Harmonic dynamics of arbitrary set of atoms (no periodic symmetry)

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{ij} u_i \Phi_{ij} u_j - \sum_i f_i u_i$$

§1. Normal coordinates

- Equations: $\frac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i \;,\; \frac{\partial \mathcal{H}}{\partial q_i} = -\dot{p}_i$ where $q_i \equiv u_i$

The Lagrangian:

$$\mathcal{L} = \sum_i \frac{m_i \dot{u}_i^2}{2} - \frac{1}{2}\sum_{ij} u_i \Phi_{ij} u_j + \sum_j f_j u_j$$

- We first diagonalise $\mathcal{L}$ and $\mathcal{H}$.

$$x_i = \sqrt{m_i}\, u_i \;,\quad x = M^{1/2} u \quad \text{and} \quad u = M^{-1/2} x$$

$$\mathcal{L} = \frac{1}{2}(M^{1/2}\dot{u})^{\dagger}(M^{1/2}\dot{u}) - \frac{1}{2} u^{\dagger}\Phi u + f^{\dagger} u$$

(although all are real so far, i.e. $\dagger$ is equiv. to T).

$$\to \mathcal{L} = \frac{1}{2}\dot{x}^{\dagger}\dot{x} - \frac{1}{2} x^{\dagger}\underbrace{(M^{-1/2}\Phi M^{-1/2})}_{D} x + \underbrace{(f^{\dagger} M^{-1/2})}_{\varphi^{\dagger}} x$$

$$\mathcal{L} = \frac{1}{2}\dot{x}^{\dagger}\dot{x} - \frac{1}{2} x^{\dagger} D x + \varphi^{\dagger} x \;,\quad \boxed{\varphi = M^{-1/2} f}$$

If we know all eigenvectors / values of D:

$$\boxed{D e_\lambda = \omega_\lambda^2 e_\lambda} \quad \boxed{\sum_\lambda e_\lambda e_\lambda^{\dagger} = \mathbb{1}} \quad \boxed{e_\lambda^{\dagger} e_{\lambda'} = \delta_{\lambda\lambda'}}$$

$$\boxed{D = \sum_\lambda e_\lambda e_\lambda^{\dagger}\omega_\lambda^2} \quad \text{(spectral theorem)}$$

then: $$\mathcal{L} = \frac{1}{2}\dot{x}^{\dagger}\dot{x} - \frac{1}{2}\sum_\lambda \omega_\lambda^2 x^{\dagger} e_\lambda e_\lambda^{\dagger} x + \varphi^{\dagger} x$$

$$= \frac{1}{2}\dot{x}^\dagger \dot{x} - \frac{1}{2}\sum_\lambda \omega_\lambda^2 (e_\lambda^\dagger x)^{\dagger}(e_\lambda^\dagger x) + \varphi^\dagger x$$

We introduce:

$$\boxed{\xi_\lambda = e_\lambda^\dagger x} \qquad \left(\xi_\lambda = \sum_i e_{i\lambda}^* x_i \right)$$

real!

$$\boxed{\xi_\lambda = \sum_i e_{i\lambda}^* \sqrt{m_i}\, u_i} \leftarrow \underline{\underline{\text{real!}}}$$

Then,

$$\sum_\lambda e_\lambda \xi_\lambda = \sum_\lambda e_\lambda e_\lambda^\dagger x = x, \qquad \boxed{x = \sum_\lambda e_\lambda \xi_\lambda}$$

$$\boxed{u_i = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \xi_\lambda}$$

and the kinetic energy goes into

$$\frac{1}{2}\dot{x}^\dagger \dot{x} = \frac{1}{2}\left(\sum_\lambda e_\lambda \dot{\xi}_\lambda\right)^\dagger \left(\sum_{\lambda'} e_{\lambda'} \dot{\xi}_{\lambda'}\right) =$$

$$= \frac{1}{2}\sum_{\lambda\lambda'} \dot{\xi}_\lambda^* (e_\lambda^\dagger e_{\lambda'}) \dot{\xi}_{\lambda'} = \frac{1}{2}\sum_\lambda \dot{\xi}_\lambda^* \dot{\xi}_\lambda$$

$$\hookrightarrow \boxed{\mathcal{L} = \frac{1}{2}\sum_\lambda \dot{\xi}_\lambda^* \dot{\xi}_\lambda - \frac{1}{2}\sum_\lambda \omega_\lambda^2 \xi_\lambda^* \xi_\lambda + \sum_\lambda (\varphi^\dagger e_\lambda)\xi_\lambda}$$

