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Relative Equilibria of Molecules

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Summary. We describe a method for finding the families of relative equilibria of molecules that bifurcate from an equilibrium point as the angular momentum is increased from 0. Relative equilibria are steady rotations about a stationary axis during which the shape of the molecule remains constant. We show that the bifurcating families correspond bijectively to the critical points of a function h on the two-sphere which is invariant under an action of the symmetry group of the equilibrium point. From this it follows that for each rotation axis of the equilibrium configuration there is a bifurcating family of relative equilibria for which the molecule rotates about that axis. In addition, for each reflection plane there is a family of relative equilibria for which the molecule rotates about an axis perpendicular to the plane.

We also show that if the equilibrium is nondegenerate and stable, then the minima, maxima, and saddle points of h correspond respectively to relative equilibria which are (orbitally) Liapounov stable, linearly stable, and linearly unstable. The stabilities of the bifurcating branches of relative equilibria are computed explicitly for XY_2, X_3, and XY_4 molecules.

These existence and stability results are corollaries of more general theorems on relative equilibria of G-invariant Hamiltonian systems that bifurcate from equilibria with finite isotropy subgroups as the momentum is varied. In the general case, the function h is defined on the Lie algebra dual $\mathfrak{g}^*$ and the bifurcating relative equilibria correspond to critical points of the restrictions of h to the coadjoint orbits in $\mathfrak{g}^*$.

Key words. relative equilibria, molecules, symmetry, symplectic reduction, bifurcation, stability
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Introduction

In the theory of molecular spectra, a molecule is treated as a system of point particles, the atomic nuclei, and electrons, interacting through conservative forces. The resulting mechanical system is impossible to “solve,” even for very simple molecules. For example, the water molecule, H_2O has 3 nuclei and 10 electrons, and hence a 39 dimensional configuration space. Considerable simplification is achieved by applying the Born-Oppenheimer approximation in which the electron motion responds adiabatically to that of the nuclei (see, e.g., [15]). The result is a model for the nuclei alone, interacting via a potential energy function that incorporates the effects of the electrons.

Although considerably simpler than the original model, H_2O now has three particles and a nine-dimensional configuration space, understanding the dynamics of the resulting system is still highly nontrivial. The classical approach to computing and interpreting molecular spectra is based on a further approximation which effectively decouples the vibrational motion of the molecule from the rotational motion. For the rotational motion, the molecule is assumed to maintain a constant shape, namely that of a stable equilibrium position, and to rotate as a rigid body. Both the classical and quantum mechanics of rigid bodies are well understood and the latter gives reasonably accurate predictions of spectra for many “rigid” molecules. The classical mechanics of a rigid body includes among its features motions in which the body rotates about a stationary axis. Such motions are examples of *relative equilibria*. Provided the three principal moments of inertia of the body are all different, there are precisely six of these relative equilibria for each nonzero value of the angular momentum, one rotating in each direction about each of the three principal axes of the inertia tensor.

For a molecule, a relative equilibrium is a motion during which it rotates steadily about a fixed axis, which we call the *dynamical axis,* while the shape remains constant. In this paper we describe an approach to finding families of relative equilibria of molecules that bifurcate from equilibrium configurations as the total angular momentum is increased from zero. We do this for the full Born-Oppenheimer model for the motion of the nuclei. For example, we show that if an equilibrium configuration has distinct principal moments of inertia then, as one would expect, the six relative equilibria of the rigid body approximation persist to this model, together with their stabilities, and these are the only relative equilibria near the equilibrium configuration (Corollary 3.2).

More interesting is the case of molecules near equilibria with either two or all three principal moments of inertia equal, which in the molecular spectroscopy literature are called *symmetric top* and *spherical top* molecules, respectively. In the rigid body approximation, symmetric top molecules have a whole circle of relative equilibria with dynamical axes in the plane spanned by the two principal axes of the inertia tensor with equal moments of inertia. They also have two isolated relative equilibria that are rotations about the other principal axis. Similarly, the spherical top molecules have a sphere of relative equilibria. Indeed, in this case every trajectory of the rigid body approximation is a relative equilibrium. We show that typically in each of these cases only a finite number of these relative equilibria persist in the Born-Oppenheimer model, including the two isolated relative equilibria of symmetric top molecules. In Section 3 of this paper, we show how to calculate these for specific molecules, or rather for specific equilibria of specific molecules: A molecule can have more than one equilibrium, some

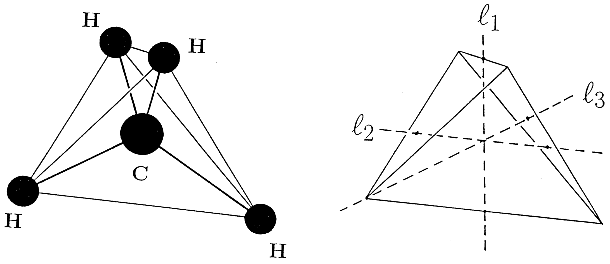

Fig. 1. The methane molecule and its symmetry axes.

stable and some unstable (as noted in Example 1.4), and our analysis applies to each one separately.

For symmetric top and spherical top molecules, the degeneracy of the rigid body approximation is caused by symmetries. The Born-Oppenheimer model is invariant under the action of two groups, the group $\mathbf{O}(3)$ of all orthogonal rotations and reflections of $\mathbf{R}^3$ and the group Σ of all permutations of identical nuclei. We define the *symmetry group* Γ of an equilibrium configuration to be the subgroup of $\mathbf{O}(3) \times \Sigma$ that fixes each nucleus. Its elements are pairs (A, σ) for which the action of the orthogonal transformation A on the equilibrium configuration is the same as that of the permutation σ.

Consider for example the methane molecule CH_4, consisting of four light hydrogen atoms distributed around a central massive carbon atom; see Figure 1. In its equilibrium state, the hydrogen nuclei are positioned at the vertices of a regular tetrahedron. The symmetry group Γ is isomorphic to the subgroup of $\mathbf{O}(3)$, which consists of orthogonal rotations and reflections that map the tetrahedron to itself. Chemists denote this group by $\mathbb{T}_d$. Each of these transformations gives a nontrivial permutation of the hydrogen nuclei, and every such permutation is realised by an element of $\mathbb{T}_d$. Thus Γ is also isomorphic to the symmetric group S_4. Note that in general Γ will be a finite group if and only if the equilibrium configuration is not collinear.

The tetrahedral symmetry of the methane equilibrium configuration forces its inertia tensor to be scalar and so methane is a spherical top molecule and has a whole two-sphere of relative equilibria in the rigid body approximation. These correspond to the tetrahedral configuration rotating about arbitrary axes through the centre of mass of the equilibrium configuration, i.e., the carbon nucleus. In Section 2 we will show that those relative equilibria with dynamical axes corresponding to symmetry axes of the equilibrium configuration persist for the full Born-Oppenheimer Hamiltonian.

More precisely, consider the action of Γ on $\mathbf{R}^3$ determined by its projection into $\mathbf{O}(3)$. Let the *axes of rotation* of Γ be the one-dimensional fixed point sets of the rotations in this projection and the *axes of reflection* the lines through the origin perpendicular to the planes fixed by the reflections. The following result is a consequence of Theorem 2.7, the main theorem of this paper (or of its subsidiary Theorem 2.1), as explained in Example 2.4. The nondegeneracy condition on the equilibrium is described in Section 2.1.

Theorem 0.1. *Consider a molecule with a nondegenerate equilibrium with symmetry group* $\Gamma < \mathbf{O}(3) \times \Sigma$. *There exists* $\mu_0 > 0$ *such that for all* $\mu \in \mathbf{R}^3$ *with* $|\mu| < \mu_0$ *there* *are at least six relative equilibria with angular momentum* μ*. Moreover, for each axis* ℓ *of rotation or reflection in* Γ*, there are two relative equilibria with angular momentum* μ *and dynamical axis* ℓ*, one rotating in each direction.*

The tetrahedral equilibrium of the methane molecule has 13 axes of symmetry, divided into 3 types, and representatives of each type are shown in Figure 1. There are four axes of threefold rotational symmetry joining the carbon nucleus to each of the hydrogen nuclei (denoted ℓ_3 in the figure), three axes of twofold rotational symmetry joining mid-points of opposite edges of the tetrahedron (ℓ_1 in the figure), and six axes of reflection passing through the carbon nucleus, parallel to an edge of the tetrahedron (ℓ_2 in the figure). By the theorem, there are two families of relative equilibria bifurcating from the equilibrium for each of these axes, a total of 26 families. Since this existence result depends only on the tetrahedral symmetry group $\mathbb{T}_d$ of the equilibrium, precisely the same result is true of any other molecule with an equilibrium with the same symmetry group such as P_4 (white phosphorous). Moreover, it turns out that the same symmetry analysis holds for molecules with the cubic or octahedral symmetry group $\mathbb{O}_h$, such as SF_6. On the other hand, the details regarding which of the relative equilibria are stable will depend on the molecule in question.

Theorem 2.7 is a generalization of a result of Montaldi [12] on bifurcations of relative equilibria of Hamiltonian systems given by Hamiltonians H that are invariant under free actions of a group G. In this paper, we relax this by requiring only that the connected component of the identity of G acts freely, and so the isotropy subgroup, Γ, of the equilibrium point from which the relative equilibria are bifurcating is finite. By using a combination of the Moncrief decomposition of the tangent space to a symplectic manifold [11], [13] and the equivariant splitting lemma, we show that a G-invariant Hamiltonian H induces a Γ-invariant function h on $\mathfrak{g}^*$, the dual of the Lie algebra of G, such that the bifurcating relative equilibria are given by the critical points of restrictions of h to the orbits of the coadjoint action of G on $\mathfrak{g}^*$. For a precise statement, see Theorems 2.1 and 2.7.

For molecular Hamiltonians, the symmetry group G is the group $\mathbf{O}(3) \times \Sigma$ described above. The space $\mathfrak{g}^*$ is the space of angular momentum values and is isomorphic to $\mathbf{R}^3$, and the coadjoint action of G is generated by the standard action of $\mathbf{SO}(3)$ on $\mathbf{R}^3$ together with trivial actions of $-I \in \mathbf{O}(3)$ and of Σ. The coadjoint orbits are just the two-spheres centred at the origin in $\mathbf{R}^3$. These are invariant under the action of Γ on $\mathbf{R}^3$ obtained by restricting the action of $\mathbf{O}(3) \times \Sigma$ and the search for bifurcating relative equilibria reduces to finding critical points of Γ-invariant functions h on these spheres. The relative equilibria described in Theorem 0.1 correspond to points on the spheres that are critical points for all Γ-invariant functions h by virtue of being the fixed-point sets of *maximal isotropy subgroups* of the Γ action.

In this paper we also incorporate the effects of the time-reversal symmetry possessed by any Hamiltonian that is the sum of a quadratic kinetic energy function and a potential energy function. This leads to the function h on $\mathfrak{g}^*$ being even (invariant under $\mu \mapsto -\mu$) in addition to being Γ-invariant. In some cases, the presence of this extra symmetry enables us to deduce that there must be extra bifurcating relative equilibria in addition to those predicted by Theorem 0.1. We show that this occurs for XY_3 molecules such as ammonia (NH_3) in Example 2.5.

The results we have described so far give the existence of relative equilibria with particular symmetries and are proved using symmetry considerations alone. To find out whether there are any others, the Taylor series of h at 0 in $\mathfrak{g}^*$ has to be calculated to a sufficiently high order. In Section 3 we describe how to do this for molecular Hamiltonians using the reduced form of the Hamiltonian function H obtained by Eckart in 1935 [4]. In the final subsections this is applied to molecules of type XY_2, XY_4, and X_3. In particular we show that the 26 relative equilibria described above are generically the only relative equilibria that bifurcate from a tetrahedral equilibrium configuration of an XY_4 molecule.

In Section 2 we also give some general results on the stability of the relative equilibria bifurcating from an equilibrium. See Theorem 2.8. For molecular Hamiltonians, these imply that if the equilibrium point is a nondegenerate minimum of the potential energy function, then relative equilibria that correspond to minima of h on the angular momentum spheres are Liapounov stable; those corresponding to maxima are linearly stable; but typically not Liapounov stable, while those corresponding to saddle points are linearly unstable. Here stability is always to be interpreted in an orbital sense [16]. Thus, the calculations of Section 3 also enable us to determine the stabilities of the bifurcating relative equilibria.

The stabilities of the bifurcating relative equilibria are determined by the low-order terms in the Γ-invariant even function h discussed above, and which terms one needs depends upon the symmetry group Γ of the equilibrium. For nonsymmetric molecules where the principal moments of inertia are distinct, the second-order terms of h are sufficient to determine the stabilities. These second-order terms depend only on the inertia tensor of the equilibrium configuration. It follows then that the stabilities are precisely those found in the rigid body approximation discussed above.

In the case of spherical top molecules, for tetrahedral $\mathbb{T}_d$ symmetry, or octahedral $\mathbb{O}_h$ symmetry, the fourth-order terms are required, whereas for icosahedral $\mathbb{I}_h$ symmetry (such as for buckminsterfullerene), the sixth-order terms are required as well. For the symmetric top molecules with dihedral or cyclic symmetry, those with square symmetry require fourth-order terms, while those with triangular or hexagonal symmetry require sixth-order terms.

In terms of physical molecular parameters, the fourth-order terms depend on the so-called *inertia derivatives* (the derivatives of the inertia tensor as a function of shape evaluated at the equilibrium configuration—our $\mathbf{I}_s(0)$, or the $a_k^{\alpha\beta}$ of [1]) together with the harmonic force constants (the quadratic part of the potential energy function). The sixth-order terms of h require in addition knowledge of the Coriolis coupling constants (our matrix $\mathbf{C}$, denoted Z in [20], or the ζ_{ij}^{α} in [1]), the second inertia derivatives, and certain anharmonic force constants (third derivatives of the potential energy function). The quadratic and quartic parts of h are given in closed form in Proposition 3.1, while the degree-six part is computed only for X_3 molecules in Section 3.5.

Using data on molecular parameters taken from a standard textbook on molecular spectroscopy [7], we show, for example, that for methane the six relative equilibria with dynamical axes along the twofold rotation axes are Liapounov stable, the eight relative equilibria with dynamical axes along the threefold rotation axes are linearly stable, and the twelve relative equilibria with dynamical axes along the reflection axes are unstable. This is in agreement with [3], where they also derive these results by considering a function h on two-spheres, although their functions derive from quantum-mechanical considerations. Using more recent data [2], we show in Section 3.5 that for the H_3^+ molecule the relative equilibria with dynamical axis along the twofold rotation axis (ℓ_2 in Figure 3) are linearly unstable, while those with dynamical axis along the reflection axis (ℓ_3 in Figure 3) are linearly stable.

