Stationary-State Perturbation Theory

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I Theory

Let us consider some Hamiltonian H^0, whose exact eigenstates are known; we then apply a perturbation to this system:

$$H = H^0 + \lambda\,\delta H. \tag{1.1}$$

where $\lambda\,\delta H$ is small compared to H^0. Note that λ can be varied so that this perturbation remains small (often, however it is taken to be 1). For many perturbations, it is extremely difficult to exactly solve for the eigenstates and eigenenergies; perturbation theory is a method by which we can approximate these objects. In practice, the exact solutions to the eigenstates and eigenenergies are written as power series in λ such that the $\mathcal{O}(\lambda^0)$ terms are the eigenstates and eigenenergies of H^0 (which are already known); we then solve order-by-order for the higher-order terms (called "corrections").

I.i Preliminaries and Goals

We start by noting that H^0 satisfies

$$H^0 \left|k^{(0)}\right\rangle = E_k^{(0)} \left|k^{(0)}\right\rangle, \tag{1.2}$$

where $\left|k^{(0)}\right\rangle$ is an eigenstate of the unperturbed Hamiltonian, H^0, and $E_k^{(0)}$ is the corresponding eigenenergy. Note that we are only considering Hamiltonians with non-degenerate energies, i.e.:

$$E_1^{(0)} < E_2^{(0)} < \cdots < E_{k-1}^{(0)} < E_k^{(0)} < E_{k+1}^{(0)} \ldots, \tag{1.3}$$

where $E_1^{(0)}$ is the ground-state energy of H^0. Now our goal is to find how the states and energies change with our perturbation.

$$H\left|k'\right\rangle = E_k' \left|k'\right\rangle, \tag{1.4}$$

where

$$\left|k'\right\rangle \equiv \left|k^{(0)}\right\rangle + \left|\delta k\right\rangle, \tag{1.5a}$$

$$E_k' \equiv E_k^{(0)} + \delta E_k, \tag{1.5b}$$

where $\left|\delta k\right\rangle$ and δE_k are the total corrections to the eigenstates and eigenenergies, which we will solve for order-by-order in λ.

I.ii Order-by-Order Corrections

Now we can write the corrections to the eigenstates and eigenenergies as power series in λ:

$$\left|\delta k\right\rangle = \lambda \left|k^{(1)}\right\rangle + \lambda^2 \left|k^{(2)}\right\rangle + \ldots, \tag{1.6a}$$

$$\delta E_k = \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots. \tag{1.6b}$$

Now we have reduced the problem to determining these corrections to the eiegenstates and eigenenergies; note that the higher the order of the correction, the less it contributes to the total correction—this is more obvious when λ is a small parameter. To actually solve for these corrections, we start by substituting Equation 1.1 into Equation 1.4:

$$(H^0 + \lambda\delta H - E'_k)\left|k'\right\rangle = 0; \tag{1.7}$$

We then substitute Equations 1.6a and 1.6b into this:

$$\begin{aligned}&[(H^0 - E_k^{(0)}) - \lambda(E_k^{(1)} - \delta H) - \lambda^2 E_k^{(2)} - \cdots - \lambda^n E_k^{(n)} - \dots] \\ &\qquad \times [\left|k^{(0)}\right\rangle + \lambda\left|k^{(1)}\right\rangle + \lambda^2\left|k^{(2)}\right\rangle + \cdots + \lambda^n\left|k^{(n)}\right\rangle + \dots] = 0,\end{aligned} \tag{1.8}$$

where $\lambda \in (0, 1]$. Since powers of λ are linearly-independent, we can separate Equation 1.8 up according to the powers of λ. We start with the zeroth-order equation, which reads:

$$(H^0 - E_k^{(0)})\left|k^{(0)}\right\rangle = 0; \tag{1.9}$$

you will recognize this as the eigenvalue equation for the unperturbed Hamiltonian. The situation gets somewhat more complicated when we gather the $\mathcal{O}(\lambda^1)$ terms:

$$(H^0 - E_k^{(0)})\left|k^{(1)}\right\rangle = (E_k^{(1)} - \delta H)\left|k^{(0)}\right\rangle. \tag{1.10}$$

In general, the $\mathcal{O}(\lambda^n)$ term will be of the form:

$$(H^0 - E_k^{(0)})\left|k^{(n)}\right\rangle = (E_k^{(1)} - \delta H)\left|k^{(n-1)}\right\rangle + E_k^{(2)}\left|k^{(n-2)}\right\rangle + \cdots + E_k^{(n)}\left|k^{(0)}\right\rangle. \tag{1.11}$$

Notice from the form of these equations that we will need to solve sequentially for the corrections, since the $\mathcal{O}(\lambda^n)$ equation contains all of the lower-order corrections as well.

