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Time-Independent Perturbation Theory

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1 The central problem in time-independent perturbation theory:

Let H_0 be the unperturbed (a.k.a. 'background' or 'bare') Hamiltonian, whose eigenvalues and eigenvectors are known. Let $E_n^{(0)}$ be the n^{th} unperturbed energy eigenvalue, and $|n^{(0)}\rangle$ be the n^{th} unperturbed energy eigenstate. They satisfy

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \tag{1}$$

and

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

Let V be a Hermitian operator which 'perturbs' the system, such that the full Hamiltonian is

$$H = H_0 + V. \tag{3}$$

The standard approach is to instead solve

$$H = H_0 + \lambda V, \tag{4}$$

and use λ as for book-keeping during the calculation, but set $\lambda = 1$ at the end of the calculation.

The goal is to find the eigenvalues and eigenvectors of the full Hamiltonian (4). Let E_n and $|n\rangle$ be the n^{th} eigenvalue of the full Hamiltonian, and its corresponding eigenstate, respectively. They satisfy

$$H|n\rangle = E_n|n\rangle \tag{5}$$

and

$$\langle n|n\rangle = 1. \tag{6}$$

Because λ is a small parameter, it is assumed that accurate results can be obtained by expanding E_n and $|n\rangle$ in powers of λ, and keeping only the leading term(s). Formally expanding the perturbed quantities gives

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots, \tag{7}$$

and

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots, \tag{8}$$

where $E_n^{(j)}$ and $|n^{(j)}\rangle$ are yet-to-be determined expansion coefficients Inserting these expansions into the eigenvalue equation (5) then gives

$$(H_0+\lambda V)(|n^{(0)}\rangle+\lambda|n^{(1)}\rangle+\lambda^2|n^{(2)}\rangle+\ldots.) = (E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\ldots)(|n^{(0)}\rangle+\lambda|n^{(1)}\rangle+\lambda^2|n^{(2)}\rangle+\ldots.). \tag{9}$$

Because of the linear independence of terms in a power series, this equation can only be satisfied for arbitrary λ if all terms with the same power of λ cancel independently. Equating powers of λ thus gives

$$\lambda^0 : \qquad H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle, \tag{10}$$
$$\lambda^1 : \qquad (H_0 - E_n^{(0)})|n^{(1)}\rangle = -\,V|n^{(0)}\rangle + E_n^{(1)}|n^{(0)}\rangle \tag{11}$$
$$\lambda^2 : \qquad (H_0 - E_n^{(0)})|n^{(2)}\rangle = -V|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle + E_n^{(1)}|n^{(1)}\rangle \tag{12}$$
$$\text{etc} \ldots \tag{13}$$

This generalizes to

$$\lambda^j : \qquad (H_0 - E_n^{(0)})|n^{(j)}\rangle = -V|n^{(j-1)}\rangle + \sum_{k=1}^{j} E_n^{(k)}|n^{(j-k)}\rangle. \tag{14}$$

Similiarly, we can expand the normalization equation in powers of λ, giving

$$1 = \langle n^{(0)}|n^{(0)}\rangle + \lambda(\langle n^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n^{(1)}\rangle) + \lambda^2(\langle n^{(2)}|n^{(0)}\rangle + \langle n^{(1)}|n^{(1)}\rangle + \langle n^{(0)}|n^{(2)}\rangle) + \ldots. \tag{15}$$

Again, we require that all terms of the same power in λ cancel independently, resulting in the set of equations:

$$\lambda^0 : \qquad \langle n^{(0)}|n^{(0)}\rangle = 1, \tag{16}$$
$$\lambda^1 : \qquad \langle n^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n^{(1)}\rangle = 0, \tag{17}$$
$$\lambda^2 : \qquad \langle n^{(2)}|n^{(0)}\rangle + \langle n^{(1)}|n^{(1)}\rangle + \langle n^{(0)}|n^{(2)}\rangle, \tag{18}$$

which readily generalizes to

$$\lambda^j : \qquad \sum_{k=0}^{j} \langle n^{(j-k)}|n^{(k)}\rangle = 0. \tag{19}$$

