T^*S\), or \((\mathfrak{g}_{q_e}^\perp)^* \times T^*S\), respectively, coordinates. In our context, we have \(\mathfrak{g}_{q_e} = so(2)_y\) and \(\mathfrak{g}_{q_e}^\perp = so(2)_{x,z}\) (infinitesimal rotations about \(Ox\) and \(Oz\) axes).

Practically, we apply a change of coordinates that re-organises the dynamics as a coupled system with two parts: a rigid-body-like system corresponding to the invertible part of the locked inertia tensor \(I\), and a simple mechanical system. The metric matrix is re-arranged into a reduced locked inertia \(I_{\text{red}}\) block and a reduced mass \(M_{\text{red}}\) block, the two being coupled by a Coriolis-type term \(C\). Next we write the Lagrangian in these coordinates, pass to the Hamiltonian side and calculate the linearization of the corresponding Hamiltonian system.
We calculate:

\[ S = \{(r, s) = (0, r_e + \sigma_1, 0, \sigma_2, \sigma_3, \sigma_4) \mid \sigma_i \in \mathbb{R}\} \cong \{\sigma \mid \sigma = (\sigma_1, \sigma_2, \sigma_3, \sigma_4) \in \mathbb{R}^4\} \]

\[ \mathbb{I}_{\text{red}}(\sigma) = \begin{bmatrix} M_1(r_e + \sigma_1)^2 + M_2(\sigma_2^2 + \sigma_3^2) & -M_2\sigma_2\sigma_4 \\ -M_2\sigma_2\sigma_4 & M_1(r_e + \sigma_1)^2 + M_2(\sigma_3^2 + \sigma_4^2) \end{bmatrix}, \]

\[ \mathbb{C}(\sigma) = \begin{bmatrix} 0 & 0 & M_2\sigma_4 & M_2\sigma_3 \\ 0 & -M_2\sigma_3 & M_2\sigma_2 & 0 \end{bmatrix}, \]

\[ \mathbb{M}(\sigma) = \begin{bmatrix} M_1 & 0 & 0 & 0 \\ 0 & M_2 & 0 & 0 \\ 0 & 0 & M_2 & 0 \\ 0 & 0 & 0 & M_2 \end{bmatrix} =: \mathbb{M}. \]

Note that the RE \((r_e, s)\) corresponds to \(0 = (0, 0, 0, 0) \in S\). In slice coordinates the Lagrangian (1) becomes \(L : so(3)_{x, z} \times T^*S \rightarrow \mathbb{R}\)

\[ L(\xi_x, \xi_z, \sigma, \dot{\sigma}) = \frac{1}{2} [\xi_x, \xi_z] \mathbb{I}_{\text{red}}(\sigma) \begin{bmatrix} \xi_x \\ \xi_z \end{bmatrix} + [\xi_x, \xi_z] \mathbb{C}(\sigma) \dot{\sigma} + \frac{1}{2} \dot{\sigma}^T \mathbb{M}(\sigma) \dot{\sigma} - V(\sigma). \]

Applying the Legendre transform, the reduced Hamiltonian takes the form \(H : so(3)_{x, z}^* \times T^*S \rightarrow \mathbb{R}\)

\[ H(\mu_x, \mu_z, \sigma, p_\sigma) = \frac{1}{2} [\mu_x, \mu_z] \mathbb{I}_{\text{red}}^{-1}(\sigma) \begin{bmatrix} \mu_x \\ \mu_z \end{bmatrix} + \frac{1}{2} \left( p_\sigma - \mathbb{A}(\sigma) \begin{bmatrix} \mu_x \\ \mu_z \end{bmatrix} \right)^T \mathbb{M}^{-1} \left( p_\sigma - \mathbb{A}(\sigma) \begin{bmatrix} \mu_x \\ \mu_z \end{bmatrix} \right) + V(\sigma) \]

where \(\mathbb{A}(\sigma) = \mathbb{I}_{\text{red}}^{-1}(\sigma) \mathbb{C}(\sigma)\) and \(\mathbb{A}(0) = 0\). Finally, to decide stability, we calculate Hessian \(D_2H(0, 0, 0, 0)\) and, if the later is not positive definite, the spectrum of the linearization of corresponding Hamiltonian system at the equilibrium \((0, 0, 0, 0)\).

### 6 Numerical examples

In this section we determine the RE numerically, verifying the qualitative findings stated in Proposition 4.1 and apply the stability methods presented in the previous section. Then we determining the stability of RE using the above geometric.

As apparent from the previous section, determining the stability of RE involves the second order derivatives of the diatomic potentials at the RE. Specifically, one must consider the relative positions of the critical points and the inflection points (called dissociation distances in chemical-physics terminology), leading to cumbersome classification diagrams. Rather then focusing on such an analysis, we use explicit Lennard-Jones type models.

We consider triatomic molecules with outer atoms with greater, equal and smaller mass then the central atom; we call these \(D_2H, H_3\) and \(H_2D\)-type molecules, respectively.

