Matrix Mechanics

should have read CDTL pages 94-121
read CTDL pages 121-144 ASAP

Last time: Numerov-Cooley Integration of 1-D Schr. Eqn. Defined on a Grid.
2-sided boundary conditions
nonlinear system - iterate to eigenenergies (Newton-Raphson)

So far focussed on $\psi(x)$ and Schr. Eq. as differential equation.
Variety of methods $\{E_i, \psi_i(x)\} \leftrightarrow V(x)$

Often we want to evaluate integrals of the form

overlap of special ψ on standard functions $\{\phi\}$

$$\int \psi^*(x)\phi_i(x)dx = a_i$$

a_i is "mixing coefficient"
$\{\phi\}$ is complete set of "basis functions"

OR

expectation values
transition moments

$$\int \phi_i^* \hat{x}^n \phi_j dx \equiv \left(x^n\right)_{ij}$$

There are going to be elegant tricks for evaluating these integrals and relating one integral to others that are already known. Also "selection" rules for knowing automatically which integrals are zero: symmetry, commutation rules

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Today: begin matrix mechanics - deal with matrices composed of these integrals - focus on manipulating these matrices rather than solving a differential equation - find eigenvalues and eigenvectors of matrices instead (COMPUTER "DIAGONALIZATION")

HIGHLIGHTS

* Perturbation Theory: tricks to find approximate eigenvalues of <u>infinite</u> matrices
* Wigner-Eckart Theorem and 3-j coefficients: use symmetry to identify and inter-relate values of nonzero integrals
* Density Matrices: information about state of system as separate from measurement operators

First Goal: Dirac notation as convenient NOTATIONAL simplification
It is actually a new abstract picture
(vector spaces) — but we will stress the utility ($\psi \leftrightarrow | \,\rangle$ relationships) rather than the philosophy!

Find equivalent matrix form of standard $\psi(x)$ concepts and methods.

1. Orthonormality $\int \psi_i^* \psi_j dx = \delta_{ij}$

2. completeness $\psi(x)$ is an arbitrary function

(expand ψ) A. Always possible to expand $\psi(x)$ uniquely in a COMPLETE BASIS SET $\{\phi\}$

$$\psi(x) = \sum_i a_i \phi_i(x)$$

a_i — mixing coefficient — how to get it? left multiply by $\int \phi_j^*$

$$* \quad a_i = \int \phi_i^* \psi dx$$

(expand $\mathbf{B}\psi$) B. Always possible to expand $\hat{B}\psi$ in $\{\phi\}$ since we can write ψ in terms of $\{\phi\}$.
So simplify the question we are asking to $\hat{B}\phi_i = \sum_j b_j \phi_j$ What are the $\{b_j\}$? Multiply by $\int \phi_j^*$

$$b_j = \int \phi_j^* \hat{B} \phi_i dx \equiv B_{ji}$$

$$\hat{B}\phi_i = \sum_j B_{ji}\phi_j$$

note counter-intuitive pattern of indices. We will return to this.

* The effect of any operator on ψ_i is to give a linear combination of ψ_j's.

3. <u>Products of Operators</u>

$$\left(\hat{A}\hat{B}\right)\phi_i = \hat{A}\left(\hat{B}\phi_i\right) = \hat{A}\sum_j B_{ji}\phi_j$$

can move numbers (but not operators) around freely

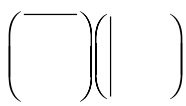
$$= \sum_j B_{ji}\hat{A}\phi_j = \sum_j\sum_k \underbrace{B_{ji}A_{kj}}\phi_k \qquad \text{note repeated index}$$

$$= \sum_{j,k}\left(A_{kj}B_{ji}\right)\phi_k = \sum_k (\mathbf{AB})_{ki}\phi_k$$

* Thus product of 2 operators follows the rules of matrix multiplication:

$\hat{A}\hat{B}$ acts like **A B**

Recall rules for matrix multiplication:



indices are $A_{\text{row,column}}$

must match # of columns on left to # of rows on right

$$(N \times N) \otimes (N \times N) \rightarrow (N \times N) \quad \text{a matrix}$$

order matters!

$$(1 \times N) \otimes (N \times 1) \rightarrow (1 \times 1) \quad \text{a number}$$

"row vector" "column vector"

$$(N \times 1) \otimes (1 \times N) \rightarrow (N \times N) \quad \text{a matrix!}$$

column vector row vector

Need a notation that accomplishes all of this *memorably* and compactly.