The restriction in Theorem 2.7 to equilibria with finite isotropy subgroups means that our results only apply to bifurcations of relative equilibria from equilibrium configurations that are not collinear. A bifurcation theorem for group actions with nonfinite isotropy subgroups has been obtained by Roberts and Sousa Dias [18]. That paper also contains a brief discussion of relative equilibria bifurcating from collinear equilibrium configurations of molecules.

In this paper, we are concerned only with the classical dynamics of molecular Hamiltonians. If the methods and results are to be applied to molecular spectra, then they must be related to the quantum mechanics, presumably by semiclassical techniques. This is a project for the future. However, we note that some elements of the theory developed here are reminiscent of the work of Harter and Patterson [6] on the spectra of SF_6, and of Pavlichenkov, Zhilinskii, and coworkers, see [17], [19], and the survey [22]. In particular, these methods also generate Γ-invariant functions on angular momentum spheres similar to the functions h of this paper. These are obtained as the classical limits of quantum Hamiltonians restricted to certain finite-dimensional spaces of quantum states, rather than by a purely classical reduction procedure. Moreover, the methods are used to explain observed patterns in high angular momenta spectra, rather than the low angular momentum regime considered in this paper. Nevertheless, we believe that new insights into the structure of ro-vibrational spectra may be obtained by exploring the relationship between these two approaches.

1. Molecules

Consider a molecule consisting of N interacting atoms in $\mathbf{R}^3$. Regarding the atomic nuclei as point masses, the configuration space is $\mathbf{R}^{3N}$, which it is useful to view as

$$\mathcal{C} = \mathbf{R}^N \otimes \mathbf{R}^3 \simeq L(N, 3).$$

Here $L(N, 3)$ is the space of real $3 \times N$ matrices. The N columns of a configuration matrix Q represent the positions q_i of the N nuclei ($i = 1, \ldots, N$). The total phase space is then $\mathcal{P} = T^*\mathcal{C} \simeq \mathbf{R}^{6N}$, which we can identify with the space of pairs (P, Q) of $3 \times N$ matrices. The columns of P are the momenta p_i of the nuclei.

If the mass of the ith nucleus is m_i, the dynamics of the system is given by the Hamiltonian

$$H(p, q) = \sum_i \frac{1}{2m_i} |p_i|^2 + V(q_1, \ldots, q_N),$$

where $V(q_1, \ldots, q_N)$ is the potential energy of the configuration Q due to the electronic bonding between the nuclei. In terms of matrices, we have

$$H(P, Q) = \tfrac{1}{2}\,\mathrm{tr}(P\mathbf{M}^{-1}P^T) + V(Q), \tag{1.1}$$

where $\mathbf{M}$ is the diagonal mass matrix with entries $m_1, \ldots, m_N$. For any motion $Q(t)$, the momentum P is related to the velocity $\dot{Q}$ by

$$P = \dot{Q}\mathbf{M}.$$

The centre of mass of the molecule is given by the sum of the columns of the matrix $Q\mathbf{M}$. If there are no external forces on the molecule, the centre of mass moves in an inertial frame, which we can take to be fixed (corresponding to taking total momentum equal to zero), and we can choose the origin to coincide with the centre of mass. Thus, henceforth, we assume that the sum of the columns of $Q\mathbf{M}$ is zero. That is,

$$\mathcal{C} = L_0(N,3) = \left\{ Q \in L(N,3) \,\middle|\, \sum_j q_{ij} = 0,\ i = 1,2,3 \right\}.$$

Consequently,

$$\mathcal{P} = T^*L_0(N,3) \cong L_0(N,3) \times L_0(N,3).$$

1.1. *Symmetries of the Model*

There are three types of symmetry of this model: Euclidean motions, internal particle relabelling, and time-reversal. These are described below.

Of the Euclidean motions, we have already eliminated the translational component by fixing the centre of mass. Rotation or reflection of the molecule (or change of basis in $\mathbf{R}^3$) by an orthogonal matrix A acts on configuration space $\mathcal{C} = L_0(N,3)$ by multiplication by A on the left: $A \cdot Q = AQ$. In the absence of external forces, this leaves the potential energy invariant.

The relabelling symmetry group can be described as follows. If some of the nuclei are identical, then a finite subgroup Σ of the permutation group S_N acts by permuting the N nuclei, in such a way that for $\sigma \in \Sigma < S_N$, the nuclei i and $\sigma(i)$ are indistinguishable. Thus, $\sigma \in \Sigma$ if and only if

$$V(q_{\sigma(1)}, \ldots, q_{\sigma(N)}) = V(q_1, \ldots, q_N), \qquad m_{\sigma(i)} = m_i, \tag{1.2}$$

for all $(q_1, \ldots, q_N) \in \mathcal{C}$, and all i.

For $\sigma \in \Sigma$, we also denote by σ the associated $N \times N$ permutation matrix, which acts on $\mathcal{C}$ by multiplication by σ^T on the right. Note that this matrix commutes with $\mathbf{M}$, by (1.2).

There is thus an action of $\mathbf{O}(3) \times \Sigma$ on the configuration space $\mathcal{C} = L_0(N,3)$ leaving the potential energy invariant,

$$(A,\sigma) \cdot Q = AQ\sigma^T. \tag{1.3}$$

It is simple to see that the induced action of $\mathbf{O}(3) \times \Sigma$ on $\mathcal{P} = T^*L_0(N,3)$ is a symmetry of the Hamiltonian system, for P transforms in the same way as Q, so that

$$H((A,\sigma)\cdot(P,Q)) = \tfrac{1}{2}\operatorname{tr}\left((AP\sigma^T)\mathbf{M}^{-1}(\sigma P^T A^T)\right) + V(AQ\sigma^T) = H(P,Q),$$

where we have used the fact that $\mathbf{M}$ and σ commute.

Note that the group Σ of relabelling symmetries is not in general the same as the group that is often thought of as being *the* symmetry group of a molecule, namely the symmetry group of its equilibrium configuration. For example, buckminsterfullerene, C_{60}, has Σ equal to S_{60}, but its equilibrium only has icosahedral symmetry $\mathbb{I}_h$. For the symmetry group of a given equilibrium configuration, which we will denote by Γ, see Section 1.2 below.

As with any classical Hamiltonian system of the form 'kinetic + potential', the molecule model is time reversible. That is, H is invariant under the involution

$$\tau : (P, Q) \mapsto (-P, Q).$$

We denote by $\mathbf{Z}_2^\tau$ the group generated by τ. Note that the action of $\mathbf{Z}_2^\tau$ commutes with the action of any group G that is induced from an action on $\mathcal{C}$. In particular, it commutes with the action of $\mathbf{O}(3) \times \Sigma$ described above. Thus, when time reversal is included, the symmetry group of the system becomes $\mathbf{O}(3) \times \Sigma \times \mathbf{Z}_2^\tau$.

One of the important consequences of the $\mathbf{SO}(3)$-symmetry is that angular momentum is conserved. The usual expression for the angular momentum of a system of point masses, $\mathbf{J} = \sum_i q_i \wedge p_i$, here becomes

$$\mathbf{J}(P, Q) = \tfrac{1}{2}(PQ^T - QP^T), \tag{1.4}$$

where we consider angular momentum as a skew-symmetric matrix rather than a vector. In fact, it is naturally an element of the dual space $\mathfrak{so}(3)^*$, but we identify $\mu \in \mathfrak{so}(3)^*$ with a skew-symmetric matrix by the usual formula: $\langle \mu, \xi \rangle = \mathrm{tr}(\mu^T \xi)$. Note that $\mathbf{J}(-P, Q) = -\mathbf{J}(P, Q)$, so that the time-reversal operator reverses angular momentum. For the orthogonal symmetries, $\mathbf{J}(AP, AQ) = A\mathbf{J}(P, Q)A^T$. If we identify the skew-symmetric matrices with vectors in $\mathbf{R}^3$, then this transformation becomes

$$\mathbf{J} \mapsto \det(A)A\mathbf{J}. \tag{1.5}$$

The angular momentum is also invariant under the action of the relabelling symmetry group Σ on the phase space, $\mathbf{J}(P\sigma^T, Q\sigma^T) = \mathbf{J}(P, Q)$. Thus $\mathbf{J}$ is equivariant with respect to the action of $\mathbf{O}(3) \times \Sigma \times \mathbf{Z}_2^\tau$ on phase space defined above and the action on momentum space $\mathfrak{so}(3)^* \cong \mathbf{R}^3$ given by

$$\begin{aligned} (A, \sigma).\mu &= \det(A)A\mu, &(1.6)\\ \tau.\mu &= -\mu. &(1.7)\end{aligned}$$

For $A \in \mathbf{SO}(3)$, the action on μ is just $\mu \mapsto A\mu$, while for $A \in \mathbf{O}(3)\backslash\mathbf{SO}(3)$ the action is $\mu \mapsto -A\mu$, and $-A$ is a rotation about the axis of reflection of A.

1.2. Configuration Symmetries

The symmetry group of a particular configuration Q_0 of a molecule is the *isotropy subgroup* of Q_0 for the action of $\mathbf{O}(3) \times \Sigma$ on configuration space. In other words, it is the subgroup, $\Gamma(Q_0)$, of $\mathbf{O}(3) \times \Sigma$ consisting of elements which map Q_0 to itself:

$$\Gamma(Q_0) = \{(A, \sigma) \in \mathbf{O}(3) \times \Sigma \mid (A, \sigma) \cdot Q_0 = Q_0\}.$$

Note that if Q_1 is a configuration that can be obtained from a configuration Q_0 by applying an element of $\mathbf{O}(3) \times \Sigma$, i.e., $Q_1 = (A, \sigma) \cdot Q_0$, then (A, σ) *conjugates* the isotropy subgroup $\Gamma(Q_0)$ to $\Gamma(Q_1)$:

$$\Gamma(Q_1) = (A, \sigma)\Gamma(Q_0)(A, \sigma)^{-1}.$$

Let $\Gamma = \Gamma(Q_0)$ be an isotropy subgroup. Away from collinear configurations, $\mathbf{SO}(3)$ acts freely. This fact is essential in what follows, and so collinear configurations will not be considered in this paper (see [18] for a brief discussion of them). Moreover, it is clear that a configuration is fixed by an element of $\mathbf{O}(3)\backslash\mathbf{SO}(3)$ if and only if it is planar, and if the planar configuration is not collinear, then the element of $\mathbf{O}(3)$ in question is a reflection. Thus for nonplanar configurations the projection, Γ_2, of $\Gamma < \mathbf{O}(3) \times \Sigma$ into Σ is an isomorphism. For planar noncollinear configurations, Γ is isomorphic to an extension of Γ_2 by the group of order two. In both cases, the group Γ is finite.

Fixed points for the action of the pure relabelling group Σ are not of interest, since they correspond to points where two or more nuclei coincide. However, there are interesting isotropy groups of mixed type, where $\sigma \in \Sigma$ acts in the same way as some $A \in \mathbf{O}(3)$. For example, in the methane molecule at equilibrium (Figure 1), every permutation of the four hydrogen nuclei can be realised by an orthogonal transformation. The same is true of the water molecule. But, as has already been pointed out, it is not true of buckminsterfullerene.

The fact that Σ acts freely on configurations without coincident nuclei implies that the isotropy subgroup of such a configuration is isomorphic to its projection, Γ_1, to $\mathbf{O}(3)$. The *axes of rotation and reflection* of the configuration are, respectively, the axes of rotation (one-dimensional fixed-point spaces) of elements $A \in \Gamma_1 \cap \mathbf{SO}(3)$, and the axes perpendicular to the reflection planes for $A \in \Gamma_1 \cap (\mathbf{O}(3)\backslash\mathbf{SO}(3))$. Note that in the latter case the axis of reflection of A is the axis of rotation of $-A$.

1.3. Examples

We now describe the relative equilibria obtained by applying Theorem 0.1 to a number of different types of small molecules. In the introduction there is a similar discussion of the methane molecules. The stabilities of these relative equilibria will be calculated in Section 3.

Example 1.1 (Planar Molecules). Consider a planar equilibrium configuration of a molecule, for example any equilibrium configuration of a molecule with three atoms. Its symmetry group will contain the element of $\mathbf{O}(3)$ corresponding to reflection in that plane. If the atoms are all different and the configuration is not collinear, then this will be the only symmetry. The groups Γ and Γ_1 are both isomorphic to $\mathbf{Z}_2$ and Γ_2 is trivial. The chemists' notation for this symmetry group Γ is C_s. We denote the reflection itself by r_s. The configuration has one axis of reflection, perpendicular to the plane containing the molecule.

Theorem 0.1 says that these molecules will have two families of bifurcating relative equilibria with dynamical axes equal to the reflection axis, together with at least four more families. In Section 3 (see Corollary 3.2) we will show that generically these

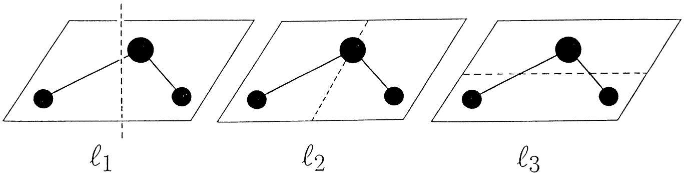

Fig. 2. Axes for the XY_2 molecule.

molecules have precisely six families and that their dynamical axes are close to the principal axes of inertia of the equilibrium configuration. One of these axes coincides with the reflection axis, so in this case the dynamical axis remains equal to the inertia axis.

Example 1.2 (Noncollinear XY_2 Molecules). In addition to the reflection r_s described in the previous example, a configuration of a triatomic molecule with two identical atoms can also be invariant under a reflection in $\mathbf{O}(3)$ through a plane perpendicular to that containing the molecule, combined with permutation of the two identical nuclei. We denote this reflection by r_t and the permutation by π. The composition of the two reflections gives a rotation of order two about the axis defined by the intersection of the two reflection planes. This we denote by ρ. It follows that (ρ, π) is also a symmetry of the configuration. The symmetry group Γ consists of the identity together with the elements (r_s, I), (r_t, π), and (ρ, π), where I is the identity in Σ. The nontrivial elements of the projection Γ_1 are r_s, r_t, and ρ. Both Γ and Γ_1 are isomorphic to $\mathbf{Z}_2 \times \mathbf{Z}_2$. The projection Γ_2 is isomorphic to $\mathbf{Z}_2$ and is generated by π. The chemists' notation for this symmetry group is C_{2v}. There are many molecules with equilibria with this symmetry, including water, H_2O.

This symmetry group has two axes of reflection (ℓ_1 and ℓ_3 in Figure 2) and one of rotation (ℓ_2), all mutually perpendicular. Each of these gives two families of relative equilibria branching from the equilibrium point. Two of the families are similar to those of the previous example: the dynamical axis is the axis of the reflection in the plane containing the molecule.

