DEGENERATE PERTURBATION THEORY (still TIME-INDEPENDENT)

Let us suppose that the unperturbed states of the Hamiltonian H^0 are degenerate, i.e., more than one state is an eigenstate of H^0 corresponding to the same eigenvalue. E.g., let us imagine a two-fold degeneracy. We can write:

examples: 2-D oscillator; particle in a box; H atom

$$H^0 \psi_a^0 = E^0 \psi_a^0$$
$$H \psi_b^0 = E^0 \psi_b^0$$

and choose ψ_a^0 and ψ_b^0 such that $\langle \psi_a^0 | \psi_b^0 \rangle = \phi$

Let me extend this already to the case in which I have a p-fold degeneracy (p being the number of independent states that share the same eigenvalue E^0):

$$H^0 \psi_j^0 = E^0 \psi_j^0 \qquad j = 1 \dots p \qquad \text{and} \qquad \langle \psi_j^0 | \psi_e^0 \rangle = \delta_{je}$$

Kronecker

All these p states have a common unperturbed energy E^0.
(note: in the previous lecture notes, the lower index indicated the n-th eigenstate, corresponding to the n-th energy level; here it indicates the j-th state, in a set of p states, all of which have the <u>same</u> energy)

The perturbation typically breaks the degeneracy. Our problem is that we do <u>not</u> know if the ψ_j^0 we choose are indeed the eigenstates of the perturbed Hamiltonian.

Let us posit that there exists a linear combination of ψ_j^0 that is an eigenstate of the perturbed Hamiltonian. This will simplify our calculations a lot. We can write:

$$\psi^0 = \sum_j \alpha_j \psi_j^0$$

where ψ^0 is our magical linear combination. Let us take ψ^0 normalized $\Rightarrow \sum_j \alpha_j^* \alpha_j = 1$.

Let us remember that $\langle \psi_j^\circ | \psi_\ell^\circ \rangle = \delta_{j\ell}$ and write the usual expansion in powers of λ:

$$\psi = \psi^\circ + \lambda\psi^1 + \lambda^2\psi^2 + \dots$$
$$E = E^\circ + \lambda E^1 + \lambda^2 E^2 + \dots \quad \xRightarrow{\text{substitute into}} \quad H\psi = E\psi$$
$$H = H^\circ + \lambda H'$$

The first-order equation is (again):

$$H\psi^1 + H'\psi^\circ = E^\circ\psi^1 + E^1\psi^\circ$$

Let us project the equation on $\langle \psi_K^\circ |$:

$$\cancel{\langle \psi_K^\circ | H | \psi^1 \rangle} + \langle \psi_K^\circ | H' | \psi^\circ \rangle = \cancel{E^\circ \langle \psi_K^\circ | \psi^1 \rangle} + E^1 \langle \psi_K^\circ | \psi^\circ \rangle$$

H is Hermitian: $\langle \psi_K^\circ | H = \langle H\psi_K^\circ |$
$= E^\circ \langle \psi_K^\circ |$

But $\psi^\circ = \sum_j \alpha_j \psi_j^\circ$, then:

$$\langle \psi_K^\circ | H' | \psi^\circ \rangle = \sum_j \alpha_j \langle \psi_K^\circ | H' | \psi_j^\circ \rangle$$

$$E^1 \langle \psi_K^\circ | \psi^\circ \rangle = \sum_j \alpha_j E^1 \langle \psi_K^\circ | \psi_j^\circ \rangle = \sum_j \alpha_j E^1 \delta_{Kj} = E^1 \alpha_K$$

This is a matrix eigenvalue problem!

$$\vec{\alpha} = \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_p \end{pmatrix}$$

$$\Longrightarrow \quad \underset{\text{matrix}}{W} \vec{\alpha} = \underset{\text{number}}{E^1} \vec{\alpha}$$

$W = p \times p$ matrix

$W_{jK} = \langle \psi_j^\circ | H' | \psi_K^\circ \rangle$

in general, W will have <u>p</u> eigenvalues and <u>p</u> eigenvectors.

What do we get by solving the eigenvector problem (note: this is really a linear algebra problem!)

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ?$$

In general, a $p \times p$ matrix will have p eigenvalues, and p corresponding eigenvectors.

Each eigenvector corresponds to a linear combination of ψ_i^0 and its corresponding eigenvalue E^1 is the first-order correction energy to the unperturbed energy E^0. I started with p independent wavefunctions ψ_i^0, each of which satisfies:

$$H^0\psi_i^0 = E^0\psi_i^0$$

Therefore, also each combination of ψ_i^0 satisfies the same zero-th order equation for free:

$$H^0\psi^0 = E^0\psi^0 \quad \text{where} \quad \psi^0 = \sum_i \alpha_i \psi_i^0$$

If $\vec{\alpha}_{(s)}$ is an eigenvector of the matrix W, with eigenvalue $E^1_{(s)}$, we have that:

s = index running over eigenvectors of W

$$E^1_{(s)} = \langle \psi^0_{(s)} | H' | \psi^0_{(s)} \rangle \quad \text{, i.e.,} \quad \sum \alpha_{i(s)} \psi_i^0 \text{ is the special combination I was looking for}$$

remember: $\langle \psi_i^0 | \psi_j^0 \rangle = \delta_{ij}$ and $\sum_i \alpha_i^* \alpha_i = 1$: ψ^0 is normalized

Proof that $\psi^0_{(s)}$ is eigenstate of H' (and therefore of $H = H^0 + H'$):

$$\underline{\underline{H'|\psi^0_{(s)}\rangle}} = \underbrace{\sum_i |\psi_i^0\rangle\langle\psi_i^0|}_{\substack{|\psi_i^0\rangle \text{ are complete orthonormal} \\ \text{set: } \sum_i |\psi_i^0\rangle\langle\psi_i^0| = \mathbb{1} \text{ : identity operator}}} H'|\psi^0_{(s)}\rangle = \sum_i \sum_j |\psi_i^0\rangle\langle\psi_i^0| H' |\psi_j^0\rangle \alpha_{j(s)}$$

$$= \sum_i |\psi_i^0\rangle \underbrace{\sum_j W_{ij}\alpha_{j(s)}}_{E^1_{(s)} \cdot \alpha_{i(s)}} = \sum_i E^1_{(s)} \alpha_{i(s)} |\psi_i^0\rangle = \underline{\underline{E^1_{(s)} |\psi^0\rangle}}$$