Dirac's bra and ket notation

Heisenberg's matrix mechanics

ket $| \rangle$ is a column matrix, i.e. a vector $\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$

contains all of the "mixing coefficients" for ψ expressed in some basis set.
[These are projections onto unit vectors in N-dimensional vector space.]
Must be clear what state is being expanded in what basis

$$\psi(x) = \sum_i \overbrace{\left[\int \phi_i^* \psi dx\right]}^{a_i} \phi_i(x)$$

$$|\psi\rangle = \begin{pmatrix} \int \phi_1^* \psi dx \\ \int \phi_2^* \psi dx \\ \vdots \\ \int \phi_N^* \psi dx \end{pmatrix}_{\phi}$$

* ψ expressed in ϕ basis
* a column of complex #s
* nothing here is a function of x

$\phi \leftarrow$ bookkeeping device (RARE)

OR, a pure state in its own basis

$$|\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}_{\phi} \quad \text{one 1, all others 0}$$

bra $\langle \, |$ is a row matrix $(b_1, b_2 \ldots b_N)$

$\langle \, |$ contains all mixing coefficients for ψ^* in $\{\phi^*\}$ basis set

$$\psi^*(x) = \sum_i \left[\int \phi_i \psi^* dx\right] \phi_i^*(x) \qquad \text{(This is * of } \psi(x) \text{ above)}$$

The * stuff is needed to make sure $\langle \psi | \psi \rangle = 1$ even though $\langle \phi_i | \psi \rangle$ is complex.

The symbol $\langle a|b\rangle$, a bra–ket, is defined in the sense of product of $(1 \times N) \otimes (N \times 1)$ matrices $\rightarrow$ a 1×1 matrix: a number!

<u>Box Normalization in both ψ and $\langle \ | \ \rangle$ pictures</u>

$$1 = \int \psi^* \psi dx$$

$$\psi = \sum_i \left(\int \phi_i^* \psi dx \right) \phi_i$$

$$\psi^* = \sum_j \left(\phi_j \psi^* dx \right) \phi_j^*$$

expand both in ϕ basis

$$1 = \int \psi^* \psi dx = \sum_{i,j} \left(\int \underline{\phi_j \psi^*} dx \right) \left(\int \underline{\phi_i^* \psi} dx \right) \underbrace{\int \phi_j^* \phi_i dx}_{\delta_{ij}}$$

c.c.

δ_{ij}: forces 2 sums to collapse into 1

$$1 = \sum_j \underbrace{\left| \int \phi_j^* \psi dx \right|^2}_{\text{real, positive \#'s}}$$

We have proved that sum of $|\text{mixing coefficients}|^2 = 1$. These are called "mixing fractions" or "fractional character".

now in $\langle \ | \ \rangle$ picture

$$\langle \psi | \psi \rangle = \left(\underbrace{\int \phi_1 \psi^* dx \quad \int \phi_2 \psi^* dx \quad \cdots}_{\text{row vector: "bra"}} \right) \left(\underbrace{\begin{matrix} \int \phi_1^* \psi dx \\ \int \phi_2^* \psi dx \\ \vdots \end{matrix}}_{\text{column vector "ket"}} \right)$$

$$= \sum_j \left| \int \phi_j^* \psi dx \right|^2$$

same result

[CTDL talks about dual vector spaces — best to walk before you run. Always translate $\langle\rangle$ into ψ picture to be sure you understand the notation.]

Any symbol $\langle\ \rangle$ is a complex number.
Any symbol $|\ \rangle\langle\ |$ is a square matrix.

$$\text{again } \langle\psi|\psi\rangle = \big(\langle\psi|\phi_1\rangle\ \langle\psi|\phi_2\rangle \ldots\big)\begin{pmatrix}\langle\phi_1|\psi\rangle \\ \langle\phi_2|\psi\rangle \\ \vdots\end{pmatrix}$$

$$= \sum_i \langle\psi\underbrace{|\phi_i\rangle\langle\phi_i|}_{\mathbb{1}\text{ unit matrix}}\psi\rangle = \langle\psi|\psi\rangle = 1$$