We will see in Section 3.3 that, generically, these are the only families of relative equilibria that branch from the equilibrium solution.

Example 1.3 (Equilateral X_3 Molecules). A configuration of a molecule with three identical atoms in which the three nuclei lie at the corners of an equilateral triangle has the reflectional symmetry r_s together with three further reflectional symmetries through planes perpendicular to the reflection plane of r_s, each of which must be combined with an appropriate permutation. Composing one of these three reflections with r_s gives a rotation of order two which is also a symmetry when combined with a permutation. In addition, there is an order three rotation about an axis perpendicular to the reflection plane of r_s, again with corresponding permutation. Together these give a symmetry group Γ which is isomorphic to $\mathbf{Z}_2 \times \mathbf{D}_3$ (where $\mathbf{D}_3$ is the dihedral group of order six) and is denoted by chemists by D_{3h}. The projection Γ_2 is equal to $\Sigma = S_3$, which is isomorphic to $\mathbf{D}_3$. An example of a molecule with an equilibrium with this symmetry is the molecular ion H_3^+.

This configuration has three reflectional axes (similar to ℓ_3 in Figure 2), three rotational axes (similar to ℓ_2), and an axis (similar to ℓ_1) that is both rotational (for the rotation of order three) and reflectional (for r_s) . By Theorem 0.1, for low angular momentum an X_3 molecule has 14 relative equilibria rotating about these axes. Again, we will see in Section 3.5 that generically these are the only relative equilibria for sufficiently small values of angular momentum. We will also discuss their stabilities.

Example 1.4 (Ammonia: NH_3). The ammonia molecule consists of one nitrogen atom and three hydrogen atoms and has an equilibrium configuration in which the three hydrogens lie at the corners of an equilateral triangle and the nitrogen lies on the axis of threefold rotational symmetry of the triangle, but not in the same plane. This configuration is therefore nonplanar and its symmetry group Γ, denoted C_{3v} by chemists, is isomorphic to a $\mathbf{D}_3$ subgroup of the previous example. The configuration has one axis of (threefold) rotational symmetry and three axes of reflectional symmetry, and therefore eight bifurcating relative equilibria rotating about these axes.

We will see in Example 2.5 that these are not the only relative equilibria of the ammonia molecule near the equilibrium. There are at least a further six relative equilibria that are not geometric, in the sense that their precise location depends on the form of the interatomic bonding. In fact, their axes lie in the planes containing an N—H bond and the centre of mass. There is thus a total of 14 relative equilibria near the equilibrium for the ammonia molecule.

The ammonia molecule is also interesting because it has two symmetrically related stable equilibria, one with the N atom above the H_3-plane, and one with it below. They are separated by a potential barrier, and between the two stable equilibria there is a planar equilibrium configuration with $\mathbf{Z}_2 \times \mathbf{D}_3$ symmetry. This is the same symmetry group as in Example 1.3, although here the equilibrium is unstable. Each of the stable equilibria will have 14 relative equilibria nearby, as described above, and furthermore the unstable equilibrium will also have 14 relative equilibria nearby, as described in the previous example, since the existence arguments depend only on the symmetry and not on either the number of atoms or the stability of the equilibrium. The potential barrier between the stable equilibria is very low, accounting for the 'inversion flip' seen in ammonia. This means that the local bifurcation analysis performed in this paper is truly local, and the existence of the other equilibria will interfere with extending it to high energy or angular momentum. A more global analysis of ammonia would therefore be useful.

There are other molecules with this C_{3v} symmetry, such as CHD_3, where the potential barrier is very high, and the relative equilibria found by our analysis can be expected to persist to much higher values of the angular momentum.

2. Existence and Stability of Relative Equilibria

Let $\mathcal{P}$ be a symplectic manifold with a symplectic action of a compact Lie group G and a G-equivariant momentum map $\mathbf{J} : \mathcal{P} \to \mathfrak{g}^*$. Let H be a G-invariant smooth Hamiltonian function defined on $\mathcal{P}$. If G acts freely (i.e., the isotropy subgroups are all trivial), then the reduced phase spaces $\mathcal{P}_\mu = \mathbf{J}^{-1}(\mu)/G_\mu$ are themselves symplectic manifolds and the relative equilibria of H in $\mathcal{P}$ are given by the critical points of the induced functions

H_μ on the $\mathcal{P}_\mu$. In [12] it was shown that, near a nondegenerate equilibrium point p of H with $\mathbf{J}(p) = 0$, the critical points of H_μ correspond bijectively to those of a function defined on the coadjoint orbit $G.\mu$.

Essentially the same technique will be used in this paper to find the relative equilibria of molecules. Of course the action of $G = \mathbf{O}(3) \times \Sigma$ on $\mathcal{P}$ described in Section 1.1 is not free. However, away from collinear configurations of molecules, the action of $\mathbf{SO}(3)$ is free and we can reduce by it as in [12]. The new ingredient in this paper is that we then consider the action of the (finite) quotient group $(\mathbf{O}(3) \times \Sigma)/\mathbf{SO}(3) \cong \mathbf{Z}_2 \times \Sigma$ on the reduced spaces.

We also incorporate time-reversal symmetry, restricting for simplicity to the case when $\mathcal{P} = T^*\mathcal{C}$ is a cotangent bundle. In this setting, the reduction procedure can be made more explicit than in the general case. It is also global, as described in [11], although the results in this paper are purely local. In this section, we will work in the general setting of a cotangent action of a compact Lie group G on $\mathcal{P}$ for which the connected component containing the identity, denoted by G_0, acts freely. In the next subsection, we state our main existence theorem for relative equilibria of Hamiltonians that are also invariant under the time-reversal operator $\tau(p, q) = (-p, q)$. We will use $\widehat{G}$ to denote the product $G \times \mathbf{Z}_2^\tau$.

2.1. An Existence Theorem

Let $\mathfrak{g}$ denote the Lie algebra of G and G_0. The momentum map $\mathbf{J} : \mathcal{P} = T^*\mathcal{C} \to \mathfrak{g}^*$ is given by

$$\mathbf{J}_\xi(p, q) = \langle \mathbf{J}(p, q), \xi \rangle = \big\langle p, X_\xi(q) \big\rangle, \tag{2.1}$$

where $\xi \in \mathfrak{g}$ and X_ξ is the vector field corresponding to the action of ξ on $\mathcal{C}$. The angular momentum (1.4) is a special case. A straightforward calculation shows that this commutes with the action of G on $\mathcal{P}$ and the coadjoint action on $\mathfrak{g}^*$. It also commutes with the action of the time-reversal operator τ on $\mathcal{P}$ given by $\tau.(p, q) = (-p, q)$ and its action on $\mathfrak{g}^*$ by $-I$.

Since G_0 is acting freely, the orbit space $\mathcal{P}/G_0$ is a smooth manifold and the momentum map (2.1) is a submersion $\mathcal{P} \to \mathfrak{g}^*$. We denote the G_0-coadjoint orbits by $\mathcal{O}_\mu = G_0.\mu$. The equivariance of the momentum map implies that there is a well-defined *orbit momentum map* $\mathbf{j} : \mathcal{P}/G_0 \longrightarrow \mathfrak{g}^*/G_0$, making the following diagram commute:

$$\begin{tikzcd}
\mathcal{P} \arrow[r, "\mathbf{J}"] \arrow[d] & \mathfrak{g}^* \arrow[d] \\
\mathcal{P}/G_0 \arrow[r, "\mathbf{j}"] & \mathfrak{g}^*/G_0.
\end{tikzcd}$$

That is, $\mathbf{j}$ is defined on $\mathcal{P}/G_0$ by $\mathbf{j}(G_0.x) = G_0.\mathbf{J}(x) = \mathcal{O}_{\mathbf{J}(x)}$. The components of the map $\mathbf{j}$ are Casimirs for the natural Poisson structure on the orbit space. The reduced spaces $\mathcal{P}_\mu$ are, by definition, the fibres of $\mathbf{j}$.

Up to now, we have understood a relative equilibrium to be a trajectory of the dynamics that lies in a group orbit, and any such trajectory has a well-defined momentum μ. Since we are now working in the orbit space $\mathcal{P}/G_0$, it is more natural to take a relative equilibrium to be a G_0-orbit of such trajectories—or equivalently, an invariant G_0-orbit (as in [12]). The momentum of such a relative equilibrium is now a group orbit $\mathcal{O}_\mu$.

As we have only reduced by the G_0 action, and not by the full $\widehat{G}$-action, there is still an action of the finite group $\widehat{G}/G_0$ remaining on $\mathcal{P}/G_0$. The quotient $\widehat{G}/G_0$ also acts on $\mathfrak{g}^*/G_0$, and with respect to these actions, $\mathbf{j}$ is equivariant. Let Π denote the projection

$$\Pi : \widehat{G} \longrightarrow \widehat{G}/G_0,$$

and let $\Pi(\widehat{G})_{\mathcal{O}_\mu}$ denote the isotropy subgroup of $\mathcal{O}_\mu \in \mathfrak{g}^*/G_0$. Then $\Pi(\widehat{G})_{\mathcal{O}_\mu}$ acts on $\mathcal{P}_\mu$. In the case of molecules, where $G_0 = \mathbf{SO}(3)$, the orbit space $\mathfrak{g}^*/G_0$ is a half line, and so $\Pi(\widehat{G})$ acts trivially on $\mathfrak{g}^*/G_0$, so that $\Pi(\widehat{G})_{\mathcal{O}_\mu} = \Pi(\widehat{G})$.

If H is a $\widehat{G}$-invariant Hamiltonian on $\mathcal{P}$, there is an induced $\widehat{G}/G_0$-invariant function on the quotient space $\mathcal{P}/G_0$ that we still denote by H. We denote the restriction of this function to $\mathcal{P}_\mu \subset \mathcal{P}/G_0$ by H_μ. This restriction is $\Pi(\widehat{G})_{\mathcal{O}_\mu}$-invariant.

Let $x = (0, q) \in \mathcal{P}$ be an equilibrium point of H with isotropy subgroup Γ for the G action and $\widehat{\Gamma} = \Gamma \times \mathbf{Z}_2^\tau$ for the $\widehat{G}$ action. Then $G_0.x$ is a critical point of H_0 in $\mathcal{P}_0 \subset \mathcal{P}/G_0$. The group $\widehat{\Gamma}$ acts on $\mathcal{P}/G_0$ via its projection $\Pi(\widehat{\Gamma})$. Since $\widehat{\Gamma} \cap G_0$ is trivial, $\Pi(\widehat{\Gamma})$ is isomorphic to $\widehat{\Gamma}$. The group $\widehat{\Gamma}$ also acts on $\mathfrak{g}^*$ by the restriction of the $\widehat{G}$ action and on $\mathfrak{g}^*/G_0$ by the restriction of the $\Pi(\widehat{G})$ action. Let $\widehat{\Gamma}_{\mathcal{O}_\mu}$ denote the isotropy subgroup of $\mathcal{O}_\mu \in \mathfrak{g}^*/G_0$ for this latter action.

The following theorem is part of the main result of this paper (Theorem 2.7), but it is stated here as it is less technical and already has several useful consequences. Recall that a critical point x of a function f is said to be nondegenerate if the second derivative $d^2f(x)$ is nondegenerate as a quadratic form.

Theorem 2.1. *Suppose that H_0 has a nondegenerate critical point at $G_0.x \in \mathcal{P}_0$. Then there exists a smooth $\widehat{\Gamma}$-invariant function $h : \mathfrak{g}^* \to \mathbf{R}$, such that for each μ the critical points of $h_\mu = h|_{\mathcal{O}_\mu}$ are in 1-1 correspondence with the relative equilibria of H with momentum $\mathcal{O}_\mu$. Moreover, this correspondence is equivariant: If ν is a critical point of h with isotropy $K < \widehat{\Gamma}$, then the corresponding relative equilibrium also has isotropy group K.*

We will see in Theorem 2.7 that the 1-1 correspondence is in fact given by a smooth embedding $\delta : \mathfrak{g}^* \to \mathcal{P}/G_0$ satisfying $\mathbf{j}(\delta(\mu)) = \mathcal{O}_\mu$, and $h = H \circ \delta$. It seems likely that the $\widehat{\Gamma}$-invariance of h can be used to give lower bounds for the number of bifurcating relative equilibria on each nearby momentum level set, generalising the Lusternick-Schnirelman category bound given in [12].

Example 2.2 (Molecules). For the application to molecules described in Section 1, we take $G = \mathbf{O}(3) \times \Sigma$. Then $G_0 = \mathbf{SO}(3)$ and $\mathfrak{g}^* = \mathfrak{so}(3)^* \cong \mathbf{R}^3$. The coadjoint orbits $\mathcal{O}_\mu$ are the two-spheres centred at the origin in $\mathbf{R}^3$. The quotient space $\mathfrak{g}^*/G_0$ is just a half-line and the action of $\Pi(\widehat{G})$ on it is trivial. Hence, $\Pi(\widehat{G})_{\mathcal{O}_\mu} = \Pi(\widehat{G})$ and $\widehat{\Gamma}_{\mathcal{O}_\mu} = \Pi(\widehat{\Gamma})$. In particular, the functions h_μ must be invariant under the action of τ by $-I$ on the two-spheres and so are given by functions on $\mathcal{O}_\mu/\mathbf{Z}_2^\tau \cong \mathbf{RP}^2$, the two-dimensional real projective space. The Lusternick-Schnirelman category of $\mathbf{RP}^2$ is equal to 3, and so the quotient functions must have at least three critical points and the h_μ must have at least six critical points. By Theorem 2.1, these give the six families of relative equilibria claimed in Theorem 0.1. If one assumes that the equilibria of h_μ are nondegenerate, then the Morse inequalities give the same result.

2.2. Symmetric Relative Equilibria

If $\widehat{G}_y$ is the isotropy subgroup for the $\widehat{G}$ action on $\mathcal{P}$ at y, then $\Pi(\widehat{G}_y)$ is the isotropy subgroup for the $\Pi(\widehat{G})$ action on $\mathcal{P}/G_0$ at $G_0.y$. Since G_0 acts freely on $\mathcal{P}$, $\Pi(\widehat{G}_y)$ is isomorphic to $\widehat{G}_y$. If $y_2 = g.y_1$ for some $g \in \widehat{G}$, then $G_{y_2} = gG_{y_1}g^{-1}$ and $\Pi(G_{y_2}) = \Pi(g)\Pi(G_{y_1})\Pi(g)^{-1}$. So, if y_1 and y_2 belong to the same G orbit, the isotropy subgroups of $G_0.y_1$ and $G_0.y_2$ in $\mathcal{P}/G_0$ are conjugate in $\Pi(\widehat{G})$.

