

Lecture 35: δ -functions, Eigenfunctions of \hat{X} , and Discrete Variable Representation

Outline for today:

I. δ -functions. $\delta(x, x_i)$ is an eigenstate of \hat{x} with eigenvalue x_i .

δ -function is a computationally convenient tool, especially convenient for representing a barrier on a potential curve or a maximally localized well. *Tunneling*.

II. Discrete Variable Representation (DVR).

How do we construct a matrix representation of a function of a matrix?

DVR allows us to express almost any $V(R)$, $\hat{x} = \hat{R} - R_e$, as a matrix, $\mathbf{V}(\hat{x})$, expressed in the harmonic oscillator basis set. It makes non-degenerate perturbation theory look like a Model-T Ford.

III. Extension of DVR to include rotation.

IV. We can obtain $\psi(x)$ from experiment after all! But we must do it via the eigenvectors and eigen-energies of an effective Hamiltonian.

I. δ -Functions

The Dirac δ -function, $\delta(x, x_i) \equiv \delta(x - x_i)$, is an extremely useful tool in spectroscopic calculations.[‡] It has the property

$$\int_{-\infty}^{\infty} f(x)\delta(x, x_i)dx = f(x_i).$$

[‡]See CTDL, pages 1468-1472.

$\delta(x, x_i)$ is sharply localized at $x = x_i$. It is also “normalized to 1” in the sense that $f(x)$ is returned evaluated at x_i *without* any additional multiplicative factor, $c f(x_i)$.

This Dirac δ -function may be viewed as an eigenfunction of \hat{x} because it satisfies the *eigenvalue equation*

$$\hat{x}\delta(x, x_i) = x_i\delta(x, x_i).$$

This seems strange because we usually regard \hat{x} as a continuous variable, regardless of whether the system we are treating is discrete or continuous in energy, finite or infinite in range of x .

We can also have δ -functions in \hat{p} , $\delta(p, p_i)$,

$$\int_{-\infty}^{\infty} g(p)\delta(p, p_i)dp = g(p_i).$$

Transformations

The set of $\delta(x, x_i)$ for all x_i or $\delta(p, p_i)$ for all p_i may be regarded as a complete set of basis functions in which any quantum mechanical state may be expressed,

$$\psi_j(x) = \oint c_{x_i}^j \delta(x - x_i) dx$$

where $c_{x_i}^j$ is the usual mixing coefficient with which we are familiar for all basis set transformations

$$\begin{aligned} \psi_j(x) &= \sum_k c_k^j \phi_k(x) \\ c_k^j &= \int \phi_k^* \psi_j dx. \end{aligned}$$

Representations

There are many mathematical representations of Dirac δ -functions, $\delta(x)$:

$$(i) \lim_{\varepsilon \rightarrow +0} \frac{1}{2\varepsilon} e^{-|x|/\varepsilon}$$

$$(ii) \lim_{\varepsilon \rightarrow +0} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2}$$

$$(iii) \lim_{\varepsilon \rightarrow +0} \pi^{-1/2} \frac{1}{\varepsilon} e^{-x^2/\varepsilon^2}$$

$$(iv) \lim_{\varepsilon \rightarrow +0} \frac{1}{\pi} \frac{\sin(x/\varepsilon)}{x}$$

$$(v) \lim_{\varepsilon \rightarrow +0} \frac{\varepsilon}{\pi} \frac{\sin^2(x/\varepsilon)}{x^2}$$

For $\delta(x, x_i)$ replace x in the above expressions for $\delta(x)$ by $x - x_i$. $\delta(x)$ is centered at $x = 0$. $\delta(x, x_i)$ is centered at x_i .

Properties of δ -functions

$$\delta(-x) = \delta(x)$$

$$\delta(cx) = \frac{1}{|c|} \delta(x)$$

$$\delta[g(x)] = \sum_j \frac{1}{\left| \frac{dg}{dx} \Big|_{x=x_j} \right|} \delta(x - x_j) \quad \text{where } \{x_j\} \text{ are the zeroes of } g(x).$$

$\delta(x)$ has units of $\frac{1}{x}$.