Let us now project $\left|k^{(1)}\right\rangle$ onto the basis formed by the eigenstates of H^0, $\left|l^{(0)}\right\rangle$:

$$\left|k^{(1)}\right\rangle = \sum_l c_l\left|l^{(0)}\right\rangle; \tag{1.12}$$

plugging this into Equation 1.10, we find:

$$\begin{aligned}(E_k^{(1)} - \delta H)\left|k^{(0)}\right\rangle &= (H^0 - E_k^{(0)})\sum_l c_l\left|l^{(0)}\right\rangle \\ &= \sum_l (E_l^{(0)} - E_k^{(0)})c_l\left|l^{(0)}\right\rangle \\ &= \sum_{l\neq k}(E_l^{(0)} - E_k^{(0)})c_l\left|l^{(0)}\right\rangle.\end{aligned} \tag{1.13}$$

Now, since this equations determines the form of $\left|k^{(1)}\right\rangle$, we see that the $\left|k^{(0)}\right\rangle$-term does not contribute to the first-order correction; consequently, we have

$$\left|k^{(1)}\right\rangle = \sum_{l\neq k} c_l\left|l^{(0)}\right\rangle. \tag{1.14}$$

Taking the inner product of this with the zeroth-order correction, we find:

$$\begin{aligned}\left\langle k^{(0)} \middle| k^{(1)} \right\rangle &= \sum_{l \neq k} c_l \left\langle k^{(0)} \middle| l^{(0)} \right\rangle \\ &= 0; \end{aligned} \tag{1.15}$$

so the zeroth- and first-order corrections are orthogonal to each other. Note that all of the higher-order corrections will also have this property, which is obvious when we look at the l.h.s. of Equation 1.11; so, we have

$$\boxed{\left\langle k^{(0)} \middle| k^{(n)} \right\rangle = 0.} \tag{1.16}$$

This will equation will be useful to us presently.

We now have all of the information we need to find the corrections to the energy. Although there are two unknowns (assuming that we have already solved for all of the lower-order corrections), we can use Equation 1.16 to remove one of these degrees of freedom. Let's start with the first-order equation and multiply from the left by the dual of $\left| k^{(0)} \right\rangle$:

$$\left\langle k^{(0)} \right| (H^0 - E_k^{(0)}) \left| k^{(1)} \right\rangle = \left\langle k^{(0)} \right| (E_k^{(1)} - \delta H) \left| k^{(0)} \right\rangle; \tag{1.17}$$

the l.h.s. cancels so that we are left with (using Equation 1.16):

$$\boxed{E_k^{(1)} = \left\langle k^{(0)} \right| \delta H \left| k^{(0)} \right\rangle.} \tag{1.18}$$

Happily, this means we do not need to know $\left| k^{(1)} \right\rangle$ in order to find the first-order correction to the energy. We need only find the matrix element of the perturbing Hamiltonian using the zeroth-order correction. We can apply the same process to Equation 1.11, where we see the l.h.s. will always be zero, so that, in general, we have:

$$\begin{aligned} 0 &= \left\langle k^{(0)} \right| (E_k^{(1)} - \delta H) \left| k^{(n-1)} \right\rangle + E_k^{(2)} \left\langle k^{(0)} \middle| k^{(n-2)} \right\rangle + \cdots + E_k^{(n)} \left\langle k^{(0)} \middle| k^{(0)} \right\rangle \\ &= E_k^{(n)} - \left\langle k^{(0)} \right| \delta H \left| k^{(n-1)} \right\rangle; \end{aligned} \tag{1.19}$$

we can then rewrite this as

$$E_k^{(0)} = \left\langle k^{(0)} \right| \delta H \left| k^{(n-1)} \right\rangle. \tag{1.20}$$

So we see that, we require knowledge of the $\mathcal{O}(\lambda^{n-1})$ correction to the eigenstate in order to find the $\mathcal{O}(\lambda^n)$ correction to the energy; so it is clear what our next step should be.

Initially we took the overlap of equation 1.10 with the same energy state; now we try its overlap with some other energy eigenstate, i.e. $l \neq k$, which yields:

$$\left\langle l^{(0)} \right| (H^0 - E_k^{(0)}) \left| k^{(1)} \right\rangle = \left\langle l^{(0)} \right| (E_k^{(1)} - \delta H) \left| k^{(0)} \right\rangle. \tag{1.21}$$

We can readily simplify rewrite this as

$$\left\langle l^{(0)} \middle| k^{(1)} \right\rangle = -\frac{\delta H_{lk}}{E_l^{(0)} - E_k^{(0)}}, \tag{1.22}$$

where

$$\delta H_{lk} \equiv \left\langle l^{(0)} \right| \delta H \left| k^{(0)} \right\rangle . \tag{1.23}$$