In Theorem 2.1, if $\nu \in \mathcal{O}_\mu$ is a critical point of h_μ with isotropy subgroup $K \subset \widehat{\Gamma}_{\mathcal{O}_\mu} \subset \Pi(\widehat{G})$, then the corresponding relative equilibrium in $\mathcal{P}/G_0$ also has isotropy subgroup K and so Π projects the isotropy subgroups of points in the corresponding orbit $G_0.y$ isomorphically to K. The following corollary of Theorem 2.1 predicts the existence of families of relative equilibria with particular isotropy subgroups. We say that an isotropy subgroup K is *maximal* if it is not contained in any other isotropy subgroup.

Corollary 2.3. *With the same hypotheses as in Theorem 2.1, if K is an isotropy subgroup of the action of $\widehat{\Gamma}_{\mathcal{O}_\mu}$ on $\mathcal{O}_\mu$, then there must be at least one family of relative equilibria bifurcating from x with isotropy subgroups that project to a subgroup of $\widehat{\Gamma}_{\mathcal{O}_\mu}$ containing K. If K is a maximal isotropy subgroup, then the isotropy subgroups project isomorphically to K.*

Proof. The fixed-point set of the action of K on $\mathcal{O}_\mu$, denoted $\mathrm{Fix}(K, \mathcal{O}_\mu)$, is a compact smooth manifold and so the restriction of h_μ to it must have a critical point. By the *principle of symmetric criticality* [14], this will also be a critical point of h_μ itself, and will have isotropy subgroup containing K. If K is a maximal isotropy subgroup, then the isotropy subgroup, of the critical point is precisely K. The result now follows from Theorem 2.1 and the remarks above. ☐

Example 2.4 (Rotation and Reflection Axes of Molecules). By Example 2.2 for molecules, we have

$$\widehat{\Gamma}_{\mathcal{O}_\mu} \cong \widehat{\Gamma} \cong \Gamma \times \mathbf{Z}_2^\tau \subset \mathbf{O}(3) \times \Sigma \times \mathbf{Z}_2^\tau.$$

The coadjoint orbits $\mathcal{O}_\mu$ can be identified with the two-spheres centred at the origin in $\mathfrak{so}(3)^* \cong \mathbf{R}^3$. The group $\widehat{\Gamma}$ acts on these by the restriction to $\widehat{\Gamma}$ of the projection of $\mathbf{O}(3) \times \Sigma \times \mathbf{Z}_2^\tau$ to $\mathbf{SO}(3) \times \mathbf{Z}_2^\tau$.

Each rotation and reflection axis ℓ of the equilibrium configuration defines a subgroup K_ℓ of $\widehat{\Gamma}$ which fixes the corresponding axis in $\mathfrak{so}(3)^*$. For a rotation axis, the group K_ℓ contains the rotations about ℓ that map the equilibrium configuration to itself, up to permutations of identical nuclei. For a reflection axis, K_ℓ contains the corresponding reflection. Note that an axis can be both a reflection axis and a rotation axis, in which case K_ℓ contains both types of elements. A rotation or reflection axis ℓ can also be fixed by a reflection in a plane that contains ℓ. In this case, K_ℓ also contains the composition of this reflection with τ.

These subgroups K_ℓ are precisely the maximal isotropy subgroups for the actions of $\widehat{\Gamma}$ on the $\mathcal{O}_\mu$. Each of them has a fixed point set consisting of two points and so h_μ must have two critical points with that isotropy subgroup. These two critical points are equivalent under the $\mathbf{Z}_2^\tau$-action. The corresponding relative equilibria have isotropy subgroups that are conjugate to K_ℓ by rotations in $\mathbf{SO}(3)$. Those with isotropy subgroup equal to K_ℓ correspond to the molecule rotating about the axis ℓ. The conjugate groups are the isotropy subgroups of spatial rotations of these motions.

These remarks complete the proof of Theorem 0.1.

Example 2.5 (Ammonia). As a particular example, we consider the case of ammonia, NH_3. By Example 1.4, the group Γ is isomorphic to $\mathbf{D}_3$. Its projection to $\mathbf{O}(3)$ contains the rotations by $2\pi/3$ about one axis and three reflections with axes perpendicular to the rotation axis. The action of Γ on $\mathcal{O}_\mu \cong S^2$ is by rotations, the 'reflections' in $\mathbf{D}_3$ acting by rotation by π about the corresponding reflection axis. In addition, τ acts by $-I$.

The combined action of $\mathbf{D}_3 \times \mathbf{Z}^\tau$ has four maximal isotropy subgroups, falling into two conjugacy classes. The three corresponding to the reflection axes are isomorphic to $\mathbf{Z}_2$ and are generated by the appropriate reflection.The isotropy subgroup corresponding to the rotation axis contains the rotations by $2\pi/3$ and also the reflections composed with τ. It is therefore isomorphic to $\mathbf{D}_3$. These four maximal isotropy subgroups lead to eight families of relative equilibria, as described above.

In addition to the maximal isotropy subgroups, this action also has three further nontrivial *submaximal* isotropy subgroups. Each of these is isomorphic to $\mathbf{Z}_2$ and is generated by a reflection composed with τ. Their fixed point sets in $\mathfrak{so}(3)^*$ are planes perpendicular to the corresponding reflection axes. The three planes intersect along the threefold rotation axis. In $\mathcal{O}_\mu \cong S^2$ these fixed point sets become circles, each containing the two points fixed by the threefold rotations. The operator τ maps each of these circles to itself and so the restrictions to them of the functions h_μ must have at least four critical points. Thus there must be at least two critical points with each of these submaximal isotropy subgroups. These give at least another three pairs of families of relative equilibria.

2.3. The Moncrief Decomposition

To prove Theorems 2.1 and 2.7, we first describe the local geometry of the reduction process by using a well-known splitting of the tangent space $T_x\mathcal{P}$ (sometimes called the Moncrief decomposition [11]; see also [13] for the more general setting away from $\mathbf{J} = 0$). For $x = (0, q) \in \mathcal{P}$, let

$$W_q := \mathfrak{g}.q \subset T_q\mathcal{C} \subset T_x\mathcal{P}$$

be the tangent space to the group orbit through x. Let

$$\mathcal{S}_q^* := \operatorname{ann}(W_q) \subset T_q^*\mathcal{C} \subset T_x\mathcal{P},$$

where $\operatorname{ann}(W)$ is the annihilator of W in the dual space. Using the kinetic energy metric (or any other G-invariant Riemannian metric on $\mathcal{C}$), we put

$$\mathcal{S}_q := (W_q)^\perp \subset T_q\mathcal{C} \subset T_x\mathcal{P},$$

$$Z_q := \operatorname{ann}(S_q) \subset T_q^*\mathcal{C} \subset T_x\mathcal{P}.$$

We have explicitly identified $T_q^*\mathcal{C}$ with a subset of $T_x\mathcal{P}$, which is allowed since $T_q^*\mathcal{C} \simeq T_x(T_q^*\mathcal{C}) \subset T_x\mathcal{P}$. The space $\mathcal{S}_q$ is a slice to the G-action on $\mathcal{C}$.

Note that the pairing of $T_q^*\mathcal{C}$ with $T_q\mathcal{C}$ identifies $\mathcal{S}_q^*$ with the dual of $\mathcal{S}_q$ (hence the notation), and Z_q with the dual of W_q. Finally, define

$$Y_q := \mathcal{S}_q \oplus \mathcal{S}_q^*. \tag{2.2}$$

The space $Y_q \subset T_x\mathcal{P}$ is called the *symplectic slice* for the G-action at x (denoted $\mathcal{S}$ by Marsden [11]). Note also that since the Riemannian metric was assumed to be G-invariant, the spaces $W_q, \mathcal{S}_q^*, \mathcal{S}_q, Z_q$ are G_q-invariant. We have an isomorphism of G_q-representations:

$$T_x\mathcal{P} \cong W_q \oplus Y_q \oplus Z_q. \tag{2.3}$$

The time-reversal operator τ fixes $x = (0, q)$ and so also acts on $T_x\mathcal{P}$. With respect to the decomposition given by (2.2) and (2.3), the action is

$$\tau(w, s, \sigma, z) = (w, s, -\sigma, -z).$$

The symplectic form on this decomposition is given by

$$\omega((w_1, s_1, \sigma_1, z_1),\ (w_2, s_2, \sigma_2, z_2)) = \langle z_2, w_1\rangle - \langle z_1, w_2\rangle + \langle \sigma_2, s_1\rangle - \langle \sigma_1, s_2\rangle.$$

Consequently (or by differentiating (2.1)), the linear part of the momentum map at $x = (0, q)$ is given by

$$\left\langle d\mathbf{J}_{(0,q)}(w, s, \sigma, z), \xi\right\rangle := \omega(X_\xi(0, q), (w, s, \sigma, z)) = \left\langle z, X_\xi(q)\right\rangle. \tag{2.4}$$

The main properties of this decomposition of $T_x\mathcal{P}$ are given in the following proposition.

Proposition 2.6. *For a free action of G_0, we have the following isomorphisms of $G_q \times \mathbf{Z}_2^\tau$ representations*

$$\begin{aligned} W_q &\simeq \mathfrak{g}, \\ Z_q &\simeq \mathfrak{g}^*, \\ Y_q &\simeq T_qQ/\mathfrak{g} \oplus (T_qQ/\mathfrak{g})^*. \end{aligned}$$

Here G_q acts on $\mathfrak{g}$ by the adjoint representation and on $\mathfrak{g}^*$ by the coadjoint representation. The group $\mathbf{Z}_2^\tau$ acts on both spaces by $-I$. The linear part $d\mathbf{J}_x$ of the momentum map at $x = (0, q)$ provides the isomorphism $d\mathbf{J}_x : Z_q \xrightarrow{\sim} \mathfrak{g}^*$.

Proof. The isomorphisms are immediate consequences of the definitions. For example, the first one is provided by $\mathfrak{g} \to W_q, \xi \mapsto X_\xi(q)$; that it is a $G_q \times \mathbf{Z}_2^\tau$ isomorphism is just the fact that the $G \times \mathbf{Z}_2^\tau$-action is indeed an action. The second part follows immediately from (2.4). ☐

We can use the Moncrief decomposition to give a local description of the reduced spaces $\mathcal{P}_\mu$ in a neighbourhood of $x = (0, q)$. The isotropy subgroup of $\widehat{G}$ at x is $\widehat{\Gamma} \cong \Gamma \times \mathbf{Z}_2^\tau$. Since $T_x(G_0.x) = W_q$, the orbit map $\pi : \mathcal{P} \to \mathcal{P}/G_0$ defines a $\widehat{\Gamma}$-equivariant isomorphism,

$$d\pi_x : Y_q \oplus Z_q \xrightarrow{\sim} T_{\pi(x)}(\mathcal{P}/G_0).$$

Moreover, the momentum map (2.1) is a submersion $\mathcal{P} \to \mathfrak{g}^*$, so we can use the $\widehat{G}$-invariant Riemannian metric to identify $Y_q \subset \ker(d\mathbf{J}_x)$ with a $\widehat{\Gamma}$-invariant submanifold of $\mathbf{J}^{-1}(0)$ transverse to the G_0-orbit, which we also denote Y_q. We can similarly identify Z_q with a submanifold of $\mathcal{P}$ transverse to $\mathbf{J}^{-1}(0)$, which is also denoted Z_q. Then $\pi : Y_q \times Z_q \to \mathcal{P}/G_0$ is a $\widehat{\Gamma}$-equivariant isomorphism onto its image, a neighbourhood of x. Moreover, the restriction of $\mathbf{J}$ to Z_q is also an isomorphism onto its image, and we have

$$\begin{aligned} \mathbf{j} : Y_q \times \mathfrak{g}^* &\longrightarrow \mathfrak{g}^*/G_0, \\ (y\,,\ \nu) &\mapsto \mathcal{O}_\nu, \end{aligned}$$

where we have used $\mathbf{J}$ to identify Z_q with $\mathfrak{g}^*$. Thus, in a neighbourhood of the point $x = (0, q)$,

$$\mathcal{P}_\mu = \mathbf{j}^{-1}(\mathcal{O}_\mu) \cong \left\{(y, \nu) \in Y_q \times \mathfrak{g}^* \mid \nu \in \mathcal{O}_\mu\right\} = Y_q \times \mathcal{O}_\mu. \tag{2.5}$$

This isomorphism is equivariant with respect to the natural actions of $\widehat{\Gamma}_\mu$, the isotropy subgroup at μ for the action of $\widehat{\Gamma}$ on $\mathfrak{g}^*$. The symplectic slice Y_q has a natural symplectic structure induced from that on $T_x\mathcal{P}$, and the isomorphism between $\mathcal{P}/G_0$ and $Y_q \times \mathfrak{g}^*$ identifies the natural Poisson structure on $\mathcal{P}/G_0$ with the product Poisson structure on $Y_q \times \mathfrak{g}^*$. For more details see [12], [18].

The G-equivariant, time-reversible flow generated by a $\widehat{G}$-invariant Hamiltonian function H on $\mathcal{P}$ induces a flow on each of the reduced spaces $\mathcal{P}_\mu$ that commutes with the action of $\Pi(G_\mu)$ and is time-reversible with respect to the action of elements of $\Pi(\widehat{G}_\mu)\backslash\Pi(G_\mu)$. This flow is generated by the restriction to $\mathcal{P}_\mu$ of the function on $\mathcal{P}/G_0$ induced by H. We will denote this *reduced Hamiltonian* by H_μ. In the neighbourhood of a point $x = (0, q)$, identifying $\mathcal{P}/G_0$ with $Y_q \times \mathfrak{g}^*$ enables us to identify the induced function on $\mathcal{P}/G_0$ with a $\widehat{\Gamma}$ invariant function on $Y_q \times \mathfrak{g}^*$ and the reduced Hamiltonians H_μ with the restrictions of this function to the symplectic manifolds $Y_q \times \mathcal{O}_\mu$. Explicit forms for the reduced Hamiltonians H_μ for molecular Hamiltonians are obtained in Section 3. The method used there extends in a straightforward way to any Hamiltonian that is the sum of a nondegenerate quadratic kinetic energy function and a potential energy function.

2.4. Main Theorem

Let $H : \mathcal{P} \to \mathbf{R}$ be a $\widehat{G} = G \times \mathbf{Z}_2^\tau$-invariant function, where G is a compact Lie group acting on $\mathcal{C}$ and by the lift of this action on $\mathcal{P} = T^*\mathcal{C}$, and $\mathbf{Z}_2^\tau$ acts as above. Suppose that G_0, the connected component of the identity of G, acts freely on $\mathcal{P}$ in a neighbourhood of an orbit $G_0.x$ where $x = (0, q)$. From Section 2.3, near $G_0.x$ we have a $\widehat{\Gamma}$-equivariant isomorphism $P/G_0 \simeq Y \oplus Z$ where Y is a symplectic slice at x and $Z \simeq \mathfrak{g}^*$. This isomorphism restricts to symplectic isomorphisms of reduced phase spaces, $\mathcal{P}_\mu \simeq Y \times \mathcal{O}_\mu$.