Solving these equations can be simplified by choosing a convenient global phase-factor. In this case, we can choose the phase of the full eigenstates to be such that $\langle n^{(0)}|n\rangle$ is real-valued. To enforce our choice of global phase, we can expand $\langle n^{(0)}|n\rangle$ in power series, giving

$$\langle n^{(0)}|n\rangle = 1 + \lambda\langle n^{(0)}|n^{(1)}\rangle + \lambda^2\langle n^{(0)}|n^{(2)}\rangle + \ldots. \tag{20}$$

Requiring that the r.h.s. be real-values for any real-valued λ requires that each term be independently real-valued, so that

$$\langle n^{(0)}|n^{(j)}\rangle = \langle n^{(j)}|n^{(0)}\rangle. \tag{21}$$

2 The non-degenerate case

We will now describe how to solve these equations in the case where none of the unperturbed energy levels are degenerate.

Step #1: To obtain the j^{th} correction to the n^{th} energy eigenvalue, simply hit the λ^j equation from the left with the bra $\langle n^{(0)}|$ and solve for $E_n^{(j)}$, giving

$$E_n^{(j)} = \langle n^{(0)}|V|n^{(j-1)}\rangle - \sum_{k=1}^{j-1} E_n^{(k)} \langle n^{(0)}|n^{(j-k)}\rangle, \tag{22}$$

where we have used $\langle n^{(0)}|(H_0 - E_n^{(0)}) = 0$ and $\langle n^{(0)}|n^{(0)}\rangle = 1$. Note that all quantities on the r.h.s are of order $< j$, and are thus presumed to be known.

Step #2: To obtain the j^{th} correction to the n^{th} eigenstate, we hit both sides of the λ^j equation with the bra $\langle m^{(0)}|$ where $m \neq n$. This gives

$$\langle m^{(0)}|n^{(j)}\rangle = -\frac{\langle m^{(0)}|V|n^{(j-1)}\rangle}{E_m^{(0)} - E_n^{(0)}} + \sum_{k=1}^{j-1} \frac{E_n^{(k)} \langle m^{(0)}|n^{(j-k)}\rangle}{E_m^{(0)} - E_n^{(0)}}, \tag{23}$$

which is the expansion coefficient of the j^{th} correction onto the m^{th} bare eigenvector.

Step #3: To obtain the remaining unknown quantity, $\langle n^{(0)}|n^{(j)}\rangle$, we simply solve the normalization equation, giving

$$\langle n^{(0)}|n^{(j)}\rangle = -\frac{1}{2} \sum_{k=1}^{j-1} \langle n^{(j-k)}|n^{(k)}\rangle. \tag{24}$$

Steps **1**, **2**, and **3** must be solved iteratively, starting with $j = 1$, and repeating for each order until the desired accuracy is achieved.

Final Step: Once these quantities are computed, we can reconstruct the n^{th} eigenvalue and eigenvector via

$$\begin{aligned} E_n &= \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \\ &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots, \end{aligned} \tag{25}$$

and

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle \sum_{j=0}^{\infty} \langle n^{(0)}|n^{(j)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \sum_{j=0}^{\infty} \langle m^{(0)}|n^{(j)}\rangle \\ &= |n^{(0)}\rangle \left[1 + \lambda \langle n^{(0)}|n^{(1)}\rangle + \lambda^2 \langle n^{(0)}|n^{(2)}\rangle + \ldots\right] + \sum_{m \neq n} |m^{(0)}\rangle \left[\lambda \langle m^{(0)}|n^{(1)}\rangle + \lambda^2 \langle m^{(0)}|n^{(2)}\rangle + \ldots\right]. \end{aligned} \tag{26}$$