$$\text{what is } |\phi_1\rangle\langle\phi_1| = (1\ \ 0\ \ \ldots\ \ 0)\begin{pmatrix}1 \\ 0 \\ \vdots \\ 0\end{pmatrix} = \begin{pmatrix}1 & 0 & \cdots \\ 0 & 0 & \\ \vdots & & \ddots\end{pmatrix}$$

a shorthand for specifying only the important part of an infinite matrix

$$\text{what is } \sum_i |\phi_i\rangle\langle\phi_i| = \begin{pmatrix}1 & & & \\ & 1 & 0 & \\ & 0 & 1 & \\ & & & \ddots\end{pmatrix}$$

unit or identity matrix = $\mathbb{1}$

"completeness" or "closure" involves insertion of $\mathbb{1}$ between any two symbols.

Use 𝟙 to evaluate matrix elements of product of 2 operators, **AB** (we know how to do this in ψ picture).

$$\langle \phi_i | \mathbf{A} | \phi_j \rangle = \underset{\text{i-th}}{(0 \ldots 1 \ldots 0)} \underset{\text{square matrix}}{(\mathbf{A})} \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}$$

1 at the j-th position – picks out j-th column of **A**

$$= \underset{\text{i-th}}{(0 \ldots 1 \ldots 0)} \begin{pmatrix} A_{1j} \\ A_{2j} \\ \vdots \end{pmatrix} = A_{ij}$$

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

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

In Heisenberg picture, how do we get <u>exact</u> equivalent of ψ(x)?
basis set $\delta(x,x_0)$ for all x_0 – this is a complete basis (eigenbasis for $\hat{x}$, eigenvalue x_0) - perfect localization at any x_0

$\langle x | \psi \rangle$ is the same thing as ψ(x) $\left(\text{i.e., } \int \delta(x,x')^* \psi(x') dx' = \psi(x)\right)$

↑

x is continuously variable ↔ δ(x)

overlap of state vector ψ with δ(x) – a complex number. ψ(*x*) is a complex function of a real variable.

other $\psi \leftrightarrow \langle | \rangle$ relationships

1. All observable quantities are represented by a Hemitian operator (Why – because expectation values are always real). Definition of Hermitian operator.

$$A_{ij} = A_{ji}^{*} \qquad \text{or} \qquad \mathbf{A} = \mathbf{A}^{\dagger}$$

Easy to prove that if all expectation values of **A** are real, then $\mathbf{A} = \mathbf{A}^{\dagger}$ and vice-versa

2. <u>Change of basis set</u>

$$\mathbf{A}^{\phi} \leftrightarrow \mathbf{A}^{u} \qquad \{\phi\} \text{ to } \{u\}$$

$$A_{ij}^{\phi} \equiv \left\langle \phi_i \middle| A \middle| \phi_j \right\rangle = \left\langle \phi_i \middle| \mathbf{1} A \mathbf{1} \middle| \phi_j \right\rangle$$

$$= \sum_{k,\ell} \left\langle \phi_i \middle| u_k \right\rangle \left\langle \mathrm{u}_k \middle| A \middle| \mathrm{u}_\ell \right\rangle \left\langle u_\ell \middle| \phi_j \right\rangle$$

1st index is u

$S_{ki}^{*} \equiv S_{ik}^{\dagger}$ (↑ u, ϕ)

$S_{\ell j} \leftarrow \phi$ (↑ u) j-th column of **S**

S is Frequently used to denote "overlap" integral

$$= \sum_{k,\ell} S_{ik}^{\leq} A_{k\ell}^{u} S_{\ell j} = \left(\mathbf{S}^{\leq} \boldsymbol{A}^{u} \mathbf{S}\right)_{ij} \equiv A_{ij}^{\phi}$$

$$\boldsymbol{A}^{\phi} = \boldsymbol{S}^{\leq} \boldsymbol{A}^{u} \boldsymbol{S}$$

a special kind of transformation (unitary)

(different from usual $\mathbf{T}^{-1}\mathbf{A}\mathbf{T}$ "similarity" transformation)

What kind of matrix is **S**?

$$S_{\ell j} = \langle u_\ell | \phi_j \rangle$$

$$S^*_{\ell j} = \left[\langle u_\ell | \phi_j \rangle\right]^* = \langle \phi_j | u_\ell \rangle \equiv S^{\leq}_{j\ell}$$

$\leq$ means take complex conjugate and interchange indices.

