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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

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

with corresponding energy eigenvalues $E(\lambda)$. 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 $H_0 + V$. 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:

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

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

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

(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 expansion for the energy eigenvalue is

$$E(\lambda) = E(0) + \dot{E}(0)\lambda + \tfrac{1}{2}\ddot{E}(0)\lambda^2 + \cdots \tag{6}$$

$$=: \varepsilon + E^{(1)}\lambda + E^{(2)}\lambda^2 + \cdots, \tag{7}$$

introducing the notation ε for the unperturbed energy and $E^{(k)}$ for the kth order contribution to $E(1)$. For the Hamiltonian (1), the perturbation equations evaluated at $\lambda = 0$ take the form

$$(H_0 - \varepsilon)|\psi\rangle = 0 \tag{8}$$

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

$$-2E^{(2)}|\psi\rangle + 2(V - E^{(1)})|\dot{\psi}\rangle + (H_0 - \varepsilon)|\ddot{\psi}\rangle = 0, \tag{10}$$

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

First order perturbation

Multiplying (9) by the bra $\langle\psi|$ yields the first order energy shift:

$$\boxed{E^{(1)} = \langle\psi|V|\psi\rangle} \tag{11}$$

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 the vector equation (9) not captured in the scalar equation (11) restricts what this limit could be. To see how, let P be the projection onto the degeneracy subspace of states with energy ε (at $\lambda = 0$), which we'll denote by $\mathcal{H}_\varepsilon$. Then $P|\psi\rangle = |\psi\rangle$, and $P(H_0 - \varepsilon) = 0$, so acting with P on (9) yields

$$\boxed{PV|\psi\rangle = E^{(1)}|\psi\rangle.} \tag{12}$$

This is called the *first order secular equation*. It tells us that $|\psi\rangle$ must be an eigenstate of PV, and that the first order energy shift is the corresponding eigenvalue. Since $P|\psi\rangle = |\psi\rangle$, we may replace PV in (12) by PVP, the perturbation projected into $\mathcal{H}_\varepsilon$. Thus (12) states that $|\psi\rangle$ must be an eigenvector of the projected perturbation. If ε is *non-degenerate*, then $P = |\psi\rangle\langle\psi|$ is a one-dimensional projector. In this case $|\psi\rangle$ automatically satisfies the secular equation (12), with $E^{(1)}$ given by (11).

To write out the first order secular equation (12) in matrix form, choose an orthonormal basis $\{|m\rangle\}$ for $\mathcal{H}_\varepsilon$. Then take the inner product of (12) with $\langle m|$, and insert $P = \sum'_m |m'\rangle\langle m'|$ before $|\psi\rangle$ on the left hand side. This yields

$$\boxed{\sum_{m'} \langle m|V|m'\rangle\langle m'|\psi\rangle = E^{(1)}\,\langle m|\psi\rangle} \tag{13}$$

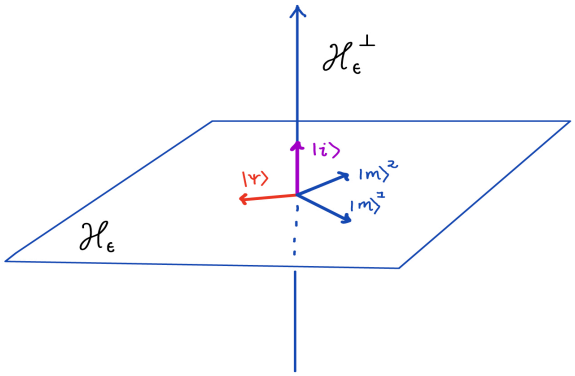

Figure 1: The degeneracy subspace $\mathcal{H}_\varepsilon$ for the H_0 eigenvalue ε, and its orthogonal complement $\mathcal{H}_\varepsilon^\perp$.

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 eigenvalue ε of H_0 is totally degenerate in the two-dimensional Hilbert space spanned by $|0\rangle$ and $|1\rangle$. If we start with the eigenvector $|0\rangle$, the first order energy shift according to (11) is $E^{(1)} = \langle 0|V|0\rangle = 0$. But this is wrong! The exact eigenstates of $H(\lambda) = \varepsilon I + \lambda V$ are $(|0\rangle \pm |1\rangle)/\sqrt{2}$, with corresponding eigenvalues $E(\lambda) = \varepsilon \pm \lambda$. The reason the perturbation formula (11) gave the wrong answer is that we started with an unperturbed state $|0\rangle$ which is not the $\lambda \to 0$ limit of an exact eigenvector. The secular equation (12) would have told us this if we hadn't noticed it by inspection: Here P is just the identity, so the secular equation reads $V|\psi\rangle = E^{(1)}|\psi\rangle$. Thus we must begin with an eigenvector of V.