2.1 First-order terms:

Introducing a more compact notation via

$$V_{mn} = \langle m^{(0)}|V|n^{(0)}\rangle. \tag{27}$$

and

$$E_{mn} := E_m^{(0)} - E_n^{(0)}, \tag{28}$$

we can compute the first-order terms from Eqs. (22), (23), and (24) with $j = 1$, yielding

$$E_n^{(1)} = V_{nn}, \tag{29}$$

$$\langle m^{(0)}|n^{(1)}\rangle = -\frac{V_{mn}}{E_{mn}}, \tag{30}$$

and

$$\langle n^{(0)}|n^{(1)}\rangle = 0. \tag{31}$$

2.2 Second-order terms:

By setting $j = 2$, and inserting the first-order solutions, eqs (22), (23), and (24) give us

$$\begin{aligned} E_n^{(2)} &= \langle n^{(0)}|V|n^{(1)}\rangle \\ &= -\sum_{m\neq 0} \frac{|V_{mn}|^2}{E_{mn}}, \end{aligned} \tag{32}$$

$$\begin{aligned} \langle m^{(0)}|n^{(2)}\rangle &= -\frac{\langle m^{(0)}|V|n^{(1)}\rangle}{E_{mn}} - \frac{V_{nn}V_{mn}}{E_{mn}^2} \\ &= \sum_{m'\neq n} \frac{V_{mm'}V_{m'n}}{E_{mn}E_{m'n}} - \frac{V_{mn}V_{nn}}{E_{mn}^2} \end{aligned} \tag{33}$$

and

$$\begin{aligned} \langle n^{(0)}|n^{(2)}\rangle &= -\frac{1}{2}\langle n^{(1)}|n^{(1)}\rangle \\ &= -\frac{1}{2}\sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}^2} \end{aligned} \tag{34}$$

2.3 Eigenvectors and eigenvalues to second-order:

Putting the first- and second-order terms together then gives the results

$$E_n = E_n^{(0)} + \lambda V_{nn} - \lambda^2 \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}} + O(\lambda^3), \tag{35}$$

and

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle \left[1 - \frac{\lambda^2}{2} \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}^2} + O(\lambda^3) \right] \\ &+ \sum_{m \neq n} |m^{(0)}\rangle \left[-\lambda \frac{V_{mn}}{E_{mn}} + \lambda^2 \left(\sum_{m' \neq n} \frac{V_{mm'} V_{m'n}}{E_{mn} E_{m'n}} - \frac{V_{mn} V_{nn}}{E_{mn}^2} \right) + O(\lambda^3) \right]. \end{aligned} \tag{36}$$

Truncating the series, and setting $\lambda = 1$ then gives the approximations

$$E_n \approx E_n^{(0)} + V_{nn} - \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}}, \tag{37}$$

and

$$|n\rangle \approx |n^{(0)}\rangle \left[1 - \frac{1}{2} \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}^2} \right] + \sum_{m \neq n} |m^{(0)}\rangle \left[- \frac{V_{mn}}{E_{mn}} + \sum_{m' \neq n} \frac{V_{mm'} V_{m'n}}{E_{mn} E_{m'n}} - \frac{V_{mn} V_{nn}}{E_{mn}^2} \right]. \tag{38}$$

2.4 The second-order Hamiltonian

With these results, we can reconstruct the full-Hamiltonian in the unperturbed basis to second-order via

$$
\begin{aligned}
H &= H_0 + V \\
&= \sum_n E_n |n\rangle\langle n| \\
&\approx \sum_n \left(E_n^{(0)} + V_{nn} - \sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}} \right) \\
&\times \left[|n^{(0)}\rangle \left(1 - \frac{1}{2} \sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}^2} \right) + \sum_{m\neq n} |m^{(0)}\rangle \left(-\frac{V_{mn}}{E_{mn}} + \sum_{m'\neq n} \frac{V_{mm'}V_{m'n}}{E_{mn}E_{m'n}} - \frac{V_{mn}V_{nn}}{E_{mn}^2} \right) \right] \\
&\times \left[\left(1 - \frac{1}{2} \sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}^2} \right) \langle n^{(0)}| + \sum_{m\neq n} \left(-\frac{V_{nm}}{E_{mn}} + \sum_{m'\neq n} \frac{V_{nm'}V_{m'm}}{E_{mn}E_{m'n}} - \frac{V_{nn}V_{nm}}{E_{mn}^2} \right) \langle m^{(0)}| \right] \quad (39)
\end{aligned}
$$

