

Chapter 1

Perturbation theory

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It is often the case that the Hamiltonian of a system differs slightly from a Hamiltonian that is well studied and completely understood. This is a situation where perturbation theory can be useful. Perturbation theory allows us to make statements about the Hamiltonian of the system using what we know about the well studied Hamiltonian.

The well studied Hamiltonian could be the that of the simple harmonic oscillator in one, two, or three dimensions. In a diatomic molecule, for example, the potential that controls the vibrations is not exactly quadratic; it has extra terms that make the vibrations slightly anharmonic. In that situation the extra terms in the potential represent perturbations of the Hamiltonian. The hydrogen atom Hamiltonian is also a well understood system. If we place the atom inside a weak external magnetic field or electric field, the situation is described by adding some small terms to the hydrogen Hamiltonian. Similarly, the interaction between the magnetic moments of the proton and the electron can be incorporated by modifying the original hydrogen atom Hamiltonian. The interaction between two neutral hydrogen atoms at a distance, leading to the van der Waals force can be studied in perturbation theory by thinking of the two atoms as electric dipoles.

The Hamiltonian of interest is written as the understood, original Hamiltonian $H^{(0)}$, plus a perturbation δH :

$$H^{(0)} + \delta H . \tag{1.0.1}$$

Since $H^{(0)}$ is Hermitian and the sum must be a Hermitian Hamiltonian, the perturbation operator δH must also be Hermitian. It is convenient to introduce a unit-free constant $\lambda \in [0, 1]$ and to consider, instead, a λ -dependent Hamiltonian $H(\lambda)$ that takes the form

$$H(\lambda) = H^{(0)} + \lambda \delta H . \tag{1.0.2}$$

When $\lambda = 1$ we have the Hamiltonian of interest, but λ allows us to consider a family of Hamiltonians that interpolate from $H^{(0)}$, when λ is equal to zero, to the Hamiltonian of interest for λ equal to one. In many cases perturbations can be turned on and off; think,

for example, of an atom in an external magnetic field that can be varied continuously. In that case we can view λ as the parameter that allows us to turn on the perturbation by letting $\lambda \neq 0$. The parameter λ is also useful in organizing the perturbation analysis, as we will see below.

We spoke of a Hamiltonian that differs slightly from $H^{(0)}$. In order to use perturbation theory we need $\lambda\delta H$ to be a ‘small’ perturbation of the Hamiltonian $H^{(0)}$. We will have to deal with the meaning of small. At first sight we may imagine that small means that, viewed as matrices, the largest entries in $\lambda\delta H$ are smaller than the largest entries in $H^{(0)}$. While this is necessary, more is needed, as we will see in our analysis. An additional advantage of using λ is that by taking it to be sufficiently small we can surely make $\lambda\delta H$ small.

We assume that the Hamiltonian $H^{(0)}$ is understood, namely, we know the eigenstates and eigenvalues of $H^{(0)}$. We want to know the eigenstates and eigenvalues of $H(\lambda)$. One may be able to calculate those exactly, but this is seldom a realistic possibility. Diagonalizing δH is seldom useful, since δH and H do not generally commute and therefore δH eigenstates are not eigenstates of $H(\lambda)$. In perturbation theory the key assumption is that the eigenvalues and eigenvectors of $H(\lambda)$ can be found as series expansions in powers of λ . We hope, of course, that there are some values of λ for which the series converges, or at least gives useful information.

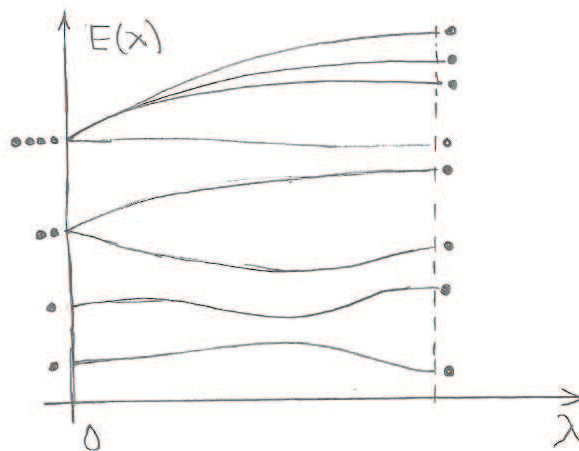


Figure 1.1: The energy eigenvalues of $H(\lambda)$ as λ varies from zero to one. On the $\lambda = 0$ vertical axis the $H^{(0)}$ eigenstates are represented by heavy dots. By the time $\lambda = 1$ the dots have shifted.

In Figure 1.1 we illustrate some of the phenomena that we may see in the spectrum of a system with Hamiltonian $H(\lambda)$. We show how the energies of the various states may change as the parameter λ is increased from zero. The two lowest energy eigenstates are non-degenerate and their energies can go up and down as λ varies. Next up in energy we have two degenerate states of $H^{(0)}$ (the Hamiltonian as $\lambda = 0$). The perturbation splits the

two levels, and that happens generically. In the figure, the perturbation splits the levels to first order in λ , as shown by the different slopes of the two curves that meet at $\lambda = 0$. In other words, viewed as power series in λ the energies of the two states have different linear terms in λ . The last level shown corresponds to four degenerate states. The perturbation to first order in λ splits the states into a group of three states and a fourth. To second order in λ the three states split further. A single Hamiltonian can exhibit behavior like this, with many possible variations.

To analyze the evolution of states and energies as functions of λ we have two possible cases: (i) we are following a non-degenerate state or, (ii) we are following a collection of degenerate states. The challenges are quite different and therefore we must analyze them separately. Clearly both situations can occur for a single Hamiltonian, depending on the spectrum of $H^{(0)}$. To follow a non-degenerate state we use *non-degenerate perturbation theory*. To follow a set of degenerate states we use *degenerate perturbation theory*. Since Hamiltonians $H^{(0)}$ generally have both non-degenerate and degenerate states we need to consider both types of perturbation theory. We begin with non-degenerate perturbation theory.

1.1 Nondegenerate perturbation theory

We begin by describing the original Hamiltonian $H^{(0)}$. We assume this Hamiltonian has a discrete spectrum with an orthonormal basis $|k^{(0)}\rangle$ of energy eigenstates, where $k \in \mathbb{Z}$ is a label that ranges over a possibly infinite set of values:

$$H^{(0)} |k^{(0)}\rangle = E_k^{(0)} |k^{(0)}\rangle, \quad \langle k^{(0)} | l^{(0)} \rangle = \delta_{kl}. \quad (1.1.1)$$

We will let $k = 0$ denote the ground state and we order the states so that the energies generally increase as the value of the label increases, so that

$$E_0^{(0)} \leq E_1^{(0)} \leq E_2^{(0)} \leq E_3^{(0)} \leq \dots \quad (1.1.2)$$

The equal signs are needed because some states may be degenerate.

In this section we focus on a non-degenerate state $|n^{(0)}\rangle$ with fixed n . This means that $|n^{(0)}\rangle$ is a single state that is separated by some finite energy from all the states with more energy and from all the states with less energy. In other words the following must be part of the sequence of inequalities in (1.1.2)

$$\dots \leq E_{n-1}^{(0)} < E_n^{(0)} < E_{n+1}^{(0)} \leq \dots \quad (1.1.3)$$

If the chosen state is the ground state, we have instead $E_0^{(0)} < E_1^{(0)}$.

As the perturbation is turned on by making λ different from zero, the energy eigenstate $|n^{(0)}\rangle$ of $H^{(0)}$ will evolve into some energy eigenstate $|n\rangle_\lambda$ of $H(\lambda)$ with energy $E_n(\lambda)$:

$$H(\lambda)|n\rangle_\lambda = E_n(\lambda)|n\rangle_\lambda, \quad (1.1.4)$$

where

$$|n\rangle_{\lambda=0} = |n^{(0)}\rangle, \quad \text{and} \quad E_n(\lambda=0) = E_n^{(0)}. \quad (1.1.5)$$

As we said, the solution is assumed to take the form of a regular power series expansion in λ . To make this clear consider a function $f(\lambda)$ such that its derivatives to all orders exist for $\lambda = 0$. In that case we have a Taylor expansion

$$f(\lambda) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0) \lambda^n = f(0) + f'(0) \lambda + \frac{1}{2} f''(0) \lambda^2 + \frac{1}{3!} f'''(0) \lambda^3 + \dots \quad (1.1.6)$$

The expansion is a power series in λ , with coefficients $f(0)$, $f'(0)$, etc, that are λ independent and reflect the value of the function and its derivatives at $\lambda = 0$.