As you may recall, we stated that this formalism is only applicable to non-degenerate states; Equation 1.22 now shows this explicitly. Note that the state $\left| l^{(0)} \right\rangle$ may be degenerate, since 1.22 would not run into a pole in this case; the trouble arrises when $\left| k^{(0)} \right\rangle$ is degenerate, since there would be at least one state $\left| l^{(0)} \right\rangle$ for which there would be a pole in $E_k^{(0)}$. Using the completeness relation, we can write the relation

$$\begin{aligned} \left| k^{(1)} \right\rangle &= \sum_l \left| l^{(0)} \right\rangle \left\langle l^{(0)} \middle| k^{(1)} \right\rangle \\ &= \sum_{l \neq k} \left| l^{(0)} \right\rangle \left\langle l^{(0)} \middle| k^{(1)} \right\rangle . \end{aligned} \tag{1.24}$$

Now if we multiply 1.22 by $\left| l^{(0)} \right\rangle$ and then sum over l, we obtain the first-order correction to the wave function:

$$\boxed{\left| k^{(1)} \right\rangle = -\sum_{l \neq k} \frac{\delta H_{lk}}{E_l^{(0)} - E_k^{(0)}} \left| l^{(0)} \right\rangle .} \tag{1.25}$$

Finally, we can rewrite our second order energy correction entirely in terms of the unperturbed states and energies along with the perturbing Hamiltonian:

$$\begin{aligned} E_k^{(2)} &= \left\langle k^{(0)} \right| \delta H \left| k^{(1)} \right\rangle \\ &= -\sum_{l \neq k} \left\langle k^{(0)} \right| \delta H \left| l^{(0)} \right\rangle \frac{\delta H_{lk}}{E_l^{(0)} - E_k^{(0)}} \\ &= \boxed{-\sum_{l \neq k} \frac{\left| \delta H_{lk} \right|^2}{E_l^{(0)} - E_k^{(0)}} .} \end{aligned} \tag{1.26}$$

II Example

II.i Problem

Consider a harmonic oscillator with characteristic frequency, ω, to which the following perturbation is added:

$$V = \beta(a^\dagger a^\dagger + aa). \tag{2.1}$$

(a): Determine the first-order corrections to the ground state energy and wave function.

(b): Compute the second-order correction to the ground state energy.

II.ii Solution

II.ii.i A

We start by finding the first-order correction to the energy this is readily done using Equation 1.18 with $\left|k^{(0)}\right\rangle = |0\rangle$, where $|0\rangle$ is the ground state of the harmonic oscillator; first of all note that when we act upon this state with the annihilation operator, we get

$$a\,|0\rangle = 0, \tag{2.2}$$

and taking the Hermitian conjugate of this, we also have

$$\langle 0|\, a^\dagger = 0. \tag{2.3}$$

From this, we very easily see that

$$\begin{aligned} E_0^{(1)} &= \langle 0|V|0\rangle \\ &= \beta\,\langle 0|a^\dagger a^\dagger + aa|0\rangle \\ &= 0. \end{aligned} \tag{2.4}$$

Well that wasn't too much of a challenge, but now we should look into the correction to the wave function, which is obtained from Equation 1.25; first of all, note that

$$\begin{aligned} \delta H_{lk} &= \left\langle l^{(0)}\right|\beta(a^\dagger a^\dagger + aa)\,|0\rangle \\ &= \sqrt{2}\beta\left\langle l^{(0)}|2\right\rangle, \end{aligned} \tag{2.5}$$

where $|2\rangle$ is the second excited state of the Harmonic oscillator. Consequently, all terms besides $l = 2$ will go to zero in the sum, and we have

$$\left|k_0^{(1)}\right\rangle = -\frac{\sqrt{2}\beta}{E_2^{(0)} - E_0^{(0)}}\,|2\rangle\,; \tag{2.6}$$

the energies, are, of course, given by

$$E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{2.7}$$

so that

$$\boxed{\left|k_0^{(1)}\right\rangle = -\frac{\beta}{\sqrt{2}\hbar\omega}\,|2\rangle\,.} \tag{2.8}$$

II.ii.ii B

Having already computed the first-order correction to the wave function, the calculation of the second-order correction to the energy should be trivial; we need merely employ Equation

1.26. We have already determined δH_{l0}, and as was the case previously, $l = 2$ will be the only non-zero term in the sum; now, noting that

$$|\delta H_{20}| = 2\beta^2, \tag{2.9}$$

we find that the second-order correction to the ground state energy is

$$\boxed{E_0^{(2)} = -\frac{\beta^2}{\hbar\omega}.} \tag{2.10}$$