The Fourier Transform of $\delta(x)$ is a delta function in p and vice versa.

$$\begin{aligned} \text{FT of } \delta(x - x_0) &= \text{FT } \delta(x, x_0) \equiv \bar{\delta}_{x_0}(p) \\ \bar{\delta}_{x_0} &= [2\pi\hbar]^{-1/2} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \delta(x - x_0) dx = [2\pi\hbar]^{-1/2} e^{ipx_0/\hbar} \end{aligned}$$

and the inverse Fourier transform of $\bar{\delta}_{x_0}(p)$ is

$$\delta(x, x_0) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{ip(x-x_0)/\hbar} dp = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)} dk$$

Note that a δ -function in x corresponds to an integral with respect to p over $\cos[p(x-x_0)/\hbar]$ and $\sin[p(x-x_0)/\hbar]$ and that perfect localization in x corresponds to complete delocalization in p . But you already knew this!

II. Discrete Variable Representation

Almost every system with an equilibrium structure “looks like” a harmonic oscillator. Often we can use Perturbation Theory to deal with the deviations from harmonic behavior. This can be an algebraic nightmare!

There is an alternative way of dealing with non-harmonic effects that is algebra-free. The computer does all of the work. It is based on how one constructs a matrix representation of **a function of a matrix**. For example, how would you compute the square root of a matrix? Let \mathbf{A} be a real and symmetric matrix. Every real symmetric matrix can be diagonalized by a unitary transformation

$$\mathbf{T}^\dagger \mathbf{A} \mathbf{T} = \tilde{\mathbf{A}} = \begin{pmatrix} a_1 & 0 & 0 & 0 \\ 0 & a_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & a_N \end{pmatrix}$$

where

$$\mathbf{T}^\dagger = \mathbf{T}^{-1}.$$

The i^{th} eigenvector is the i^{th} column of \mathbf{T}^\dagger . One can generalize to any Hermitian matrix, \mathbf{B} ,

$$\mathbf{U}^\dagger \mathbf{B} \mathbf{U} = \tilde{\mathbf{B}} = \begin{pmatrix} b_1 & 0 & 0 & 0 \\ 0 & b_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & b_N \end{pmatrix}$$

where all of the $\{b_i\}$ are real.

If we want to compute some function of the matrix \mathbf{A} or \mathbf{B} , $f(\mathbf{A})$, one diagonalizes \mathbf{A} to obtain all of the eigenvalues of \mathbf{A} . If \mathbf{A} is of infinite dimension, one can truncate \mathbf{A} , keeping only the A_{ij} elements where $0 \leq i \leq 99$ and $0 \leq j \leq 99$; call this \mathbf{A}^{100} . This would be the 100×100 block associated with the 100 smallest A_{ii} diagonal elements of \mathbf{A} .

Now we diagonalize \mathbf{A}^{100} and obtain 100 eigenvalues $\{a_i\}$ $0 < i \leq 100$.

Next we evaluate the function f at each of the eigenvalues of \mathbf{A}^{100}

$$f(\tilde{\mathbf{A}}^{100}) = \tilde{f} = \begin{pmatrix} f(a_1) & 0 & 0 & 0 \\ 0 & f(a_2) & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & f(a_{100}) \end{pmatrix}.$$

This is trivial. For $f(\mathbf{A}) = \mathbf{A}^{1/2}$, we have

$$\tilde{f}(\tilde{\mathbf{A}}^{100}) = \begin{pmatrix} a_1^{1/2} & 0 & 0 & 0 \\ 0 & a_2^{1/2} & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & a_{100}^{1/2} \end{pmatrix}.$$

To get $\mathbf{f}(\mathbf{A}^{100})$ we need to transform $\tilde{\mathbf{f}}(\tilde{\mathbf{A}}^{100})$ back to the original representation of \mathbf{A}

$$\mathbf{f}(\mathbf{A}^{100}) = \mathbf{T}\mathbf{f}(\mathbf{T}^\dagger \mathbf{A}^{100} \mathbf{T})\mathbf{T}^\dagger = \mathbf{T}\tilde{\mathbf{f}}^{100}\mathbf{T}^\dagger.$$

It is possible to prove this, but that is not a job for 5.61.

