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 (two different kinds of boundary condition)
* 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 with standard functions $\{\phi\}$

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

a_i is "mixing coefficient"
ϕ_i is a member of a "complete" set of basis functions, $\{\phi\}$

OR

expectation values and 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"). LINEAR ALGEBRA.

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* of $\psi \leftrightarrow |\rangle$ 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 $\{\phi\}$

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

mixing coefficient — how to get it?

* $\boxed{a_i = \int \phi_i^* \psi dx}$ left multiply by ϕ^*_i and integrate over x

(expand $\hat{B}\psi$) 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 $\left\{b_j\right\}$? Multiply by $\int \phi_j^*$

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

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

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. Products of Operators

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

can move numbers (but not operators) around freely

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

$$= \sum_{j,k}\left(A_{kj}B_{ji}\right)\phi_k = \sum_k (\mathbf{AB})_{ki}\phi_k \qquad \text{note repeated k-index}$$

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

$\hat{A}\hat{B}$ acts like $\mathbf{A}\,\mathbf{B}$

Recall rules for matrix multiplication:

$$\begin{pmatrix} \overline{} \\ \\ \end{pmatrix}\begin{pmatrix} | & & \\ | & & \end{pmatrix}$$ indices of a matrix are $A_{row,column}$

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

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

the order of matrices matters!

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

"row vector" "column vector"

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

column vector row vector

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

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Dirac's <u>bra</u> and <u>ket</u> notation

Heisenberg's matrix mechanics

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

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

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

$$|\psi\rangle = \begin{pmatrix} \int \phi_1^* \psi dx \\ \int \phi_2^* \psi dx \\ \vdots \\ \int \phi_N^* \psi dx \end{pmatrix}_{\phi} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

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

bookkeeping device (RARELY USED) to specify basis set

OR, a pure state in its own basis

$$|\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}_{\phi}$$ one 1, all others 0 (often expressed as $|2\rangle$)

$$|\psi\rangle = a_1 \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} + a_2 \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} + \ldots a_N \begin{pmatrix} 0 \\ \vdots \\ \vdots \\ 1 \end{pmatrix}$$

a weighted sum of unit vectors

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

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

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

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

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The symbol $\langle a|b\rangle$, a bra–ket, is defined in the sense of a 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>

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

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

take complex conjugate of ψ equation

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

expand both in ortho-normal 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.

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

forces the 2 sums (over i and j) to collapse into 1 sum (over j)

We have proved that sum of |mixing coefficients$|^2 = 1$. These mixing coefficients "squared" are called "mixing fractions" or "fractional characters".

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

$$\langle \psi | \psi \rangle = \Big(\underbrace{\int \phi_1 \psi^*\, dx \quad \int \phi_2 \psi^*\, dx \quad \cdots}_{\text{row vector: "bra"}} \Big) \left(\underbrace{\begin{matrix} \int \phi_1^* \psi\, dx \\ \int \phi_2^* \psi\, dx \\ \vdots \end{matrix}}_{\text{column vector "ket"}} \right) = 1 \times 1 \text{ matrix}$$

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

same result as in wavefunction representation

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

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

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

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

$$\text{what is } |\phi_1\rangle\langle\phi_1| = (1\,0\ldots0)\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix} = \begin{pmatrix}1 & 0 & \cdots \\ 0 & 0 & \\ \vdots & & \ddots\end{pmatrix}$$

three dots are shorthand for specifying only the important part of an infinite matrix

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

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

Large zero $(\mathbf{0})$ denotes a lot of zeroes.

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

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

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

square matrix

j-th position – picks out j-th column of **A**

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

picks out the i-th element of a column vector

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

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

a number (obtained by matrix multiplication)

In the Heisenberg picture, how do we get an <u>exact</u> equivalent of $\psi(x)$?
Use 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

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

↑

x is continuously variable ↔ $\delta(x)$

Overlap of state vector Ψ with $\delta(x)$ – a complex number. $\Psi(x)$ is a complex function of a real variable.

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

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

   For a matrix: $A_{ij} = A^*_{ji}$ or $\mathbf{A} = \mathbf{A}^\dagger$

   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>

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

$$A^\phi_{ij} \equiv \langle \phi_i | A | \phi_j \rangle = \langle \phi_i | \mathbf{1} A \mathbf{1} | \phi_j \rangle$$

$$= \sum_{k,\ell} \langle \phi_i | u_k \rangle \langle u_k | A | u_\ell \rangle \langle u_\ell | \phi_j \rangle$$

$\langle \phi_i | u_k \rangle = S^*_{ki} \equiv S^\dagger_{ik}$ (k ↑ u, i ↑ ϕ); $\langle u_\ell | \phi_j \rangle = S_{\ell j}$ (ℓ ↑ u, j ← ϕ)

S is Frequently used to denote an "overlap" integral

This is the j-th column of **S**

$$= \sum_{k,\ell} S^\dagger_{ik} \underbrace{A^u_{k\ell}}_{u \text{ basis}} S_{\ell j} = \left(\mathbf{S}^\dagger A^u \mathbf{S}\right)_{ij} \equiv \underbrace{A^\phi_{ij}}_{\phi \text{ basis}}$$