For our problem we note the values of $|n\rangle_{\lambda}$ and $E_n(\lambda)$ for $\lambda = 0$ (1.1.5) and write:

$$\begin{aligned} |n\rangle_{\lambda} &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \dots, \\ E_n(\lambda) &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \dots \end{aligned} \quad (1.1.7)$$

The superscripts on the states and energies denote the power of λ that accompanies them in the above expressions. The above equations are a natural assumption; they state that the perturbed states and energies, being functions of λ , admit a Taylor expansion around $\lambda = 0$. Our aim is to calculate the states

$$|n^{(1)}\rangle, \quad |n^{(2)}\rangle, \quad |n^{(3)}\rangle, \dots \quad (1.1.8)$$

and the energies

$$E_n^{(1)}, \quad E_n^{(2)}, \quad E_n^{(3)}, \quad \dots \quad (1.1.9)$$

Note that all these states and energies are, by definition, λ independent. Here $|n^{(1)}\rangle$ is the leading correction to the state $|n^{(0)}\rangle$ as we turn on λ , and $E_n^{(1)}$ is the leading correction to the energy as we turn on λ . We will *not* impose the requirement that $|n\rangle_{\lambda}$ is normalized. It suffices that $|n\rangle_{\lambda}$ is normalizable, which it will be for sufficiently small perturbations. For $\lambda = 1$ we would find the solution for $H(1) = H^{(0)} + \delta H$ in the form

$$\begin{aligned} |n\rangle &\equiv |n\rangle_1 = |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + |n^{(3)}\rangle + \dots, \\ E_n &\equiv E_n(1) = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \dots \end{aligned} \quad (1.1.10)$$

Substituting the ansatz (1.1.7) into the Schrödinger equation (1.1.4) we will find the conditions for such solution to exist:

$$(H^{(0)} + \lambda \delta H - E_n(\lambda)) |n\rangle_{\lambda} = 0, \quad (1.1.11)$$

which more explicitly takes the form

$$\begin{aligned} &\left((H^{(0)} - E_n^{(0)}) - \lambda (E_n^{(1)} - \delta H) - \lambda^2 E_n^{(2)} - \lambda^3 E_n^{(3)} - \dots - \lambda^k E_n^{(k)} + \dots \right) \\ &\left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \dots + \lambda^k |n^{(k)}\rangle + \dots \right) = 0. \end{aligned} \quad (1.1.12)$$

Multiplying out we get a series in λ with coefficients λ -independent vectors in the state space of the theory. If this is to vanish for all values of λ those coefficients must be zero. Collecting the coefficients for each power of λ we

$$\begin{aligned}
 \lambda^0 : \quad & (H^{(0)} - E_n^{(0)}) |n^{(0)}\rangle = 0, \\
 \lambda^1 : \quad & (H^{(0)} - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - \delta H) |n^{(0)}\rangle, \\
 \lambda^2 : \quad & (H^{(0)} - E_n^{(0)}) |n^{(2)}\rangle = (E_n^{(1)} - \delta H) |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle, \\
 \lambda^3 : \quad & (H^{(0)} - E_n^{(0)}) |n^{(3)}\rangle = (E_n^{(1)} - \delta H) |n^{(2)}\rangle + E_n^{(2)} |n^{(1)}\rangle + E_n^{(3)} |n^{(0)}\rangle, \\
 & \vdots \quad \quad \quad \vdots \\
 \lambda^k : \quad & (H^{(0)} - E_n^{(0)}) |n^{(k)}\rangle = (E_n^{(1)} - \delta H) |n^{(k-1)}\rangle + E_n^{(2)} |n^{(k-2)}\rangle + \dots + E_n^{(k)} |n^{(0)}\rangle.
 \end{aligned}
 \tag{1.1.13}$$

Each equation is the condition that the coefficient multiplying the power of λ indicated to the left vanishes. That power is reflected as the sum of superscripts on each term, counting δH as having superscript one. This gives a simple consistency check on our equations. These are equations for the kets $|n^{(1)}\rangle, |n^{(2)}\rangle, \dots$ as well as the energy corrections $E_n^{(1)}, E_n^{(2)}, \dots$. Note again that λ does not enter into the equations, and thus the kets and energy corrections are λ independent.

The first equation, corresponding to λ^0 , is satisfied by construction. The second equation, corresponding to λ^1 , should allow us to solve for the first correction $|n^{(1)}\rangle$ to the state and the first correction $E_n^{(1)}$ to the energy. Once these are known, the equation corresponding to λ^2 involves only the unknowns $|n^{(2)}\rangle$ and $E_n^{(2)}$, and should determine them. At each stage each equation has only two unknowns: a state correction $|n^{(k)}\rangle$ and an energy correction $E_n^{(k)}$.

A useful choice. We now claim that without loss of generality we can assume that all the state corrections $|n^{(k)}\rangle$, with $k \geq 1$ contain no vector along $|n^{(0)}\rangle$. Explicitly:

$$\boxed{0 = \langle n^{(0)} | n^{(1)} \rangle = \langle n^{(0)} | n^{(2)} \rangle = \langle n^{(0)} | n^{(3)} \rangle = \dots} \tag{1.1.14}$$

To show this we explain how we can manipulate a solution that does not have this property into one that does. Suppose you have solution in which the state corrections $|n^{(k)}\rangle$ have components along $|n^{(0)}\rangle$:

$$|n^{(k)}\rangle = |n^{(k)}\rangle' - a_k |n^{(0)}\rangle, \quad k \geq 1, \tag{1.1.15}$$

with some constants a_k and with $|n^{(k)}\rangle'$ orthogonal to $|n^{(0)}\rangle$. Then the solution for the full

corrected state is

$$\begin{aligned} |n\rangle_\lambda &= |n^{(0)}\rangle + \lambda (|n^{(1)}\rangle' - a_1|n^{(0)}\rangle) + \lambda^2 (|n^{(2)}\rangle' - a_2|n^{(0)}\rangle) + \dots \\ &= (1 - a_1\lambda - a_2\lambda^2 - \dots)|n^{(0)}\rangle + \lambda|n^{(1)}\rangle' + \lambda^2|n^{(2)}\rangle' + \dots \end{aligned} \quad (1.1.16)$$

Since this is an eigenstate of the Hamiltonian $H(\lambda)$, it will still be an eigenstate if we change its normalization by dividing it by any function of λ . Dividing by the coefficient of $|n^{(0)}\rangle$ we have the physically identical solution $|n\rangle'_\lambda$ given by

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \frac{1}{(1 - a_1\lambda - a_2\lambda^2 - \dots)} [\lambda|n^{(1)}\rangle' + \lambda^2|n^{(2)}\rangle' + \dots] \quad (1.1.17)$$

We can expand the denominator so that we get

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle' + \lambda^2(|n^{(2)}\rangle' + a_1|n^{(1)}\rangle') + \dots \quad (1.1.18)$$

The explicit expressions do not matter, the key point, actually visible in (1.1.17), is that we have a physically identical solution of the same equation in which the state corrections are all orthogonal to $|n^{(0)}\rangle$. This shows that we can impose the conditions (1.1.14) without loss of generality.

Solving the equations. Let us finally begin solving equations (1.1.13). For this we note that the Schrodinger equation for the ket $|n^{(0)}\rangle$ implies that for the bra we have

$$\langle n^{(0)}|(H^{(0)} - E_n^{(0)}) = 0. \quad (1.1.19)$$

This means that acting with $\langle n^{(0)}|$ on the left-hand side of any of the equations in (1.1.13) will give zero. Consistency requires that acting with $\langle n^{(0)}|$ on the right-hand side of any of the equations in (1.1.13) also give zero, and presumably some interesting information. For the λ -equation this gives:

$$0 = \langle n^{(0)}|(E_n^{(1)} - \delta H)|n^{(0)}\rangle. \quad (1.1.20)$$

Since $|n^{(0)}\rangle$ is normalized and $E_n^{(1)}$ is a number, this means that

$$\boxed{E_n^{(1)} = \langle n^{(0)}|\delta H|n^{(0)}\rangle.} \quad (1.1.21)$$

This is the *most famous* result in perturbation theory: the first correction to the energy of an energy eigenstate is simply the expectation value of the correction to the Hamiltonian in the *uncorrected* state. You need not know the correction to the state to determine the first correction to the energy! Note that the hermicity of δH implies the required reality of the energy correction.

