Eigenvalues, Eigenvectors, and Discrete Variable Representation (DVR)

should have read CDTL pages 94-144

Last time:

bra $\langle\ |$ $\begin{pmatrix} a_1^* & \dots & a_N^* \end{pmatrix}_\phi$

ket $|\ \rangle$ $\begin{pmatrix} a_1 \\ \vdots \\ a_N \end{pmatrix}_\phi$

$|\ \rangle\langle\ |$ $N \times N$ matrix

$\langle\ |\ \rangle$ (complex) #

ψ in $\{\phi\}$ basis set

$$|\psi_i\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \\ a_N \end{pmatrix}_\phi$$

$$a_j = {}_\phi\langle\phi_j|\psi_i\rangle_\phi$$

$$\mathbb{1} = \begin{pmatrix} 1 & & & \\ & 1 & & 0 \\ & & 1 & \\ & 0 & & \ddots \\ & & & \end{pmatrix} = \sum_k |k\rangle\langle k|$$

at end of lecture

$$\langle\phi_i|\mathbf{AB}|\phi_j\rangle = \sum_k \langle\phi_i|\mathbf{A}\underbrace{|\phi_k\rangle\langle\phi_k|}_{\mathbf{1}}\mathbf{B}|\phi_j\rangle$$

$$= \sum_k A_{ik}B_{kj} = (\mathbf{AB})_{ij}$$

What is the connection between the Schrödinger and Heisenberg representations?

$$\psi_i(x) = \langle x | \psi_i \rangle$$

$$|x_0\rangle = \delta(x, x_0)$$ eigenfunction of **x** with eigenvalue x_0

Using this formulation for $\psi_i(x)$, you can go freely (and rigorously) between the Schrödinger and Heisenberg approaches.

$$\mathbf{1} = \sum_k |k\rangle\langle k| = \int |x\rangle\langle x| dx$$

Today: eigenvalues of a matrix – what are they? how do we get them? (secular equation). Why do we need them?

eigenvectors – how do we get them?

Arbitrary V(x) in Harmonic Oscillator Basis Set (DVR)

Schr. Eq. is an eigenvalue equation

$$\hat{A}\psi = a\psi$$

in matrix language

$$\mathbf{A}|\psi_i\rangle = a_i|\psi_i\rangle \quad A = \begin{pmatrix} a_1 & & & 0 \\ & a_2 & & \\ & & \ddots & \\ 0 & & & a_N \end{pmatrix}_{\psi}$$

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}_{\psi} \quad \text{satisfies } \mathbf{A}|\psi_1\rangle = a_1|\psi_1\rangle$$

but that is the eigen-basis representation – a <u>special</u> representation!

What about an arbitrary representation? Call it the ϕ representation.

$$*** \begin{cases} \mathbf{A}\left(\sum_{i=1}^{N} c_i|i\rangle_{\phi}\right) = a\left(\sum_{i} c_i|i\rangle_{\phi}\right) *** \\ \mathbf{A} \text{ as transformation on each } |\phi_i\rangle \end{cases} \quad \textbf{Eigenvalue equation}$$

N unknown coefficients $\{c_i\}$ $\quad i = 1$ to N

How to determine $\{c_i\}$ and a ? **Secular Eqn. derive it.**

first, left multiply by ${}_{\phi}\langle j|$

$$\sum_i A_{ji}^{\phi} c_i = a\sum_i c_i\langle j|i\rangle = a\sum_i c_i\delta_{ij}$$

$$0 = \sum_{i=1}^{N} c_i\left[A_{ji}^{\phi} - a\delta_{ij}\right] \quad \text{one equation}$$

(arrow pointing to c_i: N unknowns)

next, multiply original equation by ${}_{\phi}\langle k|$

$$0 = \sum_{i=1}^{N} c_i\left[A_{ki}^{\phi} - a\delta_{ik}\right] \quad \text{another equation}$$

etc. for all ${}_{\phi}\langle\ |$.

N linear homogeneous equations in N unknowns – Condition that a nontrivial (i.e. not all 0's) solution exists is that determinant of coefficients = 0.

$$0 = \begin{vmatrix} A_{11} - a & A_{12} & \dots & A_{1N} \\ A_{21} & A_{22} - a & & \\ & & \ddots & \\ & & & A_{NN} - a \end{vmatrix}$$

Nth order equation – as many as N different values of a satisfy this equation (if fewer than N, some values of a are "degenerate").

