

Dynamics in State Space and in Q, P Space

Readings: Chapter 9.4.7, 9.4.8, and 9.4.11, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

Polyatomic Molecule Vibrations
 Polyads — example: $\omega_1 \approx 2\omega_2 \approx \omega_3$
 with two anharmonic resonances

interconnected manifold of resonances
 rapid increase in number of near-degenerate zero-order states

Today

causal dynamics based on Heisenberg equation of motion rather than $\langle \mathbf{A} \rangle_t = \text{Trace}(\mathbf{A}\rho(t))$

We are able to compute the time evolution of any observable quantity using $\langle \mathbf{A} \rangle_t = \text{Trace}(\mathbf{A}\rho(t))$. Need to know $\rho(t)$.

But this merely tells us *what happens*, not *why it happens*. NO CAUSALITY.

One of the most interesting classes of information will be the early time behavior of precisely specifiable pluck of the system. So we are interested in $\frac{d}{dt}\langle \mathbf{A} \rangle$ and $\frac{d^2}{dt^2}\langle \mathbf{A} \rangle$ at $t = 0$.

Intrapolyad Dynamics

1. $\langle \mathbf{a}_j^\dagger \mathbf{a}_j \rangle_t$ number operator \mathbf{N}_j
2. $\langle \mathbf{Q}_j \rangle$ or $\langle \mathbf{P}_j \rangle$ coordinate and momentum operators
3. $\langle \mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger \rangle, \langle \mathbf{\Omega}_1 - \mathbf{\Omega}_1^\dagger \rangle, \langle \mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger \rangle, \langle \mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger \rangle$ [recall $\mathbf{\Omega}_1 = k'_{11,33} \mathbf{a}_1^2 \mathbf{a}_3^{+2}$, $\mathbf{\Omega}_2 = k'_{1,22} \mathbf{a}_1 \mathbf{a}_2^{+2}$], resonance and transfer rate operators.
4. Fractional importance of resonance 1 vs. 2 for various plucks.
5. Find a new set of $\mathbf{a}, \mathbf{a}^\dagger, \mathbf{N}$ for local rather than normal modes. $\mathbf{a}_L = 2^{-1/2} (\mathbf{a}_1 + \mathbf{a}_3)$, $\mathbf{a}_R = 2^{-1/2} (\mathbf{a}_1 - \mathbf{a}_3)$

$\mathbf{N} = \mathbf{N}_1 + \mathbf{N}_2 + \mathbf{N}_3$

We start with the **Heisenberg Equation of Motion**

$$\frac{d}{dt} \langle \mathbf{A} \rangle = \frac{1}{i\hbar} \langle [\mathbf{A}, \mathbf{H}] \rangle + \left\langle \frac{\partial \mathbf{A}}{\partial t} \right\rangle$$

If we want to know about (the number of quanta in mode j), we need to compute $[\mathbf{a}_j^\dagger \mathbf{a}_j, \mathbf{H}]$

Useful simplifications:

number operators, \mathbf{N}_j , commute with other number operators

all operators commute with constants

a number operator for oscillator j commutes with resonance operators that do not involve oscillator j .

So, for the $\frac{d}{dt}$ of \mathbf{N}_1 , \mathbf{N}_2 , and \mathbf{N}_3 we need to work out

$$\begin{aligned} & [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{Q}_1] \\ & [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{Q}_1^\dagger] \\ & [\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{Q}_2] \\ & [\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{Q}_2^\dagger] \end{aligned}$$

Since all of the resonance operators operate within a polyad, the polyad quantum number is conserved

$$\begin{aligned} \mathbf{P} &= 2\mathbf{a}_1^\dagger \mathbf{a}_1 + \mathbf{a}_2^\dagger \mathbf{a}_2 + 2\mathbf{a}_3^\dagger \mathbf{a}_3 \\ \frac{d}{dt} \langle \mathbf{P} \rangle_t &= 0 \quad \left(\text{also } \frac{d^2}{dt^2} \langle \mathbf{P} \rangle_t = 0 \right) \end{aligned}$$

Therefore the expectation value of the more difficult of the number operators ($\mathbf{a}_1^\dagger \mathbf{a}_1$) can be obtained from the two easy ones.

$$\langle \mathbf{a}_1^\dagger \mathbf{a}_1 \rangle_t = \frac{1}{2} \left[\mathbf{P} - \langle \mathbf{a}_2^\dagger \mathbf{a}_2 \rangle_t - 2 \langle \mathbf{a}_3^\dagger \mathbf{a}_3 \rangle_t \right]$$

a number, not an operator. Conserved.

