Chem237: Lecture 16

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1 Note

I have just transcribed the lecture notes, no thought has gone in yet. We need to sit down and analyze this. 9-15-19

2 Normal Mode Analysis; Quantum Case

We begin by writing the Hamiltonian for our system of interest with N vibrational degrees of freedom,

$$\begin{aligned}\widehat{H} &= \sum_{i=1}^{N} \frac{-1}{2m}\frac{\partial^2}{\partial r_i^2} + V(r_1,\ldots,r_N) \\ &= -\frac{1}{2}\nabla^T\mathbf{M}^{-1}\nabla + \frac{1}{2}\mathbf{r}^T\mathbf{K}\mathbf{r}\end{aligned} \tag{1}$$

Where ∇ refers to a set of partial derivitives $\nabla = \frac{\partial}{\partial r_i}$.

We will begin by mass-scaling our coordinates (no momentum).

$$\begin{aligned}\mathbf{r}' &:= \mathbf{M}^{1/2}\mathbf{r} \\ \nabla' &:= \mathbf{M}^{-1/2}\nabla = \begin{bmatrix} \frac{1}{\sqrt{m_1}}\frac{\partial}{\partial r_i} \\ \vdots \\ \frac{1}{\sqrt{m_N}}\frac{\partial}{\partial r_i} \end{bmatrix} \\ \mathbf{K}' &:= \mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2}\end{aligned} \tag{2}$$

In our new coordinates the Hamiltonian reads

$$\widehat{H} = -\frac{1}{2}\nabla'^T\nabla + \frac{1}{2}\mathbf{r}'^T\mathbf{K}'\mathbf{r}' \tag{3}$$

Which is analagous to the classical case.

Normal mode analysis is useful for chemistry and physics problems, for example the simple harmonic oscillator.

2.1 Example

Consider an example of two classical masses attached to three springs as shown in the figure below. The Hamiltonian for the system is simple to write because we just have coupled harmonic oscillators.

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{k_1}{2}r_1^2 + \frac{k_2}{2}(r_1 - r_2)^2 + \frac{k_3}{2}r_2^2 \tag{4}$$

For simplicity, let's just say that the spring constants are the same, i.e. $k_1 = k_2 = k_3 = k$, and the masses are the same, i.e. $m_1 = m_2 = m$. So now our Hamiltonian simplifies to,

$$\begin{aligned}H &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{k}{2}r_1^2 + \frac{k}{2}(r_1 - r_2)^2 + \frac{k}{2}r_2^2 \\ &= \frac{1}{2m}\Big(p_1^2 + p_2^2\Big) + \frac{k}{2}\Big(2r_1^2 - 2r_1r_2 + 2r_2^2\Big)\end{aligned} \tag{5}$$

where r_1 and r_2 are each mass's coordinates measured from the equilibrium position. By creating mass, coordinate, momenta, and Hessian matrices, we can make this look like equation (**??**),

$$\begin{aligned}\mathbf{H} &= \frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p} + \frac{1}{2}\mathbf{r}^T\mathbf{K}\mathbf{r} \\ &= \frac{1}{2}\begin{bmatrix}p_1\\p_2\end{bmatrix}^T\begin{bmatrix}m & 0\\0 & m\end{bmatrix}^{-1}\begin{bmatrix}p_1\\p_2\end{bmatrix} + \frac{1}{2}\begin{bmatrix}r_1\\r_2\end{bmatrix}^T\begin{bmatrix}2k & -k\\-k & 2k\end{bmatrix}\begin{bmatrix}r_1\\r_2\end{bmatrix}\end{aligned} \tag{6}$$

The mass matrix is simply a diagonal matrix because there are no cross terms in the kinetic energy. However, the cross terms in the Hessian come from the $(r_1 - r_2)^2$ term in the potential. If you're not sure where each matrix element came from, recall equation (8),

$$K_{ij} = \frac{\partial^2 V}{\partial r_i r_j}. \tag{7}$$

Since the potential is equal to,

$$V = \frac{k}{2}\Big(2r_1^2 - 2r_1r_2 + 2r_2^2\Big) \tag{8}$$

we can say that the matrix elements for the Hessian are,

$$K_{11} = \frac{\partial^2 V}{\partial r_1^2} = 2k \quad ; \quad K_{12} = \frac{\partial^2 V}{\partial r_1 r_2} = K_{21} = -k \quad ; \quad K_{22} = \frac{\partial^2 V}{\partial r_2^2} = 2k. \tag{9}$$

You can verify that equation 15 and 16 are the same.