The dynamics on P/G_0 are determined by the $\Pi(\widehat{G})$-invariant quotient function $H : P/G_0 \to \mathbf{R}$. The relative equilibria with momentum μ are given by the critical points of the restriction $H_\mu = H|_{P_\mu}$. Using the identifications described in Section 2.3, we can regard H_{G_0} as a $\widehat{\Gamma}$-invariant function on $Y \oplus \mathfrak{g}^*$ and H_μ as a $\widehat{\Gamma}_\mu$-invariant function on $Y \oplus \mathcal{O}_\mu$.

Remark. Although for simplicity we have restricted attention to the cotangent bundle setting, the theorem below holds under the more general setting of an arbitrary symplectic manifold with a locally free 'pseudo-symplectic' action of a compact Lie group $\widehat{G}$ (that is, $g^*\omega = \pm\omega$ for each $g \in \widehat{G}$). This is because the Moncrief decomposition is still valid, although it is not defined in the same manner; see, for example, [12], [13], or [18].

Theorem 2.7. *Suppose that H_0 has a nondegenerate critical point at $G_0.x \in \mathcal{P}_0$. Identifying $\mathcal{P}/G_0$ with $Y \times \mathfrak{g}^*$, there is a smooth map $\delta : \mathfrak{g}^* \to \mathcal{P}/G_0$ of the form $\delta(\mu) = (\delta_1(\mu), \mu)$ such that the condition*

$$d_y H(y, \mu) = 0 \tag{2.6}$$

is satisfied if and only if $y = \delta_1(\mu)$. Let $h = H \circ \delta : \mathfrak{g}^* \to \mathbf{R}$. Then,

1. *$\nu \in \mathcal{O}_\mu$ is a critical point of $h_\mu = h|_{\mathcal{O}_\mu}$ if and only if $\delta(\nu) \in \mathcal{P}/G_0$ is a relative equilibrium for H, and moreover every relative equilibrium is of this form. (This implies Theorem 2.1.)*
2. *There exists a $\widehat{\Gamma}$- equivariant diffeomorphism Φ of $\mathcal{P}/G_0$ of the form*

   $$\Phi(y, \mu) = (\phi(y, \mu), \mu),$$

   satisfying

   $$H \circ \Phi(y, \mu) = Q(y) + h(\mu),$$

   where $Q(y) = \frac{1}{2} d^2 H_0(0)$ is a nondegenerate quadratic form.
3. *If the identification of $\mathcal{P}/G_0$ with $Y \times \mathfrak{g}^*$ is such that $d^2 H(0, 0)$ splits (that is, all the mixed partial derivatives vanish: $\frac{\partial^2 H}{\partial y_i \partial \mu_j}(0, 0) = 0$), then δ_1 is of order $O(\mu^2)$ and the linear approximation to Φ at $(0, 0)$ can be chosen to be the identity.*

Here and elsewhere we write $O(\mu^k)$ to mean $O(\|\mu\|^k)$ for the vector variable μ.

Note that although Φ decouples the reduced Hamiltonian into a sum of independent functions on Y and $\mathcal{O}_\mu$, it does not preserve the natural product symplectic structure on $Y \times \mathcal{O}_\mu$, so the corresponding vector field is not decoupled.

Proof. For the purposes of this proof, we write $H|_\mu$ for $H|_{Y \times \{\mu\}}$. This is not to be confused with $H_\mu = H|_{Y \times \mathcal{O}_\mu}$.

First note that since $dH_0(0) = 0$ and $Q := \frac{1}{2}d^2H_0(0)$ is nondegenerate, it follows from the implicit function theorem that for each sufficiently small μ there is a unique point $\delta_1(\mu)$ near $y = 0$ such that $dH|_\mu(\delta_1(\mu)) = 0$. We put $\delta(\mu) = (\delta_1(\mu), \mu)$.

The theorem follows essentially from the equivariant splitting lemma, or equivariant parametrized Morse lemma. For μ near 0, we have a function $H|_\mu$ with a nondegenerate critical point at $y = \delta_1(\mu)$, so by the equivariant Morse lemma, there is an equivariant diffeomorphism $y \mapsto \phi_\mu(y)$ such that $H|_\mu \circ \phi_\mu = Q + const$, where $const$ is a constant depending on μ, and is just the value of $H|_\mu$ at $\delta(\mu) = \phi_\mu(0)$. The point of the equivariant splitting lemma is that this procedure can be carried out smoothly and equivariantly in μ. The constant depending on μ is also smooth and is equal to $h(\mu)$. Writing $\Phi(y, \mu) = (\phi_\mu(y), \mu)$, we have part (2) of the theorem.

For part (3), if d^2H splits, then H is already in the desired form up to order two, and so the linear part of δ_1 vanishes and the linear part of Φ can be chosen equal to the identity.

For part (1), let $\nu \in \mathcal{O}_\mu$. The function $H_\mu = H|_{Y \times \mathcal{O}_\mu}$ has a critical point at (y, ν) if and only if the derivatives of H_μ with respect to the y-variables and the $\mathcal{O}_\mu$-variables vanish. The first condition is by definition equivalent to $y = \delta_1(\nu)$, and the second is then equivalent to ν being a critical point of h_μ, as required. Indeed,

$$dh_\mu(\nu) = d(H_\mu \circ \delta)(\nu) = d_yH_\mu(\delta(\nu)).d\delta_1(\nu) + d_\nu H_\mu(\delta(\nu)),$$

and by definition d_yH_μ vanishes at $\delta(\nu)$. Since critical points of H_μ are relative equilibria for H with momentum μ (or $\mathcal{O}_\mu$), the result is proved. □

2.5. *Stability of Relative Equilibria*

In this subsection we relate the stability of a relative equilibrium near the orbit $G_0.(0, q)$ with momentum μ to the Morse type of the corresponding critical point of the function h_μ on the coadjoint orbit $\mathcal{O}_\mu$.

Recall that a relative equilibrium with $\mathbf{J} = \mu$ is an equilibrium point of the flow on $Y \times \mathcal{O}_\mu$ generated by H_μ. A critical point ν_0 of h_μ corresponds to a relative equilibrium $\delta(\nu_0) = (\delta_1(\nu_0), \nu_0)$.

In practice, the critical points of the functions h_μ occur in smooth families bifurcating from 0 as $||\mu||$ increases. We therefore assume that $\nu_0 = \nu_0(s)$ and $\mu = \mu(s)$ are continuous curves in $\mathfrak{g}^*$ such that $||\mu(s)|| = s$ and $\nu_0(s) \in \mathcal{O}_{\mu(s)}$ is a critical point of $h_{\mu(s)}$.

Recall that $Q = \frac{1}{2}d^2H_0(0)$ (as in Theorem 2.7). The linearization near the equilbrium is thus given by $L_0 = 2J_Y(0)Q$. The following theorem relates the stability of nearby relative equilibria to the stability of L_0 and the type of critical point of h_μ at ν_0. Recall also that an infinitesimally symplectic matrix L is said to be

- *spectrally stable* if all its eigenvalues are purely imaginary,
- *linearly stable* if it is spectrally stable and semisimple, and
- *strongly stable* if it lies in the interior of the set of linearly stable, infinitesimally symplectic matrices.

In particular, $L_0 = 2J_Y(0)Q$ is strongly stable if Q is definite. If the Hamiltonian function H is of the "kinetic energy + potential energy" type, then this is equivalent to the orbit $G_0.x$ of equilibrium points being a nondegenerate critical orbit of local minima of the potential energy function. If the orbit is a nondegenerate saddle or maximum, then L_0 is unstable.

Theorem 2.8. *The following statements hold for* $\nu_0 = \nu_0(s)$ *and* $\mu = \mu(s)$ *when* s *is sufficiently small.*

1. *If* Q *is positive-definite and* ν_0 *is a strict local minimum of* h_μ*, then* $\delta(\nu_0)$ *is Liapounov stable.*
2. *If* L_0 *is unstable, then* $\delta(\nu_0)$ *is linearly and nonlinearly unstable.*
3. *If* L_0 *is strongly stable and the coadjoint orbits in* $\mathfrak{g}^*$ *are two-dimensional, then* $\delta(\nu_0)$ *is*
   - (a) *strongly stable (elliptic) if* ν_0 *is a nondegenerate local extremum of* h_μ*;*
   - (b) *linearly and nonlinearly unstable (hyperbolic) if* ν_0 *is a nondegenerate saddle point of* h_μ*.*

Proof. Recall that there exists a change of coordinates Φ on $Y \times \mathfrak{g}^*$ such that

$$H_\mu(\Phi(y, \nu)) = Q(y) + h_\mu(\nu).$$

If Q is positive-definite and ν_0 is a strict local minimum of h_μ, then $(0, \nu_0)$ is a strict local minimum of $Q(u) + h_\mu(\nu)$. This property is preserved by the diffeomorphism Φ and so $\delta(\nu_0)$ is a strict local minimum of H_μ. It must therefore be Liapounov stable. This proves part (1).

For the remaining statements, we need to estimate the eigenvalues of the linearization of the vector field at $\delta(\nu_0)$ generated by H_μ. This satisfies

$$L(\delta(\nu_0)) = J(\delta(\nu_0))d^2H_\mu(\delta(\nu_0)), \tag{2.7}$$

where $J(\delta(\nu_0))$ is the Poisson structure on $Y \times \mathcal{O}_\mu$ at $(\delta(\nu_0))$. From Section 2.3, this is the product structure

$$J(\delta(\nu_0)) = \begin{pmatrix} J_Y(\delta_1(\nu_0)) & 0 \\ 0 & J_\mu(\nu_0) \end{pmatrix},$$

where J_Y is the Poisson structure on Y given by its symplectic form and J_μ is the restriction to $\mathcal{O}_\mu$ of the natural Poisson structure on $\mathfrak{g}^*$,

$$J_\mu(\nu_0)\xi = ad^*_\xi \nu_0. \tag{2.8}$$

As $s \to 0$, we have

$$J_Y(\delta_1(\nu_0(s))) \to J_Y(0); \qquad J_\mu(\nu_0(s)) \to 0,$$

and

$$L(\delta(\nu_0(s))) \to L(0) = L_0 \oplus 0.$$

The nondegeneracy of Q implies that the eigenvalues of L_0 are nonzero. The eigenvalues of $L(\delta(\nu_0(s)))$ therefore form two distinct groups, those that are perturbations of eigenvalues of L_0 and those that are perturbations of 0.

If L_0 is unstable, then it has eigenvalues with nonzero real part, and hence so must $L(\delta(\nu_0(s)))$ for sufficiently small s. This proves part (2).

If L_0 is strongly stable, then its eigenvalues all lie on the imaginary axis, as do the eigenvalues of any small perturbation of L_0. It follows that the corresponding eigenvalues of $L(\delta(\nu_0(s)))$ will remain on the imaginary axis for all sufficiently small s. To complete the proof of the theorem we need to determine what happens to the eigenvalues that perturb from zero.

The change of coordinates Φ transforms $d^2H_\mu(\delta(\nu_0(s)))$ to $2Q \oplus d^2h_{\mu(s)}(\nu_0(s))$. If $\nu_0(s)$ is a nondegenerate critical point of $h_{\mu(s)}$, then $2Q \oplus d^2h_{\mu(s)}(\nu_0(s))$ will be nondegenerate and hence so will $d^2H_{\mu(s)}(\delta(\nu_0(s)))$. It follows that for $s \neq 0$ there will be no eigenvalues of $L(\delta(\nu_0(s)))$ at zero. If the coadjoint orbits are two-dimensional, there are only two possibilities, either the two eigenvalues of $L(0)$ at zero perturb to a real pair or to an imaginary pair. The first will happen if and only if $d^2H_\mu(\delta(\nu_0(s)))$ has a single negative eigenvalue while the second possibility occurs if it has either zero or two negative eigenvalues. The number of negative eigenvalues of $d^2H_\mu(\delta(\nu_0(s)))$ is preserved by the coordinate change Φ and so is equal to the number of negative eigenvalues of $2Q \oplus d^2h_{\mu(s)}(\nu_0(s))$. This is one if $\nu_0(s)$ is a nondegenerate saddle point and two if it is a nondegenerate maximum and zero if it is a nondegenerate minimum. This completes the proof of part (3). ☐

For the proof of part (3) of the Theorem, it was necessary to restrict to cases (such as $\mathfrak{g}^* = \mathfrak{so}(3)^*$) for which the coadjoint orbits are two-dimensional. For higher dimensional cases the number of negative eigenvalues of $d^2H_\mu(\delta(\nu_0))$ is not sufficient to determine whether the eigenvalues of $L(\delta(\nu_0(s)))$ that perturb from zero remain on the imaginary axis or not.

3. Calculating Relative Equilibria

To calculate exactly how many families of relative equilibria bifurcate from an equilibrium, and to determine their stabilities, we need to go beyond symmetry considerations and use an explicit form for the Hamiltonian. The standard reduced Hamiltonian for molecules near noncollinear equilibria was established by C. Eckart in 1935 [4]. We describe this in the next subsection, following very closely the exposition of Sutcliffe [20] (though changing the notation somewhat). See also [1], [10]. Then we show how the splitting lemma can be applied to compute the Taylor series of the function h on momentum space $\mathfrak{so}(3)^*$. In the final subsections, we apply this to a number of examples.