Using the definitions of **S** and $\mathbf{S}^{\leq}$:

$$S_{\ell j} S^{\dagger}_{jk} = \langle u_\ell | \phi_j \rangle \langle \phi_j | u_k \rangle$$

$$\sum_j S_{\ell j} S^{\dagger}_{jk} = \sum_j \langle u_\ell | \phi_j \rangle \langle \phi_j | u_k \rangle = \langle u_l | \mathbb{1} | u_k \rangle$$

$$= \langle u_\ell | u_k \rangle = \delta_{\ell k} = \mathbb{1}_{\ell k}$$

$\therefore$ $\mathbf{SS}^\dagger = \mathbb{1}$ OR $\mathbf{S}^\dagger = \mathbf{S}^{-1}$ "Unitary" a very special and convenient property.

Unitary transformations preserve both normalization and orthogonality.

$$A^{\phi} = S^{\dagger} A^{u} S$$

$$S A^{\phi} S^{\dagger} = S S^{\dagger} A^{u} S S^{\dagger} = A^{u}$$

$$A^{u} = S A^{\phi} S^{\dagger}$$

Take matrix element of both sides of equation:

$$A_{ij}^{u} = \left\langle u_i \mid A \mid u_j \right\rangle = \left(S A^{\phi} S^{\dagger} \right)_{ij}$$

$$= \sum_{k,l} S_{ik} \left\langle \phi_k \mid A \mid \phi_l \right\rangle S_{lj}^{\dagger}$$

$$\therefore \left| u_j \right\rangle = \sum_{\ell} \left| \phi_{\ell} \right\rangle \mathbf{S}_{\ell j}^{\leq} \qquad \text{j - th column of } \mathbf{S}^{\leq}$$

$$\phi \rightarrow u \quad \text{via} \quad \mathbf{S}^{\dagger}, \mathbf{S} \; : \; \left| u_j \right\rangle \text{ is j-th column of } \mathbf{S}^{\dagger}$$

Thus,

j-th

$$\left|u_j\right\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} S^{\leq}_{1j} \\ S^{\leq}_{2j} \\ \vdots \\ \vdots \\ S^{\leq}_{nj} \end{pmatrix}_{\phi}$$

Alternatively,

$$\mathrm{A}^{\phi}_{\mathrm{pq}} = \left\langle \phi_p \right| \mathbf{A} \left| \phi_q \right\rangle = \left(\mathbf{S}^{\leq}\mathbf{A}^{u}\mathbf{S}\right)_{pq}$$

$$= \sum_{mn} S^{\leq}_{pm} \left\langle u_m \right| \mathbf{A} \left| u_n \right\rangle S_{nq}$$

$$\therefore \left|\phi_q\right\rangle = \sum_n \left|u_n\right\rangle S_{nq} \qquad q\text{ - th column of } \mathbf{S}$$

$$\left|\phi_{\mathrm{q}}\right\rangle = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_{\phi} = \begin{pmatrix} S_{1q} \\ S_{2q} \\ \vdots \\ S_{nq} \end{pmatrix}_{u}$$

q-th

Commutation Rules

* $\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$

e.g. $\left[\hat{x},\hat{p}\right] = i\hbar$ means $(xp - px)\phi = x\frac{\hbar}{i}\frac{d\phi}{dx} - \frac{\hbar}{i}\left(\phi + x\frac{d\phi}{dx}\right)$

$= i\hbar\phi$

* If $\hat{A}$ and $\hat{B}$ are Hermitian, is $\hat{A}\hat{B}$ Hermitian?

$$(AB)_{ij} = \sum_k A_{ik}B_{kj} = \sum \overbrace{A^*_{ki}B^*_{jk}}^{\text{Hermitian } \mathbf{A} \text{ and } \mathbf{B}} = \sum B^*_{jk}A^*_{ki} = (BA)^*_{ji}$$

but this is **not** what we need to say **AB** is Hermitian: That would be:

$(\mathbf{AB})_{ij} = (\mathbf{AB})^*_{ji}$

AB is Hermitian only if $[\mathbf{A},\mathbf{B}] = 0$

However, $\frac{1}{2}[\mathbf{AB} + \mathbf{BA}]$ is Hermitian if **A** and **B** are Hermitian.

This is the foolproof way to construct a new Hermitian operator out of simpler Hermitian operators.

Standard prescription for the Correspondence Principle.