Work out a few examples

$$\begin{aligned} [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{\Omega}_1] &= [\mathbf{a}_3^\dagger \mathbf{a}_3, k'_{1,33} \mathbf{a}_1^2 \mathbf{a}_3^{\dagger 2}] \\ &= k'_{1,33} \mathbf{a}_1^2 [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{a}_3^{\dagger 2}] = 2k'_{1,33} \mathbf{a}_1^2 \mathbf{a}_3^{\dagger 2} \\ [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{\Omega}_1^\dagger] &= k'_{1,33} \mathbf{a}_1^{\dagger 2} [\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{a}_3^2] = -2k'_{1,33} \mathbf{a}_1^{\dagger 2} \mathbf{a}_3^2 \end{aligned}$$

thus

$$[\mathbf{a}_3^\dagger \mathbf{a}_3, \mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger] = 2 \underbrace{(\mathbf{\Omega}_1 - \mathbf{\Omega}_1^\dagger)}_{\substack{\text{The exclusive cause} \\ \text{of the dynamics of} \\ \mathbf{N}_3}}$$

Similarly,

$$\begin{aligned} [\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{\Omega}_2] &= [\mathbf{a}_2^\dagger \mathbf{a}_2, k'_{1,22} \mathbf{a}_1 \mathbf{a}_2^{\dagger 2}] \\ &= k'_{1,22} \mathbf{a}_1 [\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{a}_2^{\dagger 2}] = 2k'_{1,22} \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} \\ [\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{\Omega}_2^\dagger] &= -2k'_{1,22} \mathbf{a}_1^\dagger \mathbf{a}_2^2 \end{aligned}$$

thus

$$[\mathbf{a}_2^\dagger \mathbf{a}_2, \mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger] = 2 \underbrace{(\mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger)}_{\substack{\text{The exclusive cause} \\ \text{of the dynamics of} \\ \mathbf{N}_3}}$$

$$\boxed{\begin{aligned} \frac{d}{dt} \langle \mathbf{N}_2 \rangle &= \frac{2}{i\hbar} \langle \mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger \rangle_t \\ \frac{d}{dt} \langle \mathbf{N}_3 \rangle &= \frac{2}{i\hbar} \langle \mathbf{\Omega}_1 - \mathbf{\Omega}_1^\dagger \rangle_t \end{aligned}}$$

Now, suppose we start in the $|0, P, 0\rangle$ basis state, a pure-bender pluck.

$$\langle \mathbf{N}_2 \rangle_0 = P$$

$$\langle \mathbf{Q}_2 \rangle_t = \langle 0P0 | k'_{1,22} \mathbf{a}_1 \mathbf{a}_2^\dagger | 0P0 \rangle = 0$$

$$\langle \mathbf{Q}_2^\dagger \rangle_t = 0, \text{ thus } \frac{d}{dt} \langle \mathbf{N}_2 \rangle = 0 \text{ at } t=0 \text{ for this choice of pluck.}$$

$$\langle \mathbf{N}_2 \rangle_t = P + O(t^2) \left(\begin{array}{l} \text{because we have just shown that the first} \\ \text{derivative is zero at } t=0 \end{array} \right)$$

Not very interesting. The extreme pure bender pluck gives no motion in \mathbf{N}_2 (or \mathbf{N}_1 or \mathbf{N}_3) at $t=0$. All

$\frac{d}{dt} \langle \mathbf{N}_i \rangle = 0$. It is likely that the second derivative is not zero. We may return to this later or on the final exam.