Conjugate variable to ξ_λ is

$$\eta_\lambda = \frac{\partial \mathcal{L}}{\partial \dot{\xi}_\lambda} = \dot{\xi}_\lambda \qquad \boxed{\eta_\lambda = \dot{\xi}_\lambda}$$

~~In the Hamiltonian~~:

$$\cancel{\mathcal{H} = \frac{1}{2}\sum_\lambda \xi_\lambda (M^{-1/2}p)^T (M^{-1/2}p) \; (pM^{-1/2})^T (pM^{-1/2})}$$

$$\cancel{+ \frac{1}{2}u^T \Phi u - f^T u = (M^{1/2}u)^T (M^{1/2}u)}$$

Then, the Hamiltonian becomes:

$$\mathcal{H} = \frac{1}{2}\sum_\lambda \eta_\lambda^2 + \frac{1}{2}\sum_\lambda \omega_\lambda^2 \xi_\lambda^2 - \sum_\lambda (\varphi^\dagger e_\lambda)\xi_\lambda$$

$$\boxed{\mathcal{H} = \sum_\lambda \left[\frac{1}{2}\left(\eta_\lambda^2 + \omega_\lambda^2 \xi_\lambda^2\right) - (\varphi^T e_\lambda)\, \xi_\lambda \right]}$$

and eq. of motion are separated:

$$\frac{\partial \mathcal{H}}{\partial \eta_\lambda} = \eta_\lambda \equiv \dot{\xi}_\lambda$$

$$-\frac{\partial \mathcal{H}}{\partial \xi_\lambda} = -\omega_\lambda^2 \xi_\lambda + (\varphi^T e_\lambda) \equiv \dot{\eta}_\lambda = \ddot{\xi}_\lambda$$

i.e. $$\boxed{\ddot{\xi}_\lambda + \omega_\lambda^2 \xi_\lambda = \varphi^T e_\lambda \equiv g_\lambda}$$

Its solution:

$$\overset{*}{\xi}_\lambda(t) = A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t} + \int_0^t g_\lambda(\tau) \frac{\sin \omega_\lambda (t-\tau)}{\omega_\lambda} d\tau$$

§2. General solution

$$u_i(t) = \frac{1}{\sqrt{m_i}} X_i(t) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \xi_\lambda(t)$$

$$= \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \left[A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t} + \int_0^t g_\lambda(\tau) \frac{\sin \omega_\lambda (t-\tau)}{\omega_\lambda} d\tau \right]$$

~~Initial cond~~ Velocity:

$$v_i(t) = \dot{u}_i(t) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \Big\{ i\omega_\lambda \left(A_\lambda e^{i\omega_\lambda t} - B_\lambda e^{-i\omega_\lambda t} \right)$$

$$+ \int_0^t g_\lambda(\tau) \cos(\omega_\lambda (t-\tau))\, d\tau$$

Initial conditions:

$$u_i(0) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \left[A_\lambda + B_\lambda \right]$$

$$V_i(0) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \cdot i\omega_\lambda (A_\lambda - B_\lambda)$$

These should be real, so that:

$$u_i^* = u_i \to A_\lambda^* e^{-i\omega_\lambda t} + B_\lambda^* e^{i\omega_\lambda t} \equiv A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t}$$

$$\hookrightarrow A_\lambda^* \equiv B_\lambda \ ,$$

Should solve for initial ~~velocities~~ A_λ, B_λ:

$$\sum_i \sqrt{m_i}\, e_{i\lambda} u_i(0) = \sum_i \sqrt{m_i}\, e_{i\lambda} \frac{1}{\sqrt{m_i}} \sum_{\lambda'} e_{i\lambda'} (A_{\lambda'} + B_{\lambda'})$$

$$= \sum_{\lambda'} \underbrace{\Big(\sum_i e_{i\lambda} e_{i\lambda'}\Big)}_{= \delta_{\lambda\lambda'}} (A_{\lambda'} + B_{\lambda'}) = A_\lambda + B_\lambda \ ,$$

