Perturbation theory for energy levels[1]

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I offer here some background for Chapter 5 of J. J. Sakurai, *Modern Quantum Mechanics*.

1 Notation

I try to follow the notation of Sakurai fairly closely. We are interested in the eigenvalues of a hamiltonian of the form

$$H = H_0 + \lambda V \quad . \tag{1}$$

Here H_0 is a hamiltonian for which we know the energy levels. When we add an additional piece λV, the problem is too hard to solve exactly, so we want to obtain an answer in powers of λ, considering that λV is a small perturbation on H_0. In the end, one may set $\lambda \to 1$, but we keep it in the derivation in order to keep track of how small contributions are.

The unperturbed problem, which we assume has been solved exactly, is specified by

$$H_0 \big| n^{(0)} \big\rangle = E_n^{(0)} \big| n^{(0)} \big\rangle \quad . \tag{2}$$

The perturbed problem that we wish to solve is

$$(H_0 + \lambda V) \big| n(\lambda) \big\rangle = [E_n^{(0)} + \Delta_n(\lambda)] \big| n(\lambda) \big\rangle \quad . \tag{3}$$

We will be interested in one of the states $\big| n(\lambda) \big\rangle$ and the corresponding eigenvalue $E_n^{(0)} + \Delta_n(\lambda)$. Generally, we will use the index n for this state and eigenvalue. Then other states can be labelled by indices k, l, *etc.*

We take the unperturbed eigenvectors to have the conventional normalization

$$\big\langle m^{(0)} \big| n^{(0)} \big\rangle = \delta_{n,m} \quad . \tag{4}$$

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For the perturbed eigenvectors, it is convenient to choose

$$\langle n^{(0)} | n(\lambda) \rangle = 1 \quad . \tag{5}$$

The states and the eigenvalues have an expansion in powers of λ, which we write as

$$\begin{aligned} |n(\lambda)\rangle &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \quad , \\ \Delta_n(\lambda) &= \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \cdots \quad . \end{aligned} \tag{6}$$

Note that the normalization condition (5) gives

$$\begin{aligned} 1 &= \langle n^{(0)} | n^{(0)} \rangle + \lambda \langle n^{(0)} | n^{(1)} \rangle + \lambda^2 \langle n^{(0)} | n^{(2)} \rangle + \cdots \\ &= 1 + \lambda \langle n^{(0)} | n^{(1)} \rangle + \lambda^2 \langle n^{(0)} | n^{(2)} \rangle + \cdots \end{aligned} \tag{7}$$

Therefore all of the higher order components of $|n(\lambda)\rangle$ are orthogonal to $|n^{(0)}\rangle$,

$$0 = \langle n^{(0)} | n^{(1)} \rangle = \langle n^{(0)} | n^{(2)} \rangle = \cdots \quad . \tag{8}$$

We let P_n be the projection onto states with unperturbed energy $E_n^{(0)}$,

$$P_n = \sum_k \theta(E_k^{(0)} = E_n^{(0)}) \, |k^{(0)}\rangle \langle k^{(0)}| \quad . \tag{9}$$

We let Q_n be the projection onto states with unperturbed energy different from $E_n^{(0)}$,

$$Q_n = \sum_k \theta(E_k^{(0)} \neq E_n^{(0)}) \, |k^{(0)}\rangle \langle k^{(0)}| \quad . \tag{10}$$

Then

$$P_n + Q_n = 1 \quad . \tag{11}$$

If the energy level $E_n^{(0)}$ is non-degenerate, then P_n is the projection onto a single state. However, it could be that the energy level $E_n^{(0)}$ is degenerate. Then P_n is the projection onto a subspace with more than one dimension of the quantum state space. Sakurai uses ϕ_n for my Q_n in the non-degenerate case, but switches notation for the degenerate case.

2 Non-degenerate case

Here we assume that P_n projects onto a single state, $|n^{(0)}\rangle$. This case is pretty straightforward. Arrange the equation in the form

$$[E_n^{(0)} - H_0]\big|n(\lambda)\big\rangle = [-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ . \tag{12}$$

First, take the inner product of Eq. (12) with $\langle n^{(0)}|$ to get

$$\big\langle n^{(0)}\big|E_n^{(0)} - H_0\big|n(\lambda)\big\rangle = \big\langle n^{(0)}\big|[-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ . \tag{13}$$

The left hand side vanishes. On the right hand side, we can use

$$\big\langle n^{(0)}\big|\Delta_n(\lambda)\big|n(\lambda)\big\rangle = \Delta_n(\lambda) \ . \tag{14}$$