3.1. Reduction to the Eckart Hamiltonian

Consider a molecular equilibrium configuration $Q_0 \in \mathcal{C} = L_0(N,3)$. The kinetic energy is given by

$$T = \tfrac{1}{2}\,\mathrm{tr}(\dot{Q}\mathbf{M}\dot{Q}^T).$$

This defines an $\mathbf{O}(3)\times\Sigma$-invariant Riemannian metric on $\mathcal{C}$, which at $Q\in\mathcal{C}$ is given by

$$\left\langle \widehat{Q}_1,\,\widehat{Q}_2\right\rangle_Q=\operatorname{tr}(\widehat{Q}_1\mathbf{M}\widehat{Q}_2^T),\tag{3.1}$$

for $\widehat{Q}_1,\,\widehat{Q}_2\in T_Q\mathcal{C}$. The subscript Q on the metric is redundant, but is kept to distinguish the metric from other pairings. Using this metric, we choose the slice $\mathcal{S}$ in $\mathcal{C}$ to the $\mathbf{SO}(3)$ orbit through Q_0 to be the affine linear subspace of $\mathcal{C}$ through Q_0 orthogonal to $\mathfrak{so}(3).Q_0$. That is,

$$\mathcal{S}:=\left\{S\in\mathcal{C}\mid\langle\Omega Q_0,(S-Q_0)\rangle_{Q_0}=0,\ \forall\Omega\in\mathfrak{so}(3)\right\}.$$

Choosing the slice to be orthogonal to the group orbit ensures that the Coriolis interaction matrix $\mathbf{C}$ below vanishes at the equilibrium; this is called the *Eckart condition* in the molecular spectroscopy literature. Note that since the metric is $\mathbf{SO}(3)$-invariant, it follows that $\langle\Omega Q_0,\,Q_0\rangle_{Q_0}=0$, whence $0\in\mathcal{S}$ and $\mathcal{S}$ is a linear subspace of $\mathcal{C}$. Consequently, the definition of $\mathcal{S}$ can be replaced by the simpler expression,

$$\mathcal{S}=\left\{S\in\mathcal{C}\mid\langle\Omega Q_0,S\rangle_{Q_0}=0,\ \forall\Omega\in\mathfrak{so}(3)\right\}.\tag{3.2}$$

By the slice theorem, any point in $\mathcal{C}$ can be decomposed as a product of matrices,

$$Q=AS,\qquad A\in\mathbf{SO}(3),\qquad S\in\mathcal{S}.$$

Any motion $Q(t)$ has a corresponding decomposition, which differentiates to give

$$\dot{Q}=\dot{A}S+A\dot{S}=A(\Omega S+\dot{S}),$$

where $\Omega=A^{-1}\dot{A}$. The kinetic energy is then given by

$$T=\tfrac{1}{2}\operatorname{tr}(\Omega\mathcal{E}\Omega^T)+\tfrac{1}{2}\operatorname{tr}(\dot{S}\mathbf{M}\dot{S}^T)+\operatorname{tr}(\Lambda\Omega),$$

where

$$\begin{aligned}\mathcal{E}&=S\mathbf{M}S^T,\\ \Lambda&=\tfrac{1}{2}(S\mathbf{M}\dot{S}^T-\dot{S}\mathbf{M}S^T).\end{aligned}$$

Note that the *inertia dyadic* $\mathcal{E}$ is symmetric, while Λ is skew-symmetric. Note also that, with the choice of slice $\mathcal{S}$ we have made, if $S=Q_0\in\mathcal{S}$ then $\Lambda=0$ (for all $\dot{S}$) by (3.2).

We now introduce coordinates on $\mathcal{S}$ by fixing a basis of matrices $\{S_1,\dots,S_n\}$ and putting $S=\sum_i s_iS_i$. Let $\mathcal{E}_{ij}=S_i\mathbf{M}S_j^T$, and define n^2 symmetric matrices E_{ij}, n^2 skew-symmetric matrices Z_{ij}, and an $n\times n$ matrix $\mathbf{N}=(\mathbf{N}_{ij})$ by

$$\begin{aligned}E_{ij}&=\tfrac{1}{2}(\mathcal{E}_{ij}+\mathcal{E}_{ji}),\\ Z_{ij}&=\tfrac{1}{2}(\mathcal{E}_{ij}-\mathcal{E}_{ji}),\\ \mathbf{N}_{ij}&=\operatorname{tr}\mathcal{E}_{ij}.\end{aligned}$$

These are all constant matrices, depending only on the choice of basis in the slice $\mathcal{S}$, and

$$\begin{aligned} \mathcal{E} &= \sum_{ij} s_i s_j E_{ij}, \\ \Lambda &= \sum_{ij} s_i \dot{s}_j Z_{ij}. \end{aligned}$$

We will also find it more convenient to identify skew-symmetric matrices with vectors in $\mathbf{R}^3$ in the usual way. If Ω is identified with ω, then we define matrices $\mathbf{I}$ and $\mathbf{C}$ by identifying $\frac{1}{2}(\mathcal{E}\Omega + \Omega\mathcal{E})$ with $\mathbf{I}\omega$ and $\mathrm{tr}(\Lambda\Omega)$ with $\omega^T \mathbf{C}\dot{s}$. Then $\mathbf{I}$ is a symmetric 3×3 matrix, the *inertia tensor,* and $\mathbf{C}$ is a $3 \times n$ matrix that gives the *Coriolis interaction* between the vibrational and rotational dynamics. Note that $\mathbf{I}$ depends quadratically on s, while $\mathbf{C}$ is linear and vanishes at the equilibrium configuration. In terms of these coordinates, the kinetic energy becomes

$$T = \tfrac{1}{2}\omega^T \mathbf{I}\omega + \tfrac{1}{2}\dot{s}^T \mathbf{N}\dot{s} + \omega^T \mathbf{C}\dot{s}. \tag{3.3}$$

To put this into Hamiltonian form, we introduce the momentum variables μ and σ conjugate to ω and s, respectively. These can be expressed in terms of the other coordinates by

$$\begin{aligned} \mu &= \frac{\partial T}{\partial \omega} = \mathbf{I}\omega + \mathbf{C}\dot{s}, \\ \sigma &= \frac{\partial T}{\partial \dot{s}} = \mathbf{N}\dot{s} + \mathbf{C}^T \omega. \end{aligned}$$

Eliminating $\dot{s}$ from these equations gives

$$\mu = \mathbf{K}^{-1}\omega + \pi,$$

where

$$\begin{aligned} \mathbf{K} &= (\mathbf{I} - \mathbf{C}\mathbf{N}^{-1}\mathbf{C}^T)^{-1}, \\ \pi &= \mathbf{C}\mathbf{N}^{-1}\sigma. \end{aligned}$$

Substituting for ω and $\dot{s}$ in equation (3.3) gives the Hamiltonian form for the kinetic energy

$$T = \tfrac{1}{2}(\mu - \pi)^T \mathbf{K}(\mu - \pi) + \tfrac{1}{2}\sigma^T \mathbf{N}^{-1}\sigma. \tag{3.4}$$

The full $\mathbf{SO}(3)$ reduced Hamiltonian is obtained from this by simply adding the potential energy function $V(s)$, restricted to the slice $\mathcal{S}$,

$$H(\mu, s, \sigma) = \tfrac{1}{2}(\mu - \pi)^T \mathbf{K}(\mu - \pi) + \tfrac{1}{2}\sigma^T \mathbf{N}^{-1}\sigma + V(s). \tag{3.5}$$

This is a function of μ, s, and σ, defined on $\mathfrak{so}(3)^* \times T^*\mathcal{S}$, and invariant under the action of $\widehat{\Gamma} = \Gamma \times \mathbf{Z}_2^\tau$. It is known as the Eckart Hamiltonian [4].

It follows from (1.5) that the angular momentum $\mathbf{J}$ can be expressed as

$$\mathbf{J} = A\mu$$

(since $\det(A) = 1$). Hence, μ can be interpreted as the angular momentum of the molecule in a coordinate system that rotates with the molecule.

3.2. Applying the Main Theorem

Next we must apply Theorem 2.7 to reduce the Hamiltonian (3.5) to a function h on $\mathfrak{so}(3)^*$ only. For simplicity we will assume throughout the rest of this section that the equilibrium configuration Q_0 is a nondegenerate local minimum of the restriction of the potential energy function V to the slice $\mathcal{S}$. This implies that the nondegeneracy hypothesis of Theorem 2.7 is satisfied and also that the unperturbed linearization L_0 in Theorem 2.8 is strongly stable. In fact, the bifurcation results remain unchanged if Q_0 is a nondegenerate saddle point of V, but since L_0 is then unstable, all the bifurcating relative equilibria will also be unstable.

We will be interested in the critical points of h when restricted to small two-spheres around the origin, so we only need to compute its Taylor series to sufficiently high order. Since h is always invariant under the time-reversal operator τ, acting by $-I$ on $\mathfrak{so}(3)^*$, all terms of odd degree must vanish. The following result gives general formulae for the first two nonzero terms, the quadratic h_2 and the quartic h_4. These turn out to be sufficient for some, although not all, of the examples considered below.

Proposition 3.1.

1. $h_2(\mu) = \frac{1}{2}\mu^T \mathbf{I}(0)^{-1}\mu$;
2. $h_4(\mu) = -\frac{1}{16} V_2^{-1}(\mu^T \mathbf{I}_s^{-1}(0)\mu, \mu^T \mathbf{I}_s^{-1}(0)\mu)$,

where $\mathbf{I}(0)$ *is the inertia tensor of the equilibrium configuration of the molecule;* $\mathbf{I}_s^{-1}(0)$ *is the derivative with respect to s of the inverse inertia tensor* $\mathbf{I}(s)^{-1}$ *(regarded as a function on* $\mathcal{S}$*), evaluated at the equilibrium configuration;* $V_2 = \frac{1}{2}d^2V(Q_0)$ *is the quadratic approximation to the potential energy function at the equilibrium configuration; and* V_2^{-1} *is the inverse matrix to* V_2.

To interpret the formula for h_4, regard V_2^{-1} as a quadratic form on $\mathcal{S}^*$, the dual to the slice, and $\mathbf{I}_s^{-1}(0)$ as a quadratic form on $\mathfrak{so}(3)^*$ that takes values in $\mathcal{S}^*$. Note that $\mathbf{I}_s^{-1}(0)$ satisfies

$$\mathbf{I}_s^{-1}(0) \;=\; -\mathbf{I}(0)^{-1}\mathbf{I}_s(0)\mathbf{I}(0)^{-1},$$

where $\mathbf{I}_s(0)$ is the derivative of $\mathbf{I}(s)$ with respect to s at the equilibrium configuration; the entries of $\mathbf{I}_s(0)$ are called *inertia derivatives* in the molecular spectroscopy literature. If we choose a basis $\{S_1, \ldots, S_n\}$ for $\mathcal{S}$, and write V_2^{-1} as a matrix u_{ij}, and $\partial(\mathbf{I}^{-1})/\partial s_i = K_{iab}$, then

$$h_4(\mu_1, \mu_2, \mu_3) = -\frac{1}{16} \sum_{i,j,a,b,c,d} u_{ij} K_{iab} K_{jcd} \mu_a \mu_b \mu_c \mu_d,$$

where i, j run from 1 to n and a, b, c, d from 1 to 3.

It follows from the propositions that h_2 depends only on the inertia tensor $\mathbf{I}$ at the equilibrium, while h_4 depends in addition on the harmonic force constants and the inertia derivatives.

Proof. Recall from Theorem 2.7 that the function h and the reduced Hamiltonian H are related by

$$h(\mu) = H(\delta_1(\mu), \mu), \tag{3.6}$$

where δ_1 satisfies $d_y H(\delta_1(\mu), \mu) = 0$. It will be convenient to write $y = (s, \sigma)$ and $\delta_1(\mu) = (s(\mu), \sigma(\mu))$. For the Eckart Hamiltonian, it is clear that $d^2_{s\mu} H(0, 0, 0) = 0$ and $d^2_{\sigma\mu} H(0, 0, 0) = 0$, so that $\delta_1(\mu) = O(\mu^2)$, and δ_1 is equivariant. In particular, the $\mathbf{Z}_2^\tau$ symmetry implies that $s(\mu)$ is even and $\sigma(\mu)$ is odd, so $\sigma(\mu) = O(\mu^3)$.

To obtain the second- and fourth-order parts of h, we use (3.6) and the explicit form of the Eckart Hamiltonian (3.5). We use subscripts to denote Taylor series coefficients; i.e., f_k is the order k part in the Taylor series of f at the origin, where the order is defined in terms of its arguments. Then, to order four in μ,

$$h(\mu) = \tfrac{1}{2}\mu^T (K_0 + K_1(s_2(\mu)))\mu + s_2(\mu)^T V_2 s_2(\mu) + O(\mu^6), \tag{3.7}$$

where we have used the facts that $\sigma(\mu) = O(\mu^3)$ and $s(\mu) = O(\mu^2)$, which imply that all the terms involving σ are $O(\mu^6)$, and we have represented $s(\mu)$ as a vector and V_2 as a symmetric matrix. Note that $K_1(s)$ is the linear part of $K(s)$, which is precisely the $\mathbf{I}_s^{-1}$ of the proposition.

From this Taylor series, we see immediately that $h_2(\mu) = \frac{1}{2}\mu^T K_0 \mu$, as required in part (1).

For the fourth-order part of h, we need to find $s_2(\mu)$, which can be found from the leading order part of (2.6),

$$0 = \frac{\partial H}{\partial s}(s(\mu), \sigma(\mu), \mu) = \tfrac{1}{2}\mu^T K_1 \mu + 2V_2 s_2(\mu) + O(\mu^4).$$

Consequently,

$$s_2(\mu) = -\frac{1}{4} V_2^{-1}(\mu^T K_1 \mu), \tag{3.8}$$

where V_2^{-1} is considered as a linear map $\mathcal{S}^* \to \mathcal{S}$. Substituting for this in (3.7) gives

$$\begin{aligned} h_4(\mu) &= \frac{1}{2}\mu^T (K_1(s_2(\mu)))\mu + s_2(\mu)^T V_2 s_2(\mu) \\ &= -\frac{1}{8}(\mu^T K_1 \mu)^T V_2^{-1}(\mu^T K_1 \mu) + \frac{1}{16}(\mu^T K_1 \mu)^T V_2^{-1}(\mu^T K_1 \mu) \\ &= -\frac{1}{16}(\mu^T K_1 \mu)^T V_2^{-1}(\mu^T K_1 \mu), \end{aligned}$$

as required. □

The following results can be deduced from the form of h_2.

Corollary 3.2.

1. *If the equilibrium configuration Q_0 has three distinct principal moments of inertia, then there are precisely six families of relative equilibria bifurcating from it. The*

relative equilibria have dynamical axes that are aligned, at least approximately, with the principal axes of the equilibrium configuration. Those corresponding to the principal axis with largest (resp., smallest) moment of inertia are Liapounov stable (resp., linearly stable), while those corresponding to the intermediate moment of inertia are linearly unstable.

2. *If the equilibrium configuration Q_0 is planar, the nearby relative equilibria with dynamical axes perpendicular to the plane containing the equilibrium are Liapounov stable.*

Proof. If $\mathbf{I}(0)^{-1}$ has three distinct eigenvalues, h_2 has precisely six nondegenerate critical points on each sphere around zero. These are at the points corresponding to the eigenvectors of $\mathbf{I}(0)^{-1}$. The maxima, saddle points, and minima are given by the eigenvectors with the smallest, middle, and largest eigenvalues, respectively. On sufficiently small spheres, the function h is a small perturbation of h_2 and so will have nearby critical points. Part (1) now follows from Theorem 2.1 and Theorem 2.8.

For part (2) we use the fact that the principle moment of inertia of a planar body perpendicular to the plane is the sum of the other two principal moments of inertia and so must be the largest. ☐

Part (1) of this corollary states that if the molecule has little or no symmetry, and the three moments of inertia are distinct, then for small values of angular momentum the molecule behaves like a rigid body, and the relative equilibria and their stabilities depend only on the equilibrium shape. On the other hand, this is not true for symmetric molecules, as the examples below show.