We can actually find some interesting formulae (but not yet fully explicit!) for the higher energy corrections. For the λ^2 equation, acting with $\langle n^{(0)}|$ on the right-hand side gives

$$0 = \langle n^{(0)}|\left((E_n^{(1)} - \delta H)|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle\right). \quad (1.1.22)$$

Recalling our orthogonality assumption, we have $\langle n^{(0)} | n^{(1)} \rangle = 0$ and the term with $E_n^{(1)}$ drops out. We get

$$E_n^{(2)} = \langle n^{(0)} | \delta H | n^{(1)} \rangle, \quad (1.1.23)$$

which states that the second correction to the energy is determined if we have the first correction $|n^{(1)}\rangle$ to the state. Note that this expression is not explicit enough to make it manifest that $E_n^{(2)}$ is real. This and the earlier result for the first correction to the energy have a simple generalization. Acting with $\langle n^{(0)} |$ on the last equation of (1.1.13) we get

$$0 = \langle n^{(0)} | \left((E_n^{(1)} - \delta H) | n^{(k-1)} \rangle + E_n^{(2)} | n^{(k-2)} \rangle + \dots + E_n^{(k)} | n^{(0)} \rangle \right). \quad (1.1.24)$$

Using the orthogonality of $|n^{(0)}\rangle$ and all the state corrections, we have

$$0 = -\langle n^{(0)} | \delta H | n^{(k-1)} \rangle + E_n^{(k)}, \quad (1.1.25)$$

and therefore we have

$$\boxed{E_n^{(k)} = \langle n^{(0)} | \delta H | n^{(k-1)} \rangle.} \quad (1.1.26)$$

At any stage of the recursive solution, the energy at a fixed order is known if the state correction is known to previous order. So it is time to calculate the corrections to the states!

Let us solve for the first correction $|n^{(1)}\rangle$ to the state. This state must be some particular superposition of the original energy eigenstates $|k^{(0)}\rangle$. For this we look at the equation

$$(H^{(0)} - E_n^{(0)}) | n^{(1)} \rangle = (E_n^{(1)} - \delta H) | n^{(0)} \rangle. \quad (1.1.27)$$

This is a vector equation: the left-hand side vector set equal to the right-hand side vector. As in any vector equation, we can check it using a basis set of vectors. Forming the inner product of each and every basis vector with both the left-hand side and the right-hand side, we must get equal numbers. We already acted on the above equation with $\langle n^{(0)} |$ to figure out $E_n^{(1)}$. The remaining information in this equation can be obtained by acting with all the states $\langle k^{(0)} |$ with $k \neq n$:

$$\langle k^{(0)} | (H^{(0)} - E_n^{(0)}) | n^{(1)} \rangle = \langle k^{(0)} | (E_n^{(1)} - \delta H) | n^{(0)} \rangle. \quad (1.1.28)$$

On the left-hand side we can let $H^{(0)}$ act on the bra. On the right-hand side we note that with $k \neq n$ the term with $E_n^{(1)}$ vanishes

$$(E_k^{(0)} - E_n^{(0)}) \langle k^{(0)} | n^{(1)} \rangle = -\langle k^{(0)} | \delta H | n^{(0)} \rangle. \quad (1.1.29)$$

To simplify notation we define the matrix elements of δH in the original basis

$$\delta H_{mn} \equiv \langle m^{(0)} | \delta H | n^{(0)} \rangle. \quad (1.1.30)$$

Note that the Hermiticity of δH implies that

$$\delta H_{nm} = (\delta H_{mn})^*. \quad (1.1.31)$$

With this notation, equation (1.1.29) gives

$$\langle k^{(0)} | n^{(1)} \rangle = - \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}, \quad k \neq n. \quad (1.1.32)$$

Since we now know the overlap of $|n^{(1)}\rangle$ with all basis states, this means that the state has been determined. Indeed we can use the completeness of the basis to write

$$|n^{(1)}\rangle = \sum_k |k^{(0)}\rangle \langle k^{(0)} | n^{(1)} \rangle = \sum_{k \neq n} |k^{(0)}\rangle \langle k^{(0)} | n^{(1)} \rangle, \quad (1.1.33)$$

since the term with $k = n$ does not contribute because of the orthogonality assumption. Using the overlaps (1.1.32) we now get

$$\boxed{|n^{(1)}\rangle = - \sum_{k \neq n} \frac{|k^{(0)}\rangle \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}.} \quad (1.1.34)$$

This shows that the first correction $|n^{(1)}\rangle$ can have components along all basis states, except $|n^{(0)}\rangle$. The component along a state $|k^{(0)}\rangle$ vanishes if the perturbation δH does not couple $|n^{(0)}\rangle$ to $|k^{(0)}\rangle$, namely, if δH_{kn} vanishes. Note that the assumption of non-degeneracy is needed here. We are summing over all states $|k^{(0)}\rangle$ that are not $|n^{(0)}\rangle$ and if any such state has the same $H^{(0)}$ energy as $|n^{(0)}\rangle$ the energy denominator will vanish causing trouble!

Now that we have the first order correction to the states we can compute the *second order* correction to the energy. Using (1.1.23) we have

$$E_n^{(2)} = \langle n^{(0)} | \delta H | n^{(1)} \rangle = - \sum_{k \neq n} \frac{\langle n^{(0)} | \delta H | k^{(0)} \rangle \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}. \quad (1.1.35)$$

In the last numerator we have $\langle n^{(0)} | \delta H | k^{(0)} \rangle = \delta H_{nk} = (\delta H_{kn})^*$ and therefore

$$E_n^{(2)} = - \sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}}. \quad (1.1.36)$$

This is the second-order energy correction. This explicit formula makes the reality of $E_n^{(2)}$ manifest.

In summary, going back to (1.1.7), we have that the states and energies for $H(\lambda) = H^{(0)} + \lambda \delta H$ are, to this order,

$$\boxed{\begin{aligned} |n\rangle_\lambda &= |n^{(0)}\rangle - \lambda \sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} |k^{(0)}\rangle + \mathcal{O}(\lambda^2), \\ E_n(\lambda) &= E_n^{(0)} + \lambda \delta H_{nn} - \lambda^2 \sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \mathcal{O}(\lambda^3), \end{aligned}} \quad (1.1.37)$$

Remarks:

1. The first order corrected energy of the (non-degenerate) ground state *overstates* the true exact ground state energy. To see this consider the first order corrected ground state energy $E_0^{(0)} + \lambda E_0^{(1)}$. Writing this in terms of expectation values, with $|0^{(0)}\rangle$ denoting the unperturbed ground state, we have

$$\begin{aligned} E_0^{(0)} + \lambda E_0^{(1)} &= \langle 0^{(0)} | H^{(0)} | 0^{(0)} \rangle + \lambda \langle 0^{(0)} | \delta H | 0^{(0)} \rangle \\ &= \langle 0^{(0)} | (H^{(0)} + \lambda \delta H) | 0^{(0)} \rangle \\ &= \langle 0^{(0)} | H(\lambda) | 0^{(0)} \rangle. \end{aligned} \quad (1.1.38)$$

By the variational principle, the expectation value of the Hamiltonian on an arbitrary (normalized) state is larger than the ground state energy $E_0(\lambda)$, therefore

$$E_0^{(0)} + \lambda E_0^{(1)} = \langle 0^{(0)} | H(\lambda) | 0^{(0)} \rangle \geq E_0(\lambda), \quad (1.1.39)$$

which is what we wanted to prove. Given this overestimate at first order, the second order correction to the ground state energy is always negative. Indeed,

$$-\lambda^2 \sum_{k \neq 0} \frac{|\delta H_{k0}|^2}{E_k^{(0)} - E_0^{(0)}}, \quad (1.1.40)$$

and each term is negative because the unperturbed excited state energies $E_k^{(0)}$ ($k \neq 0$) exceed the unperturbed ground state energy $E_0^{(0)}$.

2. The second order correction to the energy of the $|n^{(0)}\rangle$ eigenstate exhibits *level repulsion*: the levels with $k > n$ push the state down and the levels with $k < n$ push the state up. Indeed,

$$-\lambda^2 \sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} = -\lambda^2 \sum_{k > n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \lambda^2 \sum_{k < n} \frac{|\delta H_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}. \quad (1.1.41)$$

The first term gives the negative contribution from the higher energy states and the second term gives the contribution from the lower energy states (see Figure 1.2).

The systematics of solving the equations is now apparent. For each equation we take inner products with all states in the state space. That gives the full content of the equation. We first take the inner product with $\langle n^{(0)} |$, as this makes the left-hand side equal to zero and is thus simpler. Then we take the inner product with $\langle k^{(0)} |$ with all $k \neq n$ and that gives the remainder of the information that is contained in the equation.

Exercise 1. Calculate $|n^{(2)}\rangle$ and $E_n^{(3)}$.

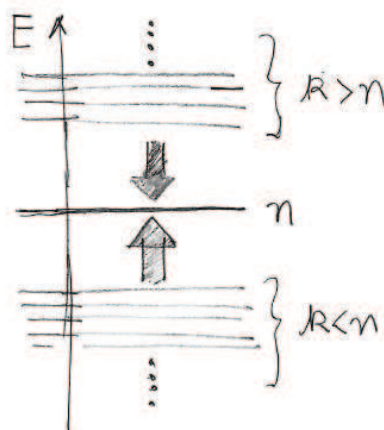


Figure 1.2: The second order corrections to the energy of the state $|n^{(0)}\rangle$ receives negative contributions from the higher energy states and positive contributions from the lower energy states. We have, effectively, a repulsion preventing the state $|n^{(0)}\rangle$ from approaching the neighboring states.