Choose a less extreme pluck.

$$|\psi(0)\rangle = a|0P0\rangle + b|1P-20\rangle$$

$$a = |a|e^{i\phi_a}$$

$$b = |b|e^{i\phi_b} = [1 - |a|^2]^{1/2} e^{i\phi_b} \quad (\text{normalized})$$

(ϕ_a and ϕ_b are time dependent! Why must this be true?)

$$\begin{aligned} \langle \mathbf{N}_2 \rangle_0 &= \langle \Psi(0) | \mathbf{N}_2 | \Psi(0) \rangle = |a|^2 P + |b|^2 (P - 2) \\ &= P - 2 + 2|a|^2 \end{aligned}$$

If $|a| = 2^{-1/2}$ $\langle \mathbf{N}_2 \rangle_0 = P - 1$ as expected (average of P and $P - 2$)

Now to get $\left. \frac{d}{dt} \langle \mathbf{N}_2 \rangle \right|_{t=0}$ we need

$$\begin{aligned}
 \langle \psi(0) | \mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger | \psi(0) \rangle &= k'_{1,22} \left[a^* b \langle 0P0 | \mathbf{a}_1 \mathbf{a}_2^{\dagger 2} | 1P-20 \rangle - ab^* \langle 1P-20 | \mathbf{a}_1^\dagger \mathbf{a}_2^2 | 0P0 \rangle \right] \\
 &= k'_{1,22} 2i \operatorname{Im}(a^* b) [P(P-1)]^{1/2} \\
 &= k'_{1,22} [P(P-1)]^{1/2} |a| [1-|a|^2]^{1/2} 2i \sin(\phi_b - \phi_a)
 \end{aligned}$$

Thus

$$\begin{aligned}
 \left. \frac{d}{dt} \langle \mathbf{N}_2 \rangle \right|_{t=0} &= \frac{2}{i\hbar} \langle \mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger \rangle_0 \\
 &= \frac{4k'_{1,22}}{\hbar} [P(P-1)]^{1/2} |a| (1-|a|^2)^{1/2} \sin(\phi_b - \phi_a)
 \end{aligned}$$

note that if $\phi_b = \phi_a$, $\langle \mathbf{N}_2 \rangle_t$ is at an extremum at $t = 0$. (1st derivative is zero)

but if $\phi_b - \phi_a = \pi/2$

$\langle \mathbf{N}_2 \rangle_{t=0}$ is experiencing its maximum rate of increase.

We can ask a question: what is the two-component superposition state that exhibits the maximum rate of change in $\langle \mathbf{N}_2 \rangle$ at $t = 0$?

Want Maximum matrix element of $\mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger$. Polyad # $P = 2v_1 + v_2 + 2v_3$.

Let: $v_3 = 0$, $v_1 = n$, $v_2 = P - 2n$.

$$\begin{aligned}
 \langle n(P-2n)0 | \mathbf{a}_1^\dagger \mathbf{a}_2^2 | (n-1)(P-2n+2)0 \rangle &= [n(P-2n+2)(P-2n+1)]^{1/2} \\
 &= [n(P^2 - 4nP + 3P - 6n + 4n^2 + 2)]^{1/2} \\
 0 &= \frac{d}{dn} (4n^3 - 6n^2 - 4n^2P + n(P^2 + 3P + 2)) \\
 0 &= 12n^2 - 12n - 8nP + P^2 + 3P + 2 \\
 n &= \frac{(12 + 8P) \pm [(12 + 8P)^2 - 48(P^2 + 3P + 2)]^{1/2}}{24}
 \end{aligned}$$

If $P = 10$

$$n_{\max} = \frac{92 \pm [92^2 - 48(132)]^{1/2}}{24} = \frac{92 \pm 46}{24} = 6 \text{ or } 2$$

$$\begin{array}{ll}
 n_{\max} = 2 & ME = 10.6 \\
 n_{\min} = 6 & ME = 0 \quad (\text{not possible})
 \end{array}$$

<u>n</u>	<u>ME</u>
0	0
1	9.5
2	10.6 maximum
3	9.5
4	6.9

Maximum matrix element is always nearer the middle than the extreme edges of a polyad.

To get $\frac{d^2}{dt^2}$ we need to do a much more elaborate calculation

$$\frac{d^2}{dt^2} \langle \mathbf{N}_2 \rangle_t = \frac{2}{i\hbar} \frac{d}{dt} \langle \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger \rangle_t = \frac{2}{i\hbar} \frac{1}{i\hbar} \langle [\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{H}] \rangle_t$$

We need the following evaluated commutators (because the operators included are all of the operators that appear in \mathbf{H} which do not commute with $\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger$).