Now we can define the mass-scaled Hessian,

$$\mathbf{K}' = \begin{bmatrix}\frac{2k}{\sqrt{m_1^2}} & -\frac{k}{\sqrt{m_1 m_2}}\\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{2k}{\sqrt{m_2^2}}\end{bmatrix} = \begin{bmatrix}\frac{2k}{m} & -\frac{k}{m}\\ -\frac{k}{m} & \frac{2k}{m}\end{bmatrix} \tag{10}$$

and find it's eigenvalues and eigenvectors. This can be easily done with Mathematica, but we can also do this by hand since our system is 2 dimensional. To find the eigenvalues, we set up the characteristic equation,

$$\det(\mathbf{K}' - \lambda\mathbf{I}) = 0 \Longrightarrow \Big(\frac{2k}{m} - \lambda\Big)^2 - \Big(\frac{k}{m}\Big)^2 = 0 \Longrightarrow \Big(\lambda - \frac{2k}{m}\Big)^2 - \Big(\frac{k}{m}\Big)^2 = 0 \tag{11}$$

and solve for λ.

$$\begin{aligned}\lambda - \frac{2k}{m} = \pm\frac{k}{m} \Longrightarrow \lambda = \frac{2k}{m} \pm \frac{k}{m} \\ \lambda_1 = \frac{3k}{m}, \lambda_2 = \frac{k}{m}\end{aligned} \tag{12}$$

Now we find the eigenvector for each eigenvalue.

For λ_1, we have

$$\mathbf{K}'\mathbf{x} = \lambda_1\mathbf{x} \Longrightarrow (\mathbf{K}' - \lambda_1\mathbf{I})\mathbf{x} = \mathbf{0} \Longrightarrow \begin{bmatrix}\frac{2k}{m} - \lambda_1 & \frac{-k}{m}\\ \frac{-k}{m} & \frac{2k}{m} - \lambda_1\end{bmatrix}\begin{bmatrix}x_1\\x_2\end{bmatrix} = \begin{bmatrix}0\\0\end{bmatrix} \tag{13}$$

which is just solving two equations with two unknowns.

$$\begin{aligned}\frac{-k}{m}x_1 - \frac{k}{m}x_2 = 0 \\ \frac{-k}{m}x_1 - \frac{k}{m}x_2 = 0\end{aligned} \tag{14}$$

Since both equations are the same, we are really only left with one equation and two unknowns. To get around the problem, we can assign any value to x_1, like $x_1 = 1$, and just solve for x_2.

$$\frac{-k}{m}(1) - \frac{k}{m}x_2 = 0 \Longrightarrow x_2 = -1 \tag{15}$$

So our eigenvector for λ_1 is $\begin{bmatrix}1\\-1\end{bmatrix}$. If you don't understand why I was able to do this, refer to Lecture 14.

For λ_2, we have

$$\mathbf{K}'\mathbf{x} = \lambda_2\mathbf{x} \Longrightarrow (\mathbf{K}' - \lambda_2\mathbf{I})\mathbf{x} = \mathbf{0} \Longrightarrow \begin{bmatrix} \frac{2k}{m} - \lambda_2 & \frac{-k}{m} \\ \frac{-k}{m} & \frac{2k}{m} - \lambda_2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}. \tag{16}$$

So our two equations are:

$$\begin{aligned} \frac{k}{m}x_1 - \frac{k}{m}x_2 &= 0 \\ \frac{-k}{m}x_1 + \frac{k}{m}x_2 &= 0 \end{aligned} \tag{17}$$

The bottom equation is just the top equation multiplied by -1. To solve this, we again assign $x_1 = 1$ and solve for x_2.

$$\frac{k}{m}(1) - \frac{k}{m}x_2 \Longrightarrow x_2 = 1 \tag{18}$$

So our eigenvector for λ_2 is $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$. The eigendecomposition equation for the mass-scaled Hessian becomes,

$$\mathbf{K}' = \mathbf{U}\Lambda\mathbf{U}^\dagger = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \frac{3k}{m} & 0 \\ 0 & \frac{k}{m} \end{bmatrix} \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}^\dagger. \tag{19}$$

Remember that each column of $\mathbf{U}$ is the ith eigenvector that corresponds to the ith eigenvalue.

