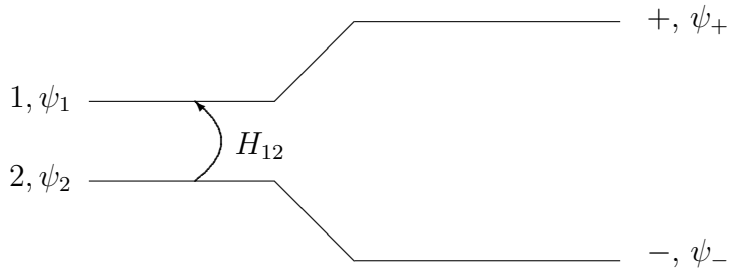
Lectures 13 & 14: From H_{ij} Integrals to H Matrices

I. The Two–Level Problem



$$H_{11} = \int \psi_1^\star \widehat{\mathbf{H}} \psi_1 d\tau$$
$$H_{22} = \int \psi_2^\star \widehat{\mathbf{H}} \psi_2 d\tau$$
$$H_{12} = \int \psi_1^\star \widehat{\mathbf{H}} \psi_2 d\tau = H_{21}^\star = \int \psi_2 \widehat{\mathbf{H}}^\star \psi_1^\star d\tau = V$$

$\widehat{\mathbf{H}}$ is Hermitian. If $\widehat{\mathbf{H}}$ is real, $H_{12} = H_{21}$

$$\psi_\pm = c_1^\pm \psi_1 + c_2^\pm \psi_2 \quad \text{“completeness”}$$
$$\widehat{\mathbf{H}} \psi_\pm = E_\pm \psi_\pm \quad \textbf{an eigenvalue equation.}$$

Left multiply by $\psi_1^\star$ and integrate

$$\int \psi_1^\star \widehat{\mathbf{H}} \psi_\pm d\tau = \int \psi_1^\star \widehat{\mathbf{H}} \left(c_1^\pm \psi_1 + c_2^\pm \psi_2 \right) d\tau = c_1^\pm H_{11} + c_2^\pm V = \int \psi_1^\star E_\pm \psi_\pm d\tau = E_\pm (c_1^\pm + 0 c_2^\pm)$$

$$\boxed{c_1^\pm (H_{11} - E_\pm) + c_2^\pm V = 0.} \tag{1}$$

Similarly, left multiply by $\psi_2^\star$ and integrate

$$\int \psi_2^\star \widehat{\mathbf{H}}(c_1^\pm \psi_1 + c_2^\pm \psi_2) d\tau = c_1^\pm V + c_2^\pm H_{22}$$

$$\int \psi_2^\star E_\pm \psi_\pm d\tau = E_\pm c_2^\pm$$

$$\boxed{c_1^\pm V + c_2^\pm (H_{22} - E_\pm) = 0.} \tag{2}$$

Thus we have two equations for $\frac{c_1^\pm}{c_2^\pm}$. We must temporarily eliminate $c_1^\pm$ and $c_2^\pm$ in order to determine $E_\pm$.

Before we can solve for $c_1^\pm$ and $c_2^\pm$, we must solve for $E_\pm$.

$$\frac{c_1^\pm}{c_2^\pm} = -\frac{V}{H_{11} - E_\pm}$$
$$\frac{c_1^\pm}{c_2^\pm} = -\frac{H_{22} - E_\pm}{V}$$

Thus

$$\frac{V}{H_{11} - E_\pm} = \frac{H_{22} - E_\pm}{V}$$
$$V^2 = (H_{11} - E_\pm)(H_{22} - E_\pm)$$
$$0 = E_\pm^2 - E_\pm(H_{11} + H_{22}) + H_{11}H_{22} - V^2.$$

This is a *quadratic equation* in $E_\pm$.

$$E_\pm = \frac{(H_{11} + H_{22}) \pm [(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - V^2)]^{1/2}}{2} \tag{3}$$

Some simplifying notation:

$$\overline{E} \equiv \frac{H_{11} + H_{22}}{2}$$
$$\Delta \equiv \frac{H_{11} - H_{22}}{2}.$$

Insert $\overline{E}$ and Δ into Eq. (3):

$$(H_{11} + H_{22})^2 - 4H_{11}H_{22} = (H_{11} - H_{22})^2$$
$$E_\pm = \overline{E} \pm [\Delta^2 + V^2]^{1/2}$$
$$x \equiv \Delta^2 + V^2$$
$$E_\pm = \overline{E} \pm x^{1/2}.$$

Next we must solve for $c_1^{\pm}$ and $c_2^{\pm}$. The algebra is very complicated and there are many phase-related pitfalls. We will need to use all possible tricks to ensure self-consistency, as I will attempt to illustrate here.