3.3. *Noncollinear* XY_2 *Molecules*

In Example 1.2 we noted that a noncollinear equilibrium configuration of an XY_2 molecule has three mutually perpendicular symmetry axes, one of rotation and two of reflection. By Theorem 0.1 for each of these, there are two families of relative equilibria bifurcating from the equilibrium with dynamical axes equal to the symmetry axis. These three axes are also the three principal axes of the inertia tensor of the equilibrium. So by Corollary 3.2 these will be the only bifurcating relative equilibria, provided the three moments of inertia are different. Note that the symmetry means that the dynamical axes of the relative equilibria are *precisely* the principal axes of the inertia tensor in this case.

The stability properties of the relative equilibria are also determined by the moments of inertia. In particular, by the second part of Corollary 3.2, the relative equilibria rotating about the reflection axis perpendicular to the plane containing the equilibrium will be stable. For the other two families, we need to compute the corresponding moments of inertia.

Let the distance between the X nucleus and one of the Y nuclei at equilibrium be ℓ and the angle between the X—Y bonds be 2θ. Let the masses of the X and Y nuclei be m_X and m_Y, respectively. Put $\mathbf{M} = m_X + 2m_Y$ and $\rho = m_X/\mathbf{M}$. Let I_1 denote the moment of inertia about the reflection axis lying in the plane containing the equilibrium (ℓ_3 in

Figure 2) and I_2 the moment of inertia about the rotation axis (ℓ_2 in Figure 2). Then,

$$\begin{aligned} I_1 &= \mathbf{M}\rho(1-\rho)\ell^2\cos^2\theta, \\ I_2 &= \mathbf{M}(1-\rho)\ell^2\sin^2\theta. \end{aligned}$$

Thus, $I_1 < I_2$ if and only if $\tan^2\theta > \rho$. In this case the relative equilibrium rotating about the reflection axis is linearly (although not Liapounov) stable, and that rotating about the rotation axis is linearly unstable. If $\tan^2\theta < \rho$, these stability properties are reversed.

The bond angles for over 25 XY_2 molecules are listed in [8] and [9]. In all these cases, the bond angle is greater than 90° and so we can conclude that it is the relative equilibria with dynamical axes along the reflection axis that are linearly stable, and that those with dynamical axes along the rotation axis are linearly unstable. However, there are also molecules with $I_1 > I_2$ such as H_2D^+, where $\rho = 1/2$ and $2\theta = 60^\circ$ (D is deuterium, with $m_D = 2m_H$), and for these the stabilities are reversed.

3.4. Tetrahedral XY_4 Molecules

In the introduction we saw that (at least) three different types of relative equilibria bifurcate from a tetrahedral equilibrium configuration of an XY_4 molecule such as methane (CH_4). Their dynamical axes are, respectively, the threefold rotation axes, the twofold rotation axes, and the reflection axes. In this subsection we will compute the quadratic and quartic terms of the function h on $\mathfrak{so}(3)^*$ and show that generically these determine the stabilities of the bifurcating relative equilibria and that no other relative equilibria bifurcate.

The function h on $\mathfrak{so}(3)^*$ is invariant under the induced action of both $\Gamma = \mathbb{T}_d \cong S_4$ and the time-reversing $\mathbf{Z}_2^\tau$. Together these give an action of the group of symmetries of the cube, denoted $\mathbb{O}_h$, which is isomorphic to the standard action on $\mathbf{R}^3$. The three types of bifurcating relative equilibria correspond to the three conjugacy classes of maximal isotropy subgroups for this action, namely, the isotropy subgroups conjugate to $\mathbf{D}_3$ (threefold rotation axis denoted ℓ_3 in Figure 1), $\mathbf{D}_4$ (twofold rotation axis, ℓ_1 in Figure 1), and $\mathbf{D}_2$ (reflection axis, ℓ_2 in Figure 1). The restriction of any $\mathbb{O}_h$-invariant function to spheres centred on $0 \in \mathfrak{so}(3)^*$ must have the points with these isotropy subgroups as critical points. The following proposition says that generically there won't be any others near zero, and determines the generic possibilities for their stabilities.

Proposition 3.3.

1. *The quadratic and quartic terms of the Taylor series at zero of a general $\mathbb{O}_h$-invariant function h on $\mathfrak{so}(3)^*$ have the form*

$$\begin{aligned} h_2 &= \alpha\left(\mu_1^2+\mu_2^2+\mu_3^2\right), \\ h_4 &= \beta\left(\mu_1^2+\mu_2^2+\mu_3^2\right)^2 + \gamma\left(\mu_1^2\mu_2^2+\mu_2^2\mu_3^2+\mu_3^2\mu_1^2\right). \end{aligned}$$

2. *If $\alpha, \gamma \neq 0$, then the restriction of h to a small sphere centred at $0 \in \mathfrak{so}(3)^*$ has only critical points with isotropy subgroups conjugate to $\mathbf{D}_4$, $\mathbf{D}_3$, and $\mathbf{D}_2$.*

3. *Suppose* $\alpha > 0$. *If* $\gamma < 0$, *the critical points with isotropy subgroups conjugate to* $\mathbf{D}_3$, $\mathbf{D}_2$, *and* $\mathbf{D}_4$ *are, respectively, minima, saddle points, and maxima. If* $\gamma > 0$, *the maxima and minima are interchanged.*

Proof. Part (1) follows from the fact that every smooth function on $\mathbf{R}^3$ which is invariant under the standard action of $\mathbb{O}_h$ is a smooth function of the polynomials $\mu_1^2 + \mu_2^2 + \mu_3^2$, $\mu_1^2\mu_2^2 + \mu_2^2\mu_3^2 + \mu_3^2\mu_1^2$, and $\mu_1^2\mu_2^2\mu_3^2$ (see for example [5, p. 48, Ex. 4.7]). Parts (2) and (3) are straightforward calculations. ☐

It follows from this proposition and Theorem 2.8 that we should expect the relative equilibria with dynamical axes equal to the reflection axis to be linearly unstable when they bifurcate from the equilibrium. To determine the stabilities of the other two types, we need to calculate γ in terms of the physical parameters of the molecule.

Let the masses of the X nucleus and Y nuclei be m_X and m_Y, respectively. Let ρ denote the mass ratio m_Y/m_X. Let ℓ denote the distance between the X nucleus and a Y nucleus at equilibrium. The inertia tensor of the equilibrium configuration is then

$$\mathbf{I}(0) = \frac{8}{3} m_Y \ell^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{3.9}$$

We take the following symmetry-adapted basis for the slice $\mathcal{S}$:

$$\text{A} \quad \begin{pmatrix} 0 & 1 & 1 & -1 & -1 \\ 0 & 1 & -1 & 1 & -1 \\ 0 & 1 & -1 & -1 & 1 \end{pmatrix},$$

$$\text{E} \quad \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 & 1 \end{pmatrix} \quad \frac{1}{\sqrt{3}} \begin{pmatrix} 0 & 2 & 2 & -2 & -2 \\ 0 & -1 & 1 & -1 & 1 \\ 0 & -1 & 1 & 1 & -1 \end{pmatrix},$$

$$\text{F}_1 \quad \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & -1 & 1 \\ 0 & 1 & -1 & 1 & -1 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 & -1 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & -1 & -1 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 & -1 & 1 & -1 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\text{F}_2 \quad \begin{pmatrix} -4\rho & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ -4\rho & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -4\rho & 1 & 1 & 1 & 1 \end{pmatrix}.$$

We denote these matrices by $S_1, \ldots, S_9$ in the order they appear above. The columns of each matrix give the coordinates of the five nuclei, with X in the first column. Note that the position of X is determined by the positions of the Y's and the requirement that the centre of mass of the system is always at the origin. Each row of matrices defines a subspace of $\mathcal{S}$ on which Γ acts irreducibly. All the matrices are orthogonal to each other and to the tangent space to the $\mathbf{SO}(3)$ orbit through the equilibrium configuration with respect to the inner product (3.1). The labels A, E, F_1, and F_2 are those commonly used in the molecular spectroscopy literature. The representations of Γ on the two F_i subspaces are isomorphic. The subspaces A and E are uniquely defined, but the F_i are not. We have chosen F_1 to be the subspace consisting of configurations in which X remains stationary. The subspace F_2 is then determined by the orthogonality requirement.

The tetrahedral equilibrium configuration is given by

$$Q_0 = \frac{\ell}{\sqrt{3}} S_1.$$

A general configuration of the molecule in $\mathcal{S}$ is defined by

$$Q = Q(s) = Q_0 + \sum_{i=1}^{9} s_i S_i.$$

To compute h_4 (and hence γ) we need to find $\mathbf{I}_s(0)$ and hence

$$\mathbf{I}_s^{-1}(0) \;=\; -\mathbf{I}(0)^{-1}\mathbf{I}_s(0)\mathbf{I}(0)^{-1}.$$

To do this, we compute the inertia derivatives $\mathbf{I}_i(0)$ $(i = 1, \ldots, 9)$ of $\mathbf{I}(s)$ in the directions given by each of the matrices listed above in the basis for $\mathcal{S}$. Explicitly, these are given by

$$\mathbf{I}_i(0) = \mathrm{tr}(\mathcal{E}_i)I - \mathcal{E}_i,$$

where $\mathcal{E}_i$ is the derivative of $\mathcal{E} = S\mathbf{M}S^T$ in the direction given by the ith basis element of $\mathcal{S}$,

$$\mathcal{E}_i = S_i\mathbf{M}Q_0^T + Q_0\mathbf{M}S_i^T.$$

With these formulae it is an easy computation (using MAPLE, for example) to obtain the derivatives

$$\mathbf{I}_i^{-1}(0) = -\mathbf{I}(0)^{-1}\mathbf{I}_i(0)\mathbf{I}(0)^{-1}.$$

These are the components of the linear map $\mathbf{I}_s^{-1}(0)$ from the tangent space to $\mathcal{S}$ at the equilibrium point, which we identify with $\mathcal{S}$ itself, to the space of quadratic forms (or symmetric matrices) on $\mathfrak{so}(3)^* \cong \mathbf{R}^3$. Using the coordinates μ_1, μ_2, μ_3 on $\mathfrak{so}(3)^*$, the calculations give

$$\begin{aligned}
\mu^T\mathbf{I}_1^{-1}(0)\mu &= -C(\mu_1^2 + \mu_2^2 + \mu_3^2),\\
\mu^T\mathbf{I}_2^{-1}(0)\mu &= \frac{C}{2}(\mu_3^2 - \mu_2^2),\\
\mu^T\mathbf{I}_3^{-1}(0)\mu &= \frac{C}{2\sqrt{3}}(2\mu_1^2 - \mu_2^2 - \mu_3^2),\\
\mu^T\mathbf{I}_4^{-1}(0)\mu &= C\mu_2\mu_3,\\
\mu^T\mathbf{I}_5^{-1}(0)\mu &= C\mu_3\mu_1,\\
\mu^T\mathbf{I}_6^{-1}(0)\mu &= C\mu_1\mu_2,\\
\mu^T\mathbf{I}_i^{-1}(0)\mu &= 0, \quad \text{for } i = 7, 8, 9,
\end{aligned}$$

where $C = 3\sqrt{3}/(4m_Y\ell^3)$. Note in particular that the subspace F_2 of $\mathcal{S}$ lies in the kernel of $\mathbf{I}_s^{-1}(0)$.

By Schur's lemma, the (symmetric) matrix of $V_2^{-1} = \left(\frac{1}{2}d^2V(Q_0)\right)^{-1}$, with respect to the basis of $\mathcal{S}$ given above, will have the form

$$V_2^{-1} = \begin{pmatrix} u_{11} & & & \\ & u_{22}I_2 & & \\ & & u_{33}I_3 & u_{34}I_3 \\ & & u_{34}I_3 & u_{44}I_3 \end{pmatrix},$$

where I_k is the $k \times k$ identity matrix and the missing entries are all zero. It follows from Proposition 3.1 that

$$\begin{aligned} -\frac{16}{C^2}h_4(\mu) &= \frac{1}{C^2}V_2^{-1}(\mu^T\mathbf{I}_s^{-1}(0)\mu, \mu^T\mathbf{I}_s^{-1}(0)\mu) \\ &= u_{11}(\mu_1^2+\mu_2^2+\mu_3^2)^2 \\ &\quad +\frac{u_{22}}{4}\left((\mu_3^2-\mu_2^2)^2+\frac{1}{3}(2\mu_1^2-\mu_2^2-\mu_3^2)^2\right) \\ &\quad +u_{33}(\mu_2^2\mu_3^2+\mu_3^2\mu_1^2+\mu_1^2\mu_2^2) \\ &= \left(u_{11}+\frac{u_{22}}{3}\right)(\mu_1^2+\mu_2^2+\mu_3^2)^2+(u_{33}-u_{22})(\mu_2^2\mu_3^2+\mu_3^2\mu_1^2+\mu_1^2\mu_2^2). \end{aligned}$$

Hence, $\gamma = (u_{22} - u_{33})C^2/16$ and the sign of this determines the stability of the relative equilibria that bifurcate from the equilibrium.

To obtain the values of the nonzero entries u_{ij} in V_2^{-1} for specific molecules is not straightforward. The methods of molecular spectroscopy determine the vibrational frequencies corresponding to the four distinct eigenvalues of V_2^{-1}. However, this is not enough information to determine the five nonzero u_{ij}. This problem can be side-stepped by assuming a specific form for the quadratic part of the potential energy function that depends on four parameters or less, and then using the experimentally determined vibrational frequencies to estimate these. See for example the account given in [7]. As an example, we use the *valence force potential* given by

$$V_2 = \frac{k}{2}\sum_{i=1}^{4} r_i^2 + \frac{k_\delta}{2}\sum_{i<j}\delta_{ij}, \tag{3.10}$$

where r_i is the change in the distance between the X-nucleus and the ith Y-nucleus, and δ_{ij} is the change in the angle between XY_i and XY_j (see [7] page 181). A routine, although tedious, calculation shows that in the basis given above for $\mathcal{S}$ the quadratic form corresponding to V_2 is

$$V_2 = \begin{pmatrix} v_{11} & & & \\ & v_{22}I_2 & & \\ & & v_{33}I_3 & v_{34}I_3 \\ & & v_{34}I_3 & v_{44}I_3 \end{pmatrix},$$

where:

$$\begin{aligned}
v_{11} &= 12k,\\
v_{22} &= 24\frac{k_\delta}{\ell^2},\\
v_{33} &= \frac{16}{3}\left(k+\frac{k_\delta}{\ell^2}\right),\\
v_{34} &= \frac{8}{3}(1+4\rho)\left(k-2\frac{k_\delta}{\ell^2}\right),\\
v_{44} &= \frac{4}{3}(1+4\rho)^2\left(k+4\frac{k_\delta}{\ell^2}\right).
\end{aligned}$$

Inverting this gives

$$\begin{aligned}
u_{22} &= \frac{\ell^2}{24k_\delta},\\
u_{33} &= \frac{\ell^2}{48k_\delta}+\frac{1}{12k},
\end{aligned}$$

and hence

$$\gamma = \frac{C^2}{768}\left(\frac{\ell^2}{k_\delta}-\frac{4}{k}\right).$$

The values of k and k_δ/ℓ^2 obtained by fitting the valence force potential (3.10) to spectroscopic data from a number of XY_4 molecules (including methane) are listed in Table 46 of [7]. In all cases γ is positive, and so we can predict that the bifurcating relative equilibria with dynamical axes along the twofold rotation axes (see ℓ_1 in Figure 1) will be Liapounov stable; those with dynamical axes along the threefold rotation axes (ℓ_3 in Figure 1) will be linearly stable, but typically Liapounov unstable; while those with dynamical axes along the reflection axes (ℓ_2 in Figure 1) will be linearly unstable (hyperbolic).