Exercise 2. The state $|n\rangle_\lambda$ is not normalized. Use (1.1.37) to calculate to order λ^2 the quantity $Z_n(\lambda)$ defined by

$$\frac{1}{Z_n(\lambda)} \equiv \langle n|n\rangle_\lambda . \quad (1.1.42)$$

What is the probability that the state $|n\rangle_\lambda$ will be observed to be along its unperturbed version $|n^{(0)}\rangle$?

1.1.1 Validity of the perturbation expansion

We now return to a question we did not address: What do we mean when we say that $\lambda\delta H$ is small? We have said that $\lambda\delta H$ must be small compared to the original Hamiltonian $H^{(0)}$, but it is not clear what this means, as both expressions are operators. For some insight into this matter consider an example where $H^{(0)}$ is a two-by-two diagonal matrix with non-degenerate eigenvalues

$$H^{(0)} = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix} . \quad (1.1.43)$$

The perturbation, called $\lambda\hat{V}$, only has off-diagonal elements so that

$$H(\lambda) = H^{(0)} + \lambda\hat{V} \equiv \begin{pmatrix} E_1^{(0)} & \lambda V \\ \lambda V^* & E_2^{(0)} \end{pmatrix} . \quad (1.1.44)$$

In this simple example there is no need to use perturbation theory since the eigenvalues, E_+ and E_- , can be calculated exactly as functions of λ

$$E_{\pm}(\lambda) = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}(E_1^{(0)} - E_2^{(0)}) \sqrt{1 + \left[\frac{\lambda|V|}{\frac{1}{2}(E_1^{(0)} - E_2^{(0)})} \right]^2}. \quad (1.1.45)$$

The perturbative expansion of the energies is obtained by Taylor expansion of the square

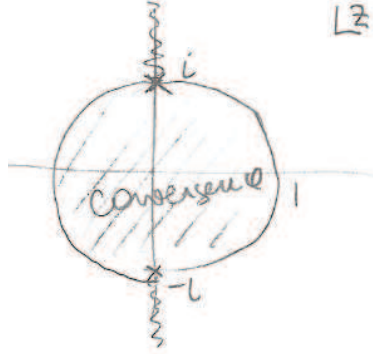


Figure 1.3: The Taylor expansion of the function $f(z) = \sqrt{1+z^2}$ about $z = 0$ has a radius of convergence equal to one.

root in powers of λ . To perform this expansion we need the result

$$f(z) \equiv \sqrt{1+z^2} = 1 + \frac{z^2}{2} - \frac{z^4}{8} + \frac{z^6}{6} + \frac{5}{128}z^8 + \mathcal{O}(z^{10}). \quad (1.1.46)$$

The function $f(z)$ exhibits branch cuts at $z = \pm i$ (see Figure 1.3), thus the expansion of $f(z)$ around $z = 0$ has radius of convergence equal to one: the series converges for $|z| < 1$ and diverges for $|z| > 1$. Table 1 shows $f(z)$ evaluated for $z = 0.9, 1.2$, and 1.5 . The various approximations to the full series are shown.

For our expansion of (1.1.45), convergence for $|z| < 1$ implies convergence when

$$\frac{|\lambda||V|}{\frac{1}{2}|E_1^{(0)} - E_2^{(0)}|} < 1 \implies |\lambda V| < \frac{1}{2}|E_1^{(0)} - E_2^{(0)}|. \quad (1.1.47)$$

For $|\lambda V| > \frac{1}{2}|E_1^{(0)} - E_2^{(0)}|$ the perturbation series does not converge. We learn that for convergence the perturbation must be small compared with *energy differences* in $H^{(0)}$. It is not sufficient that the magnitude of the matrix elements of $\lambda\delta H$ be small compared to those in $H^{(0)}$, energy differences matter. This result leads us to expect complications when energy differences go to zero and $H^{(0)}$ has degeneracies.

z	0.9	1.2	1.5
$f(z)$	1.34536	1.56205	1.80278
$f_8(z)$	1.33939	1.47946	1.20297
$f_{14}(z)$	1.33939	1.67280	4.82288
$f_{20}(z)$	1.34490	1.36568	-18.4895
$f_{30}(z)$	1.34545	2.23047	641.772

Table 1.1: $f(z) \equiv \sqrt{1+z^2} = \sum_i c_i z^i$ and $f_n(z) = \sum_{i=0}^n c_i z^i$.

1.1.2 Example: Anharmonic oscillator

Consider the simple harmonic oscillator

$$H^{(0)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \quad (1.1.48)$$

We want to explore the effect of a perturbation proportional to $\sim \hat{x}^4$. This has the effect of changing the original quadratic potential for a more complicated potential that includes a quartic term. To do analysis in a clear way, we must consider units. Using the constants \hbar, m, ω of the harmonic oscillator a length scale d can be uniquely build:

$$d^2 = \frac{\hbar}{m\omega}. \quad (1.1.49)$$

The unit-free coordinate \hat{x}/d then has a simple expression in terms of creation and annihilation operators:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger) = d \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) \quad \rightarrow \quad \frac{\hat{x}}{d} = \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger). \quad (1.1.50)$$

It follows that an \hat{x}^4 perturbation with units of energy takes the form

$$\delta H = \hbar\omega \frac{\hat{x}^4}{d^4} = \frac{m^2\omega^3}{\hbar}\hat{x}^4 = \frac{1}{4}\hbar\omega(\hat{a} + \hat{a}^\dagger)^4. \quad (1.1.51)$$

Using the unit-free parameter λ , the perturbed Hamiltonian will therefore be

$$\boxed{H(\lambda) = H^{(0)} + \lambda \frac{m^2\omega^3}{\hbar}\hat{x}^4 = H^{(0)} + \lambda \frac{1}{4}\hbar\omega(\hat{a} + \hat{a}^\dagger)^4.} \quad (1.1.52)$$

We will identify the states $|k^{(0)}\rangle$ of $H^{(0)}$ with the number eigenstates $|k\rangle$, $k = 0, 1, \dots$, of the harmonic oscillator. Recall that

$$E_k^{(0)} = \hbar\omega(k + \frac{1}{2}), \quad |k\rangle = \frac{(\hat{a}^\dagger)^k}{\sqrt{k!}}|0\rangle. \quad (1.1.53)$$

The Hamiltonian $H(\lambda)$ defines an anharmonic oscillator. In a classical anharmonic oscillator the frequency of oscillation depends on the amplitude of oscillation. In the quantum harmonic oscillator all levels are equally spaced. The frequencies associated with transitions between various levels are therefore integer multiples (*i.e.* harmonics) of the basic frequency associated to a transition between the first excited state and the ground state. In the quantum anharmonic oscillator the spacing between the energy levels is not uniform.

First the simplest question: What is the first-order correction $E_0^{(1)}$ to the energy of the ground state? For this, following (1.1.21) we simply calculate the expectation value of the perturbation on the ground state:

$$E_0^{(1)} = \langle 0 | \frac{1}{4} \hbar \omega (\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle = \frac{1}{4} \hbar \omega \langle 0 | (\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle = \frac{3}{4} \hbar \omega, \quad (1.1.54)$$

where we used

$$\langle 0 | (\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle = 3, \quad (1.1.55)$$

as you should verify. It follows that the corrected energy is

$$E_0(\lambda) = E_0^{(0)} + \lambda E_0^{(1)} + \mathcal{O}(\lambda^2) = \frac{1}{2} \hbar \omega + \lambda \frac{3}{4} \hbar \omega + \mathcal{O}(\lambda^2) = \frac{1}{2} \hbar \omega \left(1 + \frac{3}{2} \lambda + \mathcal{O}(\lambda^2) \right) \quad (1.1.56)$$

We note that the energy of the ground state increases with $\lambda > 0$. This is reasonable as the quartic term in the modified potential squeezes the ground state. How about second order correction to the ground state energy? For this we use (1.1.36) taking $n = 0$:

$$E_0^{(2)} = - \sum_{k \neq 0} \frac{|\delta H_{k0}|^2}{E_k^{(0)} - E_0^{(0)}}. \quad (1.1.57)$$

The sum is over all $k \geq 1$ such that δH_{k0} is non-vanishing. Here

$$\delta H_{k0} = \frac{1}{4} \hbar \omega \langle k | (\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle. \quad (1.1.58)$$

We consider $(\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle$ which corresponds, up to constants to acting on the ground state wavefunction φ_0 with x^4 . This should give an even wavefunction. So $(\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle$ must be a superposition of $|0\rangle, |2\rangle$, and $|4\rangle$. We cannot get states with higher number because there are at most four creation operators acting on the vacuum. A short calculation (do it!) confirms that

$$(\hat{a} + \hat{a}^\dagger)^4 | 0 \rangle = 3|0\rangle + 6\sqrt{2}|2\rangle + \sqrt{4!}|4\rangle. \quad (1.1.59)$$