Does everyone know how to expand a determinant?

$\{a_i\}$ are the eigenvalues of **A** (same as what we would have obtained by solving differential operator eigenvalue equation)

If we know the eigenvalues, then we can find the N $\{|\psi_i\rangle\}$ such that

$$|\psi_i\rangle = \sum_j c_j |j\rangle_\phi$$

expand the eigenbasis in (computationally convenient) basis

$$\langle\psi_i|\mathbf{A}^\psi|\psi_j\rangle = a_j\delta_{ij}$$

$$\mathbf{A}^\psi = \begin{pmatrix} a_1 & & 0 \\ 0 & \ddots & a_N \end{pmatrix}$$

$$\mathbf{A}^\psi|\psi_1\rangle = a_1\begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

But we generally start with $\mathbf{A}^\phi$ in nondiagonal form

computer
1. transform to diagonal form by $\mathbf{T}^{\dagger}\mathbf{A}^\phi\mathbf{T} = \mathbf{A}^\psi$
2. the diagonal elements are eigenvalues
3. the diagonalizing transformation is composed of eigenvectors, column by column of $\mathbf{T}^{\dagger}$.

<u>Hermitian Matrices</u>

$$\mathbf{A} = \mathbf{A}^{\dagger} \qquad A^{\dagger}_{ij} = A^{*}_{ji}$$

(can use this property to show that all expectation values of **A** are real)

These matrices can be "diagonalized" (i.e. the set of all eigenvalues can be found) by a **unitary** transformation.

$$\mathbf{T}^{-1} = \mathbf{T}^{\leq} \qquad \text{unitary matrix}$$

diagonalization

$$\mathbf{T}^{\leq}\mathbf{A}^{\phi}\mathbf{T} = \begin{pmatrix} a_1 & & & 0 \\ & a_2 & & \\ & & \ddots & \\ 0 & & & a_N \end{pmatrix}_{\psi} \equiv \mathbf{A}^{\psi}$$

not diagonal ($\mathbf{A}^{\phi}$) — diagonal ($\mathbf{A}^{\psi}$)

$$\underbrace{\mathbf{T}^{\leq}\mathbf{A}^{\phi}\mathbf{T}}_{\text{diagonal } \mathbf{A}^{\psi}}\underbrace{\mathbf{T}^{\leq}\left|\phi_j\right\rangle}_{\text{Eigenvector expressed in } \phi \text{ basis set}}$$

diagonal $\mathbf{A}^{\psi}$

Eigenvector expressed in ϕ basis set eigenvector

$$\mathbf{T}^{\leq}\left|\phi_i\right\rangle = \mathbf{T}^{\leq}\begin{pmatrix}0\\ \vdots\\ 1\\ \vdots\\ 0\end{pmatrix}_{\phi} = \begin{pmatrix}\mathbf{T}^{\leq}_{1i}\\ \mathbf{T}^{\leq}_{2i}\\ \vdots\\ \mathbf{T}^{\leq}_{Ni}\end{pmatrix}_{\phi} = \left|\psi_i\right\rangle = \begin{pmatrix}0\\ \vdots\\ 1\\ \vdots\\ 0\end{pmatrix}_{\psi} \leftarrow \text{i - th position}$$

i-th position (arrow pointing to the 1)

i-th column of $\mathbf{T}^{\dagger}$

suppose we apply

$$\mathbf{A}^{\psi}\left|\psi_i\right\rangle = \mathbf{A}^{\psi}\begin{pmatrix}0\\ \vdots\\ 1\\ \vdots\\ 0\end{pmatrix}_{\psi} = \begin{pmatrix}0\\ \vdots\\ a_i\\ \vdots\\ 0\end{pmatrix}_{\psi} = a_i\begin{pmatrix}0\\ \vdots\\ 1\\ \vdots\\ 0\end{pmatrix}_{\psi}$$

i-th (arrow pointing to the 1)

RECAPITULATE:

Start with arbitrary basis set $|\phi\rangle$

Construct $\mathbf{A}^{\phi}$: Not Diagonal, but basis set was computationally convenient.

