5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #1: Matrices are Useful in Spectroscopic Theory

For next time, read handout on the Van Vleck transformation and look at the notes on coupled harmonic oscillators.

Outline

* Correspondences

bra: $\psi_i \rightarrow |i\rangle = \begin{pmatrix} \\ \end{pmatrix}$ row column — N × 1 — column vector

ket: $\psi_i^* \rightarrow \langle i| = \begin{pmatrix} & \end{pmatrix}$ — 1 × N — row vector

operator $\hat{O} \rightarrow \mathbf{O}$ — N × N square matrix

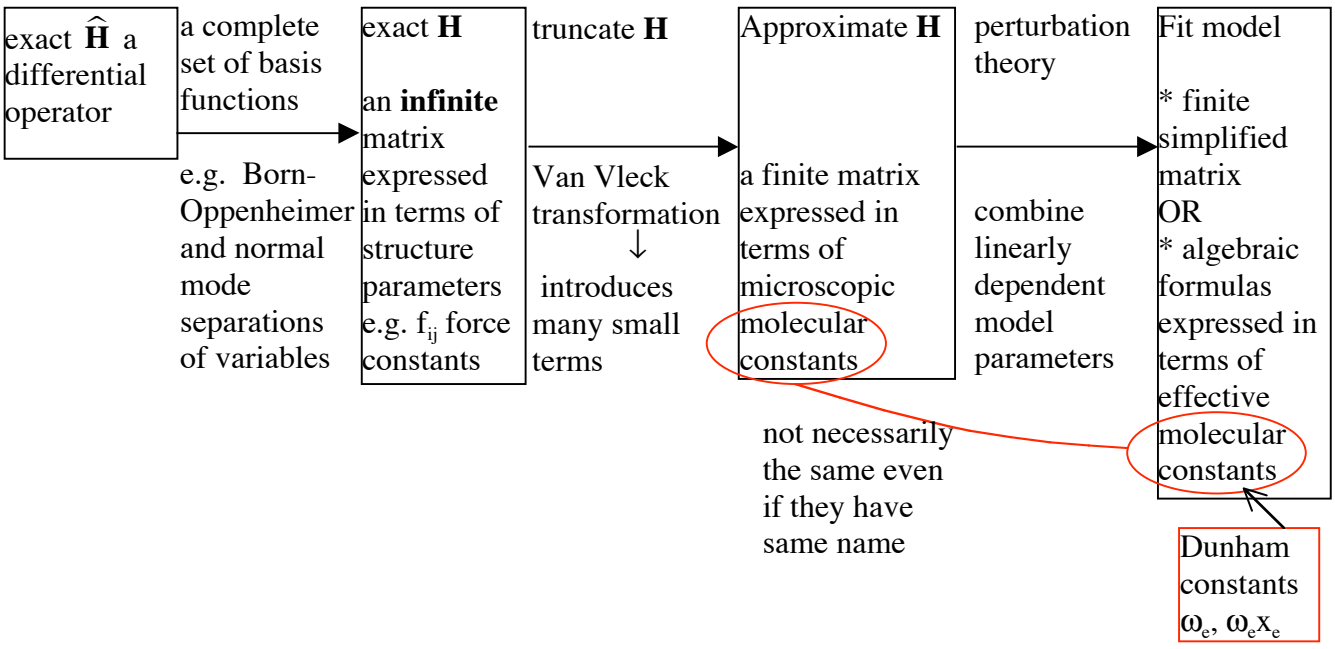
* Solution of Schrödinger Equation corresponds to solving a determinantal secular equation for the $\{E_k\}$

* The $\{E_k\}$ are the $\mathbf{H}^{\psi}_{kk}$ in the special "diagonal" representation of $\hat{\mathbf{H}}$;

* The $\{\psi_k\}$ are obtained from the basis states $\{\phi_k\}$ as columns of the unitary matrix **T** from the similarity transformation $\mathbf{T}^{\dagger}\mathbf{H}^{\phi}\mathbf{T} = \mathbf{H}^{\psi}$ that "diagonalizes" $\mathbf{H}^{\phi}$;

* Matrix representation of arbitrary f(**Q**).

Usual procedure to obtain a fit model.



Matrices are useful because:

* they display all necessary information;

* can be "read" and simplified by perturbation theory "order sorting" via $\frac{H_{ij}}{E_i^o - E_j^o}$;

* labor saving tricks for avoiding the evaluation of unnecessary integrals, such as formulas for all matrix elements of $\hat{Q}$ and $\hat{P}$ in the Harmonic Oscillator basis set.
  No integrals actually evaluated.
  No functions actually looked at.