This immediately gives

$$\delta H_{00} = \frac{3}{4} \hbar \omega, \quad \delta H_{20} = \frac{3\sqrt{2}}{2} \hbar \omega, \quad \delta H_{40} = \frac{\sqrt{6}}{2} \hbar \omega, \quad (1.1.60)$$

the first of which we had already determined and is not needed for the second order computation. Back in (1.1.57) we have

$$E_0^{(2)} = - \frac{|\delta H_{20}|^2}{2\hbar\omega} - \frac{|\delta H_{40}|^2}{4\hbar\omega} = - \frac{(\hbar\omega)^2 9}{2\hbar\omega 2} - \frac{(\hbar\omega)^2 3}{4\hbar\omega 2} = - \left(\frac{9}{4} + \frac{3}{8} \right) \hbar\omega = - \frac{21}{8} \hbar\omega. \quad (1.1.61)$$

Therefore the corrected ground state energy to quadratic order is

$$E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} = \frac{1}{2} \hbar \omega \left(1 + \frac{3}{2} \lambda - \frac{21}{4} \lambda^2 \right). \quad (1.1.62)$$

The computation can be carried to higher order, as first done by Bender and Wu (Phys. Rev. **184** (1969)1231). They find that¹

$$E_0(\lambda) = \frac{1}{2} \hbar \omega \left(1 + \frac{3}{2} \lambda - \frac{21}{4} \lambda^2 + \frac{333}{8} \lambda^3 - \frac{30885}{64} \lambda^4 + \frac{916731}{128} \lambda^5 - \frac{65518401}{512} \lambda^6 + \mathcal{O}(\lambda^7) \right) \quad (1.1.63)$$

As it turns out the coefficients keep growing and the series does not converge for any nonzero λ ; the radius of convergence is actually zero! This does not mean the series is not useful. It is an asymptotic expansion. This means that for a given small value of λ the magnitude of successive terms generally decrease until, at some point, they start growing again. A good approximation to the desired answer is obtained by including only the part of the sum where the terms are decreasing.

Exercise 3. Calculate the first order correction $E_n^{(1)}$ to the energy for the state $|n\rangle$ of number n . Exhibit the anharmonicity of the oscillator by using this result to find, to first order in λ , the energy separation $\Delta E_n(\lambda) = E_n(\lambda) - E_{n-1}(\lambda)$ between levels.

Let us now find the first order correction to the ground-state wavefunction. Using (1.1.34) with $n = 0$ we have

$$|0^{(1)}\rangle = - \sum_{k \neq 0} \frac{\delta H_{k0}}{E_k^{(0)} - E_0^{(0)}} |k\rangle. \quad (1.1.64)$$

We then find

$$\begin{aligned} |0^{(1)}\rangle &= - \frac{\delta H_{20}}{2\hbar\omega} |2\rangle - \frac{\delta H_{40}}{4\hbar\omega} |4\rangle = - \frac{3}{4} \sqrt{2} |2\rangle - \frac{1}{16} \sqrt{4!} |4\rangle \\ &= - \frac{3}{4} \hat{a}^\dagger \hat{a}^\dagger |0\rangle - \frac{1}{16} \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger |0\rangle. \end{aligned} \quad (1.1.65)$$

This means that to first order the ground state of the perturbed oscillator is

$$|0\rangle_\lambda = |0\rangle - \lambda \left(\frac{3}{4} \hat{a}^\dagger \hat{a}^\dagger |0\rangle + \frac{1}{16} \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger |0\rangle \right) + \mathcal{O}(\lambda^2). \quad (1.1.66)$$

1.2 Degenerate perturbation theory

If the spectrum of $H^{(0)}$ has degenerate states, as shown in Figure 1.1, tracking the evolution of those states as λ becomes nonzero presents new challenges. We first show that naive extrapolation of our results for a non-degenerate state do not work. We will also be able to appreciate the basic difficulty.

¹Bender and Wu's results, in eqns. (2.12) of their paper must all be multiplied by a factor of 2, as they take $A_0 = 1/2$.

1.2.1 Degenerate toy model

Consider an example with two-by-two matrices. The unperturbed matrix $H^{(0)}$ will be set equal to the identity matrix:

$$H^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (1.2.1)$$

We have a degeneracy here as the two eigenvalues are identical (and equal to one). The perturbation matrix δH is chosen to be off diagonal:

$$\delta H = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (1.2.2)$$

We then have

$$H(\lambda) = H^{(0)} + \lambda \delta H = \begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix}. \quad (1.2.3)$$

Using labels $n = 1, 2$ the unperturbed eigenstates can be taken to be

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E_1^{(0)} = E_2^{(0)} = 1, \quad (1.2.4)$$

with the corresponding eigenvalues indicated as well. To first order in λ , the eigenvalues predicted from non-degenerate perturbation theory (1.1.37) are $E_n(\lambda) = E_n^{(0)} + \lambda \delta H_{nn}$. This gives

$$\begin{aligned} E_1(\lambda) &= E_1^{(0)} + \lambda \delta H_{11} = 1 + \lambda \cdot 0 = 1? \\ E_2(\lambda) &= E_2^{(0)} + \lambda \delta H_{22} = 1 + \lambda \cdot 0 = 1? \end{aligned} \quad (1.2.5)$$

The eigenvalues are unperturbed to first order in λ since the matrix δH is off-diagonal. These answers, however, are wrong. We can compute the exact eigenvalues of $H(\lambda)$ and they are $1 \pm \lambda$. There is also a problem with the state corrections. Equation (1.1.37) states that

$$|n\rangle_\lambda = |n^{(0)}\rangle - \lambda \sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} |k^{(0)}\rangle. \quad (1.2.6)$$

but this time, with $E_1^{(0)} = E_2^{(0)}$ the denominator is zero, and the δH matrix element is also zero, giving us an ambiguous result.

So what can we do? A direct calculation shows that

$$H(\lambda) \text{ has eigenvectors } \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{with eigenvalue } = 1 + \lambda, \quad (1.2.7)$$

$$\text{and } \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{with eigenvalue } = 1 - \lambda. \quad (1.2.8)$$

You may think the eigenvectors jump from those of $H^{(0)}$ indicated in (1.2.4) to those of $H(\lambda)$ as soon as λ becomes nonzero. Such discontinuity is totally against the spirit of

perturbation theory. Happily, this is not really true. The eigenvectors of $H^{(0)}$ are in fact *ambiguous*, precisely due to the degeneracy. The eigenvectors of $H^{(0)}$ are actually the *span* of the two vectors listed in (1.2.4). The perturbation selected a particular combination of these eigenvectors. This particular combination is the one that we should use even for $\lambda = 0$. The lesson is that to get states that vary continuously as λ is turned on we must choose the basis in the degenerate subspace of $H^{(0)}$ carefully. We will call that carefully selected basis the “good” basis.

1.2.2 Systematic Analysis

Again, we are looking at the perturbed Hamiltonian

$$H(\lambda) = H^{(0)} + \lambda\delta H, \quad (1.2.9)$$

where $H^{(0)}$ has known eigenvectors and eigenvalues. We will focus this time on a degenerate subspace of eigenvectors of dimension $N > 1$, that is, a space with N linearly independent eigenstates of the same energy. In the basis of eigenstates, $H^{(0)}$ is a diagonal matrix that contains a string of $N > 1$ identical entries:

$$H^{(0)} = \text{diag} \{ E_1^{(0)}, E_2^{(0)}, \dots, \underbrace{E_n^{(0)}, \dots, E_n^{(0)}}_N, \dots \}. \quad (1.2.10)$$

In the degenerate subspace we choose a collection of N orthonormal eigenstates

$$|n^{(0)}; 1\rangle, |n^{(0)}; 2\rangle, \dots, |n^{(0)}; N\rangle. \quad (1.2.11)$$

Accordingly, we have

$$\langle n^{(0)}; p | n^{(0)}; l \rangle = \delta_{p,l}, \quad (1.2.12)$$

$$H^{(0)} |n^{(0)}; k\rangle = E_n^{(0)} |n^{(0)}; k\rangle. \quad (1.2.13)$$

This set of vectors span a degenerate subspace of dimension N that we will call \mathbb{V}_N

$$\mathbb{V}_N \equiv \text{span}\{|n^{(0)}; k\rangle, k = 1, \dots, N\}. \quad (1.2.14)$$

The total state space of the theory, denoted by \mathcal{H} is written as a direct sum:

$$\mathcal{H} = \mathbb{V}_N \oplus \hat{V}, \quad (1.2.15)$$

where \hat{V} is spanned by those eigenstates of $H^{(0)}$ that are not in \mathbb{V}_N . We denote by $|p^{(0)}\rangle$ with $p \in \mathbb{Z}$ a basis for \hat{V} . That basis may include both degenerate and non degenerate states. Together with the states in \mathbb{V}_N we have an orthonormal basis for the whole state space:

$$\langle p^{(0)} | q^{(0)} \rangle = \delta_{pq}, \quad \langle p^{(0)} | n^{(0)}; k \rangle = 0. \quad (1.2.16)$$

Our notation distinguishes the states in \mathbb{V}_N from those in \hat{V} because the former have two labels and the latter have only one.