This gives

$$\Delta_n(\lambda) = \big\langle n^{(0)}\big|\lambda V\big|n(\lambda)\big\rangle \tag{15}$$

That is

$$\begin{aligned} \Delta_n^{(1)} &= \big\langle n^{(0)}\big|V\big|n^{(0)}\big\rangle \ , \\ \Delta_n^{(2)} &= \big\langle n^{(0)}\big|V\big|n^{(1)}\big\rangle \ , \\ \Delta_n^{(3)} &= \big\langle n^{(0)}\big|V\big|n^{(2)}\big\rangle \ , \\ &\ \ \vdots \end{aligned} \tag{16}$$

This gives $\Delta_n^{(1)}$ immediately. For the higher order corrections to the energy, we need the corrections to the state vector.

Next, project Eq. (12) with Q_n to get

$$[E_n^{(0)} - H_0]Q_n\big|n(\lambda)\big\rangle = Q_n[-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ . \tag{17}$$

That is

$$Q_n\big|n(\lambda)\big\rangle = \frac{Q_n}{E_n^{(0)} - H_0}[-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ . \tag{18}$$

Here

$$\frac{Q_n}{E_n^{(0)} - H_0} = \sum_k \theta(E_k^{(0)} \neq E_n^{(0)})\,\frac{\big|k^{(0)}\big\rangle\big\langle k^{(0)}\big|}{E_n^{(0)} - E_k^{(0)}} \ . \tag{19}$$

Only states that do *not* have a zero in the denominator contribute.

Expand Eq. (18) perturbatively. On the left hand side, note that for $j \geq 1$,

$$Q_n \big| n^{(j)} \big\rangle = \big| n^{(j)} \big\rangle - \big| n^{(0)} \big\rangle \big\langle n^{(0)} \big| n^{(j)} \big\rangle = \big| n^{(j)} \big\rangle \ . \tag{20}$$

We obtain

$$\begin{aligned} \lambda \big| n^{(1)} \big\rangle + \lambda^2 \big| n^{(2)} \big\rangle + \cdots = {} & \frac{Q_n}{E_n^{(0)} - H_0} \\ & \times [\lambda(-\Delta_n^{(1)} + V) - \lambda^2 \Delta_n^{(2)} + \cdots] \\ & \times [\big| n^{(0)} \big\rangle + \lambda \big| n^{(1)} \big\rangle + \lambda^2 \big| n^{(2)} \big\rangle + \cdots] \ . \end{aligned} \tag{21}$$

That is (noting that $Q_n \big| n^{(0)} \big\rangle = 0$),

$$\begin{aligned} \big| n^{(1)} \big\rangle &= \frac{Q_n}{E_n^{(0)} - H_0} V \big| n^{(0)} \big\rangle \ , \\ \big| n^{(2)} \big\rangle &= \frac{Q_n}{E_n^{(0)} - H_0} (V - \Delta_n^{(1)}) \big| n^{(1)} \big\rangle \ , \\ &\vdots \end{aligned} \tag{22}$$

Now we can solve Eqs. (16) and (22) by iteratively substituting lower order results into the higher order equations. This gives the first three contributions to the energy:

$$\begin{aligned} \Delta_n^{(1)} &= \big\langle n^{(0)} \big| V \big| n^{(0)} \big\rangle \ , \\ \Delta_n^{(2)} &= \big\langle n^{(0)} \big| V \frac{Q_n}{E_n^{(0)} - H_0} V \big| n^{(0)} \big\rangle \ , \\ \Delta_n^{(3)} &= \big\langle n^{(0)} \big| V \frac{Q_n}{E_n^{(0)} - H_0} (V - \Delta_n^{(1)}) \frac{Q_n}{E_n^{(0)} - H_0} V \big| n^{(0)} \big\rangle \ . \end{aligned} \tag{23}$$

One can continue this in a pretty much automatic way, although it gets messier as one goes to higher orders. I think that in all but the most sophisticated calculations, one would stop at second order.

3 Degenerate case

Let's now allow for a degenerate state. This is more complicated, so we will stop at second order.

We again start with

$$[E_n^{(0)} - H_0]\big|n(\lambda)\big\rangle = [-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ \ . \tag{24}$$

We will first project both sides of this equation with Q_n to get one set of relations, then project both sides of this equation with P_n to get another set of relations.