$$\sum_i \sqrt{m_i}\, e_{i\lambda} V_i(0) = \sum_{\lambda'} \underbrace{\Big(\sum_i e_{i\lambda} e_{i\lambda'}\Big)}_{= \delta_{\lambda\lambda'}} i\omega_{\lambda'} (A_{\lambda'} - B_{\lambda'}) = i\omega_\lambda (A_\lambda - B_\lambda) \ ,$$

so that:

$$\begin{cases} A_\lambda + B_\lambda = \sum_j \sqrt{m_j}\, e_{j\lambda} u_j(0) \\ A_\lambda - B_\lambda = \frac{1}{i\omega_\lambda} \sum_j \sqrt{m_j}\, e_{j\lambda} V_j(0) \end{cases}$$

$$\hookrightarrow \begin{cases} A_\lambda = \frac{1}{2} \sum_j \sqrt{m_j}\, e_{j\lambda} \left(u_j(0) + \frac{1}{i\omega_\lambda} V_j(0) \right) \\ B_\lambda = \frac{1}{2} \sum_j \sqrt{m_j}\, e_{j\lambda} \left(u_j(0) - \frac{1}{i\omega_\lambda} V_j(0) \right) \end{cases}$$

We indeed ~~see~~ that $B_\lambda^* = A_\lambda$.

We now calculate

$$A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t} = \frac{1}{2} \sum_j \sqrt{m_j}\, e_{j\lambda} \Big[u_j(0) \left(e^{i\omega_\lambda t} + e^{-i\omega_\lambda t} \right)$$

$$+ \frac{1}{i\omega_\lambda} V_j(0) \left(e^{i\omega_\lambda t} - e^{-i\omega_\lambda t} \right) \Big]$$

$$= \frac{1}{2} \sum_j \sqrt{m_j}\, e_{j\lambda} \left[u_j(0)\, 2\cos\omega_\lambda t + \frac{v_j(0)}{\omega_\lambda}\, 2\sin\omega_\lambda t \right],$$

$$= \sum_j \sqrt{m_j}\, e_{j\lambda} \left[u_j(0) \cos\omega_\lambda t + v_j(0) \frac{\sin\omega_\lambda t}{\omega_\lambda} \right].$$

Also,

$$\omega_\lambda\left(A_\lambda e^{i\omega_\lambda t} - B_\lambda e^{-i\omega_\lambda t}\right) = \frac{i\omega_\lambda}{2} \sum_j \sqrt{m_j}\, e_{j\lambda}\Big[u_j(0)\, 2i\sin\omega_\lambda t$$

$$+ \frac{1}{i\omega_\lambda} v_j(0)\, 2\cos\omega_\lambda t\Big] = \sum_j \sqrt{m_j}\, e_{j\lambda}\Big[-u_j(0)\,\omega_\lambda \sin\omega_\lambda t$$

$$+ v_j(0)\cos\omega_\lambda t\Big],$$

so that:

$$u_i(t) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \left\{ \sum_j \sqrt{m_j}\, e_{j\lambda} \left(u_j(0)\cos\omega_\lambda t + v_j(0)\frac{\sin\omega_\lambda t}{\omega_\lambda} \right) \right.$$

$$\left. + \int_0^t g_\lambda(\tau) \frac{\sin\omega_\lambda(t-\tau)}{\omega_\lambda}\, d\tau \right\}$$

Here:

$$g_\lambda(\tau) = \varphi^T(\tau)\, e_\lambda = \sum_j \varphi_j(\tau)\, e_{j\lambda} = \sum_j \frac{1}{\sqrt{m_j}} f_j(\tau)\, e_{j\lambda}$$

$u_i(t)$ consists of two parts:

(i) <u>integral</u>

$$\frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \int_0^t \sum_j \frac{1}{\sqrt{m_j}} f_j(\tau)\, e_{j\lambda} \frac{\sin\omega_\lambda(t-\tau)}{\omega_\lambda}\, d\tau$$

$$= \sum_j \frac{1}{\sqrt{m_i m_j}} \int_0^t \left[\sum_\lambda \frac{e_{i\lambda} e_{j\lambda}}{\omega_\lambda} \sin\omega_\lambda(t-\tau) \right] f_j(\tau)\, d\tau$$

We introduce:

$$\boxed{\mathcal{G}_{ij}(t) = \sum_\lambda \frac{e_{i\lambda} e_{j\lambda}}{\omega_\lambda} \sin\omega_\lambda t}$$

Then the integral $= \sum_j \frac{1}{\sqrt{m_i m_j}} \int_0^t \Omega_{ij}(t-\tau) f_j(\tau) d\tau$.