Dropping all terms beyond second-order then gives

$$
\begin{aligned}
H &\approx \sum_n |n^{(0)}\rangle\langle n^{(0)}| \left[E_n^{(0)} + V_{nn} - \sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}} \left(1 + \frac{E_n^{(0)}}{E_{mn}} \right) \right] \\
&- \sum_n \sum_{m\neq n} |n^{(0)}\rangle\langle m^{(0)}| \left[\left(E_n^{(0)} + V_{nn} \right) \frac{V_{nm}}{E_{mn}} - \sum_{m'\neq n} \frac{E_n^{(0)} V_{nm'}V_{m'm}}{E_{mn}E_{m'n}} + \frac{E_n^{(0)} V_{nn}V_{nm}}{E_{mn}^2} \right] \\
&- \sum_n \sum_{m\neq n} |m^{(0)}\rangle\langle n^{(0)}| \left[\left(E_n^{(0)} + V_{nn} \right) \frac{V_{mn}}{E_{mn}} - \sum_{m'\neq n} \frac{E_n^{(0)} V_{mm'}V_{m'n}}{E_{mn}E_{m'n}} + \frac{E_n^{(0)} V_{mn}V_{nn}}{E_{mn}^2} \right] \\
&+ \sum_n \sum_{m\neq n} \sum_{m'\neq n} |m^{(0)}\rangle\langle m'^{(0)}| \left[\frac{E_n^{(0)} |V_{mn}|^2}{E_{mn}^2} \right]. \quad (40)
\end{aligned}
$$

With this Hamiltonian as the generator of the unitary time-propagator, we see how the perturbation will introduce dynamical coupling between the bare eigenstates, as described by the off-diagonal terms.

2.5 Examples

2-Level system: The first example we can consider is the two-level system. Here we have $H_0 = \delta S_z$ and $V = \Omega S_x$, so that

$$H = \delta S_z + \Omega S_x. \tag{41}$$

Here the Rabi-frequency Ω will take the place of the perturbation parameter λ. Let the ground state of H_0 be $|\downarrow\rangle$, with eigenvalue $E_\downarrow = -\hbar\delta/2$, and let the excited state be $|\uparrow\rangle$, with eigenvalue $E_\uparrow = \hbar\delta/2$, where clearly we have assumed $\delta > 0$. Let $|0\rangle$ be the ground state of the full Hamiltonian, with eigenvalue E_0 and let $|1\rangle$ be the excited state of the full Hamiltonian, with eigenvalue E_1. The zeroth order terms in the expansions of E_n and $|n\rangle$ are therefore $E_0^{(0)} = -\hbar\delta/2$, $E_1^{(0)} = \hbar\delta/2$, $|0^{(0)}\rangle = |\downarrow\rangle$ and $|1^{(0)}\rangle = |\uparrow\rangle$. Thus we have

$$H_0 = \frac{\hbar\delta}{2}(|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|) \tag{42}$$

and

$$V = \frac{\hbar}{2}(|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|). \tag{43}$$

To second-order in perturbation theory we then find the perturbed eigenvalues to be

$$\begin{aligned} E_0 &= E_\downarrow + \Omega V_{\downarrow\downarrow} - \Omega^2 \frac{|V_{\uparrow\downarrow}|^2}{E_{\uparrow\downarrow}} \\ &= \hbar\left[-\frac{\delta}{2} - \frac{\Omega^2}{4\delta} + O(\Omega^3)\right] \end{aligned} \tag{44}$$

and

$$\begin{aligned} E_1 &= E_\uparrow + \Omega V_{\uparrow\uparrow} - \Omega^2 \frac{|V_{\downarrow\uparrow}|^2}{E_{\downarrow\uparrow}} \\ &= \hbar\left[\frac{\delta}{2} + \frac{\Omega^2}{4\delta} + O(\Omega^3)\right] \end{aligned} \tag{45}$$

This clearly indicates the phenomena of level repulsion. Regardless of the sign of Ω, the leading-order effect of the perturbation is to push the energy levels apart.