Quantum Mechanics Operators follow the rules of matrix multiplication.

$$\text{e.g.} \quad \int \psi_i^* \left(\hat{A}\hat{B}\right) \psi_j d\tau = \sum_k \left(\int \psi_i^* \hat{A} \underbrace{\psi_k d\tau}_{\substack{\text{completeness} \\ \text{of } \{\psi\}}} \right) \left(\int \psi_k^* \hat{B} \psi_j d\tau \right)$$

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

This is very useful because we can generate <u>many</u> matrices by simple operations on <u>one</u> matrix.

E.g. $\mathbf{Q} = R - R_e$

$$V(\mathbf{Q}) = \sum_n c_n \mathbf{Q}^n$$

matrix of $\widehat{\mathbf{Q}^n}$ $\quad (\mathbf{Q}^n) = (\mathbf{Q})^n \quad \mathbf{Q} \times \mathbf{Q} \times \ldots \mathbf{Q}$

so instead of evaluating $\mathbf{Q}^1$, $\mathbf{Q}^2$, $\mathbf{Q}^3$, etc. we just evaluate $\mathbf{Q}$ and derive all the rest by matrix operations.
↑ formulas, not integrals!

There is even some diagrammatic insight [* shortcuts to selection rules; * calculations of a specific element of $\mathbf{Q}^n$

$$\mathbf{Q} = \begin{pmatrix} 0 & & & & & \\ & 0 & & & \mathbf{0} & \\ & & 0 & & & \\ & & & 0 & & \\ & \mathbf{0} & & & \ddots & \\ & & & & & 0 \end{pmatrix}$$

$\Delta v = \pm 1$ non-zero matrix elements of $\mathbf{Q}$

$$(\mathbf{Q}^2) = \begin{pmatrix} 0 & & 0 & & & \\ & 0 & & 0 & \mathbf{0} & \\ 0 & & 0 & & & \\ & 0 & & 0 & & \\ & & 0 & & \ddots & \\ \mathbf{0} & & & 0 & & 0 \\ & & & & 0 & \end{pmatrix}$$

$\Delta v = 0, \pm 2$ selection rules

etc.

At the end of this lecture we will see that we are not restricted to integer powers of $\mathbf{Q}$.

Suppose we have a convenient and complete (orthonormal) basis set $\{\phi_i\}$.

Any arbitrary function (including an eigenfunction of $\widehat{\mathbf{H}}$) can be expanded in terms of the $\{\phi\}$.

wavefunction picture

$$\psi_k = \sum_{i=1}^{N} a_i^k \phi_i \qquad \int \phi_i^* \psi_k d\tau = a_i^k$$

can be ∞

matrix picture

$\boldsymbol{\psi} = \mathbf{U}\boldsymbol{\phi}$ $\mathbf{U}$ is a transformation that converts $\{\phi\}$ into $\{\psi\}$.

$$\psi_k \rightarrow |k\rangle_\psi = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi \qquad \phi_i \rightarrow |i\rangle_\phi = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\phi$$

$$\psi_k^* \rightarrow {}_\psi\langle k| = \underbrace{0 \ldots 1 \ldots 0}_{\psi} \qquad \phi_i^* \rightarrow {}_\phi\langle i| = \underbrace{0 \ldots 1 \ldots 0}_{\phi}$$

$N \times 1$ column matrix

We know $\psi_k = \sum_{i=1}^{N} a_i^k \phi_i$

We want $\boldsymbol{\psi} = \mathbf{U}\boldsymbol{\phi}$ where $\mathbf{U}$ is $N \times N$ matrix that transforms $\boldsymbol{\phi}$ into $\boldsymbol{\psi}$.

By this we mean

$$\psi_k = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi = \sum_i U_{ki}\phi_i = \begin{pmatrix} U_{k1} \\ 0 \\ \vdots \\ \vdots \\ 0 \end{pmatrix}_\phi + \begin{pmatrix} 0 \\ U_{k2} \\ \vdots \\ \vdots \\ 0 \end{pmatrix}_\phi + \ldots \begin{pmatrix} 0 \\ \vdots \\ \vdots \\ \vdots \\ U_{kN} \end{pmatrix}_\phi$$

k-th row of U

$$\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi = \begin{pmatrix} U_{k1} \\ \vdots \\ \vdots \\ \vdots \\ U_{kN} \end{pmatrix}_\phi$$

$$U_{ki} = a_i^k = \int \phi_i^* \psi_k \, d\tau$$

We can go in the opposite direction

$U^{-1}\boldsymbol{\psi} = \boldsymbol{\phi}$

and show that $U^{-1} = U^\dagger$ $\quad U_{ij}^{-1} = U_{ji}^*$

ϕ_i is the i-th row of U^{-1} or the i-th column of U*.