(ii) Term with initial positions / velocities

$$\frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \sum_j \sqrt{m_j}\, e_{j\lambda} \left[u_j(0) \cos\omega_\lambda t + v_j(0) \frac{\sin\omega_\lambda t}{\omega_\lambda} \right]$$

$$= \sum_j \sqrt{\frac{m_j}{m_i}} \left\{ u_j(0) \left(\sum_\lambda e_{i\lambda} e_{j\lambda} \cos\omega_\lambda t \right) + v_j(0) \left(\sum_\lambda e_{i\lambda} e_{j\lambda} \frac{\sin\omega_\lambda t}{\omega_\lambda} \right) \right\}$$

$$= \sum_j \sqrt{\frac{m_j}{m_i}} \left[u_j(0)\, \dot{\Omega}_{ij}(t) + v_j(0)\, \Omega_{ij}(t) \right]$$

Finally,

$$\boxed{u_i(t) = \sum_j \left\{ \sqrt{\frac{m_j}{m_i}} \left(\dot{\Omega}_{ij}(t)\, u_j(0) + \Omega_{ij}(t)\, v_j(0) \right) + \frac{1}{\sqrt{m_i m_j}} \int_0^t \Omega_{ij}(t-\tau) f_j(\tau)\, d\tau \right\}}$$

The integral can also be rewritten by integrating by parts,

$$\int_0^t \overbrace{\Omega(t-\tau) \underbrace{f(\tau)}_{u} d\tau}^{dv} \Rightarrow uv| - \int u\, dv$$

$u \Rightarrow f(\tau)$

$dv \Rightarrow \Omega(t-\tau)\, d\tau\,, \quad v(\tau) = \int_t^\tau \Omega(t-\tau')\, d\tau' \cancel{= \Lambda(t-\tau)}$

$$\cancel{\hookrightarrow \int_0^t \cdots d\tau =} \int_t^\tau = \left| \begin{array}{l} x = t-\tau' \\ dx = -d\tau' \end{array} \right| = -\int_0^{t-\tau} \Omega(x)\, dx \equiv \Lambda(t-\tau)$$

$$\boxed{\Lambda(t) = -\int_0^t \Omega(\tau)\, d\tau}$$

then,

$$\int_0^t \Omega(t-\tau) f(\tau)\, d\tau = f(\tau)\Lambda(t-\tau)\Big|_0^t - \int_0^t \dot{f}(\tau)\Lambda(t-\tau)\, d\tau$$

$$= f(t)\underset{0}{\underset{\shortparallel}{\Lambda(0)}} - f(0)\Lambda(t) - \int_0^t \Lambda(t-\tau)\dot{f}(\tau)\, d\tau$$

$$= - f(0)\Lambda(t) - \int_0^t \Lambda(t-\tau)\dot{f}(\tau)\, d\tau \qquad \checkmark$$

Then,

$$\boxed{u_i(t) = \sum_j \left[\sqrt{\frac{m_j}{m_i}} \left(\dot{\Omega}_{ij}(t)\, u_j(0) + \Omega_{ij}(t)\, v_j(0) \right) - \frac{1}{\sqrt{m_i m_j}} \left(\Lambda_{ij}(t) f_j(0) + \int_0^t \Lambda_{ij}(t-\tau) \dot{f}(\tau)\, d\tau \right) \right]}$$

Now, for the velocities:

$$v_i(t) = \frac{1}{\sqrt{m_i}} \sum_\lambda e_{i\lambda} \Big\{ \sum_j \sqrt{m_j}\, e_{j\lambda} \left(-u_j(0)\,\omega_\lambda \sin\omega_\lambda t + v_j(0)\cos\omega_\lambda t \right)$$

$$+ \sum_j \frac{1}{\sqrt{m_j}} e_{j\lambda} \int_0^t f_j(\tau) \cos\omega_\lambda (t-\tau)\, d\tau \Big\}$$

$$= \frac{1}{\sqrt{m_i}} \sum_j \Big[\sqrt{m_j} \Big\{ -u_j(0) \Big(\sum_\lambda e_{i\lambda} e_{j\lambda} \omega_\lambda \sin\omega_\lambda t \Big) +$$