We now consider the evolution of the degenerate eigenstates as we turn on the perturbation. Again we assume that the states vary continuously in λ and thus write:

$$\begin{aligned} |n^{(0)}; k\rangle \rightarrow |n; k\rangle_\lambda &= |n^{(0)}; k\rangle + \lambda |n^{(1)}; k\rangle + \lambda^2 |n^{(2)}; k\rangle + \mathcal{O}(\lambda^3), \\ E_n^{(0)} \rightarrow E_{n,k}(\lambda) &= E_n^{(0)} + \lambda E_{n,k}^{(1)} + \lambda^2 E_{n,k}^{(2)} + \mathcal{O}(\lambda^3). \end{aligned} \quad (1.2.17)$$

These equations hold for $k = 1, \dots, N$. Note that for each value of k the energy corrections might be different and that's why the energy corrections carry the label k . Our goal is to find the state corrections $|n^{(p)}; k\rangle$ and the energy corrections $E_{n,k}^{(p)}$ for $p \geq 1$ and for each k . As before we demand that $|n^{(p)}; k\rangle$ for $p \geq 1$ has no component along $|n^{(0)}; k\rangle$, i.e.

$$\langle n^{(0)}; k | n^{(p)}; k \rangle = 0 \quad \text{for } p \geq 1 \quad (1.2.18)$$

Note, however, that $|n^{(p)}; k\rangle$ may have components along $|n^{(0)}; \ell\rangle$ with $\ell \neq k$. So $|n^{(0)}; k\rangle$ may and in fact will have a component in \mathbb{V}_N .

The perturbed eigenstates must satisfy

$$H(\lambda) |n; k\rangle_\lambda = E_{n,k}(\lambda) |n; k\rangle_\lambda, \quad (1.2.19)$$

and substituting the perturbative expansions above we obtain equations completely analogous to the ones in Eq.(1.1.13)

$$\lambda^0 : \quad (H^0 - E_n^{(0)}) |n^{(0)}; k\rangle = 0, \quad (1.2.20)$$

$$\lambda^1 : \quad (H^0 - E_n^{(0)}) |n^{(1)}; k\rangle = (E_{n,k}^{(1)} - \delta H) |n^{(0)}; k\rangle, \quad (1.2.21)$$

$$\lambda^2 : \quad (H^0 - E_n^{(0)}) |n^{(2)}; k\rangle = (E_{n,k}^{(1)} - \delta H) |n^{(1)}; k\rangle + E_{n,k}^{(2)} |n^{(0)}; k\rangle, \quad (1.2.22)$$

$$\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots$$

In the following we will discuss a solution to first order for the case in which the degeneracy in \mathbb{V}_N is completely broken to first order in perturbation theory; that is, the first order corrections to the energies split the N states completely. Our solution will proceed in three steps:

1. Hit the $\mathcal{O}(\lambda)$ equation with $\langle n^{(0)}; \ell |$ to learn that δH must be diagonal in the chosen basis for \mathbb{V}_N and to determine the first-order energy shifts.
2. Use the $\mathcal{O}(\lambda)$ equation to calculate the components of $|n^{(1)}; k\rangle$ in \hat{V} .
3. Hit the $\mathcal{O}(\lambda^2)$ equation with $\langle n^{(0)}; \ell |$ to determine the second order energy correction $E_{n,k}^{(2)}$ and the component of $|n^{(1)}; k\rangle$ in \mathbb{V}_N .

Step 1. Recalling that $\langle n^{(0)}; \ell | (H^{(0)} - E_n^{(0)}) = 0$, as we hit the $\mathcal{O}(\lambda)$ equation with $\langle n^{(0)}; \ell |$ the left-hand side vanishes and we find

$$\langle n^{(0)}; \ell | (E_{n,k}^{(1)} - \delta H) | n^{(0)}; k \rangle = 0. \quad (1.2.23)$$

Since the basis states in \mathbb{V}_N are orthonormal, this implies that

$$\langle n^{(0)}; \ell | \delta H | n^{(0)}; k \rangle = E_{n,k}^{(1)} \delta_{\ell,k}. \quad (1.2.24)$$

This equation holds for all $k, \ell = 1, \dots, N$. Remarkably, this equation is telling us that the basis $|n^{(0)}; k\rangle$ *must be chosen* to make the matrix δH diagonal in the subspace \mathbb{V}_N ! This is required in order to get the perturbation theory going. Setting ℓ equal to k we read the values of the first order energy shifts

$$E_{n,k}^{(1)} = \langle n^{(0)}; k | \delta H | n^{(0)}; k \rangle = \delta H_{nk,nk}, \quad (1.2.25)$$

where the last equality is a definition. The energies to first order are then

$$\boxed{E_{n,k}(\lambda) = E_n^{(0)} + \lambda \delta H_{nk,nk}.} \quad (1.2.26)$$

A few remarks:

1. The above result for the first order energy shifts is true *always*, even if the degeneracy is not lifted. The degeneracy is lifted when

$$E_{n,k}^{(1)} \neq E_{n,\ell}^{(1)}, \quad \text{whenever } k \neq \ell, \quad (1.2.27)$$

for all values of $k, \ell = 1, \dots, N$. This assumption will be used in the later steps. If the degeneracy is lifted, the basis states $|n^{(0)}; k\rangle$ that make δH diagonal in \mathbb{V}_N are called “good states” or a “good basis”. This means that they are the basis states in \mathbb{V}_N that get deformed continuously as λ becomes non-zero. If the degeneracy is not lifted to first order the determination of the good basis has to be attempted to second order.

2. The perturbation δH is diagonalized in the subspace \mathbb{V}_N . The perturbation δH is *not* diagonal on the whole space \mathcal{H} , only within the block representing \mathbb{V}_N is δH a diagonal matrix. Alternatively we can see this via the action of δH on the basis states. Introducing a resolution of the identity, we have

$$\begin{aligned} \delta H | n^{(0)}; \ell \rangle &= \sum_q | n^{(0)}; q \rangle \langle n^{(0)}; q | \delta H | n^{(0)}; \ell \rangle + \sum_p | p^{(0)} \rangle \langle p^{(0)} | \delta H | n^{(0)}; \ell \rangle \\ &= \sum_q E_{n,\ell}^{(1)} \delta_{\ell,q} | n^{(0)}; q \rangle + \sum_p | p^{(0)} \rangle \langle p^{(0)} | \delta H | n^{(0)}; \ell \rangle \\ &= E_{n,\ell}^{(1)} | n^{(0)}; \ell \rangle + \sum_p | p^{(0)} \rangle \langle p^{(0)} | \delta H | n^{(0)}; \ell \rangle. \end{aligned} \quad (1.2.28)$$

This shows that the states $|n^{(0)}; \ell\rangle$ are *almost* δH eigenstates with eigenvalues equal to the first order energy corrections. The failure is an extra state along \hat{V} .

3. We can sometimes assess without computation that a certain basis in \mathbb{V}_N makes δH diagonal. Here is a rule: *the matrix δH is diagonal for a choice of basis in \mathbb{V}_N if there is a Hermitian operator K that commutes with δH for which the chosen basis vectors are K eigenstates with different eigenvalues.* This is quickly established. Consider two different basis states in \mathbb{V}_N : $|n^{(0)}; p\rangle$ and $|n^{(0)}; q\rangle$, with $p \neq q$. Assume these have K eigenvalues λ_p and λ_q , respectively. Since $[\delta H, K] = 0$:

$$0 = \langle n^{(0)}; p | [\delta H, K] | n^{(0)}; q \rangle = (\lambda_q - \lambda_p) \langle n^{(0)}; p | \delta H | n^{(0)}; q \rangle. \quad (1.2.29)$$

Since the eigenvalues λ_p and λ_q are presumed to be different, the non-diagonal matrix elements of δH vanish.

