From Quantum Mechanical $\underline{\underline{\mathbf{H}}}^{\mathbf{eff}}$ to Classical Mechanical $\mathcal{H}^{\mathbf{eff}}$

Readings:	Chapter 9.4.14 and 9.4.15, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

Transformation $\mathbf{H}^{\text{eff}}_{\text{LOCAL}} \leftrightarrow \mathbf{H}^{\text{eff}}_{\text{NORMAL}}$

analytical transformation of basis states
analytical transformation of $\mathbf{H}^{\text{eff}}$
numerical transformation of $\mathbf{H}^{\text{eff}}$ by setting limit preserving parameter to zero

limit-preserving and limit-destroying terms in $\mathbf{H}^{\text{eff}}$: reversal of role in opposite representations

2-level illustration
Two identical coupled Morse oscillators
3-parameter model (some inconsistencies wrt the Darling-Dennison term)
6-parameter model → basis for today's QM → CM conversion.

Today:

Convert from Quantum Mechanical $\mathbf{H}^{\text{eff}}$ to equivalent Classical Mechanical $\mathbf{H}^{\text{eff}}$.

Why? The QM $\mathbf{H}^{\text{eff}}$ is vastly simpler than the exact QM $\mathbf{H}$. In addition, the parameters in $\mathbf{H}^{\text{eff}}$ are determined by experimental observations. So we have a QM representation of reality and we would like to obtain an equivalent CM representation. It is easier to gain insight from the form of trajectories than from attempting to discern the nodal structure of a QM wavefunction.

Begin with Heisenberg's Correspondence Principle

But first an aside about classical mechanics

$\mathcal{H}$ is a function of pairs of conjugate variables

i.e. Q_i and P_i (coordinate and momentum)

Hamilton's equations of motion:

$$\dot{Q}_i = \frac{\partial \mathcal{H}}{\partial P_i} \quad , \quad \dot{P}_i = -\frac{\partial \mathcal{H}}{\partial Q_i}$$

I_i and ϕ_i (action and angle)

$$\dot{\phi}_i = \frac{\partial \mathcal{H}}{\partial I_i} \quad , \quad \dot{I}_i = -\frac{\partial \mathcal{H}}{\partial \phi_i}$$

PQ has dimension of action.

The action-angle representation is most convenient for going from QM to CM (or vice versa).

Heisenberg's Correspondence Principle

$$\text{replace} \begin{cases} \mathbf{a}_j^\dagger \to (v_j + 1/2)^{1/2} e^{i\phi_j} = I_j^{1/2} e^{i\phi_j} \\ \mathbf{a}_j \to (v_j + 1/2)^{1/2} e^{-i\phi_j} = I_j^{1/2} e^{-i\phi_j} \end{cases}$$

Prescription:

1. express $\mathbf{H}^{\text{eff}}$ entirely in terms of constants times products of $\mathbf{a}_j^\dagger, \mathbf{a}_j$ v_j is replaced by $\mathbf{a}_j^\dagger \mathbf{a}_j$.
2. replace $\mathbf{a}_j^\dagger$ and $\mathbf{a}_j$ everywhere by $I_j^{1/2} e^{\pm i\phi_j}$.
3. simplify by algebra. There are no commutation restrictions.

$$\mathbf{H}_{\text{LOCAL}}^{\text{eff}}/hc = \omega_0(v_R + v_L + 1) + \frac{1}{2}[\beta + (\varepsilon/2)(v_R + v_L + 1)][\mathbf{a}_R^\dagger \mathbf{a}_L + \mathbf{a}_L^\dagger \mathbf{a}_R]$$
$$+(\alpha_1/4)(v_R + v_L + 1)^2 + (\alpha_2/4)[v_R - v_L]^2$$
$$+\delta'[\mathbf{a}_R^{\dagger 2} \mathbf{a}_L^2 + \mathbf{a}_L^{\dagger 2} \mathbf{a}_R^2]$$

This is the same as $\mathbf{H}_{\text{LOCAL}}^{\text{eff}}$ from Lecture #18, where the 6 independent parameters are:

$$\omega_0 = \frac{\omega_s + \omega_a}{2}$$
$$\frac{\alpha_1}{4} = \frac{3x_{ss} + 3x_{aa} + x_{sa} - K_{ssaa}/8hc}{2}$$
$$\frac{\alpha_2}{4} = \frac{3K_{ssaa}/16hc - x_{ss} - x_{aa} + x_{sa}}{4}$$
$$\beta/2 = \frac{\omega_s - \omega_a}{2}$$
$$\varepsilon/4 = \frac{x_{ss} - x_{aa}}{2}$$
$$\delta' = \frac{K_{ssaa}/32hc + x_{ss} + x_{aa} - x_{sa}}{4}.$$