Derivation of Secular Determinant

Now for every operator there is a matrix representation.

$$\hat{O} \rightarrow \mathbf{O}^{\phi} = \begin{pmatrix} O_{11} & \cdots & O_{1N} \\ \vdots & & \vdots \\ O_{N1} & \cdots & O_{NN} \end{pmatrix}$$

$$O_{ij} = \int \phi_i^* \hat{O} \phi_j d\tau$$

Schrödinger Equation in ψ eigenbasis picture

$$\hat{\mathbf{H}}\psi_k = E_k \psi_k$$

$$\psi_k = \sum_{i=1}^{\infty} a_i^k \phi_i$$

mixing coefficient

basis function - convenient

usually defined as eigenfunctions of a part of $\hat{\mathbf{H}}$ called $\hat{\mathbf{H}}^{\circ}$

$\hat{\mathbf{H}}^{\circ}\phi_i = E_i^{\circ}\phi_i$

Matrix notation:

$$\mathbf{H}_{ij}^{\phi} = \int \phi_i^* \hat{\mathbf{H}} \phi_j d\tau = {}_{\phi}\langle i|\mathbf{H}|j\rangle_{\phi}$$

$$\begin{pmatrix} \mathbf{H}^{\phi}_{11} & \cdots & \mathbf{H}^{\phi}_{1N} \\ \mathbf{H}^{\phi}_{21} & & \\ \vdots & & \\ \mathbf{H}^{\phi}_{N1} & & \end{pmatrix}_{\phi} \begin{pmatrix} a^k_1 \\ \vdots \\ \vdots \\ a^k_N \end{pmatrix}_{\phi} = E_k \begin{pmatrix} a^k_1 \\ \vdots \\ \vdots \\ a^k_N \end{pmatrix}_{\phi}$$

convenient representation — initially unknown mixing coefficients — initially unknown energies

$$\text{LHS} = \begin{pmatrix} \sum_i & \mathbf{H}^{\phi}_{1i} & a^k_i \\ \sum_i & \mathbf{H}_{2i} & a^k_i \\ & \vdots & \\ \sum_i & \mathbf{H}_{Ni} & a^k_i \end{pmatrix} = E_k \begin{pmatrix} a^k_1 \\ \vdots \\ \vdots \\ a^k_N \end{pmatrix}$$

move everything into one column matrix

$$\begin{pmatrix} \sum_i \left(\mathbf{H}_{1i} a^k_i - \delta_{1i} E_k a^k_i\right) \\ \sum_i \left(\mathbf{H}_{2i} a^k_i - \delta_{2i} E_k a^k_i\right) \\ \text{etc.} \end{pmatrix} = \begin{pmatrix} \sum_i a^k_i \left(\mathbf{H}_{1i} - \delta_{1i} E_k\right) \\ \text{etc.} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

A system of N linear homogeneous equations in N unknowns $\left(a^k_i \; i = 1 \ldots N\right)$. A nontrivial solution exists if the determinant of coefficients of the unknown $\left\{a^k_i\right\}$ is zero.

$$0 = \begin{vmatrix} \mathbf{H}_{11} - E_k & \mathbf{H}_{12} & \cdots \mathbf{H}_{1N} \\ \mathbf{H}_{21} & \mathbf{H}_{22} - E_k & \\ & & \mathbf{H}_{NN} - E_k \end{vmatrix} = \left|\mathbf{H}^{\phi} - \mathbb{1} E_k\right| \quad \text{(unit matrix)}$$

This is the secular determinant. Must solve for special values of E_k which satisfy the requirement $0 = |\mathbf{H}^{\phi} - \mathbb{1}E_k|$.

These are eigenvalues of $\widehat{\mathbf{H}}$. $\{E_k\}$ $k = 1, 2, \ldots N$
COMPUTERS!

1. start with complete set $\{\phi\}$
2. compute all $\mathbf{H}^{\phi}$ matrix elements
3. "diagonalize" $\mathbf{H}^{\phi}$ time required $\propto N^3$
4. solve for $\left\{a_i^k\right\}$: one set of N coefficients for each of the N eigenvalues.

