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Perturbation theory for stationary states

Consider a Hamiltonian

$$H(\lambda) = H_0 + \lambda V, \tag{1}$$

depending on a parameter λ, and suppose that for λ sufficiently near $\lambda = 0$ one can follow the energy eigenstates as differentiable functions of λ. For a particular one parameter family of such eigenstates $|\psi(\lambda)\rangle$ we then have

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle. \tag{2}$$

If the state can be followed all the way from $\lambda = 0$ to $\lambda = 1$ then it makes sense to say that $E(1)$ is the energy of the eigenstate $|\psi(1)\rangle$ of the Hamiltonian $H_0 + V$ which aries from $|\psi(0)\rangle$. Perturbation theory gives an approximation to $E(1)$ and $|\psi(1)\rangle$ by Taylor expansion of $E(\lambda)$ and $|\psi(\lambda)\rangle$ about $\lambda = 0$.

Perturbation equations

We begin by writing out the Schrödinger equation (2) and its first two derivatives with respect to λ:

$$(H - E)|\psi\rangle = 0 \tag{3}$$

$$(\dot{H} - \dot{E})|\psi\rangle + (H - E)|\dot{\psi}\rangle = 0 \tag{4}$$

$$-\ddot{E}|\psi\rangle + 2(\dot{H} - \dot{E})|\dot{\psi}\rangle + (H - E)|\ddot{\psi}\rangle = 0. \tag{5}$$

(Overdot denotes $d/d\lambda$.) These equations hold for all values of λ, but for the purpose of Taylor expansion we are only interested in evaluating them at $\lambda = 0$.

The Taylor expansion for the energy eigenvalue is $E(\lambda) = E(0)+\dot{E}(0)\lambda+\frac{1}{2}\ddot{E}(0)\lambda^2+\cdots$. With the notation $E(0) = \varepsilon$, $\dot{E}(0) = E^{(1)}$, and $\ddot{E}(0) = 2E^{(2)}$, the perturbation expansion for the energy at $\lambda = 1$ takes the form

$$E(1) = \varepsilon + E^{(1)} + E^{(2)} + \cdots. \tag{6}$$

With this notation, and using $H(0) = H_0$ and $\dot{H} = V$, the perturbation equations evaluated at $\lambda = 0$ take the form

$$(H_0 - \varepsilon)|\psi\rangle = 0 \tag{7}$$

$$(V - E^{(1)})|\psi\rangle + (H_0 - \varepsilon)|\dot{\psi}\rangle = 0 \tag{8}$$

$$-2E^{(2)}|\psi\rangle + 2(V - E^{(1)})|\dot{\psi}\rangle + (H_0 - \varepsilon)|\ddot{\psi}\rangle = 0, \tag{9}$$

where *here and hereafter all kets are implicitly evaluated at* $\lambda = 0$.

First order perturbation

Multiplying (8) by the bra $\langle\psi|$ yields the first order energy shift:

$$E^{(1)} = \langle\psi|V|\psi\rangle. \tag{10}$$

Remember that we have assumed $|\psi\rangle$ is the limit as $\lambda \to 0$ of a one-parameter family of eigenstates $|\psi(\lambda)\rangle$ of $H(\lambda)$ with eigenvalues $E(\lambda)$ that converge to ε. The information in (8) not captured in (10) restricts what this limit could be. To see how, let P be the projection onto the subspace of states with energy ε (at $\lambda = 0$). Then $P|\psi\rangle = |\psi\rangle$, and $P(H_0 - \varepsilon) = 0$, so acting with P on (8) yields

$$PV|\psi\rangle = E^{(1)}|\psi\rangle. \tag{11}$$

This is called the *first order secular equation*. It tells us that the limit as $\lambda \to 0$ of the eigenstates $|\psi(\lambda)\rangle$ of $H(\lambda)$ must be an eigenstate of PV, and the first order energy shift is the corresponding eigenvalue.

If ε is *non-degenerate*, then P is a one-dimensional projector. In this case $|\psi\rangle$ automatically satisfies the secular equation (11), with $E^{(1)}$ given by (10). If ε is *degenerate*, we may only use (10) for $|\psi\rangle$ that are solutions to the first order secular equation. If we do not know in advance what the limiting eigenvectors are, we must solve the secular equation to find the correct eigenvalue perturbations $E^{(1)}$ and the limiting eigenvectors if needed.