First, project with Q_n,

$$\begin{aligned} Q_n[E_n^{(0)} - H_0]\big|n(\lambda)\big\rangle = & -\Delta_n(\lambda) Q_n\big|n(\lambda)\big\rangle \\ & + \lambda Q_n V Q_n\big|n(\lambda)\big\rangle + \lambda Q_n V P_n\big|n(\lambda)\big\rangle \ \ . \end{aligned} \tag{25}$$

That is

$$\begin{aligned} Q_n\big|n(\lambda)\big\rangle = & -\Delta_n(\lambda)\frac{Q_n}{E_n^{(0)} - H_0}\big|n(\lambda)\big\rangle \\ & + \frac{Q_n}{E_n^{(0)} - H_0}\lambda V Q_n\big|n(\lambda)\big\rangle + \frac{Q_n}{E_n^{(0)} - H_0}\lambda V P_n\big|n(\lambda)\big\rangle \ \ . \end{aligned} \tag{26}$$

We will need the first order part of this,

$$\begin{aligned} Q_n\big|n^{(1)}\big\rangle = & -\Delta_n^{(1)}\frac{Q_n}{E_n^{(0)} - H_0}\big|n^{(0)}\big\rangle \\ & + \frac{Q_n}{E_n^{(0)} - H_0} V Q_n\big|n^{(0)}\big\rangle + \frac{Q_n}{E_n^{(0)} - H_0} V P_n\big|n^{(0)}\big\rangle \ \ . \end{aligned} \tag{27}$$

The first two terms on the right hand side vanish because $Q_n\big|n^{(0)}\big\rangle = 0$. This gives

$$Q_n\big|n^{(1)}\big\rangle = \frac{Q_n}{E_n^{(0)} - H_0} V\big|n^{(0)}\big\rangle \ \ . \tag{28}$$

We will use this result below.

Next, project Eq. (24) with P_n,

$$P_n[E_n^{(0)} - H_0]\big|n(\lambda)\big\rangle = P_n[-\Delta_n(\lambda) + \lambda V]\big|n(\lambda)\big\rangle \ \ . \tag{29}$$

The left hand side vanishes. Then (inserting $1 = P_n + Q_n$ to the right of V)

$$\Delta_n(\lambda) P_n\big|n(\lambda)\big\rangle = \lambda P_n V P_n\big|n(\lambda)\big\rangle + \lambda P_n V Q_n\big|n(\lambda)\big\rangle \ \ . \tag{30}$$

At first order, Eq. (30) is

$$\Delta_n^{(1)} \big| n^{(0)} \big\rangle = P_n V P_n \big| n^{(0)} \big\rangle \ . \tag{31}$$

This is really straightforward in the non-degenerate case, when P_n projects onto the single state $\big|n^{(0)}\big\rangle$. Now, for the degenerate case, it is more subtle. In fact, we know that P_n projects onto a subspace. But so far, we don't know what $\big|n^{(0)}\big\rangle$ is except that it is the limit of $\big|n(\lambda)\big\rangle$ for $\lambda \to 0$, where $\big|n(\lambda)\big\rangle$ is the state vector that we were hoping to find. Thus, we need to find $\big|n^{(0)}\big\rangle$. In fact, Eq. (31) is an eigenvalue equation for $\Delta_n^{(1)}$ and $\big|n^{(0)}\big\rangle$. The vector $\big|n^{(0)}\big\rangle$ is in the space $P_n\mathcal{H}$ and $P_n V P_n$ is a linear operator in this space. Thus we can solve the eigenvalue equation. (As a practical, matter, this means that we choose a convenient basis for $P_n\mathcal{H}$ and solve the corresponding matrix equation.) Let us denote the eigenvalues of $P_n V P_n$ by v_l. The eigenvalue that we seek is one of them and the state we seek is one of the eigenvectors. Which one is up to us; we have not said whether we wanted the lowest eigenvalue or the next lowest or what. Note that if the eigenvalues of $P_n V P_n$ are non-degenerate, we have no choice about what the eigenvectors are; we just choose the one corresponding to the eigenvalue we want. But if the eigenvalues are still degenerate, then at the present first order there is an ambiguity, which may (or maybe not) be removed if we work to one more order.

In the case that $P_n\mathcal{H}$ is one dimensional, the eigenvector is already determined. In this case,

$$\Delta_n^{(1)} = \big\langle n^{(0)} \big| V \big| n^{(0)} \big\rangle \ . \tag{32}$$

This is true also when $P_n\mathcal{H}$ has more than one dimension, but it does not help determine $\big|n^{(0)}\big\rangle$. Note that this is actually the same result that we found for a non-degenerate level. We conclude that Eq. (31) specifies *both* the possibilities for the eigenvalue $\Delta_n^{(1)}$ and the eigenvector $\big|n^{(0)}\big\rangle$, possibly with some ambiguity with respect to the eigenvector.