And now we make the conversion to CM

$$\mathbf{a}_R, \mathbf{a}_R^\dagger, \mathbf{a}_L, \mathbf{a}_L^\dagger \to (v + 1/2)^{1/2} e^{\pm i\phi_{R \text{ or } L}}$$
$$v_R + v_L + 1 = 2I$$
$$v_R - v_L = 2I_z$$
$$(v_R + 1/2)(v_L + 1/2) = I^2 - I_z^2$$
$$\phi_R - \phi_L = \psi$$

$$\mathscr{H}_{\text{LOCAL}}/hc = 2\omega_0 I + \left[\beta + \varepsilon I\right]\left[I^2 - I_z^2\right]^{1/2}\cos\psi$$
$$+\alpha_1 I^2 + \alpha_2 I_z^2 + 2\delta'\left[I^2 - I_z^2\right]\cos 2\psi$$

2 actions: I and I_z
one angle: ψ which is associated with I_z

other angle: θ, associated with I, does not appear in $\mathscr{H}$, which implies that $\frac{\partial \mathscr{H}}{\partial \theta} = -\dot{I} = 0$, thus I is conserved. (This is the assumed block-diagonalization of $\mathbf{H}^{\text{eff}}$ into polyads.)

Let $\mathscr{H} = E$ and I is conserved. This means we have one equation that relates the non-conserved I_z to the non-conserved ψ. This is a **trajectory**!

$I_z(E, I, \psi)$ or $\psi(E, I, I_z)$

So all information about the exploration of action-angle space is given by single equation. A different choice of E, I gives a different trajectory.

We can determine the time-dependence for motion on this trajectory by integrating

$$\frac{\partial \mathscr{H}_{\text{LOCAL}}}{\partial \psi} = -\dot{I}_z \qquad \text{or} \qquad \frac{\partial \mathscr{H}_{\text{LOCAL}}}{\partial I_z} = \dot{\psi}$$

along the trajectory. We pick $E, I, \psi \rightarrow$ get I_z and $\dot{I}_z$, take a step $dt\dot{I}_z = dI_z$ along trajectory. We are now at a new ψ, then recalculate $\dot{I}_z$, etc.

What about $\mathscr{H}_{\text{NORMAL}}$?

$$\mathbf{H}^{\text{eff}}_{\text{NORMAL}} = \omega_0\left(v_s + v_a + 1\right) + \frac{1}{2}\left[\beta + (\varepsilon/2)\left(v_s + v_a + 1\right)\right]\left(v_s - v_a\right)$$
$$+(\gamma_1/4)\left(v_s + v_a + 1\right)^2 + (\gamma_2/4)\left(v_s - v_a\right)^2$$
$$+\delta\left(\mathbf{a}_s^{\dagger 2}\mathbf{a}_a^2 + \mathbf{a}_a^{\dagger 2}\mathbf{a}_s^2\right)$$

$$\omega_0 = \frac{\omega_s + \omega_a}{2}$$

$$\gamma_1/4 = \frac{x_{ss} + x_{aa} + x_{sa}}{4}$$

$$\gamma_2/4 = \frac{x_{ss} + x_{aa} - x_{sa}}{4}$$

$$\beta/2 = \frac{\omega_s - \omega_a}{2}$$

$$\varepsilon/2 = \frac{x_{ss} - x_{aa}}{2}$$

$$\delta = K_{ssaa}/16hc$$

Define Normal mode action-angle variables: (use over-bar to distinguish from Local mode variables).

$$v_s + v_a + 1 \equiv 2\bar{I} \qquad (\bar{I} = I)$$

$$v_s - v_a = 2\bar{I}_z \qquad (\bar{I}_z = I_x)$$

$$\mathbf{a}_s, \mathbf{a}_s^\dagger, \mathbf{a}_a, \mathbf{a}_a^\dagger \rightarrow (v + 1/2)^{1/2} e^{\pm i\phi}$$

$$(v_s + 1/2)(v_a + 1/2) = \bar{I}^2 - \bar{I}_z^2$$

$$\bar{\psi} = \phi_s - \phi_a$$

So now we have

$$\mathscr{H}_{\text{NORMAL}}/hc = 2\omega_0\bar{I} + (\beta + \varepsilon\bar{I})\bar{I}_z + \gamma_1\bar{I}^2$$
$$+\gamma\bar{I}_z^2 + 2\delta(\bar{I}^2 - \bar{I}_z^2)\cos 2\bar{\psi}$$

* $\bar{\theta}$ conjugate to $\bar{I}$ is absent from $\mathscr{H}$, thus I is conserved.
* choose $\mathscr{H} = E$ and a conserved value of I, have trajectory I_z vs ϕ.
* can get time dependence along trajectory

But how do we look at all of this? Phase space trajectories.