Matrix form of the first order secular equation

To write out the first order secular equation (11) in matrix form, choose an orthonormal, unperturbed energy eigenbasis $\{|m\rangle, |i\rangle\}$, where the $\{|m\rangle\}$ span the degenerate subspace with unperturbed energy ε (i.e. $P|m\rangle = |m\rangle$) and the $\{|i\rangle\}$ span the space of states with unperturbed energy ε_i other than ε (i.e. $P|i\rangle = 0$). Then (11) takes the form

$$\sum_{m'} \langle m|V|m'\rangle\langle m'|\psi\rangle = E^{(1)}\,\langle m|\psi\rangle. \tag{12}$$

Example of the degenerate case

For a simple example consider a two-dimensional system with

$$H_0 = \varepsilon I, \qquad V|0\rangle = |1\rangle, \qquad V|1\rangle = |0\rangle.$$

The exact eigenstates of $H(\lambda) = \lambda V$ are $(|0\rangle \pm |1\rangle)/\sqrt{2}$, with corresponding eigenvalues $E(\lambda) = \varepsilon \pm \lambda$. How is this result obtained in perturbation theory? The eigenvalue ε of H_0 is totally degenerate, hence the projector P is just the identity, and so the secular equation reads $V|\psi\rangle = E^{(1)}|\psi\rangle$. The eigenvectors of V agree with those of $H(\lambda)$, and the eigenvalues are ± 1 so $E^{(1)} = \pm 1$. Note however that $E^{(1)} \neq \langle 0|V|0\rangle = \langle 1|V|1\rangle = 0$. This is because the states $|0\rangle$ and $|1\rangle$ are not solutions of the secular equation, hence are not $\lambda \to 0$ limits of the eigenstates of $H(\lambda)$.

First order perturbation of the eigenstate

To find the first order correction to the state we need to solve (4) for $|\dot{\psi}\rangle$. Only that part of $|\dot{\psi}\rangle$ which is *orthogonal* to all the states of energy ε is determined by (4), however this will be enough to determine the second order energy shift. Acting with $(1 - P)$ on (4) yields

$$(1 - P)|\dot{\psi}\rangle = (\varepsilon - H_0)^{-1}(1 - P)V|\psi\rangle. \tag{13}$$

(Note that the inverse $(\varepsilon - H_0)^{-1}$ is well-defined acting on states with energy other than ε.)

Second order perturbation

We now find the second order correction to the energy, supposing that $|\psi\rangle$ is an eigenvector of the secular equation (11) as well as of the Schrödinger equation (7). Let P' be the projection onto the states with unperturbed energy ε which are *also* eigenvectors of the secular equation (11) with the same eigenvalue $E^{(1)}$ as $|\psi\rangle$. Acting with P' on (9) yields

$$P'(V - E^{(1)})|\dot{\psi}\rangle = E^{(2)}|\psi\rangle. \tag{14}$$

By definition $P'|\psi\rangle = |\psi\rangle$, and

$$P'(V - E^{(1)})P = 0. \tag{15}$$

On account of (15), we can replace $|\dot{\psi}\rangle$ by $(1 - P)|\dot{\psi}\rangle$ in (14), and then inserting (13) yields the *second order secular equation*,

$$P'V(\varepsilon - H_0)^{-1}(1 - P)V|\psi\rangle = E^{(2)}|\psi\rangle. \tag{16}$$

Taking the inner product of (16) with $\langle\psi|$ we obtain

$$E^{(2)} = \langle\psi|V(\varepsilon - H_0)^{-1}(1-P)V|\psi\rangle. \tag{17}$$

If $E^{(1)}$ is a non-degenerate eigenvalue of PV, then P' projects onto a one-dimensional subspace, and the second order secular equation (16) tells us no more than (17). If $E^{(1)}$ is degenerate however, i.e. if the degeneracy is not completely lifted by the first order perturbation, then we must solve (16) to find the correct energy shifts and limiting eigenvectors.

Matrix form of the second order perturbation equations

Replacing $1-P$ by $\sum_i |i\rangle\langle i|$ (with the same notation as before) in (17) yields an explicit formula for the second order energy shift:

$$E^{(2)} = \sum_i \frac{\langle\psi|V|i\rangle\langle i|V|\psi\rangle}{\varepsilon - \varepsilon_i}. \tag{18}$$

The sum is over all states with unperturbed energy not equal to ε.

If $E^{(1)}$ is degenerate we may only use (18) with solutions to the second order secular equation (16), whose eigenvalues give us $E^{(2)}$ directly. To write out this equation in matrix form, choose an orthonormal, unperturbed energy eigenbasis $\{|m\rangle, |n\rangle, |i\rangle\}$, where now the $\{|m\rangle\}$ span the degenerate subspace with unperturbed energy ε *and* first order perturbation $E^{(1)}$, the $\{|n\rangle\}$ span the rest of the degenerate subspace with unperturbed energy ε, and as before the $\{|i\rangle\}$ span the space of states with unperturbed energy ε_i other than ε. Taking the inner product of (16) with $\langle m|$, replacing $1-P$ by $\sum_i |i\rangle\langle i|$, and inserting $\sum_{m'} |m'\rangle\langle m'|$ before $|\psi\rangle$, we obtain

$$\sum_{m'} \left[\sum_i \frac{\langle m|V|i\rangle\langle i|V|m'\rangle}{\varepsilon - \varepsilon_i} \right] \langle m'|\psi\rangle = E^{(2)} \langle m|\psi\rangle. \tag{19}$$