The normal mode coordinates and momenta are then defined from the mass-scaled coordinates and momenta.

$$\begin{aligned} \tilde{\mathbf{r}} = \mathbf{U}^\dagger\mathbf{r}' = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}^\dagger \begin{bmatrix} \sqrt{m}r_1 \\ \sqrt{m}r_2 \end{bmatrix} = \begin{bmatrix} \sqrt{m}(r_2 - r_1) \\ \sqrt{m}(r_1 + r_2) \end{bmatrix} = \begin{bmatrix} \tilde{r}_1 \\ \tilde{r}_2 \end{bmatrix} = \sqrt{m} \begin{bmatrix} (r_2 - r_1) \\ (r_1 + r_2) \end{bmatrix} \\ \tilde{\mathbf{p}} = \mathbf{U}^\dagger\mathbf{p}' \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}^\dagger \begin{bmatrix} \frac{1}{\sqrt{m}}p_1 \\ \frac{1}{\sqrt{m}}p_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{m}}(p_2 - p_1) \\ \frac{1}{\sqrt{m}}(p_1 + p_2) \end{bmatrix} = \begin{bmatrix} \tilde{p}_1 \\ \tilde{p}_2 \end{bmatrix} = \frac{1}{\sqrt{m}} \begin{bmatrix} (p_2 - p_1) \\ (p_1 + p_2) \end{bmatrix} \end{aligned} \tag{20}$$

And with this, we have effectively turned our original coupled system into a system of independent harmonic oscillators! In other words, in the normal mode basis, we can think of our system as having 2 normal modes: one where both masses oscillate with frequency $\omega_1 = \sqrt{\frac{3k}{m}}$ and another where both masses oscillate with frequency $\omega_2 = \sqrt{\frac{k}{m}}$. Also, the position and momenta of both masses in each normal mode can be described with $(\tilde{r_1}, \tilde{p_1})$ and $(\tilde{r_2}, \tilde{p_2})$.

You may wonder why the position and momenta do not look sinusoidal. This is because we never explicitly defined r_1 and r_2. However, we expect both masses to osciallte sinusoidally so we can assume that the solutions will be sinusoidal.

3 Normal Mode Analysis of Time Signals

A time signal is simply data as a function of time (c(t)), an important tdata type for most experiments, andis usualy a set of discrete measurements made in time. A standard analysis of time signals is to describte c(t) as a sum of expotnetials.

$$c(t) = \sum_{k=1}^{K} d_k e^{-\lambda_k t} \tag{21}$$

Where c(t) is know data and d, λ are unknown parameters. The central numerical problem then is to fit a signal to a expotentials.

time analysis data is usualy a set of N discrete measurements made in time.

$$c(t) \Rightarrow c(n\tau) = \sum_{n=0}^{N-1} c_n \tag{22}$$

A nieve approach would be to use a non-linear least square optimization. You can define an optimizaiton function F in terms of our parameters.

$$F(\lambda_k, d_k) := \sum_{n=1}^{N-1} \left(c_n - \sum_{k=1}^{K} d_k e^{-\lambda_k n\tau} \right)^2 \tag{23}$$

And there are tons of variations for taking this approach.

I fyou can exactly fit your data the actual form of the fitting function is not important, normally there is no exact solution .

N is the numer of data points in teh experiment, k is the number of expotentials to use int eh fitting process, usually N >> k, so you have an overdetermined problem. This means you are trying to find the best solution, which therefore epend s on the function you use to minimize (F). This means we are really trying to minimize F itself, we have an optimization problem to minimize F.

$$\min_{\lambda_k, d_k} F(\lambda_k, d_k) \tag{24}$$

If you have a non-linear function F, it will typically have many minima and typically the global minimum is the best fit. Unfortunately teh number of minima grows with the size of the space, $\approx e^{\alpha k}$. roughly speaking with about 10 parameters global optimizaiton becomes very dificult numerically.

Although eq. 21 looks bad is is actually a special case (Proxy 1793 maybe discovered).

Disconnected you could solve this problem using linear algebra, find the roots of a polynomial degree k.

convex optimizationL function is a special case where the function of parameters only has 1 minimum.