The derivation takes advantage of normalization

$$1 = (c_1^{\pm})^2 + (c_2^{\pm})^2.$$

After a lot of algebra:

$$c_1^{\pm} = \left[\frac{1}{2}\left(1 \pm \frac{\Delta}{x^{1/2}}\right)\right]^{1/2}$$
$$c_2^{\pm} = \pm\left[\frac{1}{2}\left(1 \mp \frac{\Delta}{x^{1/2}}\right)\right]^{1/2}.$$

Note that, in the limits $V \to 0$ and $V \to \infty$

$$V \to 0 \qquad c_1^{\pm} = \left[\frac{1}{2}(1 \pm 1)\right]^{1/2}, \qquad c_2^{\pm} = \pm\left[\frac{1}{2}(1 \mp 1)\right]^{1/2}$$
$$V \to \infty \qquad c_1^{\pm} = \left[\frac{1}{2}(1)\right]^{1/2} = 2^{-1/2}, \qquad c_2^{\pm} = \mp 2^{-1/2}.$$

Both of these limits are consistent with expectations.

It is always a good idea to verify the algebra by showing

$$\int \psi_{\pm}^{\star}\psi_{\pm}d\tau = 1 \qquad \text{normalization}$$
$$\int \psi_{\mp}^{\star}\psi_{\pm}d\tau = 0 \qquad \text{orthogonality}$$
$$\int \psi_{\pm}^{\star}\widehat{\mathbf{H}}\psi_{\pm}d\tau = E_{\pm} \qquad \text{correct eigen–energy}$$
$$\int \psi_{\mp}^{\star}\widehat{\mathbf{H}}\psi_{\pm}d\tau = 0 \qquad \text{eigenstates of } \widehat{\mathbf{H}} \text{ are orthogonal.}$$

The most difficult of these tests is to show that $\psi_{\pm} \to E_{\pm}$.

Non-Lecture

$$\psi_{\pm} = c_1^{\pm}\psi_1 + c_2^{\pm}\psi_2$$

$$\begin{aligned}
\int \psi_{\pm}^{\star}\widehat{\mathbf{H}}\psi_{\pm}d\tau &= (c_1^{\pm})^2 H_{11} + (c_2^{\pm})^2 H_{22} \mp 2(c_1^{\pm})(c_2^{\pm})V \\
&= \left[\frac{1}{2}\left(1 \pm \frac{\Delta}{x^{1/2}}\right)\right] H_{11} + \left[\frac{1}{2}\left(1 \mp \frac{\Delta}{x^{1/2}}\right)\right] H_{22} \pm \left[\left(1 - \frac{\Delta^2}{x}\right)^{1/2}\right] V \\
&= \frac{1}{2}(H_{11} + H_{22}) \pm \frac{\Delta}{2x^{1/2}}(H_{11} - H_{22}) \pm \left[\left(1 - \frac{\Delta^2}{x}\right)^{1/2}\right] V \\
&= \overline{E} \pm \frac{\Delta}{2x^{1/2}}(2\Delta) \pm \left[\left(\frac{x - \Delta^2}{x}\right)^{1/2}\right] V \\
&= \overline{E} \pm \frac{\Delta^2}{x^{1/2}} \pm \left[\frac{V}{x^{1/2}}\right] V \\
&= \overline{E} \pm \frac{\Delta^2}{x^{1/2}} \pm \frac{V^2}{x^{1/2}} \\
&= \overline{E} \pm \frac{x - V^2}{x^{1/2}} \pm \frac{V^2}{x^{1/2}} = \overline{E} \pm x^{1/2}
\end{aligned}$$

which is the expected and required result.