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When there is only one non-conserved action and one non-conserved conjugate angle, it is possible to display how trajectories explore all of phase space with a single family of 2-dimensional phase space trajectory maps (Fig. 9.13ab) or polyad phase spheres (Fig. 9.13cd). $P = v_R + v_L = v_s + v_a = 3$ for H_2O. 4 eigenstates.

* One Map (or sphere) for each value of I. In CM I is not necessarily integer.
* Trajectories plotted at each QM eigen-energy. In CM E is not quantized, so we can vary E continuously if we wish. It is informative to see the specific CM trajectory that corresponds to a particular eigen-energy in a particular polyad.

The phase space trajectories can be mapped in either the Local Mode (I_z, ψ) representation or the Normal Mode ($\bar{I}_z$, $\overline{\psi}$) representation. Both pictures contain the same information even though they look very different. These differences arise from flat projection onto 2D (Fig. 9.13ab) rather than onto the surface of a sphere (Fig 9.13cd).

The information on the phase space maps:

dotted line: separatrix. Divides phase space into two non-communicating regions. No trajectory can cross the separatrix. On one side is local mode behavior (trajectories 1a, 1b and 2a, 2b) and on the other is normal mode behavior (trajectories 3, 4)

Letters A, B, and C respectively stable (A and C) and unstable (B) “fixed points”. Trajectories that surround a fixed point are named by the character of that fixed point. As E is varied at constant I, a trajectory can collapse onto a fixed point, “fall through it”, and emerge as a qualitatively different class of trajectory on the other side of the separatrix, disappear, or bifurcate into two new classes of trajectories.

Bold curves 1a, 2a and 1b, 2b are two superposed local mode eigen-trajectories. The a,b specify two branches of the same trajectory.

The qualitative structures can change as I is varied. Bifurcations. Qualitative changes in the way phase space is explored.

We label trajectories #1, 2 as "local" because they explore the full 0 to 2π range of ψ. We label trajectories #3, 4 as "normal" because they explore the full 0 to 2π range of $\overline{\psi}$. This is a rigorous classification criterion.

The *complete* trajectories are not shown in Figure 9.13. For that you also need the non-conserved angle, θ, associated with the conserved action, I.

θ is not conserved because $\frac{\partial \mathcal{H}}{\partial I}$ is expressed in terms of non-conserved I_z and ψ. θ is time -dependent even though I is conserved. See Figure 9.14 for the invariant torus.

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The full trajectories lie on the surface of such a torus. The θ angle corresponds to rotation around the torus. The position on one invariant torus is specified by I_z, ψ, and θ.

For each E, there is another torus nested inside (or outside) the previous one.

One can intersect the torus with a plane. The one shown could be the normal mode $\bar{I}_z, \overline{\psi}$, one or the local mode I_z, ψ one. As the trajectory runs for a long time (and the winding number is not an integer) it will cut many times through the 2-D dividing surface. If a mark is placed on the dividing surface each time the trajectory crosses it, we have the solid curve trajectory on the I_z, ψ or I_z, ψ, ψ plane. This is called a **"SURFACE OF SECTION"**.

Qualitative changes in the motion on the phase sphere are shown in Figures 9.15, 9.16, and 9.17.

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Figure 9.16. Shows the evolution of the phase space structure for H_2O as $P = 1$ (two states) up to $P = 5$ (six states). At $P = 1$ (a) both states are normal. At $P = 2$ (b) the lowest energy state (#1) has become local. At $P = 5$, 4 states are local and 2 are normal.

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Figure 9.17. Shows the QM wavefunctions and the configuration space trajectories for all 6 states in the H_2O $P = 5$ polyad.

When there are more degeres of freedom, the task of mapping the exploration of phase space becomes more complicated. Surfaces of section provide a useful way of seeing key structures and qualitative changes.

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Figure 9.18. Shows surface of section for the $[N_{bend}, \ell] = [4, 0]$ and [8, 0] polyads of acetylene. For [4, 0] there are only 2 families of quasi-periodic trajectories which surround the normal mode *cis*-bend and *trans*-bend periodic trajectories (the separatrices $\psi_b = \pm\pi/2$). For [8, 0], chaos has emerged (unconnected dots) as well as 2 qualitatively new classes of trajectories. Can you see what they are?

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Figure 9.19 shows the evolution of the surface of section as one explores energies from the bottom (13,861 cm^{-1}) to the top (15,461 cm^{-1}) of the $[N_{bend} = 22, \ell = 0]$ polyad. Qualitative features on the 14,661 cm^{-1} SOS appear as different classes of configuration space trajectories. 1 and 2 refer to the left and right HCC local benders. Lots of chaos in the middle *E* region of the polyad.