Chem237: Lecture 16

Shane Flynn

5/10/18

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. In this problem you have 2 masses and seperate spring constants (k) and seperate distances (r).

$$\begin{aligned} \widehat{H} &= \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(r_1, \ldots, r_N) \\ \widehat{H} &= \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{K}{2} (r_1 - r_2) \end{aligned} \tag{4}$$

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.

$$c(t) = \sum_{k=1}^{K} d_k e^{-\lambda_k t} \tag{5}$$

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.

$$c(t) \Rightarrow c(n\tau) = \sum_{n=0}^{N-1} c_n \tag{6}$$

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.

$$F(\lambda_k, d_k) := \sum_{n=1}^{N-1} \left(c_n - \sum_{k=1}^{K} d_k e^{-\lambda_k n\tau} \right)^2 \tag{7}$$

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.

$$\min_{\lambda_k, d_k} F(\lambda_k, d_k) \tag{8}$$

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. 5 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

$$\begin{aligned} c_n &= \sum_{k=1}^{K} d_k e^{-in\tau\omega_k} \\ d_k &= |d_k| e^{i\theta} \\ \omega_k &= V_k - i\lambda_k \end{aligned} \tag{9}$$

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

So the general problem actually has expotential decay.

$$e^{-in\tau\omega_k} = e^{in\tau V_k} e^{-n\tau\lambda_k} \tag{10}$$

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).

$$I(\omega) := \int_0^\infty dt\ c(t)\ e^{i\omega t} \tag{11}$$

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

$$\begin{aligned} I(\omega) &\approx \tau \sum_{n=1}^{\infty} c(n\tau) e^{i\omega\tau} \\ &= \tau \sum_{n=0}^{\infty} c_n z^{-n} \end{aligned} \tag{12}$$

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

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

$$I(\omega) \approx \sum_{n=i}^{N-1} c_n z^{-n} \tag{13}$$

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

$$\begin{aligned}
&\sum_{n=0}^{\infty} c_n z^{-n} \\
c_n &= \sum_{k=1}^{K} d_k U_k^n \\
&= \sum_{n=0}^{\infty}\sum_{k=1}^{K} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K}\sum_{n=0}^{\infty} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K}\sum_{n=0}^{\infty} d_k \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K} d_k \sum_{n=0}^{\infty} \left(\frac{U_k}{z}\right)^n \\
&= \sum_{k=1}^{K} d_k \frac{1}{1-\frac{\omega_k}{z}}
\end{aligned} \tag{14}$$

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

$$\frac{1}{1-\frac{\omega_k}{z}} = \frac{1}{1-e^{i(\omega-\omega_k)\tau}} \approx \frac{1}{i(\omega_k-\omega)\tau} \tag{15}$$

$$\begin{aligned}
\frac{1}{\omega-\omega_k} &= \frac{1}{(\omega-\omega_k)+i\lambda_k} \\
&= \frac{\omega-V_k}{(\omega-V_k)^2+\lambda_k^2} - i\frac{\lambda_k}{(\omega-V_k)^2+\lambda_k^2}
\end{aligned} \tag{16}$$

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

$$c_n = \sum_{k=1}^{K} d_k U_k^n \tag{17}$$

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

$$c_n := \theta^T \widehat{U}^N \theta \tag{18}$$

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.

$$\Psi(t) = e^{-it\widehat{H}}\Psi(0) = \widehat{U}^n\phi \tag{19}$$

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

With these definition the time autocorrelation function becomes

$$\langle \Psi(t)|\Psi(0)\rangle = \phi^T\widehat{U}^N\phi \tag{20}$$

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).

$$\begin{aligned}\widehat{U}\gamma_k &= U_k\gamma \\ \widehat{U} &= \sum_k U_k\gamma_k\gamma_k^T\end{aligned} \tag{21}$$

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.

$$\left(\sum_k U_k\gamma_k\gamma_k^T\right)\gamma_l = U_l\gamma_l \tag{22}$$

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

$$c_n = \phi^T\widehat{U}^N\phi = \sum_k \phi^T U_N^N\gamma_k\gamma_k^T\phi = \sum_k d_k U_k^N \tag{23}$$

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.

$$\widehat{U}\gamma_k = U_k\gamma_k \tag{24}$$

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

$$\begin{aligned}&\phi_n := \widehat{U}\phi \\ &\phi_0 = \phi \\ &\phi_1 = \widehat{U}\phi_0 \\ &\phi_2 = \widehat{U}\phi_1 \\ &\vdots\end{aligned} \tag{25}$$

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.

$$\begin{aligned}U_{nm} &= \phi^T\widehat{U}\phi \\ \delta_{nm} &= \phi_n^T\phi_m \\ (U - U_k\mathbf{S})B_k &= 0\end{aligned} \tag{26}$$

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

$$\delta_{nk} = \phi_N^T \phi_m = (\widehat{U}^n \phi)^T (U^m \phi) \tag{27}$$

$\widehat{U}$ is symmetric therefore

$$\delta_{nk} = \phi^T \widehat{U}^{n+m} \phi = c_{m+n} \tag{28}$$

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

$$U_{nm} = \phi^T \widehat{U} \phi_m = c_{n+m+1} \tag{29}$$

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

$$\gamma_k = \sum_{n=1}^{m-1} B_{kn} \phi_n \tag{30}$$

Wxpanding the eigenfunctions nto the basis function leads to

$$d_k = \left[\sum_{n=0}^{m-1} (B_{kn} c_n) \right]^2 \tag{31}$$

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