II. Matrix Version of the Two-Level Problem

$$\widehat{\mathbf{H}}\psi = E\psi$$

is an eigenvalue problem. For every eigen-energy E_i there is an eigenfunction ψ_i. We have just seen that the exact solution to the simplest possible problem, the two–level problem, is algebraically challenging. We can approach this problem in a matrix formulism, which turns out to be the most powerful and insight–generating approach to the vast majority of quantum mechanical problems. The matrix Hamiltonian is

$$\mathbf{H} = \begin{pmatrix} \overline{E} & 0 \\ 0 & \overline{E} \end{pmatrix} + \begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix} = \overline{E}\mathbb{1} + \mathbf{H}'.$$

$\mathbf{H}'$ is a real and symmetric matrix. We have subtracted the average energy from the original $\mathbf{H}$. We can always do this. The essential structure of the problem is in $\mathbf{H}'$. We will call this $\mathbf{H}$ from now on. The "elements" of this matrix are

$$\begin{aligned} H_{11} &= \Delta \\ H_{22} &= -\Delta \\ H_{12} &= H_{21} = V. \end{aligned}$$

[Does everyone know the rules for matrix multiplication?]

$$(AB)_{mn} = \sum_{j=1}^{N} A_{mj}B_{jn}$$

This $\mathbf{H}$ matrix operates on vectors $\mathbf{c}^i$ where $i = 1$ and 2 for the two–level problem

$$\mathbf{c}^1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\mathbf{c}^2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$(\mathbf{c}^1)^T\mathbf{c}^1 = \begin{pmatrix} 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1 \quad \text{where } {}^T \text{ means "transpose". Normalized.}$$

$$(\mathbf{c}^2)^T\mathbf{c}^1 = \begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0. \text{ Orthgonal}$$

$$\mathbf{H}\mathbf{c}^1 = \begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \Delta \\ V \end{pmatrix} = \Delta\begin{pmatrix} 1 \\ 0 \end{pmatrix} + V\begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

This is an expression of completeness, analogous to

$$\widehat{\mathbf{H}}\psi_1 = a_1\psi_1 + a_2\psi_2.$$

It means that the effect of $\widehat{\mathbf{H}}$ on one function may always be expressed as a linear combination of all members of the complete set of functions. In this case, we have

$$a_1 = \Delta \quad , \quad a_2 = V.$$

This is exactly what we saw previously in the wavefunction picture where, left multiplying by $\psi_1^\star$ and integrating

$$\int \psi_1^\star \widehat{\mathbf{H}} \psi_1 d\tau = \int a_1 \psi_1^\star \psi_1 d\tau + \int a_2 \psi_1^\star \psi_2 d\tau$$

$$H_{11} = a_1 1 + a_2 0 \qquad a_1 = H_{11} = \Delta.$$

Also, multiplying by $\psi_2^\star$ and integrating

$$\int \psi_2^\star \widehat{\mathbf{H}} \psi_1 d\tau = a_1 0 + a_2 1 \quad , \quad a_2 = H_{21} = V.$$

The key point here is that we never actually look at the $\{\psi_i\}$. We start with all of the "matrix elements" of $\widehat{\mathbf{H}}$ evaluated in the complete $\{\psi_i\}$ basis set.

Next we solve for the energy eigenvalues and eigenvectors using the matrix formalism.

We want to find the eigenvalues of the $\mathbf{H}$ matrix. There must exist a unitary transformation of $\mathbf{H}$ that "diagonalizes" it. We are going to use a special class of 2×2 matrices that have the property

$$\mathbf{T}^\dagger = \mathbf{T}^{-1} \qquad \text{or} \qquad \mathbf{T}^{-1}\mathbf{T} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{1}$$

$$\mathbf{T} = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix}$$

$$\mathbf{T}^\dagger = \begin{pmatrix} T_{11}^\star & T_{21}^\star \\ T_{12}^\star & T_{22}^\star \end{pmatrix}.$$

$\mathbf{T}^\dagger$ means "conjugate transpose". For a real symmetric matrix, $\mathbf{H}$, we can forget about the complex conjugate and use $\mathbf{T}^T$ (transpose) rather than $\mathbf{T}^\dagger$.