3.5. Equilateral X_3 Molecules

Consider a molecule made up of three identical nuclei and with an equilibrium configuration with the nuclei at the vertices of an equilateral triangle. Examples include ozone, O_3, and the ionized molecule H_3^+, which plays an important role in the chemistry of the interstellar medium and the atmospheres of the giant planets [21]. For ozone, the equilateral triangle equilibrium is unstable and the stable equilibria are isosceles. However, for H_3^+ it is stable.

The symmetry group of the equilateral triangle configuration is $\mathbf{D}_3 \times \mathbf{Z}_2$, where $\mathbf{Z}_2$ acts by reflecting in the plane of the molecule. By Theorem 0.1 relative equilibria of three types bifurcate from the equilibrium: rotations about the axis perpendicular to the

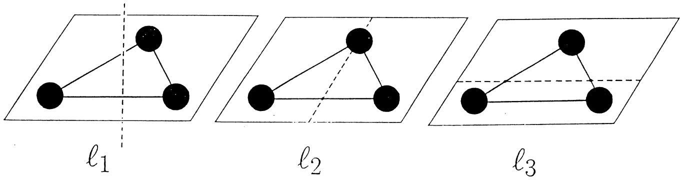

Fig. 3. Representative axes for the X_3 molecule. Note that ℓ_1 is unique, while there are three of type ℓ_2 and three of type ℓ_3.

plane of the molecule, rotations about axes passing through one of the three nuclei, and rotations about axes in the plane of the molecule that are perpendicular to these. This third set of axes are axes of reflection, where the reflection is in a plane perpendicular to that of the molecule and passing through a vertex of the equilateral triangle.

If the equilibrium point is unstable, then all the bifurcating relative equilibria will be unstable. If it is stable, then by Corollary 3.2(2) the relative equilibria with axes perpendicular to the plane of the molecule will be Liapounov stable. Generically, one of the two remaining types will be linearly stable and the other linearly unstable. In this section we show how to distinguish between the two possibilities. We also show that generically these are the only relative equilibria that bifurcate. These calculations turn out to involve computing a sixth-order coefficient in the Taylor series of h, and this depends on a third-order coefficient in the Taylor series of the potential energy function, i.e., an anharmonic force constant.

In this case the function h on $\mathfrak{so}(3)^*$ will be invariant under the action of $\mathbf{D}_3 \times \mathbf{Z}_2 \times \mathbf{Z}_2^\tau$ given by equations (1.6, 1.7). For this action $\mathfrak{so}(3)^*$ splits into the direct sum of two invariant subspaces, the two-dimensional space consisting of momentum values that lie in the plane of the molecule, and the one-dimensional space perpendicular to this. The group $\mathbf{D}_3 \times \mathbf{Z}_2$ is isomorphic to $\mathbf{D}_6$ and acts on the two-dimensional subspace by the standard action of $\mathbf{D}_6$ on the plane. The action on the one-dimensional space is determined by the fact that the subgroup that acts trivially is $\mathbf{Z}_6 \subset \mathbf{D}_6$. As usual, $\mathbf{Z}_2^\tau$ acts on $\mathfrak{so}(3)^*$ by $-I$.

Every maximal isotropy subgroup of this action on the spheres centred at zero is conjugate to one of the three groups $\widetilde{\mathbf{D}}_6$, $\mathbf{Z}_2^{(\mathrm{rot})} \times \mathbf{Z}_2^{\pi\circ\tau}$, or $\mathbf{Z}_2^{(\mathrm{ref})} \times \mathbf{Z}_2^{\pi\circ\tau}$, defined as follows. The subgroup $\widetilde{\mathbf{D}}_6$ consists of the group $\mathbf{Z}_6$ together with each of the remaining elements of $\mathbf{D}_6$ composed with τ. This fixes the momentum values perpendicular to the plane of the molecule. There are no other subgroups conjugate to this one. The subgroup $\mathbf{Z}_2^{(\mathrm{rot})}$ is generated by rotating the molecule by π about one of its twofold rotation axes (labelled ℓ_2 in Figure 3). The subgroup $\mathbf{Z}_2^{(\mathrm{ref})}$ is generated by a reflection of the molecule in one of the reflection planes perpendicular to the plane containing the molecule, with axis ℓ_1. The group $\mathbf{Z}_2^{\pi\circ\tau}$ is generated by rotating the molecule by π about its threefold rotation axis and then applying τ. These three order-two subgroups of $\mathbf{D}_6 \times \mathbf{Z}_2^\tau$ are not conjugate to each other. Each of the groups $\mathbf{Z}_2^{(\mathrm{rot})} \times \mathbf{Z}_2^{\pi\circ\tau}$ and $\mathbf{Z}_2^{(\mathrm{ref})} \times \mathbf{Z}_2^{\pi\circ\tau}$ has two other subgroups conjugate to it. The fixed point sets for each of these subgroups is a line in the plane of the molecule. Thus, there are seven maximal isotropy subgroups altogether, each of which will have two fixed points on the spheres in $\mathfrak{so}(3)^*$.

Proposition 3.4.

1. *The quadratic, quartic, and sextic terms in the Taylor series at* 0 *of a general* $\mathbf{D}_3 \times \mathbf{Z}_2 \times \mathbf{Z}_2^\tau$*-invariant function* h *on* $\mathfrak{so}(3)^*$ *have the form*

$$\begin{aligned} h_2 &= \alpha_1(\mu_1^2+\mu_2^2)+\alpha_2\mu_3^2, \\ h_4 &= \beta_1(\mu_1^2+\mu_2^2)^2+\beta_2(\mu_1^2+\mu_2^2)\mu_3^2+\beta_3\mu_3^4, \\ h_6 &= \gamma(\mu_1^3-3\mu_1\mu_2^2)^2+\sum_{i=0}^{3}\gamma_i(\mu_1^2+\mu_2^2)^i(\mu_3^2)^{3-i}. \end{aligned}$$

2. *If* $\alpha_1 \neq \alpha_2$ *and* $\gamma \neq 0$*, then the restriction of* h *to a small sphere centred at* $0 \in \mathfrak{so}(3)^*$ *has precisely 14 critical points; they have isotropy subgroups conjugate to* $\widetilde{\mathbf{D}}_6$ *(2),* $\mathbf{Z}_2^{(\mathrm{rot})} \times \mathbf{Z}_2^{\pi\circ\tau}$ *(6), and* $\mathbf{Z}_2^{(\mathrm{ref})} \times \mathbf{Z}_2^{\pi\circ\tau}$ *(6).*
3. *If* h *is the split Hamiltonian of an* X_3*-molecule, then* $\alpha_2 = \frac{1}{2}\alpha_1 > 0$*, and the critical points* $\mu = (0, 0, \pm 1)$ *with isotropy subgroups conjugate to* $\widetilde{\mathbf{D}}_6$ *are minima. Moreover, if* $\gamma > 0$*, the critical points in the orbit of* $(1, 0, 0)$ *(with isotropy subgroups conjugate to* $\mathbf{Z}_2^{(\mathrm{rot})} \times \mathbf{Z}_2^{\pi\circ\tau}$*) are maxima while those in the orbit of* $(0, 1, 0)$ *(with isotropy subgroups conjugate to* $\mathbf{Z}_2^{(\mathrm{ref})} \times \mathbf{Z}_2^{\pi\circ\tau}$*) are saddle points; if* $\gamma < 0$*, the maxima and saddles are interchanged.*

Proof. The first part is a straightforward invariant theory calculation (see, e.g., [5]). Part (2) follows from the discussion before the statement of the proposition together with a computation to verify that there are no other critical points, and part (3) is a computation. ☐

Part (3) of this proposition is used in conjunction with Theorem 2.8 to determine the stabilities of the relative equilibria. We now consider the X_3 molecule in general, and perform the computations needed to determine the sign of γ.

Let m be the mass of the X nuclei, and ℓ the equilibrium bond length. The equilibrium configuration is

$$Q_0 = \ell \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2\sqrt{3}} & -\frac{1}{2\sqrt{3}} & \frac{1}{\sqrt{3}} \\ 0 & 0 & 0 \end{pmatrix}.$$

The equilibrium inertia tensor is then

$$\mathbf{I}(0) = \frac{m\ell^2}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix},$$

and it follows from Proposition 3.1(1) that

$$h_2(\mu) = \frac{1}{m\ell^2}(2\mu_1^2+2\mu_2^2+\mu_3^2).$$

We take the following symmetry-adapted orthonormal basis for the slice $\mathcal{S}$ (with respect to the inner product (3.1), which in this case is equivalent to $\langle S, T\rangle = \operatorname{tr}(S^T T)$):

$$\text{A} \qquad S_1 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2\sqrt{3}} & -\frac{1}{2\sqrt{3}} & \frac{1}{\sqrt{3}} \\ 0 & 0 & 0 \end{pmatrix},$$

$$\text{E} \qquad S_2 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & -\frac{1}{\sqrt{3}} \\ 0 & 0 & 0 \end{pmatrix}, \qquad S_3 = \begin{pmatrix} -\frac{1}{2\sqrt{3}} & -\frac{1}{2\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The symmetry group $\Gamma = \mathbf{D}_3 \times \mathbf{Z}_2$ acts trivially on A and by the standard two-dimensional representation of $\mathbf{D}_3$ and the trivial representation of $\mathbf{Z}_2$ on E.

A general configuration is given by

$$Q = Q(s) = Q_0 + \sum_{i=1}^{3} s_i S_i.$$

The inertia tensor $\mathbf{I}(s)$ can be computed easily, and its derivatives at $s = 0$ give rise to the three quadratic forms $\mathbf{I}_i^{-1}(0) = (K_1)_i = \partial K/\partial s_i(0)$:

$$\begin{aligned} \mu^T \mathbf{I}_1^{-1}(0)\mu &= -\frac{2}{m\ell^3}(2\mu_1^2 + 2\mu_2^2 + \mu_3^2), \\ \mu^T \mathbf{I}_2^{-1}(0)\mu &= \frac{4}{m\ell^3}(\mu_1^2 - \mu_2^2), \\ \mu^T \mathbf{I}_3^{-1}(0)\mu &= \frac{8}{m\ell^3}\mu_1\mu_2. \end{aligned}$$

We wish to find an expression for γ in terms of the physical characteristics of the molecule, and in particular of its potential energy function. Since V is Γ-invariant, its third-order Taylor series can be written

$$V(s_1, s_2, s_3) = As_1^2 + B(s_2^2 + s_3^2) + Cs_1^3 + Ds_1(s_2^2 + s_3^2) + E(s_2^3 - 3s_2 s_3^2) + O(s^4). \quad (3.11)$$

Here A, B are harmonic force constants, while C, D, E are anharmonic force constants.

Recall from (3.8) that the quadratic part of $s(\mu)$ satisfies

$$s_2(\mu) = -\frac{1}{4} V_2^{-1}(\mu^T K_1 \mu)$$

(there should be no confusion arising from using s_2 both as a coordinate in (3.11) and as the quadratic part of a function). Combining this with the expressions for $(K_1)_i = \mathbf{I}_i^{-1}(0)$ above gives

$$\begin{aligned} s_{1,2}(\mu) &= \frac{1}{Am\ell^3}(\mu_1^2 + \mu_2^2 + \tfrac{1}{2}\mu_3^2), \\ s_{2,2}(\mu) &= -\frac{1}{Bm\ell^3}(\mu_1^2 - \mu_2^2), \\ s_{3,2}(\mu) &= -\frac{2}{Bm\ell^3}\mu_1\mu_2, \end{aligned}$$

where $s_{i,2}$ is the quadratic part of s_i. Substituting for this in (2.6) gives $s_4(\mu)$ and $\sigma_3(\mu)$. The expressions for $s_2, s_4,$ and σ_3 are then substituted in the expression for h. Finally, comparing with Proposition 3.4 shows that γ is given by

$$\gamma = \frac{1}{6!}\left(\frac{\partial^6 h}{\partial \mu_1^6} - \frac{\partial^6 h}{\partial \mu_2^6}\right).$$

All these computations are quite lengthy, and can most easily be performed with the aid of a computer package (again, we use MAPLE). The final result is

$$\gamma = \frac{197\, E}{3m^3\ell^9 B^3},$$

where B, E are the force constants defined in (3.11). For a stable equilibrium, $B > 0$ and so the sign of γ coincides with that of E.

As an example, consider a system of three identical point masses coupled by three identical *linear* springs with spring constant $k > 0$, and equilibrium length ℓ. Then expressing the extensions of the three springs in terms of the slice coordinates s_1, s_2, s_3, gives

$$\gamma = -\frac{9k}{4\ell}.$$

It follows from Proposition 3.4 and Theorem 2.8 that the rotation about an axis passing through one of the point masses is linearly unstable (axis ℓ_2 in Figure 3), while rotation about the orthogonal one (axis ℓ_3) is linearly stable, and indeed strongly stable.

To apply these calculations to the H_3^+ molecule, we need to know the potential energy function. The Taylor series to order seven of this function at the equilibrium has been estimated from spectroscopic data in [2]. The coordinates they use are not the same as ours, and in our coordinates, their coefficients become (cf. (3.11))

$$A = 225291, \qquad B = 146892,$$

$$C = -234030, \qquad D = -389483, \qquad E = -104648.$$

In particular, $E < 0$ and consequently so is γ. It follows that of the two horizontal axes, the one through a nucleus (axis ℓ_2 in Figure 3) is linearly unstable (hyperbolic) while the other is strongly stable (elliptic), precisely as for the linear spring model.

The world of molecules is very rich, and one would expect that there is an X_3 molecule where the stabilities differ from those of the linear spring model, but we do not know of such an example.

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