Introduction

The potential energy function derived by P. M. Morse is truly a ''workhorse" potential energy function in theoretical chemistry {% cite morse1929diatomic %}. Originally it was devised to describe the intermolecular force between the two atoms in a diatomic molecule. It has the functional form:

$$V(q) = D\left(1 - e^{-\alpha q}\right)^2, \tag{1}$$

where q represents the distance between the two atoms, $D > 0$ represents the depth of the potential well (defined relative to the dissociated atoms), and $\alpha > 0$ controls the width of the potential well (α small corresponds to a ''wide" well, α large corresponds to a narrow well).

The Morse potential defines a one degree-of-freedom Hamiltonian system, i.e. the phase space is two dimensional described by coordinates (q, p), where p is the momentum conjugate to the position variable q. The Hamiltonian has the form of the sum of the kinetic energy and the potential energy (the Morse potential). The Hamiltonian system is integrable, and all trajectories lie on the level sets of the Hamiltonian function. The level sets can be used to derive integrals that give (time) parametrizations of trajectories. Regions of closed (bounded) trajectories can be used to construct special coordinates–*action-angle coordinates*, where the angle denotes a particular location on the closed level set and the action is the area enclosed by a closed level set (divided by 2π). The transformation to action-angle coordinates for integrable Hamiltonan systems is a standard topic in good classical mechanics textbooks, see, e.g. {% cite landau1960mechanics, arnold2013mathematical %}. The transformation preserves the Hamiltonian nature of the system, i.e. it is a canonical transformation, and therefore the standard approach to constructing such transformations is through the use of generating functions. However, for one degree-of-freedom time-independent Hamiltonian systems (such as the one described by the Morse potential) there is a simpler approach to generating the action-angle transformation that uses the geometry of the closed level set of the Hamiltonian function and the explicit (time) parametrization of the trajectories that can be obtained (in principle, if the necessary integrals can be explicitly computed) for one degree-of-freedom Hamiltonian systems. The approach is inspired by the seminal paper of Melnikov {% cite melnikov1963vk %}. This approach was developed in detail in {% cite wiggins1990introduction %} (the 1990 edition, *not* the 2003 edition) and is also described in {% cite mezic1994integrability %}. This is the approach that we will follow here.

Action-angle variables are important in Hamiltonian mechanics for a number of reasons. From the point of view of classical mechanics they are the coordinate system used for the development of the Kolmogorov-Arnold-Moser and Nekhoroshev theorems {% cite dumas2014kam %}. They also play a central role in the quantization of classical Hamiltonian systems (in fact, the action and the constant $\hbar$ have the same units) {% cite stone2005einstein, keller1958corrected, keller1960asymptotic, keller1985semiclassical %}.

This paper is outlined as follows. In Section we describe the Hamiltonian system described by the Morse potential (1). In Section we describe the equilibria and determine their stability properties in the linear approximation. In Section we discuss the geometry of the region of bounded motion, i.e. the region of periodic orbits bounded by a homoclinic orbit (‘’separatrix”). In Section we compute the period of the periodic orbits and show how it depends on the energy and other system parameters. In Section we compute explicit expressions for the trajectories in the region of bounded motion. In Section we compute an explicit expression for the homoclinic orbit. In Section we compute the action-angle variables. In Section we compute explicit expressions for the trajectories in the region of unbounded motion. In section **??** we apply our results to exploring the nature of chaotic dynamics in the time periodically forced Morse oscillator and in Section **??** we discuss our conclusions.

The Hamiltonian

The dynamical system defined by the Morse potential is Hamiltonian, with Hamiltonian function given by:

$$H(q,p) = \frac{p^2}{2m} + D\left(1 - e^{-\alpha q}\right)^2, \qquad (q,p) \in \mathbb{R}^2, \tag{2}$$

and Hamilton's equations defined by:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{m}, \\ \dot{p} &= -\frac{\partial H}{\partial q} = -2D\alpha\left(e^{-\alpha q} - e^{-2\alpha q}\right). \end{aligned} \tag{3}$$

The level sets of the Hamiltonian function have the form:

$$\left\{(q,p) \in \mathbb{R}^2 \,|\, H(q,p) = h = \text{constant}\right\}. \tag{4}$$

They are (in general) one dimensional curves that are invariant under the Hamiltonian dynamics, i.e. the Hamiltonian vector field is tangent to the level sets. Since the trajectories lie on these curves, we can use the form of the level curves to obtain parametrizations of certain trajectories, as we will demonstrate.