Now, for the matrix version of the Schrödinger Equation:

$$\mathbf{Hc} = E\mathbf{c}.$$

Insert

$$\mathbb{1} = \mathbf{T}\mathbf{T}^T$$

$$\mathbf{H}\mathbf{T}\mathbf{T}^T\mathbf{c} = E\mathbf{c}$$

and left–multiply by $\mathbf{T}^T$

$$(\mathbf{T}^T\mathbf{H}\mathbf{T})(\mathbf{T}^T\mathbf{c}) = E(\mathbf{T}^T\mathbf{c})$$
$$\mathbf{T}^T\mathbf{H}\mathbf{T} = \widetilde{\mathbf{H}} \quad \text{(the transformed } \mathbf{H}\text{)}$$
$$\mathbf{T}^T\mathbf{c} = \tilde{\mathbf{c}} \quad \text{(the transformed } \mathbf{c}\text{)}.$$

We say that $\mathbf{T}$ "diagonalizes" $\mathbf{H}$

$$\widetilde{\mathbf{H}} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$
$$\tilde{\mathbf{c}}^1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ an eigenvector of } \widetilde{\mathbf{H}}$$
$$\widetilde{\mathbf{H}}\tilde{\mathbf{c}} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} E_1 \\ 0 \end{pmatrix} = E_1\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$\mathbf{T}^T\mathbf{c} = \tilde{\mathbf{c}} \qquad \text{1st column of } \mathbf{T}^T$$
$$\mathbf{T}^T\mathbf{c}^1 = \begin{pmatrix} T^T_{11} & T^T_{12} \\ T^T_{21} & T^T_{22} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} T^T_{11} \\ T^T_{21} \end{pmatrix}, \text{ notation: } T_{\text{row, column}}$$

thus

$$\widetilde{\mathbf{H}}\tilde{\mathbf{c}}^1 = E_1\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and

$$\widetilde{\mathbf{H}}\tilde{\mathbf{c}}^2 = E_2\begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

which is consistent with

$$\widetilde{\mathbf{H}}\tilde{\mathbf{c}} = E\tilde{\mathbf{c}},$$

and the eigenvector $\tilde{\mathbf{c}}^i$ is i^{th} column of $\mathbf{T}^T$, where $\widetilde{\mathbf{H}} = \mathbf{T}^\dagger\mathbf{H}\mathbf{T}$. Remember this!

III. Now we look at the general form of a unitary transformation for a 2–level problem. We think of T as a "rotation in 'state space' "

$$\mathbf{T}^T = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}, \quad \text{abbreviated as} \begin{pmatrix} c & s \\ -s & c \end{pmatrix}.$$

Determine the value of θ that results in

$$\mathbf{T}^T\mathbf{H}\mathbf{T} = \widetilde{\mathbf{H}} = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}$$

$$\begin{pmatrix} c & s \\ -s & c \end{pmatrix}\begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix}\begin{pmatrix} c & -s \\ s & c \end{pmatrix} = \begin{pmatrix} (c^2-s^2)\Delta + 2csV & (c^2-s^2)V - 2cs\Delta \\ (c^2-s^2)V - 2cs\Delta & -(c^2-s^2)\Delta - 2csV \end{pmatrix}.$$

We want the off-diagonal elements of $\widetilde{\mathbf{H}}$ to be zero

$$0 = (c^2-s^2)V - 2cs\Delta$$
$$\frac{2cs}{c^2-s^2} = \frac{V}{\Delta}$$
$$2\cos\theta\sin\theta = \sin 2\theta$$
$$\cos^2\theta - \sin^2\theta = \cos 2\theta$$
$$\frac{\sin 2\theta}{\cos 2\theta} = \tan 2\theta = \frac{V}{\Delta}$$
$$\boxed{\theta = \frac{1}{2}\tan^{-1}\left(\frac{V}{\Delta}\right).}$$