Now we turn to second order. At second order, Eq. (30) is

$$\Delta_n^{(2)} \big| n^{(0)} \big\rangle = (P_n V P_n - \Delta_n^{(1)} P_n) \big| n^{(1)} \big\rangle + P_n V Q_n \big| n^{(1)} \big\rangle \ . \tag{33}$$

This equation is supposed to tell us $\Delta_n^{(2)}$. However, it is possible that we still don't know what $\big|n^{(0)}\big\rangle$ is. Recall that $\big|n^{(0)}\big\rangle$ is an eigenvector of $P_n V P_n$ in the space $P_n\mathcal{H}$. But maybe the eigenvalue of $P_n V P_n$ that we chose to consider is degenerate. In that case $\big|n^{(0)}\big\rangle$ is only determined to lie in a certain subspace of $P_n\mathcal{H}$. Let $P_n^{(1)}$ be the projection onto this subspace.[3] Our vector $\big|n^{(0)}\big\rangle$ is, by assumption, in this subspace, so

$$\big|n^{(0)}\big\rangle = P_n^{(1)}\big|n^{(0)}\big\rangle \ . \tag{34}$$

The definition of $P_n^{(1)}$ is that it projects onto the subspace (of $P_n\mathcal{H}$) of vectors $\big|\psi\big\rangle$ such that

$$P_n V P_n\big|\psi\big\rangle = \Delta_n^{(1)} P_n\big|\psi\big\rangle \ . \tag{35}$$

Since $P_n^{(1)}$ projects onto the space of solultions of Eq. (35), we have

$$(P_n V P_n - \Delta_n^{(1)})P_n^{(1)} = 0 \ . \tag{36}$$

Equally well, we have the adjoint of this equation

$$P_n^{(1)}(P_n V P_n - \Delta_n^{(1)}) = 0 \ . \tag{37}$$

We project Eq. (33) with $P_n^{(1)}$ to get

$$\Delta_n^{(2)} P_n^{(1)}\big|n^{(0)}\big\rangle = P_n^{(1)}(P_n V P_n - \Delta_n^{(1)})\big|n^{(1)}\big\rangle + P_n^{(1)} V Q_n\big|n^{(1)}\big\rangle \ . \tag{38}$$

Because of Eq. (37), this leaves[4]

$$\Delta_n^{(2)} P_n^{(1)}\big|n^{(0)}\big\rangle = P_n^{(1)} V Q_n\big|n^{(1)}\big\rangle \ . \tag{39}$$

Substituting Eq. (28) for $\big|n^{(1)}\big\rangle$ into Eq. (39), we have

$$\Delta_n^{(2)} P_n^{(1)}\big|n^{(0)}\big\rangle = P_n^{(1)} V \frac{Q_n}{E_n^{(0)} - H_0} V P_n^{(1)}\big|n^{(0)}\big\rangle \ . \tag{40}$$

This is an eigenvalue equation that determines both the eigenvalue $\Delta_n^{(2)}$ and the eigenvector $\big|n^{(0)}\big\rangle$ in $P_n^{(1)}\mathcal{H}$.

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[3] My notation $P_n^{(1)}$ is not supposed to indicate that $P_n^{(1)}$ is a term in the expansion of something called $P_n(\lambda)$, but rather that it is the projection onto the subspace in which our eigenvector is known to be living after we have used first order perturbation theory.

[4] Sakurai assumes that there is no further degeneracy after the first step, so that $P_n^{(1)}\mathcal{H}$ is one dimensional. He displays a formula for $P_n\big|n^{(1)}\big\rangle$ and then argues that we don't need the result.

In the case that $P_n^{(1)}\mathcal{H}$ is one dimensional, the eigenvector is already determined. In this case,

$$\Delta_n^{(2)} = \left\langle n^{(0)} \middle| V \frac{Q_n}{E_n^{(0)} - H_0} V \middle| n^{(0)} \right\rangle \ . \tag{41}$$

This is true also when $P_n^{(1)}\mathcal{H}$ has more than one dimension, but it does not help determine $\left| n^{(0)} \right\rangle$. Note that this is actually the same result that we found for a non-degenerate level.

In the degenerate case, the difference is that we had to solve an eigenvalue equation to find the unperturbed state $\left| n^{(0)} \right\rangle$ in the space of states that have the same unperturbed energy. Maybe we even had to solve two eigenvalue equations.

I suppose that second order is enough orders for degenerate perturbation theory.