Perturbation theory up to second order

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1 Setup

Here we work systematically in matrix notation for a Hermitian problem doing perturbation theory. The Hamiltonian is

$$H = H_0 + H_1$$

where the perturbation is H_1 is of first order and there is no higher orders. The eigenvectors V and eigenenergies E have series expansions

$$V = V_0 + V_1 + V_2 + \ldots \quad , \quad E = E_0 + E_1 + E_2 + \ldots$$

The eigenvalue problem is

$$HV = VE$$

where the eigenvectors are columns of V, V is unitary $V^\dagger V = VV^\dagger = I$, and E is a diagonal matrix with eigenvalues on the diagonals. Plugging in the series expansions and collecting like orders to second order gives

$$\begin{aligned} H_0 V_0 &= V_0 E_0 \\ H_1 V_0 + H_0 V_1 &= V_0 E_1 + V_1 E_0 \\ H_1 V_1 + H_0 V_2 &= V_0 E_2 + V_1 E_1 + V_2 E_0 \end{aligned}$$

Now we analyze this order by order and worry about degenerate subspaces in particular.

2 Zeroth order

This seems silly but there is something to be said. Let us group degenerate states into degenerate subspaces labeled by D. All states in D have the same energy E_{0D}. We can write

$$(E_0)_{D,D'} = \delta_{D,D'} E_{0D} I_D$$

where I_D is the identity operator in the D subspace.

The main point is that we can't decide about unitary mixing of states in degenerate subspaces at all to zeroth order. So if we have some fixed set of eigenvector $\bar{V}_0$, then an equally good set is gotten by making arbitrary unitary rotations U_D in each subspace separately:

$$V_0 = \bar{V}_0 \begin{pmatrix} U_{D_1} & 0 & 0 & \cdots \\ 0 & U_{D_2} & 0 & \cdots \\ 0 & 0 & U_{D_3} & \cdots \\ \vdots & & & \end{pmatrix}$$

and V_0 is just as good as $\bar{V}_0$.

3 First order

We project the first order equation above onto the zeroth order vectors by left multiplying the equation by $V_0^\dagger$ — and using $H_0 V_0 = V_0 E_0$ — to get

$$V_0^\dagger H_1 V_0 + E_0 V_0^\dagger V_1 = E_1 + V_0^\dagger V_1 E_0$$

Computing the D, D' component gives

$$(V_0^\dagger H_1 V_0)_{D,D'} = \delta_{D,D'}(E_1)_D + (V_0^\dagger V_1)_{D,D'}(E_{0D'} - E_{0D})$$

The diagonal components in a subspace simplify to

$$(V_0^\dagger H_1 V_0)_{D,D} = (E_1)_D$$

This is a constraint: it says that the left matrix must be diagonal! Putting in the unitary matrices, we have in more detail

$$U_D^\dagger (\bar{V}_0^\dagger H_1 \bar{V}_0) U_D = (E_1)_D \tag{1}$$

This equation says that if the matrix H_1 in the subspace is not trivially zero or a multiple or identity, then U_D must be chosen so that they diagonalize H_1 in the subspace and the eigenvalues are the first order energy changes E_1 in that subspace. We have recovered first order perturbation theory for the energy and wave functions in a degenerate subspace.

The off-diagonal elements for $D \neq D'$ give the equation

$$(V_0^\dagger V_1)_{D,D'} = \frac{(V_0^\dagger H_1 V_0)_{D,D'}}{E_{0D'} - E_{0D}} \quad \text{for } D \neq D'$$

which is the just first order shift of wave functions from standard textbooks but generalized for the degenerate case. Since the U_D have been fixed by the condition to get E_1, this equation is also definite and has no degrees of freedom.

Before going to second order, we must worry about two things. First of all, there is nothing we can say about the first order shift of wave functions in the degenerate subspace itself $(V_0^\dagger V_1)_{D,D}$. It drops out of the diagonal equation due to equal energies. All we are left with is the unitary condition $V^\dagger V = I$ which just translates into $(V_0^\dagger V_1)_{D,D}$ being anti-Hermitian or i times a Hermitian operator, i.e. generator of a unitary rotation. The traditional textbook choice is to set this to zero which we do below as well.

Second, if for some reason $(\bar{V}_0^\dagger H_1 \bar{V}_0)_{D,D}$ is zero or multiple of identity, we are not able to decide on the unitary rotations U_D and thus V_0 are still somewhat arbitrary; here $(E_1)_D$ is either zero or just a multiple of identity (constant shift of all eigenvalues in D to first order).

4 Second order

Left multiplying the second order equation by $V_0^\dagger$ gives

$$V_0^\dagger H_1 V_1 + E_0 V_0^\dagger V_2 = E_2 + V_0^\dagger V_1 E_1 + V_0^\dagger V_2 E_0$$

The D, D' element is

$$(V_0^\dagger H_1 V_1)_{D,D'} - (V_0^\dagger V_1)_{D,D'}(E_1)_{D'} = \delta_{D,D'}(E_2)_D + (V_0^\dagger V_2)_{D,D'}(E_{0D'} - E_{0D})$$

We can eliminate $(E_1)_{D'}$ using the first order result for it to get

$$(V_0^\dagger H_1 V_1)_{D,D'} - (V_0^\dagger V_1)_{D,D'}(V_0^\dagger H_1 V_0)_{D',D'} = \delta_{D,D'}(E_2)_D + (V_0^\dagger V_2)_{D,D'}(E_{0D'} - E_{0D})$$

Looking at the diagonal $D = D'$ leads to

$$(V_0^\dagger H_1 V_1)_{D,D} - (V_0^\dagger V_1)_{D,D}(V_0^\dagger H_1 V_0)_{D,D} = (E_2)_D$$

We now insert $V_0 V_0^\dagger$ between H_1 and V_1 and break that into a sum over states D'':

$$\sum_{D''} (V_0^\dagger H_1 V_0)_{D,D''}(V_0^\dagger V_1)_{D'',D} - (V_0^\dagger V_1)_{D,D}(V_0^\dagger H_1 V_0)_{D,D} = (E_2)_D$$

Assuming that $(V_0^\dagger V_1)_{D,D} = 0$ so the $D = D''$ part goes away, we get the simpler

$$\sum_{D'' \neq D} (V_0^\dagger H_1 V_0)_{D,D''}(V_0^\dagger V_1)_{D'',D} = (E_2)_D$$

Plugging in for $(V_0^\dagger V_1)$ between subspaces gives us

$$\sum_{D'' \neq D} \frac{(V_0^\dagger H_1 V_0)_{D,D''}(V_0^\dagger H_1 V_0)_{D'',D}}{E_{0D} - E_{0D''}} = (E_2)_D$$

Putting the unitary matrices in gives

$$(E_2)_D = U_D^\dagger \left\{ \sum_{D' \neq D} \frac{(\bar{V}_0^\dagger H_1 \bar{V}_0)_{D,D'} (\bar{V}_0^\dagger H_1 \bar{V}_0)_{D',D}}{E_{0D} - E_{0D'}} \right\} U_D \tag{2}$$

This equation is again a condition on U_D: they must make the right hand side diagonal, and then we can find the second order energy shifts. The expression in the braces looks very much like a generalization of the standard textbook second order expression.

The above expression is also the right thing to in the case that $(V_0^\dagger H_1 V_0)_{D,D}$ vanishes so we must go to second order to get any energy shift. It tells us the eigenvalue problem we must solve to get the second order energy shifts in a degenerate subspace correctly.