Now use this result to determine energy–eigenvalues and eigenvectors:

$$\begin{aligned} E_\pm &= \overline{E} \pm [\Delta\cos 2\theta + V\sin 2\theta] \\ &= \overline{E} \pm \frac{1}{2}[\Delta^2 + V^2]^{1/2} \qquad \text{(derived earlier)} \end{aligned}$$

$$\mathbf{T} = 2^{-1/2}\begin{pmatrix} \left(1+\frac{\Delta}{[\Delta^2+V^2]^{1/2}}\right)^{1/2} & -\left(1-\frac{\Delta}{[\Delta^2+V^2]^{1/2}}\right)^{1/2} \\ +\left(1-\frac{\Delta}{[\Delta^2+V^2]^{1/2}}\right)^{1/2} & \left(1+\frac{\Delta}{[\Delta^2+V^2]^{1/2}}\right)^{1/2} \end{pmatrix}$$

You need to verify this result. The best way to convince yourself is by a few numerical examples, e.g. $\Delta = 1$, $V = 0.1$, then $\Delta = 1$, $V = 1$, and finally $\Delta = 1$, $V = 10$.

IV. Beyond the Two–Level Problem: $N > 2$ levels

The eigen–energies for the two–level problem (2×2 $\mathbf{H}$) are obtained as the solutions of a quadratic equation. The quadratic formula gives the two exact energy levels.

There are N eigen–energies for the N–level problem ($N \times N$ $\mathbf{H}$). No analytic formula exists that can provide the N values of $\{E_i\}$ as explicit functions of the $\{H_{ij}\}$ matrix elements. However, exact values of each member of the set of N $\{E_i\}$ are obtained iteratively by a variety of matrix diagonalization computer programs. We never need to concern ourselves with the algebraic complexities of finding the N eigen–energies $\{E_i\}$ and eigenfunctions $\{\psi_i\}$ or eigenvectors $\{\mathbf{c}^i\}$ of an $N \times N$ $\mathbf{H}$ matrix or the N coupled linear homogeneous equations that arise from $\widehat{\mathbf{H}}$. All we need is a "complete" set of "basis functions" $\{\phi_i\}$ with which to evaluate all H_{ij} matrix elements.

These complete sets of basis functions $\{\phi_i\}$ are almost always the eigenfunctions of one of our exactly solved problems (particle in a box, harmonic oscillator, rigid rotor, Hydrogen atom) and we have already seen several examples of problems where all $\{H_{ij}\}$ are derived semi–automatically and are expressed in terms of fundamental structural parameters. So now we are *beginning* to understand the relationship between what we want to know, the **molecular constants**, and what we are *allowed to measure* via the $\{E_i\}$ and $\{\psi_i\}$.

There are some easily verified facts about $N \times N$ $\mathbf{H}$ problems.

1. There are N eigen–energies (some might be degenerate).

2. There are N linearly independent eigen–functions or eigen–vectors, each explictly related to one of the eigen–energies.

3. The eigen–functions and eigen–vectors can be put into orthogonal and normalized form: "ortho–normal"

$$\int \psi_i^\star \psi_j d\tau = \delta_{ij} \quad \text{(Kronecker } \delta\text{)}$$

$$\mathbf{c}^{i^T}\mathbf{c}^j = \begin{pmatrix} \mathbf{c}_1^i & \mathbf{c}_2^i & \dots & \mathbf{c}_N^i \end{pmatrix} \begin{pmatrix} \mathbf{c}_1^j \\ \mathbf{c}_2^j \\ \vdots \\ \mathbf{c}_N^j \end{pmatrix} = \delta_{ij}.$$

All eigen–functions that belong to non–degenerate eigen–values are born orthogonal. Those that belong to degenerate eigen–values can be transformed into orthogonal form.

4. The value of the determinant of $\mathbf{H}$,

$$\det(\mathbf{H}) = \begin{vmatrix} H_{11} & H_{12} & \dots & H_{1N} \\ & \dots & \dots & \\ H_{N1} & H_{N2} & \dots & H_{NN} \end{vmatrix}$$

is equal to the product of the N eigen–energies

$$\prod_{i=1}^{N} E_i = \det(\mathbf{H})$$

and the trace of $\mathbf{H}$, $\chi(\mathbf{H})$, is equal to the sum of the $\{E_i\}$

$$\chi(\mathbf{H}) = \sum_{i=1}^{N} E_i.$$

5. All of the results cited here for $\mathbf{H}$ are valid for any Quantum Mechanical operator, $\mathbf{A}$, that corresponds to an observable quantity, A. All that is required is that the operator $\mathbf{A}$ is Hermitian

$$(A_{ij})^\dagger \equiv A^\star_{ji} = A_{ij}.$$

The computer program that "diagonalizes" the $N \times N$ $\mathbf{H}$ matrix also generates the complete and exact transformation