Find $\mathbf{T}$ (computer) that causes $\mathbf{T}^{\leq}\mathbf{A}^{\phi}\mathbf{T} = \begin{pmatrix}a_1 & 0 & 0\\ & \ddots & \\ 0 & & a_N\end{pmatrix} = A^{\psi}$

Eigenstates (eigenkets) are columns of $\mathbf{T}^{\leq}$ in ϕ basis set.

Columns of $\mathbf{T}$ are the linear combination of eigenvectors that correspond to each basis state. Useful for "bright state" calculations.

Can now solve many difficult appearing problems!

Start with a **matrix representation** of *any operator* that is expressable as a function of a matrix.

e.g. $e^{-i\mathbf{H}(t-t_0)/\hbar}$ propagator, $f(\mathbf{x})$ potential curve

prescription example

$$f(\mathbf{x}) = \mathbf{T} f\underbrace{\left(\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T}\right)}\mathbf{T}^{\dagger}$$

diagonalize **x** – so f( ) is applied to each diagonal element

$$\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T} = \begin{pmatrix} x_1 & & & 0 \\ & x_2 & & \\ & & \ddots & \\ 0 & & & x_N \end{pmatrix}$$

$$f\left(\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T}\right) = \begin{pmatrix} f(x_1) & & & 0 \\ & f(x_2) & & \\ & & \ddots & \\ 0 & & & f(x_N) \end{pmatrix}$$

Then perform inverse transformation $\mathbf{T}\, f(\mathbf{T}^{\dagger}\, \mathbf{x}\, \mathbf{T})\mathbf{T}^{\dagger}$ – undiagonalizes matrix, to give matrix representation of desired function of a matrix.

Show that this actually is valid for simple example

$$f(x) = \mathbf{x}^N$$

$$\underline{\underline{f(\mathbf{x})}} = \mathbf{T}\left[\underset{①}{\left(\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T}\right)}\underset{②}{\left(\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T}\right)}\cdots\underset{Ⓝ}{\left(\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T}\right)}\right]\mathbf{T}^{\dagger} \qquad \text{apply prescription}$$

$$= \mathbf{T}\left[\mathbf{T}^{\dagger}\mathbf{x}^{N}\mathbf{T}\right]\mathbf{T}^{\dagger} = \mathbf{x}^{N} \qquad \text{get expected result}$$

general proof for arbitrary f(**x**) → expand in power series. Use previous result for each integer power.

John Light: Discrete Variable Representation (DVR)
General V(x) evaluated in Harmonic Oscillator Basis Set.
we did not do H-O yet, but the general formula for all of the nonzero matrix elements of **x** is:

$$\langle n|x|n+1\rangle = \left[\frac{\hbar}{2\omega\mu}\right]^{1/2}(n+1)^{1/2} \qquad \omega = (k/\mu)^{1/2}$$

$$\text{(infinite dimension matrix)} \quad \mathbf{x} = \left[\frac{\hbar}{2\omega\mu}\right]^{1/2}\begin{pmatrix} 0 & \sqrt{1} & 0 & \cdots & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & \cdots & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 \\ \vdots & \vdots & \sqrt{3} & 0 & \sqrt{4} \\ \vdots & \vdots & \vdots & \sqrt{4} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

[CARTOON]

$$\mathbf{x}^2 = \left[\frac{\hbar}{2\omega\mu}\right]\begin{pmatrix} 1 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 0 & 5 & 0 & \sqrt{12} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 7 & 0 & & 0 & 0 & 0 \\ 0 & 0 & \sqrt{12} & 0 & 9 & 0 & & 0 & 0 \\ 0 & 0 & 0 & & 0 & 11 & 0 & & 0 \\ 0 & 0 & 0 & 0 & & 0 & 13 & 0 & \\ 0 & 0 & 0 & 0 & 0 & & 0 & 15 & \ddots \\ 0 & 0 & 0 & 0 & 0 & 0 & & \ddots & \ddots \end{pmatrix}$$

etc. matrix multiplication

to get matrix for f(**x**) diagonalize e.g., 1000×1000 (truncated) **x** matrix that was expressed in harmonic oscillator basis set.

$$\mathbf{T}^{\dagger}\mathbf{x}\mathbf{T} = \begin{pmatrix} x_1 & 0 & 0 & 0 \\ 0 & x_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & x_{1000} \end{pmatrix}_x$$

diagonalized-**x** basis $\{x_i\}$ are eigenvalues. They have no obvious physical significance.