$\tilde{\mathbf{f}}^{100}$ is a diagonal matrix. The $\mathbf{T}, \mathbf{T}^\dagger$ matrices from the unitary diagonalizing transformation of \mathbf{A}^{100} are already known by your computer. So you can ask the computer to apply the reverse transformation to obtain the non-diagonal matrix, $\mathbf{f}(\mathbf{A}^{100})$. Wonderful!

The next step is to do something related to the Harmonic Oscillator and is therefore of general usefulness.

The potential energy function is what distinguishes one oscillator problem from all others. We want the matrix representation of V in the Harmonic-Oscillator representation

$$\mathbf{V}(\mathbf{X}).$$

But you will initially think, “this is ridiculous because the displacement, X , is a *continuous variable*.” What possible meaning would the first 100 eigenvalues of the matrix \mathbf{X} have?

If the matrix representation of \mathbf{X} were chosen to be of infinite dimension, the eigenvectors of \mathbf{X} would be $\delta(x - x_i)$ Dirac δ -functions. They would be perfectly localized functions, located at each of the eigenvalues of \mathbf{X} . Each δ -function would be a linear combination of an infinite number of harmonic oscillator eigenfunctions. If \mathbf{X} is not of infinite dimension, each eigenvector is a sharply localized function, centered at one of the eigenvalues of \mathbf{X} . However, none of this matters. We can truncate \mathbf{X} at whatever dimension we choose and use it to construct a finite dimension representation of the potential energy function.

- (1) Choose a harmonic oscillator basis set where $X = x - x_e$ and $\omega = [k/\mu]^{1/2}$. It is a good idea to use a basis set where the lowest energy minimum of $V(x)$ is at $x = x_e$ and

$$k = \left. \frac{d^2V}{dx^2} \right|_{x=x_e}.$$

- (2) Truncate \mathbf{X} at some dimension close to the maximum that your computer can diagonalize in an acceptable time. If you are going to want an accurate computation of the lowest 100 eigenvalues of \mathbf{X} , you will probably want to truncate \mathbf{X} at 1000×1000 , \mathbf{X}^{1000} . You know all of the non-zero matrix elements of $\hat{\mathbf{X}}$ in the harmonic oscillator basis set: only $x_{jj\pm 1}$ matrix elements are non-zero.
- (3) Diagonalize \mathbf{X}^{1000} .

$$\tilde{\mathbf{X}}^{1000} = \mathbf{T}^{1000\dagger} \mathbf{X}^{1000} \mathbf{T}^{1000}$$

$$\tilde{\mathbf{X}}^{1000} = \begin{pmatrix} x_1 & 0 & 0 & 0 \\ 0 & x_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & x_{1000} \end{pmatrix}$$

The eigenvector that corresponds to the n^{th} eigenvalue (counting up from the lowest value) is

$$\begin{pmatrix} \mathbf{T}_{1,n}^{1000\dagger} \\ \vdots \\ \vdots \\ \mathbf{T}_{1000,n}^{1000\dagger} \end{pmatrix}.$$

- (4) $V(x)$ is some function of the harmonic oscillator displacement. Evaluate $V(x_n)$ at each value of x_n . This is $\tilde{\mathbf{V}}^{1000}$.
- (5) Transform $\tilde{\mathbf{V}}^{1000}$ back to the harmonic oscillator basis.

$$\mathbf{V}^{1000} = \mathbf{T}^{1000} \tilde{\mathbf{V}}^{1000} \mathbf{T}^{1000\dagger}.$$

Now we have expressed some arbitrary and possibly evil potential energy as a non-diagonal matrix in the harmonic oscillator basis set.