How to "diagonalize" $\mathbf{H}^{\phi}$? Seek a similarity transformation $\mathbf{T}$.

$$\mathbf{T}^{-1}\mathbf{H}^{\phi}\mathbf{T} = \mathbf{H}^{\phi} = \begin{pmatrix} \mathbf{H}_{11}^{\psi} & & \mathbf{0} \\ & \mathbf{H}_{22}^{\psi} & \\ \mathbf{0} & & \ddots \\ & & & \mathbf{H}_{NN}^{\psi} \end{pmatrix}$$

$\mathbf{H}_{ii}^{\psi} \equiv E_k$ are the eigenvalues we seek.

Computer generates $\mathbf{T}$ iteratively (Jacobi Rotations, see handout)

Special properties:

* all Quantum Mechanical operators (that correspond to real observables) are "Hermitian" (real eigenvalues) which means that their matrix representations have the property

$$\mathbf{O} = \mathbf{O}^{\dagger} \qquad O_{ij} = O_{ji}^{*}$$

* $\mathbf{T}$ is "unitary"

$$\mathbf{T}^{\dagger}\mathbf{T} = \mathbb{1} \qquad (\text{i.e., } \mathbf{T}^{\dagger} = \mathbf{T}^{-1})$$

Now I'll show that **T** contains the information we seek about the $\{a_i^k\}$.

$$\mathbf{T}^\dagger\mathbf{H}^\phi\mathbf{T} = \mathbf{H}^\phi \text{ where } \mathbf{H}^\psi \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi = E_k \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi$$

ψ_k

$$\mathbf{T}^\dagger\mathbf{H}^\phi\mathbf{T}\psi_k = E_k\psi_k$$

left multiply by **T** $\quad \mathbf{T}\mathbf{T}^\dagger = \mathbb{1}$

$$\mathbf{T}\mathbf{T}^\dagger\mathbf{H}^\phi\mathbf{T}\psi_k = \mathbf{T}E_k\psi_k$$

$$\mathbf{H}^\phi\left(\mathbf{T}\psi_k\right) = E_k\left(\mathbf{T}\psi_k\right)$$

an eigenvector of $\mathbf{H}^\phi$

an eigenvalue equation

$$\mathbf{T}\psi_k = \mathbf{T}\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}_\psi = \begin{pmatrix} T_{1k} \\ \vdots \\ \vdots \\ \vdots \\ T_{Nk} \end{pmatrix}_\psi = \begin{pmatrix} a_1^k \\ \vdots \\ \vdots \\ \vdots \\ a_N^k \end{pmatrix}_\phi$$

k^{th} column of **T**

The columns of **T** are the eigenvectors of **H** in the ϕ representation.

$$\phi = T^\psi$$

$$\psi = T^\dagger\phi$$

Special example of finding matrix representation of any general function of a matrix.

Suppose we want $\mathbf{Q}^{3/2}$

* Generate $\mathbf{Q}^{\phi}$ in the convenient ϕ basis

* diagonalize $\mathbf{Q}^{\phi}$ [not the representation that diagonalizes $\mathbf{H}$]

$$\mathbf{T}^{\dagger}\mathbf{Q}^{\phi}\mathbf{T} = \mathbf{Q}^{\theta} = \begin{pmatrix} \mathbf{Q}^{\theta}_{11} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \mathbf{Q}^{\theta}_{NN} \end{pmatrix}$$

* $$\left(\mathbf{Q}^{\theta}\right)^{3/2} = \begin{pmatrix} \left(\mathbf{Q}^{\theta}_{11}\right)^{3/2} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \left(\mathbf{Q}^{\theta}_{NN}\right)^{3/2} \end{pmatrix}$$

* transform back to ϕ basis

$\mathbf{T}(\mathbf{Q}^{\theta})^{3/2}\mathbf{T}^{\dagger} = [\mathbf{Q}^{3/2}]^{\phi}$

The only reason why this is not as wonderful and general as it seems is that it is impossible to diagonalize an infinite matrix and all Harmonic Oscillator basis sets are infinite. Still, truncation at a finite (large) dimension gives accurate results for the lowest few eigenstates. Accuracy can be tested by doing calculation twice, once for $N \times N$ and once for $(N + 1) \times (N + 1)$ and looking for stability of results for the lowest levels of interest.