Step 2. The $\mathcal{O}(\lambda)$ equation cannot determine the component of $|n^{(1)}; k\rangle$ along \mathbb{V}_N . As we will see later, such piece is required by consistency and gets determined from the $\mathcal{O}(\lambda^2)$ equation. We now determine the piece of $|n^{(1)}; k\rangle$ along \hat{V} . For this we hit the $\mathcal{O}(\lambda)$ equation with $\langle p^{(0)} |$ to find

$$\langle p^{(0)} | (H^{(0)} - E_n^{(0)}) | n^{(1)}; k \rangle = \langle p^{(0)} | \left(\cancel{E_{n,k}^{(1)}} - \delta H \right) | n^{(0)}; k \rangle \quad (1.2.30)$$

and we get

$$(E_p^{(0)} - E_n^{(0)}) \langle p^{(0)} | n^{(1)}; k \rangle = -\delta H_{p,nk}, \quad (1.2.31)$$

where we introduced the matrix element $\delta H_{p,nk} \equiv \langle p^{(0)} | \delta H | n^{(0)}; k \rangle$. Our equation above means that the piece of $|n^{(1)}; k\rangle$ in \hat{V} is now determined:

$$|n^{(1)}; k\rangle = - \sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} |p^{(0)}\rangle + |n^{(1)}; k\rangle \Big|_{\mathbb{V}_N}, \quad (1.2.32)$$

where we included explicitly the still undetermined piece of $|n^{(1)}; k\rangle$ along \mathbb{V}_N .

Step 3. We now hit we hit the $\mathcal{O}(\lambda^2)$ equation with $\langle n^{(0)}; \ell |$. The left-hand side vanishes and using the above expression for $|n^{(1)}; k\rangle$ we find

$$\begin{aligned} 0 = & - \langle n^{(0)}; \ell | (E_{n,k}^{(1)} - \delta H) \sum_p |p^{(0)}\rangle \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} \\ & + \langle n^{(0)}; \ell | (E_{n,k}^{(1)} - \delta H) | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N} + E_{n,k}^{(2)} \delta_{k,\ell}. \end{aligned} \quad (1.2.33)$$

In the first term on the right-hand side, the part proportional to $E_{n,k}^{(1)}$ vanishes by orthonormality. On the second line, the term including δH can be simplified because δH is diagonal within \mathbb{V}_N . Recalling (1.2.28) we have

$$\langle n^{(0)}; \ell | \delta H = E_{n,\ell}^{(1)} \langle n^{(0)}; \ell | + \sum_p \langle n^{(0)}; \ell | \delta H | p^{(0)} \rangle \langle p^{(0)} |. \quad (1.2.34)$$

The piece in \hat{V} vector drops out for our case of interest:

$$\langle n^{(0)}; \ell | \delta H | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N} = E_{n,\ell}^{(1)} \langle n^{(0)}; \ell | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N}. \quad (1.2.35)$$

Back into equation (1.2.33) we now get

$$\sum_p \frac{\delta H_{n\ell,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} + \left(E_{n,k}^{(1)} - E_{n,\ell}^{(1)} \right) \langle n^{(0)}; \ell | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N} + E_{n,k}^{(2)} \delta_{k,\ell} = 0. \quad (1.2.36)$$

Setting $\ell = k$ we can determine the second correction to the energies:

$$E_{n,k}^{(2)} = - \sum_p \frac{|\delta H_{p,nk}|^2}{E_p^{(0)} - E_n^{(0)}}. \quad (1.2.37)$$

For $k \neq \ell$ we get

$$\sum_p \frac{\delta H_{n\ell,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} + \left(E_{n,k}^{(1)} - E_{n,\ell}^{(1)} \right) \langle n^{(0)}; \ell | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N} = 0. \quad (1.2.38)$$

Had we not included the piece of $|n^{(1)}; k\rangle$ along the degenerate subspace we would have had an inconsistency, since there is no reason why the first term on the left-hand side must be zero. Now the above equation just fixes the components of $|n^{(1)}; k\rangle$ in the degenerate subspace *as long as* $E_{n,k}^{(1)} \neq E_{n,\ell}^{(1)}$:

$$\langle n^{(0)}; \ell | n^{(1)}; k \rangle \Big|_{\mathbb{V}_N} = - \frac{1}{E_{n,k}^{(1)} - E_{n,\ell}^{(1)}} \sum_p \frac{\delta H_{n\ell,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}, \quad k \neq \ell. \quad (1.2.39)$$

We thus have

$$|n^{(1)}; k\rangle \Big|_{\mathbb{V}_N} = - \sum_{\ell \neq k} |n^{(0)}; \ell\rangle \frac{1}{E_{n,k}^{(1)} - E_{n,\ell}^{(1)}} \sum_p \frac{\delta H_{n\ell,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}. \quad (1.2.40)$$

It may seem that this extra piece, found by using the $\mathcal{O}(\lambda^2)$ equation, is higher order than it should in the perturbation: its numerator contains two powers of δH . But this expression also has a curious energy denominator, $E_{n,k}^{(1)} - E_{n,\ell}^{(1)}$, in which each term has a power of δH . All in all, the correction to the state is properly first order in δH .

Summarizing our result we have

Degenerate perturbation theory with degeneracies lifted at $\mathcal{O}(\lambda)$:

$$\begin{aligned} |n; k\rangle_\lambda &= |n^{(0)}; k\rangle - \lambda \left(\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} |p^{(0)}\rangle + \sum_{\ell \neq k} \frac{|n^{(0)}; \ell\rangle}{E_{n,k}^{(1)} - E_{n,\ell}^{(1)}} \sum_p \frac{\delta H_{n\ell,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} \right) + \mathcal{O}(\lambda^2) \\ E_{n,k}(\lambda) &= E_n^{(0)} + \lambda \delta H_{nk,nk} - \lambda^2 \sum_p \frac{\delta H_{nk,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} + \mathcal{O}(\lambda^3), \quad E_{n,k}^{(1)} = \delta H_{nk,nk}. \end{aligned} \quad (1.2.41)$$

1.2.3 Degeneracy lifted at second order

We now investigate the case when the degeneracy is completely unbroken to first order. The situation and the setup is similar to the one we just considered: we have a degenerate subspace \mathbb{V}_N of dimension N and the rest of the space is called \hat{V} . This time, however, we will assume that the degeneracy of $H^{(0)}$ is not broken to first order in the perturbation δH . Concretely, this means that on the \mathbb{V}_N basis $|n^{(0)}; k\rangle$ with $k = 1, \dots, N$, we have

$$\langle n^{(0)}; \ell | \delta H | n^{(0)}; k \rangle = E_n^{(1)} \delta_{\ell, k}. \quad (1.2.42)$$

The first order energy correction is the same, and equal to $E_n^{(1)}$, for all basis states in \mathbb{V}_N . You should compare with (1.2.24), where the energy had an extra subscript to distinguish its various possible values.

Because the degeneracy is not broken to first order we do not know at this point what is the good basis in \mathbb{V}_N . We will consider here the case when the degeneracy is completely lifted to second order. We express our ignorance about good basis vectors by stating that we are searching for the right linear combinations:

$$|\psi^{(0)}\rangle = \sum_{k=1}^N |n^{(0)}; k\rangle a_k^{(0)}. \quad (1.2.43)$$

For some values of the constants $a_k^{(0)}$ with $k = 1, \dots, N$ the state $|\psi^{(0)}\rangle$ will be good. We can think of $a^{(0)}$ as the column vector representation of $|\psi^{(0)}\rangle$ in \mathbb{V}_N . We have written just one state, $|\psi^{(0)}\rangle$, even though we are expecting to find N good states to span the degenerate subspace. We therefore adjust the notation to reflect this. We introduce a new index $I = 1, \dots, N$ and write

$$|\psi_I^{(0)}\rangle = \sum_{k=1}^N |n^{(0)}; k\rangle a_{Ik}^{(0)}, \quad I = 1, \dots, N. \quad (1.2.44)$$

The index I now labels the different good states and their different vector representations $a_I^{(0)}$. Our most immediate goal is to find those vectors $a_I^{(0)}$ and thus the good basis. To do so we will have to consider second order energy corrections. The states $|\psi_I^{(0)}\rangle$ form an orthonormal basis in \mathbb{V}_N if the coefficients $a_I^{(0)}$ satisfy

$$\langle \psi_J^{(0)} | \psi_I^{(0)} \rangle = \delta_{IJ} \quad \rightarrow \quad \sum_k (a_{Jk}^{(0)})^* a_{Ik}^{(0)} = \delta_{IJ}. \quad (1.2.45)$$

We set up the perturbation theory as usual

$$\begin{aligned} |\psi_I\rangle_\lambda &= |\psi_I^{(0)}\rangle + \lambda |\psi_I^{(1)}\rangle + \lambda^2 |\psi_I^{(2)}\rangle + \dots, \\ E_{nI}(\lambda) &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_{nI}^{(2)} + \lambda^3 E_{nI}^{(3)} + \dots \end{aligned} \quad (1.2.46)$$