First order perturbation of the eigenstate

To find the first order correction to the state we need to solve (9) for $|\dot{\psi}\rangle$. Actually, we can only solve for the part of $|\dot{\psi}\rangle$ that is *orthogonal* to the projector P, since $(H_0 - \varepsilon)P = 0$. To do so, let $\{|i\rangle\}$ be an orthonormal basis of eigenstates for $\mathcal{H}_\varepsilon^\perp$, the subspace orthogonal to $\mathcal{H}_\varepsilon$, satisfying $H_0|i\rangle = \varepsilon_i|i\rangle$. The inner product of (9) with $\langle i|$ is

$$\langle i|(V - E^{(1)})|\psi\rangle + \langle i|(H_0 - \varepsilon)|\dot{\psi}\rangle = 0. \tag{14}$$

The $E^{(1)}$ term drops out since $\langle i|\psi\rangle = 0$. Acting to the left with H_0 in the second term thus yields

$$\boxed{\langle i|\dot{\psi}\rangle = \frac{\langle i|V|\psi\rangle}{\varepsilon - \varepsilon_i}} \tag{15}$$

We can't in general determine the component of $|\dot{\psi}\rangle$ in the degenerate subspace, because it is in general not uniquely determined!

Second order perturbation

To find the second order perturbation $E^{(2)}$ to the energy eigenvalue, suppose $|\psi\rangle$ is both an unperturbed eigenstate (8) and a solution of the first order secular equation (12). Then the inner product of $\langle\psi|$ with (10) yields

$$E^{(2)} = \langle\psi|(V - E^{(1)})|\dot{\psi}\rangle \tag{16}$$

Now suppose we insert the identity $I = P + \sum_i |i\rangle\langle i|$ just before $|\dot{\psi}\rangle$. The P-term will drop out, because ψ satisfies the first order secular equation, $\langle\psi|(V - E^{(1)})P = 0$. Therefore only the part of $|\dot{\psi}\rangle$ orthogonal to the degenerate subspace contributes, yielding

$$E^{(2)} = \sum_i \langle\psi|(V - E^{(1)})|i\rangle\langle i|\dot{\psi}\rangle. \tag{17}$$

The $E^{(1)}$ term drops out, because $\langle\psi|i\rangle = 0$. Using the expression (15) for $\langle i|\dot{\psi}\rangle$ we thus obtain an explicit formula for the second order energy shift:

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

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

Similar to what happened with the first order perturbation, if $E^{(1)}$ is degenerate for the states in $\mathcal{H}_\varepsilon$, then (18) holds only if the state satisfies an additional, vector equation. To find this vector equation, instead of taking the inner product of $\langle\psi|$ with (10) we take the inner product with any basis vector $|\tilde{m}\rangle$ in $\mathcal{H}_\varepsilon$ that is *also* a solution to the first order secular equation, $PV|\tilde{m}\rangle = E^{(1)}|\tilde{m}\rangle$. This yields

$$\langle\tilde{m}|(V - E^{(1)})|\dot{\psi}\rangle = E^{(2)}\langle\tilde{m}|\psi\rangle. \tag{19}$$

As explained above, we may insert $\sum_i |i\rangle\langle i|$ before $|\dot{\psi}\rangle$, which yields

$$\sum_i \langle\tilde{m}|(V - E^{(1)})|i\rangle\langle i|\dot{\psi}\rangle = E^{(2)}\langle\tilde{m}|\psi\rangle. \tag{20}$$

Then, again using (15), and replacing $|\psi\rangle$ by $\sum_{\tilde{m}'} |\tilde{m}'\rangle\langle\tilde{m}'|\psi\rangle$ in (15) (which is valid since we are assuming that $PV|\psi\rangle = E^{(1)}|\psi\rangle$), we obtain

$$\boxed{\sum_{\tilde{m}'} \left[\sum_i \frac{\langle\tilde{m}|V|i\rangle\langle i|V|\tilde{m}'\rangle}{\varepsilon - \varepsilon_i}\right] \langle\tilde{m}'|\psi\rangle = E^{(2)}\,\langle\tilde{m}|\psi\rangle} \tag{21}$$

This is the matrix form of the *second order secular equation.* It requires that $|\psi\rangle$ must be an eigenvector of the matrix on the left hand side of (21), in addition to being an eigenvector of PV. If $E^{(1)}$ is nondegenerate, then (21) is equivalent to the scalar equation (18).