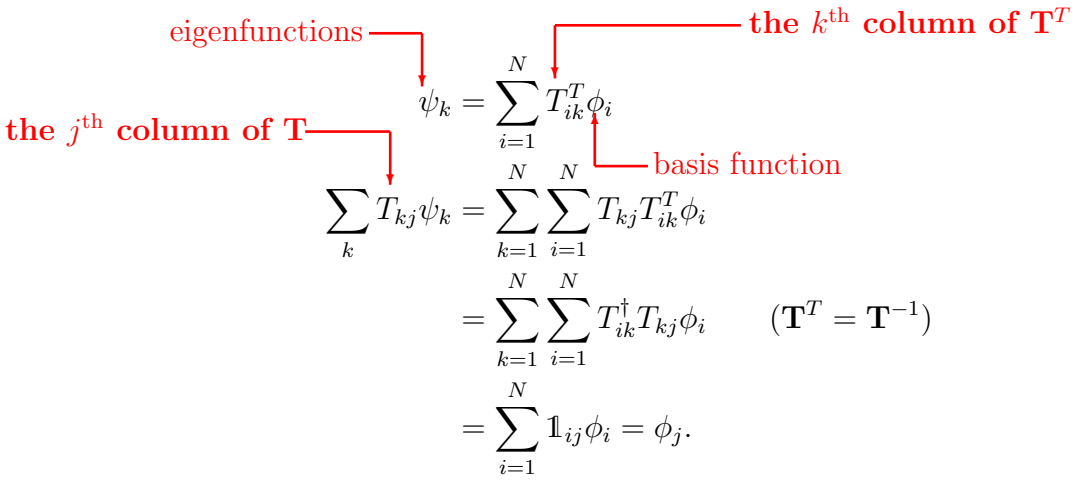
$$\mathbf{T}^\dagger \mathbf{H} \mathbf{T} = \widetilde{\mathbf{H}} = \begin{pmatrix} E_1 & & & 0 \\ & E_2 & & \\ & & \ddots & \\ 0 & & & E_N \end{pmatrix}.$$

The eigen–vector that belongs to the eigen–value E_i is

$$\begin{pmatrix} T^\dagger_{1i} \\ T^\star_{2i} \\ \vdots \\ T^\dagger_{Ni} \end{pmatrix},$$

the i^{th} column of $\mathbf{T}^\dagger$. If all of the elements of $\mathbf{H}$ are real, then $\mathbf{T}$ and $\mathbf{T}^\dagger$ are real, and $\mathbf{T}^{-1} = \mathbf{T}^T = \mathbf{T}^\dagger$. For most applications you want the columns of $\mathbf{T}^T$, but for some applications (especially time–dependent perturbation theory) you want to know the linear combination of the eigen–functions that are equal to one of the basis functions, which is the reverse transformation

$$\phi_j = \sum_{i=1}^{N} c^j_i \psi_i.$$



$$\psi_k = \sum_{i=1}^{N} T^T_{ik}\phi_i$$

$$\sum_k T_{kj}\psi_k = \sum_{k=1}^{N}\sum_{i=1}^{N} T_{kj}T^T_{ik}\phi_i$$

$$= \sum_{k=1}^{N}\sum_{i=1}^{N} T^\dagger_{ik}T_{kj}\phi_i \qquad (\mathbf{T}^T = \mathbf{T}^{-1})$$

$$= \sum_{i=1}^{N} \mathbb{1}_{ij}\phi_i = \phi_j.$$

Now for the **bummer**: most basis sets are of infinite dimension! Even the most powerful computer in the world cannot diagonalize an infinite dimension **H** matrix. Perturbation Theory provides approximate (of *a priori* known accuracy) eigen–energies and eigen–vectors, even for an infinite dimension **H**. *Perturbation Theory is a basis for both accurate numerics and for physical insight.*

V. Prelude to Perturbation Theory

We return to the two-level problem and derive some equations for

$$E_\pm \quad \text{and} \quad \psi_\pm$$

that foreshadow **Rayleigh–Schrödinger non–degenerate perturbation theory**:

Non-Lecture

Derive an equation for θ in terms of V and Δ:

$$\mathbf{H} = \overline{E} + \begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix} \qquad \text{recall } \overline{E} = \frac{H_{11}+H_{22}}{2}, \Delta = \frac{H_{11}-H_{22}}{2}$$

$$\mathbf{T} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

$$\widetilde{\mathbf{H}} = \overline{E}\mathbb{1} + \mathbf{T}^T\mathbf{H}\mathbf{T} = \overline{E}\mathbb{1} + \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}$$

What does $\mathbf{T}^T\overline{E}\mathbb{1}\mathbf{T}$ yield?

where $\mathbf{T}^T\mathbf{H}\mathbf{T} = \begin{pmatrix} (c^2-s^2)\Delta + 2csV & (c^2-s^2)V - 2cs\Delta \\ (c^2-s^2)V - 2cs\Delta & -(c^2-s^2)\Delta - 2csV \end{pmatrix}$.

The transformation $\mathbf{T}^T\mathbf{H}\mathbf{T}$ corresponds to a rotation of $\mathbf{H}$ in state space and θ is called the "mixing angle". We want to solve for θ and then derive everything we need from the value of θ that diagonalizes $\mathbf{H}$.

We determine θ by requiring the off–diagonal element of $\widetilde{\mathbf{H}}$ to be zero.

$$\theta = (c^2-s^2)V - 2cs\Delta$$

$$\frac{2cs}{c^2-s^2} = V/\Delta$$

$$\frac{\sin 2\theta}{\cos 2\theta} = \tan 2\theta = V/\Delta$$

Now that we have $\theta(V,\Delta)$ we can simplify:

$$\theta = \frac{1}{2}\tan^{-1}(V/\Delta), \quad \text{expand in a power series}$$
$$\tan^{-1}(V/\Delta) = (V/\Delta) - \frac{1}{3}(V/\Delta)^3 + \frac{1}{5}(V/\Delta)^5 - \ldots$$
$$\theta = \frac{1}{2}(V/\Delta) - \frac{1}{2}\frac{1}{3}(V/\Delta)^3 + \ldots$$

$$E_\pm = \overline{E} \pm \left[\left(c^2 - s^2\right)\Delta + 2csV\right]$$

$$\cos^2\theta - \sin^2\theta = \cos 2\theta = 1 - \frac{(2\theta)^2}{2!} + \ldots$$
$$2\cos\theta\sin\theta = \sin 2\theta = 2\theta - \frac{(2\theta)^3}{3!} + \ldots$$

After some algebra, and retaining only terms in $E_\pm$ of order up to V^2/Δ,

$$E_\pm = \overline{E} \pm \left[\Delta - \Delta\frac{\left(2\frac{1}{2}\frac{V}{\Delta}\right)^2}{2!} + V\left(2\frac{1}{2}\frac{V}{\Delta}\right)\right]$$
$$= \overline{E} \pm \left[\Delta - \frac{1}{2}\frac{V^2}{\Delta} + \frac{V^2}{\Delta}\right] = \overline{E} \pm \left[\Delta + \frac{V^2}{2\Delta}\right].$$

You will be referring to this as "matrix element squared over energy denominator."

For the eigen–states or eigen–vectors, retaining terms of order up to $(V/\Delta)^2$

$$\mathbf{T}^T = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$
$$\cos\theta \approx 1 - \frac{\theta^2}{2!} = 1 - \frac{1}{2}(V/2\Delta)^2$$
$$\sin\theta \approx \theta - \frac{\theta^3}{3!} = V/2\Delta$$
$$\psi_+ = \left[1 - \frac{1}{2}(V/2\Delta)^2\right]\phi_1 - V/2\Delta\phi_2$$
$$\psi_- = (V/2\Delta)\phi_1 + \left[1 - \frac{1}{2}(V/2\Delta)^2\right]\phi_2.$$

By casual inspection, $\int \psi_+\psi_- d\tau = 0$. Normalization is also OK if we discard terms of order $(V/2\Delta)^4$. We will see that ordinary perturbation theory through second–order gives exactly these results.

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