3.1 General Problem

The problem is generalized to complex space as

$$\begin{aligned} c_n &= \sum_{k=1}^{K} d_k e^{-in\tau\omega_k} \\ d_k &= |d_k| e^{i\theta} \\ \omega_k &= V_k - i\lambda_k \end{aligned} \tag{25}$$

Here $(d_k, \omega_k \in \mathbb{C})$

So the general problem actually has expotential decay.

$$e^{-in\tau\omega_k} = e^{in\tau V_k} e^{-n\tau\lambda_k} \tag{26}$$

In the complex case we have 2 complex numbers that are unknowns. $c_n \in mathbbC, d_k, \omega \in \mathbb{C}$. This is a well know problem, one approach to solve is the Harmonic Inversion. Here the goal is to invert the time signal with a sum of harmonic contributions. Hamonic inversion is related to spectra estimation methods.

We need to formulate the linear algebra problem to solve for frequency and amplitude. Spectral analysis: given $c_n = c(n\tau)$ estimate the spectra (I is our estimate).

$$I(\omega) := \int_0^\infty dt\ c(t)\ e^{i\omega t} \tag{27}$$

Here we have a finite interval (finite set of data measurements) and we want to estimate the result to infinity.

$$\begin{aligned} I(\omega) &\approx \tau \sum_{n=1}^{\infty} c(n\tau) e^{i\omega\tau} \\ &= \tau \sum_{n=0}^{\infty} c_n z^{-n} \end{aligned} \tag{28}$$

Where we define $(z := e^{-i\omega\tau})$.

Can we try an estimate our infinite series from the finite measurement?

$$I(\omega) \approx \sum_{n=i}^{N-1} c_n z^{-n} \tag{29}$$

This is valid, however, it converges very slowly. Also a larger problem is known as the fourier transform ncertainty principle, where resolution is given by $\delta\omega \approx \frac{1}{\alpha} N$.

In principle if N$\geq$ 2k then you can solve the problem exactly. So the paramaterization fir problem can circumvent the Fourier Transform uncertainty principle and get better resolution.

let $U_k = e^{-i\tau\omega_k}$

$$\begin{aligned}
&\sum_{n=0}^{\infty} c_n z^{-n} \\
c_n &= \sum_{k=1}^{K} d_k U_k^n \\
&= \sum_{n=0}^{\infty}\sum_{k=1}^{K} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K}\sum_{n=0}^{\infty} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K}\sum_{n=0}^{\infty} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K} d_k \sum_{n=0}^{\infty} \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K} d_k \ \frac{1}{1-\frac{\omega_k}{z}}
\end{aligned} \tag{30}$$

Where $\sum_{n=0}^{\infty}\left(\frac{U_k}{z}\right)^n$ is a geometric series. With $d_k, omega_k$ parameters you can solve.

Some approximations, $\omega_k = V_k - i\lambda_k$, but λ_k is usually small, if τ is small than

$$\frac{1}{1-\frac{\omega_k}{z}} = \frac{1}{1-e^{i(\omega-\omega_k)\tau}} \approx \frac{1}{i(\omega_k-\omega)\tau} \tag{31}$$

$$\begin{aligned}
\frac{1}{\omega-\omega_k} &= \frac{1}{(\omega-\omega_k)+i\lambda_k} \\
&= \frac{\omega-V_k}{(\omega-V_k)^2+\lambda_k^2} - i\frac{\lambda_k}{(\omega-V_k)^2+\lambda_k^2}
\end{aligned} \tag{32}$$

The last two terms are a complex lorentzian function.

The first term is the absorption (small λ_k corresponds to a narrow peak).

so if our oscillations can be dscribed by $e^{-in\tau\omega_k}$ you get a complex lorentzian function.

So how do we solv this problem

$$c_n = \sum_{k=1}^{K} d_k U_k^n \tag{33}$$

Where we have k=1,K unknown parameters and ($d_k, U_k \in \mathbb{C}$), given c_n?

3.2 Vlad Solutoin

There are many different ways to solve this problem. One solution (vlads old paper, Neuhauser 1995?) assumes the known data can be represented as

$$c_n := \theta^T \widehat{U}^N \theta \tag{34}$$

Where $\widehat{U}$ is a symmetric linear operator (a symmetric matrix $\in \mathbb{C}$), not hermitian and θ is a column vector.

This assumption is a special case for time signals. It is consistent witht he time auto correlatio nfunction for a quantum system.

$$\Psi(t) = e^{-it\widehat{H}}\Psi(0) = \widehat{U}^n\phi \tag{35}$$

If we define ($\phi := \Psi(0)$, $U := e^{-it\widehat{H}}$).