- (6) Express the kinetic energy matrix,

$$\mathbf{K}^{1000} = \mathbf{p}^2 / 2\mu$$

in the harmonic oscillator basis. This matrix has only non-zero elements K_{jj}^{1000} and $K_{jj\pm 2}^{1000}$. Now we have

$$\mathbf{H}^{1000} = \mathbf{K}^{1000} + \mathbf{V}^{1000}$$

and we can diagonalize \mathbf{H}^{1000} . This gives us the eigenvalues and eigenvectors of \mathbf{H}^{1000} .

- (7) We are probably only interested in a subset of these eigenvalues and eigenvectors. We need to check for convergence of our calculation for this subset. Repeat the calculation using a 10% smaller or larger dimension \mathbf{X} matrix, say \mathbf{X}^{900} . If the calculation has converged as far as the eigenvalues that you are interested in are concerned, the E_n for $1 < n < 100$ should agree acceptably for the \mathbf{H}^{1000} and \mathbf{H}^{900} calculations.

- (8) If you plan to perform more calculations for a family of evil $V(x)$ potential energy functions, retain your $\tilde{\mathbf{X}}^{1000}$, $\tilde{\mathbf{X}}^{900}$, \mathbf{T}^{1000} , and \mathbf{T}^{900} matrices and use them for as many problems as you choose!

III. Extension of DVR to include rotation

It is possible to extend the DVR treatment to include rotation.

$$V_J(X) = V_0(X) + B(X)J(J+1)$$

$$X = x - x_e, \quad x = X + x_e \text{ where } x \text{ is the internuclear distance}$$

$$B(X) = B_e \left(\frac{x_e^2}{(X + x_e)^2} \right)$$

Thus, once we have diagonalized \mathbf{X} we can evaluate $V_J(x_i)$ at every eigenvalue of \mathbf{X} , then transform back to the Harmonic Oscillator basis set.

We will turn the DVR crank for several values of J , perhaps $J = 0, 1, 5, 10, 20, 40, 100$. We will obtain rotational level energies for each of the vibrational levels. These energies would be fitted to the equation

$$E(J) = E_v(0) + B_v J(J+1) - D_v [J(J+1)]^2.$$

Thus obtaining the usual molecular constants G_v , B_v , and D_v for any potential energy curve, no matter how pathological.

IV. Experimental determination of wavefunctions!

At the beginning of 5.61 I told you that the central concept in the Schrödinger form of Quantum Mechanics was never directly observable. Any measurement alters the state of the system.

But $\psi(x)$ can be determined *indirectly* by experiment.

Measure a set of $\{E_n\}$, ideally from the lowest energy up to some convenient stopping point.

Design an effective Hamiltonian, \mathbf{H}^{eff} , which is defined by a set of molecular constants. These molecular constants are experimentally determined by performing a least squares fit (a form of a variational calculation) in which the deviations between the eigenvalues of \mathbf{H}^{eff} and the experimentally observed $\{E_n\}$ are minimized. When the experimental measurements are fitted to measurement accuracy, you have determined an \mathbf{H}^{eff} that is a faithful representation of reality, even though \mathbf{H}^{eff} is not of infinite dimension and is only distantly related to the exact \mathbf{H} .

The \mathbf{H}^{eff} is expressed in some convenient basis set, such as a Harmonic Oscillator basis set. The transformation that diagonalizes \mathbf{H}^{eff}

$$\mathbf{T}^\dagger \mathbf{H}^{\text{eff}} \mathbf{T} = \tilde{\mathbf{H}} = \begin{pmatrix} E_1 & & 0 \\ & \ddots & \\ 0 & & E_N \end{pmatrix}$$

gives us the eigenvectors. The columns of \mathbf{T}^\dagger are the eigenvectors

$$|j\rangle = \begin{pmatrix} T_{1j}^\dagger \\ \vdots \\ T_{Nj}^\dagger \end{pmatrix},$$

thus

$$\psi_j(x) = \sum_{n=1}^N T_{nj} \psi_n^{(0)}(x),$$

so we have a wavefunction representation of every eigenstate of \mathbf{H}^{eff} . These eigenstates can provide a picture of $\psi_j(x)$ that yields valuable insights, usually through the number and organization of nodes or nodal surfaces.

So we can obtain all of the $\psi_j(x)$ (indirectly) from experiment after all!

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