For the perturbed eigenstates we find

$$\begin{aligned} |0\rangle &= |\downarrow\rangle\left(1 - \frac{\Omega^2}{2}\frac{|V_{\uparrow\downarrow}|^2}{E_{\uparrow\downarrow}^2} + O(\Omega^3)\right) + |\uparrow\rangle\left(-\Omega\frac{V_{\uparrow\downarrow}}{E_{\uparrow\downarrow}} + \Omega^2\left[\frac{V_{\uparrow\uparrow}V_{\uparrow\downarrow}}{E_{\uparrow\downarrow}E_{\uparrow\downarrow}} - \frac{V_{\uparrow\downarrow}V_{\downarrow\downarrow}}{E_{\uparrow\downarrow}^2}\right] + O(\Omega^3)\right) \\ &= |\downarrow\rangle\left(1 - \frac{\Omega^2}{8\delta^2} + O(\Omega^3)\right) - |\uparrow\rangle\left(\frac{\Omega}{2\delta} + O(\Omega^3)\right) \end{aligned} \tag{46}$$

and

$$\begin{aligned} |1\rangle &= |\uparrow\rangle\left(1 - \frac{\Omega^2}{2}\frac{|V_{\downarrow\uparrow}|^2}{E_{\downarrow\uparrow}^2} + O(\Omega^3)\right) + |\downarrow\rangle\left(-\Omega\frac{V_{\downarrow\uparrow}}{E_{\downarrow\uparrow}} + \Omega^2\left[\frac{V_{\downarrow\downarrow}V_{\downarrow\uparrow}}{E_{\downarrow\uparrow}E_{\downarrow\uparrow}} - \frac{V_{\downarrow\uparrow}V_{\uparrow\uparrow}}{E_{\downarrow\uparrow}^2}\right] + O(\Omega^3)\right) \\ &= |\uparrow\rangle\left(1 - \frac{\Omega^2}{8\delta^2} + O(\Omega^3)\right) + |\downarrow\rangle\left(\frac{\Omega}{2\delta} + O(\Omega^2)\right). \end{aligned} \tag{47}$$

Computing the normalization gives

$$\langle 0|0\rangle = \left(1 - \frac{\Omega^2}{8\delta^2} + O(\Omega^3)\right)^2 + \left(\frac{\Omega}{2\delta} + O(\Omega^3)\right)^2 = 1 + O(\Omega^3) \tag{48}$$

and

$$\langle 1|1\rangle = \left(1 - \frac{\Omega^2}{8\delta^2} + O(\Omega^3)\right)^2 + \left(\frac{\Omega}{2\delta} + O(\Omega^3)\right)^2 = 1 + O(\Omega^3), \tag{49}$$

which verifies that the state is properly normalized, so that no re-normalization is required. Checking orthogonality gives

$$\langle 0|1\rangle = \left(1 - \frac{\Omega^2}{8\delta^2} + O(\Omega^3)\right)\left(\frac{\Omega}{2\delta} + O(\Omega^3)\right) - \left(\frac{\Omega}{2\delta} + O(\Omega^3)\right)\left(1 - \frac{\Omega^3}{8\delta^2} + O(\Omega^3)\right) = 0. \tag{50}$$