With these definition the time autocorrelation function becomes

$$\langle\Psi(t)|\Psi(0)\rangle = \phi^T\widehat{U}^N\phi \tag{36}$$

Which is exactly our c_n. So the time signal is represented by some quantum system with quantum autocoreelation funciton given by some operator.

3.3 Analysis

We now have a quantum system, so lets solve the eigenvalue problem (U our eigenvalues and γ our eigenvectors).

$$\begin{aligned} \widehat{U}\gamma_k &= U_k\gamma \\ \widehat{U} &= \sum_k U_k\gamma_k\gamma_k^T \end{aligned} \tag{37}$$

These two statements are equivalent, this is known as the eigenrepresentation of an operator, it is equivalent to eigendecomposition. We know that $\widehat{U}$ is symmetric i.e. $\widehat{U} = \widehat{U}^T$ therefore the right/left eigenvetors are the same i.e. $(\gamma_k^T\gamma_k = \delta_{kl})$, meaning the eigenvectors are orthogonal for symmetric matricies.

$$\left(\sum_k U_k\gamma_k\gamma_k^T\right)\gamma_l = U_l\gamma_l \tag{38}$$

So we see this is simply an eigenvector equivalent to the eigenvalue problem.

If we let $(\gamma_k^T\phi)^2 = \phi^T\gamma_k\gamma_k^T\phi \equiv d_k$ we have

$$c_n = \phi^T\widehat{U}^N\phi = \sum_k \phi^T U_N^N\gamma_k\gamma_k^T\phi = \sum_k d_k U_k^N \tag{39}$$

Where we used the operator as a fucntion of a matrix $(\widehat{U}^N = \sum_k U_k^N\gamma_k\gamma_K^T)$

So our time signal is defined by U and d, using $c_N = \phi^T\widehat{U}^N\phi$ reduces teh parameter estimation problem to an eigenvalue problme.

Now we can solve the eigenvalue problem.

$$\widehat{U}\gamma_k = U_k\gamma_k \tag{40}$$

We don't actually want any of these terms explicitly, we know c (the data) and we assume $c_N = \phi^T\widehat{U}^N\phi$, we don't want to find expressions for any of the other terms.

In QM we define a basis and evaluate the hamiltonian matrix to solve. So we need to express our matrix elements in terms of c.

We define our basis to be

$$\begin{aligned} \phi_n &:= \widehat{U}\phi \\ \phi_0 &= \phi \\ \phi_1 &= \widehat{U}\phi_0 \\ \phi_2 &= \widehat{U}\phi_1 \\ &\vdots \end{aligned} \tag{41}$$

This basis choice i similar to a Krylov basis (super matricies). You simply keep multiplying to get the Kryloc vectors, genearating a Krylov subspace, using these vectors you can understand the original matrix of interest.

We will use this basis to find the operator $\widehat{U}$, and therefore solve the generalized eigevalue problem.

$$\begin{aligned} U_{nm} &= \phi^T\widehat{U}\phi \\ \delta_{nm} &= \phi_n^T\phi_m \\ (U - U_k\mathbf{S})B_k &= 0 \end{aligned} \tag{42}$$

Where U and delta are square matricies of size M by M.

$$\delta_{nk} = \phi_N^T\phi_m = (\widehat{U}^n\phi)^T(U^m\phi) \tag{43}$$

$\widehat{U}$ is symmetric therefore

$$\delta_{nk} = \phi^T\widehat{U}^{n+m}\phi = c_{m+n} \tag{44}$$

Where c_{m+n} is our data. Overlap matrix is computed with teh data points directly.

$$U_{nm} = \phi^T\widehat{U}\phi_m = c_{n+m+1} \tag{45}$$

U and S are matricies we get from our data, meaning we can solve the eigenvalue problem $(U - U_k\mathbf{S})B_k = 0$. It can be shwon that $(\gamma_k^T\phi)^2 = d_k$ so we assume

$$\gamma_k = \sum_{n=1}^{m-1} B_{kn}\phi_n \tag{46}$$

Wxpanding the eigenfunctions nto the basis function leads to

$$d_k = \left[\sum_{n=0}^{m-1} (B_{kn}c_n)\right]^2 \tag{47}$$

So we solve the generalized eigenvalue problem with dtaa matricies and find U_k, d_k.