$$\mathbf{V}(x)_x = \begin{pmatrix} V(x_1) & 0 & 0 & 0 \\ 0 & V(x_2) & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & V(x_{1000}) \end{pmatrix}_x$$

next transform back from x-basis to H-O basis set

$$\mathbf{V}(x)_{H-O} = \mathbf{T}\mathbf{V}(x)_x\mathbf{T}^{\dagger} = \begin{pmatrix} \text{full} \\ \text{complicated} \\ \text{matrix} \end{pmatrix}_{\substack{1000 \times 1000 \\ H-O}}$$

T was determined when **x** was diagonalized

$$\mathbf{H} = \frac{\mathbf{p}^2}{2\mu} + V(x)$$

need matrix for $\mathbf{p}^2$, get it from **p** (the general formula for all non-zero matrix elements of **p**)

$$\langle n|p|n+1\rangle = -i\left[\frac{\hbar(\omega\mu)}{2}\right]^{1/2}(n+1)^{1/2}$$

$$\mathbf{p} = -i\left[\frac{\hbar(\omega\mu)}{2}\right]^{1/2}\begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & 0 \\ 0 & -\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & \ddots & \ddots & \ddots \\ 0 & 0 & \ddots & \ddots & \ddots \end{pmatrix}$$ same structure as **x**

$$\mathbf{p^2} = -\left[\frac{\hbar(\omega\mu)}{2}\right]\begin{pmatrix} -1 & 0 & \sqrt{2} & 0 & 0 \\ 0 & -3 & 0 & \ddots & 0 \\ \sqrt{2} & 0 & -5 & 0 & \ddots \\ 0 & \ddots & \ddots & \ddots & \ddots \\ 0 & \ddots & \ddots & \ddots & \end{pmatrix}$$

if $$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2 \qquad \left(\frac{1}{2}k = \frac{1}{2}\omega^2\mu\right)$$

$$H = \frac{\hbar\omega}{4}\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 \\ 0 & 0 & 10 & 0 \\ 0 & 0 & 0 & 14 \end{pmatrix} = \hbar\omega\begin{pmatrix} 1/2 & 0 & 0 & 0 \\ 0 & 3/2 & 0 & 0 \\ 0 & 0 & 5/2 & 0 \\ 0 & 0 & 0 & \ddots \end{pmatrix}$$

but for arbitrary V(x), express **H** in HO basis set,

$$\mathbf{H}_{HO} = \frac{\mathbf{p}_{HO}^2}{2\mu} + \underbrace{\mathbf{V}(\mathbf{x})_{HO}}_{\mathbf{TV}(\mathbf{x})_x\mathbf{T}^\dagger}$$

eigenvalues obtained by $\mathbf{S}^\dagger\mathbf{H}_{HO}\mathbf{S} = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & E_N \end{pmatrix}$

columns of $\mathbf{S}^\dagger$ are eigenvectors in HO basis set!

1. Express matrix of $\mathbf{x}$ in H-O basis (automatic; easy to program a computer to do this), get $\mathbf{x}_{HO}$.
2. Diagonalize $\mathbf{x}_{HO}$. Get $\mathbf{x}_x$ and $\mathbf{T}$.
3. Trivial to write $V(x)_x$ as $V(x_i) = \mathbf{V}(\mathbf{x})_x$ in $\mathbf{x}$ basis
4. Transform $\mathbf{V}(\mathbf{x})_x$ back to $\mathbf{V}(x)_{HO}$
5. Diagonalize $\mathbf{H}_{HO}$.

Solve many V(x) problems in this basis set.

1000×1000 $\mathbf{T}$ matrix diagonalizes $\mathbf{x} \Rightarrow 1000$ x_i's

Save the $\mathbf{T}$ and the $\{x_i\}$ for future use on *all* V(x) problems.

To verify convergence, repeat for new $\mathbf{x}$ matrix of dimension 1100 x 1100. There will be no resemblance between $\{\mathbf{x}_i\}_{1000}$ and $\{\mathbf{x}_i\}_{1100}$.

If the lowest eigenvalues of $\mathbf{H}$ (i.e. the ones you care about) do not change (by measurement accuracy), converged!

Next: Matrix solution of HO (no wave functions at all)

Start from Commutation Rule!

Then Perturbation Theory.