Equilibria and their Linearized Stability

It is straightforward to verify the the following two points are equilibria for Hamilton's equations:

$$(q, p) = (\infty, 0),\ (0, 0). \tag{5}$$

Next we check their linearized stability properties. The Jacobian matrix, denoted J, of Hamilton's equation is given by:

$$J = \begin{pmatrix} 0 & \frac{1}{m} \\ -2D\alpha^2 \left(-e^{-\alpha q} + 2e^{-2\alpha q}\right) & 0 \end{pmatrix}. \tag{6}$$

The eigenvalues of J are given by:

$$\pm \sqrt{\mathrm{det\,J}}. \tag{7}$$

Hence for the two equilibria we have:

$$(q, p) = (0, 0) \Rightarrow \mathrm{det\,J} = -\frac{\mathrm{2D\alpha^2}}{\mathrm{m}}, \tag{8}$$

with corresponding eigenvalues:

$$\pm\, i\sqrt{\frac{2D}{m}}\alpha, \tag{9}$$

and

$$(q, p) = (\infty, 0) \Rightarrow \mathrm{det\,J} = 0, \tag{10}$$

where both eigenvalues are zero.

The equilibrium $(q, p) = (0, 0)$ is stable (''elliptic" in the Hamiltonian dynamics terminology) and the $(q, p) = (\infty, 0)$ is unstable (a ''parabolic" saddle point in the Hamiltonian dynamics terminology).

The Region of Bounded Motion: Periodic Orbits

Using the Hamiltonian (2) it is straightforward to verify that the equilibria have the following energies:

$$(q,p) = (\infty, 0) \Rightarrow H = D > 0. \tag{11}$$

and

$$(q,p) = (0, 0) \Rightarrow H = 0. \tag{12}$$

Trajectories with energies larger than D have unbounded motion in q. Trajectories having energies h satisfying $0 < h < D$ correspond to periodic motions. The level sets of these periodic orbits are given by:

$$h = \frac{p^2}{2m} + D\left(1 - e^{-\alpha q}\right)^2, \quad 0 < h < D, \tag{13}$$

and surround the stable equilibrium point $(q,p) = (0,0)$ as shown in figure . The periodic orbits intersect the q axis at two distinct points, $q_+ > 0$ and $q_- < 0$, which are referred to as *turning points*. These turning points are computed as follows.

Rewriting (13) gives:

$$\frac{p^2}{2m} = h - D\left(1 - e^{-\alpha q}\right)^2. \tag{14}$$

The turning points are obtained from (14) by setting $p = 0$:

$$h = D\left(1 - e^{-\alpha q}\right)^2 \tag{15}$$

Note that we have:

$$0 \leq \sqrt{\frac{h}{D}} \leq 1, \tag{16}$$

from which we obtain the following relations:

$$1 \leq 1 + \sqrt{\frac{h}{D}} \leq 2, \tag{17}$$

$$0 \leq 1 - \sqrt{\frac{h}{D}} \leq 1, \tag{18}$$

Taking the positive root of (15) gives:

$$1 - e^{-\alpha q} = \sqrt{\frac{h}{D}}. \tag{19}$$

from which we obtain the positive turning point:

$$q_{+} = -\frac{1}{\alpha} \log \left(1 - \sqrt{\frac{h}{D}} \right) > 0. \tag{20}$$

Taking the negative root of (15) gives:

$$1 - e^{-\alpha q} = -\sqrt{\frac{h}{D}}, \tag{21}$$

from which we obtain the negative turning point:

$$q_{-} = -\frac{1}{\alpha} \log \left(1 + \sqrt{\frac{h}{D}} \right) < 0. \tag{22}$$

The level curve with energy equal to the dissociation energy $h = D$ has the form:

$$D = \frac{p^2}{2m} + D \left(1 - e^{-\alpha q} \right)^2, \tag{23}$$

and is a separatrix connecting the (parabolic) saddle point. In the terminology of Hamiltonian dynamics it is a homoclinic orbit. It separates bounded from unbounded motion as illustrated in figure .