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_1] = (\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_2] = -2(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_1^2] = 2(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_1 - (\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_2^2] = -4(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_2 - 4(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_1\mathbf{N}_2] = (\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)(\mathbf{N}_2 - 2\mathbf{N}_1) + 4(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger] = 2k'_{11,33}k'_{1,22}\mathbf{a}_2^{\dagger 2}(\mathbf{a}_1^\dagger\mathbf{a}_3^2 + \mathbf{a}_1\mathbf{a}_3^{\dagger 2})$$

$$[\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger, \boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger] = -2k'_{1,22}[\mathbf{N}_1(4\mathbf{N}_2 + 2) - \mathbf{N}_2(\mathbf{N}_2 - 1)]$$

So we have everything we need to compute the $\frac{d}{dt}$ and $\frac{d^2}{dt^2}$ of $\langle \mathbf{N}_1 \rangle_{t_0}$ if we know $\Psi(t_0)$ at $t = t_0$.

What about $\langle \mathbf{Q}_j \rangle$ and $\langle \mathbf{P}_j \rangle$? This is easy! There are no non-zero intra-polyad matrix elements of $\mathbf{Q}_j = 2^{-1/2}(\mathbf{a}_j + \mathbf{a}_j^\dagger)$ or $\mathbf{P}_j = 2^{-1/2}i(\mathbf{a}_j^\dagger - \mathbf{a}_j)$.

The only way to get motion in \mathbf{Q} or \mathbf{P} is to pluck a superposition of several polyads.

Useful Results

$$\mathbf{\Omega}_1 = k'_{11,33} \mathbf{a}_1^2 \mathbf{a}_3^{\dagger 2}$$

$$\mathbf{\Omega}_2 = k'_{1,22} \mathbf{a}_1 \mathbf{a}_2^{\dagger 2}$$

$$\begin{aligned} \mathbf{H}/hc &= \left\{ \omega_1 (\mathbf{N}_1 + 1/2) + \omega_2 (\mathbf{N}_2 + 1/2) + \omega_3 (\mathbf{N}_3 + 1/2) \right. \\ &= x_{11} (\mathbf{N}_1^2 + \mathbf{N}_1 + 1/4) + x_{22} (\mathbf{N}_2^2 + \mathbf{N}_2 + 1/4) + x_{33} (\mathbf{N}_3^2 + \mathbf{N}_3 + 1/2) \\ &\quad + x_{13} \left[\mathbf{N}_1 \mathbf{N}_3 + \frac{1}{2} (\mathbf{N}_1 + \mathbf{N}_3) + \frac{1}{4} \right] + x_{12} \left[\mathbf{N}_1 \mathbf{N}_2 + \frac{1}{2} (\mathbf{N}_1 + \mathbf{N}_2) + \frac{1}{4} \right] \\ &\quad \left. + x_{23} \left[\mathbf{N}_2 \mathbf{N}_3 + \frac{1}{2} (\mathbf{N}_2 + \mathbf{N}_3) + \frac{1}{4} \right] \right\} \\ &\quad + (\mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger) + (\mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger) \end{aligned}$$

$$\begin{aligned} \mathbf{H}/hc &= \left\{ \mathbf{N}_1 \left(\omega_1 + x_{11} + \frac{1}{2} x_{13} + \frac{1}{2} x_{12} \right) + \mathbf{N}_2 \left(\omega_2 + x_{22} + \frac{1}{2} x_{12} + \frac{1}{2} x_{23} \right) \right. \\ &\quad + \mathbf{N}_3 \left(\omega_3 + x_{33} + \frac{1}{2} x_{13} + \frac{1}{2} x_{23} \right) + \mathbf{N}_1^2 x_{11} + \mathbf{N}_2^2 x_{22} + \mathbf{N}_3^2 x_{33} \\ &\quad + \mathbf{N}_1 \mathbf{N}_2 x_{12} + \mathbf{N}_1 \mathbf{N}_3 x_{13} + \mathbf{N}_2 \mathbf{N}_3 x_{23} \\ &\quad \left. + \left(\frac{\omega_1}{2} + \frac{\omega_2}{2} + \frac{\omega_3}{2} + \frac{x_{11}}{4} + \frac{x_{22}}{4} + \frac{x_{33}}{4} + \frac{x_{13}}{4} + \frac{x_{12}}{4} + \frac{x_{23}}{4} \right) \right\} \\ &\quad + (\mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger) + (\mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger) \end{aligned}$$