Note that in the energy expansion we have accounted for the degeneracy to zeroth and first order: the index I first appears in the second-order corrections to the energy. Using the Schrödinger equation

$$H(\lambda)|\psi_I\rangle_\lambda = E_{nI}(\lambda)|\psi_I\rangle_\lambda, \quad (1.2.47)$$

gives the by now familiar equations, of which we list the first four:

$$\begin{aligned} \lambda^0 : \quad & (H^{(0)} - E_n^{(0)})|\psi_I^{(0)}\rangle = 0, \\ \lambda^1 : \quad & (H^{(0)} - E_n^{(0)})|\psi_I^{(1)}\rangle = (E_n^{(1)} - \delta H)|\psi_I^{(0)}\rangle, \\ \lambda^2 : \quad & (H^{(0)} - E_n^{(0)})|\psi_I^{(2)}\rangle = (E_n^{(1)} - \delta H)|\psi_I^{(1)}\rangle + E_{nI}^{(2)}|\psi_I^{(0)}\rangle, \\ \lambda^3 : \quad & (H^{(0)} - E_n^{(0)})|\psi_I^{(3)}\rangle = (E_n^{(1)} - \delta H)|\psi_I^{(2)}\rangle + E_{nI}^{(2)}|\psi_I^{(1)}\rangle + E_{nI}^{(3)}|\psi_I^{(0)}\rangle. \end{aligned} \quad (1.2.48)$$

The zero-th order equation is trivially satisfied. For the order λ equation the overlap with $\langle n^{(0)}; \ell |$ works out automatically, without giving any new information. Indeed, the left-hand side vanishes and we thus get

$$0 = \langle n^{(0)}; \ell | (E_n^{(1)} - \delta H) |\psi_I^{(0)}\rangle. \quad (1.2.49)$$

Since $\langle n^{(0)}; \ell |$ is a δH eigenstate with eigenvalue $E_n^{(1)}$, up to a vector in \hat{V} (see (1.2.34)), the above right-hand side vanishes. Acting on the order λ equation with $\langle p^{(0)} |$ gives useful information:

$$(E_p^{(0)} - E_n^{(0)})\langle p^{(0)} | \psi_I^{(1)} \rangle = \langle p^{(0)} | (E_n^{(1)} - \delta H) |\psi_I^{(0)}\rangle = -\langle p^{(0)} | \delta H |\psi_I^{(0)}\rangle, \quad (1.2.50)$$

using the orthogonality of \hat{V} and \mathbb{V}_N . Letting

$$\delta H_{pI} \equiv \langle p^{(0)} | \delta H |\psi_I^{(0)}\rangle, \quad (1.2.51)$$

we then have

$$\langle p^{(0)} | \psi_I^{(1)} \rangle = -\frac{\delta H_{pI}}{E_p^{(0)} - E_n^{(0)}}. \quad (1.2.52)$$

Since the ket $|\psi_I^{(0)}\rangle$ is still undetermined, it makes sense to write this information about $|\psi_I^{(1)}\rangle$ in terms of the unknown $a_I^{(0)}$ coefficients. We have

$$\delta H_{pI} \equiv \sum_{k=1}^N \langle p^{(0)} | \delta H | n^{(0)}; k \rangle a_{Ik}^{(0)} = \sum_{k=1}^N \delta H_{p,nk} a_{Ik}^{(0)}, \quad (1.2.53)$$

Back into (1.2.52) we get

$$\langle p^{(0)} | \psi_I^{(1)} \rangle = -\frac{1}{E_p^{(0)} - E_n^{(0)}} \sum_{k=1}^N \delta H_{p,nk} a_{Ik}^{(0)}. \quad (1.2.54)$$

This gives the piece of $|\psi_I^{(1)}\rangle$ in \hat{V} in terms of the unknown zeroth order eigenstates.

We have now extracted all the information from the order λ equation. We look now at the order λ^2 equation, which contains the second order corrections to the energy and therefore should help us determine the zeroth order good states. We hit that equation with $\langle n^{(0)}; \ell |$ and we get

$$0 = \langle n^{(0)}; \ell | (E_n^{(1)} - \delta H) |\psi_I^{(1)}\rangle \Big|_{\hat{V}} + \langle n^{(0)}; \ell | (E_n^{(1)} - \delta H) |\psi_I^{(1)}\rangle \Big|_{\mathbb{V}_N} + E_{nI}^{(2)} a_{I\ell}^{(0)}. \quad (1.2.55)$$

Happily, the second term, involving the components of $|\psi_I^{(1)}\rangle$ along \mathbb{V}_N , vanishes because of the by now familiar property (1.2.28) adapted to this case. The piece with $E_n^{(1)}$ on the first term also vanishes. We are thus left with

$$0 = -\langle n^{(0)}; \ell | \delta H |\psi_I^{(1)}\rangle \Big|_{\hat{V}} + E_{nI}^{(2)} a_{I\ell}^{(0)}. \quad (1.2.56)$$

Introducing a resolution of the identity to the immediate right of δH , only the basis states in \hat{V} contribute and we get

$$0 = -\sum_p \langle n^{(0)}; \ell | \delta H | p^{(0)} \rangle \langle p^{(0)} | \psi_I^{(1)} \rangle + E_{nI}^{(2)} a_{I\ell}^{(0)}, \quad (1.2.57)$$

where there is no need to copy the $|\hat{V}$ anymore. Using the result in (1.2.54) we now get

$$0 = \sum_p \delta H_{nl,p} \frac{1}{E_p^{(0)} - E_n^{(0)}} \sum_{k=1}^N \delta H_{p,nk} a_{Ik}^{(0)} + \sum_{k=1}^N E_{nI}^{(2)} \delta_{\ell k} a_{Ik}^{(0)} \quad (1.2.58)$$

Reordering sums and multiplying by minus one we get

$$\sum_{k=1}^N \left(-\sum_p \frac{\delta H_{nl,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} - E_{nI}^{(2)} \delta_{\ell k} \right) a_{Ik}^{(0)} = 0. \quad (1.2.59)$$

To understand better this equation we define the $N \times N$ Hermitian matrix $M^{(2)}$

$$M_{\ell,k}^{(2)} \equiv -\sum_p \frac{\delta H_{nl,p} \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}. \quad (1.2.60)$$

The equation then becomes

$$\sum_{k=1}^N \left(M_{\ell,k}^{(2)} - E_{nI}^{(2)} \delta_{\ell k} \right) a_{Ik}^{(0)} = 0. \quad (1.2.61)$$

Recalling that the Kronecker delta is the matrix representation of the identity, we have

$$\left(M^{(2)} - E_{nI}^{(2)} \mathbb{1} \right) a_I^{(0)} = 0. \quad (1.2.62)$$

This is an eigenvalue equation that tells us that the energy corrections $E_n^{(2)}$ are the eigenvalues of $M^{(2)}$ and the vectors $a_I^{(0)}$ are the associated normalized eigenvectors. These determine, via (1.2.44), our orthonormal basis of good zeroth order states. If δH is known, the matrix $M^{(2)}$ is computable and Hermitian and can therefore be diagonalized.

We will leave the computation of the component of $|\psi_I^{(1)}\rangle$ on the degenerate subspace. That can be done if the degeneracy is completely broken to quadratic order (the eigenvalues of $M^{(2)}$ are all different). Still, it takes some effort and one must use the order λ^3 equation. Our results so far are

$$|\psi_I\rangle_\lambda = |\psi_I^{(0)}\rangle + \lambda \left(\sum_p |p^{(0)}\rangle \frac{\delta H_{pI}}{E_n^{(0)} - E_p^{(0)}} + \sum_{J \neq I} |\psi_J^{(0)}\rangle a_{I,J}^{(1)} \right) + \mathcal{O}(\lambda^2), \quad (1.2.63)$$

$$E_{In}(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_{In}^{(2)} + \lambda^3 E_{In}^{(3)} + \dots \mathcal{O}(\lambda^3).$$

Here the $a_{I,J}^{(1)}$ are still unknown coefficients that determine the component of the first correction to the states along the degenerate subspace. If you followed the discussion, all other symbols in the above equations have been defined and are computable given δH .

The answer for the coefficients $a_{I,J}^{(1)}$ turns out to be

$$a_{I,J}^{(1)} = \frac{1}{E_n^{(2)} - E_{nJ}^{(2)}} \left[\sum_{p,q} \frac{\delta H_{Jp} \delta H_{pq} \delta H_{qI}}{(E_p^{(0)} - E_n^{(0)})(E_q^{(0)} - E_n^{(0)})} - E_n^{(1)} \sum_p \frac{\delta H_{Jp} \delta H_{pI}}{(E_p^{(0)} - E_n^{(0)})^2} \right]. \quad (1.2.64)$$

The third order corrections to the energy are

$$E_{In}^{(3)} = \sum_{p,q} \frac{\delta H_{Ip} \delta H_{pq} \delta H_{qI}}{(E_p^{(0)} - E_n^{(0)})(E_q^{(0)} - E_n^{(0)})} - E_n^{(1)} \sum_p \frac{|\delta H_{pI}|^2}{(E_p^{(0)} - E_n^{(0)})^2}. \quad (1.2.65)$$

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