$$+ v_j(0) \Big(\sum_\lambda e_{i\lambda} e_{j\lambda} \cos\omega_\lambda t \Big) + \int_0^t \frac{1}{\sqrt{m_i m_j}} \Big(\sum_\lambda e_{i\lambda} e_{j\lambda} \cos\omega_\lambda (t-\tau) \Big) f_j(\tau) d\tau \Big]$$

$$= \sum_j \Big\{ \sqrt{\frac{m_j}{m_i}} \left[+ u_j(0)\, \ddot{\Omega}_{ij}(t) + v_j(0)\, \dot{\Omega}_{ij}(t) \right] + \int_0^t \frac{1}{\sqrt{m_i m_j}} \dot{\Omega}_{ij}(t-\tau) f_j(\tau) d\tau \Big\}$$

$$\boxed{V_i(t) = \sum_j \left\{ \sqrt{\frac{m_j}{m_i}} \left(\ddot{\Omega}_{ij}(t)\, u_j(0) + \dot{\Omega}_{ij}(t)\, v_j(0) \right) + \int_0^t \frac{1}{\sqrt{m_i m_j}}\, \dot{\Omega}_{ij}(t-\tau)\, f_j(\tau)\, d\tau \right\}}$$

In the matrix form:

$$\boxed{\begin{pmatrix} u(t) \\ v(t) \end{pmatrix} = M^{-1/2} \begin{pmatrix} \dot{\Omega}(t) & \Omega(t) \\ \ddot{\Omega}(t) & \dot{\Omega}(t) \end{pmatrix} M^{1/2} \begin{pmatrix} u(0) \\ v(0) \end{pmatrix} + \int_0^t M^{-1/2} \begin{pmatrix} \Omega(t-\tau) \\ \dot{\Omega}(t-\tau) \end{pmatrix} M^{-1/2} f(\tau)\, d\tau}$$

~~§3 Statistics (as in Adelman & Doll~~

§3. Correlation functions (simple method)

In Adelman & Doll it was assumed that $u(0), v(0) = \dot{u}(0)$ are distributed as in the perfect crystal ($I_0 \cup 2$).

$$\rho(u, p) = \frac{1}{Z} e^{-\beta \mathcal{H}}, \quad \mathcal{H} =$$

$$\boxed{v_i(t) = \sum_j \Big[\sqrt{\frac{m_j}{m_i}} \left(\ddot{\Omega}_{ij}(t)\, u_j(0) + \dot{\Omega}_{ij}(t)\, v_j(0) \right) + \int_0^t \frac{1}{\sqrt{m_i m_j}} \dot{\Omega}_{ij}(t-\tau)\, f_j(\tau)\, d\tau}$$

These expressions can be written in the matrix form:

$$\boxed{\begin{pmatrix} u_{\xi}(t) \\ v_{\xi}(t) \end{pmatrix} = M^{-1/2} \begin{pmatrix} \dot{\Omega} & \Omega \\ \ddot{\Omega} & \dot{\Omega} \end{pmatrix} M^{1/2} \begin{pmatrix} u(0) \\ v(0) \end{pmatrix} + \int_0^t M^{-1/2} \begin{pmatrix} \Omega(t-\tau) \\ \dot{\Omega}(t-\tau) \end{pmatrix} M^{-1/2} f(\tau)\, d\tau}$$

§3. Statistics

We want to calculate various averages wrt initial conditions

$$\rho(u,p) = \frac{1}{Z} e^{-\beta \mathcal{H}(u,p)} \Rightarrow \rho(\xi,\eta) = \frac{1}{Z} e^{-\beta \mathcal{H}(\xi,\eta)},$$

where $\mathcal{H}(\xi,\eta) = \sum_\lambda \left[\frac{1}{2} \left(\eta_\lambda^2 + \omega_\lambda^2 \xi_\lambda^2 \right) - g_\lambda \xi_\lambda \right]$

Averages of interest:

(i) $\langle \eta_\lambda \rangle = 0$

(ii) $\langle \xi_\lambda \rangle \neq 0$. Namely:

$$\langle \xi_\lambda \rangle = \int \xi_\lambda \rho(\xi,\eta)\, d\xi\, d\eta$$