As mentioned above, the numerical experiments are performed considering Lennard-Jones potentials. For interactions between atoms of different species we adopt the average rule of Lorentz-Berthelot ([Lorentz (1881), Berthelot (1889), Kirchner & al. (2012)]), a rule that states that if atoms of species \(i\) and \(j\) have binary interacting coefficients \(a_{ii}, b_{ii}\) and \(a_{jj}, b_{jj}\), respectively, then the coefficients of the interacting potential between the atoms \(i\) and \(j\) are given by \(a_{ij} := (a_{ii} + a_{jj})/2\) and \(b_{ij} := (b_{ii} + b_{jj})/2\).

In our context, this means that if the binary potential between the identical A atoms is \(V_{AA} = F(r) = -a_{11}/r^6 + b_{11}/r^{12}\) and the binary potential between the identical B atoms is \(V_{BB} = \tilde{F}(r) = -a_{22}/r^6 + b_{22}/r^{12}\)
\[-a_{22}/r^6 + b_{22}/r^{12}\] then \(V_{AB} = G(r) = -(a_{11} + a_{22})/(2r^6) + (b_{11} + b_{22})/(2r^{12})\). Consequently, we calculate
\[
r_e^F = 2^{1/6} \left( \frac{b_{11}}{a_{11}} \right)^{1/6}, \quad l = 5^{1/6} \left( \frac{b_{11}}{a_{11}} \right)^{1/6}, \quad r_e^G = 2^{1/6} \left( \frac{b_{11} + b_{22}}{a_{11} + a_{22}} \right)^{1/6}.
\] (32)

The criteria in Proposition 4.1 become:

1. Condition \(r_e^F \geq 2r_e^G\) (no isosceles RE): \(2^6 \left(1 + \frac{b_{22}}{b_{11}}\right) - 1 \leq \frac{a_{22}}{a_{11}}\)

2. Condition \(r_e^F < 2r_e^G\): \(\frac{a_{22}}{a_{11}} < 2^6 \left(1 + \frac{b_{22}}{b_{11}}\right) - 1\).

(a) Condition \(2r_e^G < l\) (one family of isosceles RE): \(2^7 \left(1 + \frac{b_{22}}{b_{11}}\right) < 5 \left(1 + \frac{a_{22}}{a_{11}}\right)\). Together with the previous condition, this constraints the ratio \(b_{22}/b_{11}\) to

\[
\frac{b_{22}}{b_{11}} \in \left(1 - \frac{5}{2^7} \left(1 + \frac{a_{22}}{a_{11}}\right) - 1\right) = \left(\frac{1}{2^6} \left(1 + \frac{a_{22}}{a_{11}}\right) - 1, \frac{5}{2^7} \left(1 + \frac{a_{22}}{a_{11}}\right) - 1\right)
\]

(b) Condition \(l < 2r_e^G\) (two families of isosceles RE): \(5 \left(1 + \frac{a_{22}}{a_{11}}\right) < 2^7 \left(1 + \frac{b_{22}}{b_{11}}\right)\). which is equivalent to \(\frac{b_{22}}{b_{11}} > \frac{5}{2^7} \left(1 + \frac{a_{22}}{a_{11}}\right) - 1\).

The bifurcations found numerically are in agreement with the qualitative findings of Proposition 4.1. Also, the EM diagrams for the \(H_3\)-type, and the \(D_2H\) and \(H_2D\)-types molecules with chosen parameters fulfilling the \(2(b)\) case conditions of Theorem (4.1) are qualitatively in good agreement with the diagrams of [Kozin & al. (1999)] and [Kozin & al. (2000)]. Note that by Remark 5.1 isosceles RE are never Lyapunov stable.

Figure 6: The EM diagram for \(H_3\)-type molecules, in agreement with the case 2(b) of Proposition 4.1 (see Remark 4.2). The unstable and stable planar linear RE are depicted in blue and green, respectively. The isosceles RE, all unstable, are depicted in violet (color online). We used \(m_A = m_B = 1, a_{11} = a_{22} = 3, b_{11} = b_{22} = 1\).
7 Conclusions

In this paper we study isosceles triatomic “A-B-A” molecules rotating about their symmetry axis. We show that the existence and bifurcations of the rotating steady state solutions may be determined qualitatively assuming the knowledge of shape of the diatomic A-A and A-B potentials and three associated measurable parameters. Consequently, our analysis shows that the RE bifurcations of an A-B-A triatomic molecule are not specified solely by the shape of the diatomic binary potentials A-A and A-B, but additional parameters are required.

We further present two geometric mechanics methods for determining stability. For isosceles RE we employ the REM method of Marsden and co-workers [Marsden (1992)], whereas for linear RE we implement the less-known Symplectic Slice method of Roberts & al. [Roberts & al. (2006)]. We verify our qualitative results and calculate RE stability on some numerical examples using Lennard-Jones -type potentials.
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