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

$\mathbf{S}^\dagger \cdots \mathbf{S}$ is a special kind of transformation (unitary)

(different from more-familiar $\mathbf{T}^{-1}\mathbf{AT}$ "similarity" transformation)

For a state vector (ket):

$$\left|\phi_j\right\rangle = \sum_{\ell} \left|u_\ell\right\rangle\left\langle u_\ell\middle|\phi_j\right\rangle = \sum_{\ell=1}^{N} \left|u_\ell\right\rangle S_{\ell j} = \begin{pmatrix} S_{1j} \\ \vdots \\ S_{Nj} \end{pmatrix}$$

$$\left|\phi_j\right\rangle = \begin{pmatrix} S_{\ell j} \\ \vdots \\ S_{Nj} \end{pmatrix} \quad \text{This is the j-th column of } \mathbf{S}.$$

The linear combination of $\left|u_i\right\rangle$ for each $\left|\phi_j\right\rangle$ is the j-th column of S. Also, the linear combination of $\left|\phi_j\right\rangle$ for each $\left|u_i\right\rangle$ is the i-th column of $S^\dagger$. [This is a very useful thing to remember.]

$$\left|u_i\right\rangle = \underbrace{\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_u}_{\substack{\text{pure} \\ \text{state in} \\ \{u\}\text{ basis}}} \begin{matrix} \\ \\ \text{i-th} \\ \\ \\ \end{matrix} = \underbrace{\begin{pmatrix} S^\dagger_{1i} \\ \vdots \\ S^\dagger_{\mathbf{N}i} \end{pmatrix}_\phi}_{\substack{\text{mixed} \\ \text{state in} \\ \{\phi\}\text{ basis}}} = S^\dagger_{1i} \underbrace{\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}}_{\substack{\text{pure} \\ \text{state in} \\ \{\phi\}\text{ basis}}} + S^\dagger_{2i} \begin{pmatrix} 0 \\ 1 \\ \vdots \\ \vdots \end{pmatrix} + \ldots S^\dagger_{\mathbf{N}i} \begin{pmatrix} 0 \\ \vdots \\ \vdots \\ 1 \end{pmatrix}$$

What kind of matrix is **S**?

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

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

† means take complex conjugate and interchange indices.

Using the definitions of S and S† :

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

$$\sum_j S_{\ell j} S^\dagger_{jk} = \sum_j \langle u_\ell | \phi_j \rangle \langle \phi_j | u_k \rangle = \langle u_\ell | \underset{\substack{\uparrow \\ \text{identity} \\ \text{matrix}}}{\mathbb{1}} | u_k \rangle = \delta_{\ell k}$$

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

$\mathbf{SS}^\dagger = \mathbb{1}$ OR $\mathbf{S}^\dagger = \mathbf{S}^{-1}$ "Unitary"

a very special and convenient property.

$\mathbf{S}^\dagger$ is inverse of **S**!

<u>Unitary transformations preserve both normalization and orthogonality.</u>

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

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

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

Take matrix element of both sides of equation:

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

$$= \sum_{k,\ell} \mathbf{S}_{ik} \left\langle \phi_k \,|\, \mathbf{A} \,|\, \phi_\ell \right\rangle \mathbf{S}^{\dagger}_{\ell j}$$

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

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

Thus,

$$|u_j\rangle = \begin{array}{c} \\ \\ \text{j-th} \to \\ \\ \\ \end{array}\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_u = \begin{pmatrix} S^\dagger_{1j} \\ S^\dagger_{2j} \\ \vdots \\ \vdots \\ S^\dagger_{nj} \end{pmatrix}_\phi$$

Similarly,

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

$$= \sum_{mn} S^\dagger_{pm} \langle u_m \underbrace{| \mathrm{A} | u_n \rangle S_{nq}}_{|\phi_q\rangle}$$

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

$$|\phi_\mathrm{q}\rangle = \begin{array}{c} \\ \\ \text{q-th} \to \\ \\ \\ \end{array}\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\phi = \begin{pmatrix} S_{1q} \\ S_{2q} \\ \vdots \\ S_{nq} \end{pmatrix}_u$$

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 $\left(\hat{x}\hat{p}-\hat{p}\hat{x}\right)\phi = x\frac{\hbar}{i}\frac{d\phi}{dx}-\frac{\hbar}{i}\left(\phi + x\frac{d\phi}{dx}\right)=-\frac{\hbar}{i}\phi=\hbar i\phi$

$= i\hbar\phi$

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

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

but this is **not** what we need to be able to show that **AB** is Hermitian:
That would be: $(\mathbf{AB})_{ij}=(\mathbf{AB})^*_{ji}$ *or* $\mathbf{AB}=(\mathbf{AB})^\dagger \neq (\mathbf{BA})^\dagger$

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

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

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

This is the standard prescription for implementing the Correspondence Principle for constructing a quantum mechanical equivalent of a classical mechanical quantity. Quantities that commute in classical mechanics do not always commute in quantum mechanics. *Almost everything that is not classical mechanical in quantum mechanics is derivable from* $\left[\hat{x},\hat{p}_x\right]\neq 0$!