Phase portrait of the Morse oscillator for $D = 10$, $\alpha = 1$, $m = 8$. The equilibrium point at the origin is shown in black, the homoclinic orbit is shown in orange and examples of a periodic orbit and an unbounded trajectory are highlighted with blue and green respectively.

Calculation of the Period of a Periodic Orbit

In this section we calculate the period of the periodic orbits. From (3) we have $\dot{q} = \frac{p}{m}$. Using this expression, and the expression for the level set of the Hamiltonian defining a periodic orbit given in (13), we have

$$\frac{dq}{dt} = \pm \sqrt{\frac{2}{m}} \sqrt{h - D \left(1 - e^{-\alpha q}\right)^2}, \tag{24}$$

or

$$\frac{dq}{\sqrt{h - D\left(1 - e^{-\alpha q}\right)^2}} = \pm\sqrt{\frac{2}{m}}dt. \tag{25}$$

We denote the period of a periodic orbit corresponding to the level set with energy value h by $T(h)$. We can obtain the period by integrating dt around this level set. Using (25), this becomes:

$$\begin{aligned} T(h) &= \sqrt{\frac{m}{2}}\int_{q_+}^{q_-} \frac{dq}{\sqrt{h - D\left(1 - e^{-\alpha q}\right)^2}} - \sqrt{\frac{m}{2}}\int_{q_-}^{q_+} \frac{dq}{\sqrt{h - D\left(1 - e^{-\alpha q}\right)^2}}. \\ &= \sqrt{2m}\int_{q_+}^{q_-} \frac{dq}{\sqrt{h - D\left(1 - e^{-\alpha q}\right)^2}}. \end{aligned} \tag{26}$$

Computation of this integral is facilitated by the substitution:

$$u = e^{-\alpha q}. \tag{27}$$

After computing the integral using integral 2.266 in {% cite gradshteyn1980table %} we obtain:

$$T(h) = \frac{\pi\sqrt{2m}}{\alpha\sqrt{D - h}} \tag{28}$$

There are two limits in which this expression can be checked with respect to previously obtained results. First, we note that for $h = D$ (i.e. the energy of the homoclinic orbit, or ‘’separatrix’‘) $T(D) = \infty$, which is what we expect for the’‘period” of a separatrix.

Second, we consider $h = 0$, which is the energy of the elliptic equilibrium point. In this case we have $T(0) = \frac{\pi\sqrt{2m}}{\alpha\sqrt{D}}$, which is 2π divided by the imaginary part of the magnitude of eigenvalue of the Jacobian evaluated at the stable equilibrium point, as we expect.

Expressions for $q(t)$ and $p(t)$, $0 < h < D$

In this section we derive an expression for $q(t)$. Differentiating the expression for $q(t)$ will give the expression for $p(t)$ through the relation $\dot{q} = \frac{p}{m}$. Using (25), we have

$$\int_{q_+}^{q} \frac{dq'}{\sqrt{h - D\left(1 - e^{-\alpha q'}\right)^2}} = \sqrt{\frac{2}{m}} t. \tag{29}$$

Choosing the lower limit if the integral to be q_+ is arbitrary, but it is equivalent to the choice of an initial condition. After computing this integral, we obtain:

$$q(t) = \frac{1}{\alpha} \log \frac{\sqrt{Dh} \cos\left(\sqrt{\frac{2(D-h)}{m}}\, \alpha t\right) + D}{D - h}. \tag{30}$$

It is straightforward to check that the period of (30) is (28).

The Homoclinic Orbit

As noted earlier, the homoclinic orbit, corresponding to $h = D$, is given by the level set (23). Hence, the integral expression for the homoclinic orbits is obtained from (25) by setting $h = D$. Computing the integral gives:

$$q_0(t) = \frac{1}{\alpha} \log \frac{1 + \frac{2D}{m}\alpha^2 t^2}{2}. \tag{31}$$

It is a simple matter to check that $\lim_{t\to\pm\infty} q(t) = \infty$. Subsequently we obtain $p_0(t)$ from $\dot{q} = \frac{p}{m}$ as

$$p_0(t) = \frac{4mD\alpha t}{2D\alpha^2 t^2 + m}. \tag{32}$$

Expressions for Action and the Angle, $0 < h < D$

In this section we compute the action-angle representation of the orbits in the bounded region following {% cite melnikov1963vk, wiggins1990introduction, mezic1994integrability %}.