$$[\mathbf{N}_3, \boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger] = -2(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_1, \boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger] = +2(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_1, \boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger] = -1(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_2, \boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger] = +2(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \mathbf{N}_1^2] = 4[(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger) - (\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)]$$

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \mathbf{N}_3^2] = -4[(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger) + (\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)]$$

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \mathbf{N}_1 \mathbf{N}_3] = 2[(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)(\mathbf{N}_1 - \mathbf{N}_3) + 2(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)]$$

$$[\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_1^2] = 2[(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_1 - (\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)]$$

$$[\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_2^2] = -4[(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_2 + (\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)]$$

$$[\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger, \mathbf{N}_1 \mathbf{N}_2] = (\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)(\mathbf{N}_2 - 2\mathbf{N}_1) + 2(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_1, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = -(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_2, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = 2(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_1^2, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = -2(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_1 + (\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_2^2, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = 4(\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)\mathbf{N}_2 + 4(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_1 \mathbf{N}_2, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = (\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger)(2\mathbf{N}_1 - \mathbf{N}_2) - 2(\boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger)$$

$$[\mathbf{N}_1, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = -2(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_3, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = 2(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_1^2, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = -4(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)\mathbf{N}_1 + 4(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_3^2, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = 4(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)\mathbf{N}_3 + 4(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)$$

$$[\mathbf{N}_1\mathbf{N}_3, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = 2(\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger)(\mathbf{N}_1 - \mathbf{N}_3) - 2(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger)$$

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger] = 2k'_{11,33}k'_{1,22}\mathbf{a}_2^{\dagger 2}(\mathbf{a}_1\mathbf{a}_3^{\dagger 2} - \mathbf{a}_1^\dagger\mathbf{a}_3^2)$$

outside of polyad

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_1^\dagger] = 4k'_{11,33}[\mathbf{N}_1(\mathbf{N}_1 - 1)(2\mathbf{N}_3 - 1) - \mathbf{N}_3(\mathbf{N}_3 - 1)(2\mathbf{N}_1 + 1)]$$

$$[\boldsymbol{\Omega}_2 + \boldsymbol{\Omega}_2^\dagger, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = 2k'_{1,22}[\mathbf{N}_1(4\mathbf{N}_2 + 2) - \mathbf{N}_2(\mathbf{N}_2 - 1)]$$

$$[\boldsymbol{\Omega}_1 + \boldsymbol{\Omega}_1^\dagger, \boldsymbol{\Omega}_2 - \boldsymbol{\Omega}_2^\dagger] = -2k'_{11,33}k'_{1,22}\mathbf{a}_2^{\dagger 2}(\mathbf{a}_1^\dagger\mathbf{a}_3^2 + \mathbf{a}_1\mathbf{a}_3^{\dagger 2})$$

outside of polyad

$$\frac{d}{dt}\langle \mathbf{A} \rangle = \frac{1}{i\hbar}\langle [\mathbf{A}, \mathbf{H}] \rangle$$

$$\frac{d^2}{dt^2}\langle \mathbf{A} \rangle = \left(\frac{1}{i\hbar}\right)\frac{d}{dt}\langle [\mathbf{A}, \mathbf{H}] \rangle = \left(\frac{1}{i\hbar}\right)^2\langle [[\mathbf{A}, \mathbf{H}], \mathbf{H}] \rangle$$

With the above list of commutators, you should be able to express the first and second time derivatives of any observable quantity, evaluated at the instant of the initial pluck. This gives the explicit cause (expressed in terms of parameters ω_i , x_{ij} , k' , and quantum numbers) for the early time evolution of any specifiable observable.