We consider a level set defined by the Hamiltonian (4), for $0 < h < D$. i.e. we consider a periodic orbit with period $T(h)$. Choosing an arbitrary reference point on the periodic orbit, the angular displacement of a trajectory starting from this reference position after time t is given by

$$\theta = \frac{2\pi}{T(h)} \int 0^t dt' = \frac{2\pi}{T(h)} \sqrt{\frac{m}{2}} \int_{q_+}^{q} \frac{dq'}{\sqrt{h - D\left(1 - e^{-\alpha q'}\right)^2}}. \tag{33}$$

Using the substitution (27) and integral 2.266 in {% cite gradshteyn1980table %}, we have:

$$\theta = \frac{\pi}{T(h)\alpha}\sqrt{\frac{2m}{D-h}}\left(\frac{3\pi}{2} - \sin^{-1}\frac{(h-D)e^{\alpha q}+D}{\sqrt{Dh}}\right). \tag{34}$$

The action associated with this periodic orbit is the area that it encloses (in phase space) divided by 2π:

$$I = \frac{1}{2\pi}\oint_{H=h} pdq. \tag{35}$$

Recalling (25)

$$dq = \pm\sqrt{\frac{2}{m}}\sqrt{h - D\left(1-e^{-\alpha q'}\right)^2}\, dt, \tag{36}$$

we obtain

$$pdq = m\dot{q}dq = \pm\sqrt{2m}\sqrt{h - D\left(1-e^{-\alpha q'}\right)^2}\,\dot{q}dt, \tag{37}$$

and therefore

$$I = \frac{\sqrt{2m}}{\pi}\int_{q_+}^{q_-}\sqrt{h - D\left(1-e^{-\alpha q'}\right)^2}\, dq'. \tag{38}$$

Using the substitution (27) and integral 2.267 in {% cite gradshteyn1980table %}, we have:

$$I = \frac{\sqrt{2m}}{\alpha}\left(\sqrt{D} - \sqrt{D-h}\right). \tag{39}$$

Expressions for $q(t)$ and $p(t)$, $0 < D < h$

Increasing the total energy h to the value of D and beyond results in unbounded motion. Trajectories retain the turning point q_-, while q_+ becomes infinite. The expression for q_- is identical to low energies and is obtained from (2) by setting $p = 0$ and solving for q. Recall from (22) that $q_- = -\frac{1}{\alpha}\log\left(1+\sqrt{\frac{h}{D}}\right)$.

For unbounded trajectories it is not possible to define a (finite) period, but we can obtain an expression for t as a function of position. It can be derived by integrating (25) from q_- to an arbitrary position q by using the substitution (27) as follows:

$$
\begin{aligned}
t(q) &= \sqrt{\frac{m}{2}} \int_{q}^{q_-} \frac{dq'}{\sqrt{h - D\left(1 - e^{-\alpha q'}\right)^2}} = -\frac{1}{\alpha}\sqrt{\frac{m}{2}} \int_{e^{-\alpha q}}^{1+\sqrt{\frac{h}{D}}} \frac{du}{u\sqrt{h - D\left(1 - u\right)^2}}, \\
&= \frac{1}{\alpha}\sqrt{\frac{m}{2(h-D)}} \log\left(\frac{h - D + De^{-\alpha q} + \sqrt{(h-D)(h-D(1-e^{-\alpha q})^2)}}{\sqrt{hD}e^{-\alpha q}}\right).
\end{aligned}
\tag{40}
$$

We obtain an explicit solution $q = q(t)$ by inverting (40).

$$
q(t) = \frac{1}{\alpha} \log \frac{\sqrt{hD}e^{2\beta t} - 2De^{\beta t} + \sqrt{hD}}{2(h-D)e^{\beta t}}, \tag{41}
$$

where $\beta = \alpha\sqrt{\frac{2(h-D)}{m}}$. Differentiating (41) and using the relation $\dot{q} = \frac{p}{m}$ yields the expression of $p(t)$.