Square well with delta-function For the second example we consider an infinite square-well potential as the unperturbed problem, and we perturb it by placing a delta-function potential at the center. Our goal will be to compute the energy shifts to second order and the perturbed eigenstates to first order. We will attempt to explicitly evaluate all sums for the ground state only. The unperturbed Hamiltonian is

$$H_0 = \frac{P^2}{2M} + U(X), \tag{51}$$

where

$$U(x) = \begin{cases} 0: & 0 < x < L \\ \infty: & \text{else} \end{cases} \tag{52}$$

The form of the perturbation is

$$V(X) = \frac{\hbar^2}{ML}\delta(X - \frac{L}{2}), \tag{53}$$

so that the full Hamiltonian is

$$H = H_0 + \lambda V = \frac{P^2}{2M} + U(X) + \lambda\frac{\hbar^2}{ML}\delta(X - \frac{L}{2}). \tag{54}$$

The unperturbed energy levels are given by

$$E_n^{(0)} = \frac{\hbar^2\pi^2}{2ML^2}n^2; \qquad n = 1, 2, 3, \ldots, \tag{55}$$

with corresponding unperturbed wavefunctions

$$\phi_n(x) \equiv \langle x|n^{(0)}\rangle = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n}{L}x\right). \tag{56}$$

The first order energy shift is given by $E_n^{(1)} = V_{nn}$, where $V_{nn} \equiv \langle n^{(0)}|V|n^{(0)}\rangle$. Inserting the projector onto position eigenstates gives

$$V_{nn} = \int dx\, \phi_n^*(x)V(x)\phi_n(x) = \frac{2\hbar^2}{ML^2}\int dx\, \sin^2\left(\frac{n\pi}{L}x\right)\delta(x - \frac{L}{2}) = \begin{cases} \frac{2\hbar^2}{ML^2}; & n \text{ odd} \\ 0; & n \text{ even} \end{cases}. \tag{57}$$

The matrix element vanishes for even n because these wavefunctions have a node at $x = L/2.$, the odd n wavefunctions have an anti-node at $x = L/2$, so that the sin-function takes on its maximum value of unity.

The first order correction to the wavefunction is given by the usual expression $|n^{(1)}\rangle = -\sum_{m\neq n}|m^{(0)}\rangle\frac{V_{mn}}{E_{mn}}$. Thus we must evaluate the off-diagonal matrix elements, giving

$$V_{mn} = \frac{2\hbar^2}{ML^2}\int dx\, \sin\left(\frac{m\pi}{L}x\right)\delta(x - \frac{L}{2})\sin\left(\frac{n\pi}{L}x\right) = \begin{cases} -(-1)^{\frac{m+n}{2}}\frac{2\hbar^2}{ML^2}: & m \text{ and } n \text{ odd} \\ 0; & m \text{ and/or } n \text{ even} \end{cases}. \tag{58}$$

The energy denominator is $E_{mn} = E_m^{(0)} - E_n^{(0)} = \frac{\hbar^2\pi^2}{2ML^2}(m^2 - n^2)$. The perturbed wavefunction to first order is defined as $\psi_n(x) \equiv \langle x|n^{(0)}\rangle + \lambda\langle x|n^{(1)}\rangle$, giving

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) + \frac{4\lambda}{\pi^2}\sqrt{\frac{2}{L}}\sum_{\substack{m,n=1 \\ m\neq n}}^{\infty}\sin\left(\frac{(2m-1)\pi}{L}x\right)\frac{(-1)^{m+n-1}}{(2m-1)^2 - (2n-1)^2}. \tag{59}$$

In fact, this sum can be performed analytically, although the result is not very illuminating. Computing the first-order perturbed ground-state ($n = 1$) wavefunction, for example, gives

$$\psi_1(x) \approx \sqrt{\frac{2}{L}}\left(1 - \frac{\lambda}{\pi^2}\right)\sin(\pi x/L) + \frac{2\lambda}{\pi L}\left(x - Lu(x - L/2)\right)\sqrt{\frac{2}{L}}\cos(\pi x/L), \tag{60}$$

where $u(x)$ is the unit step function. The discontinuous derivative at $x = L/2$ is characteristic of eigenstates with delta-potentials.

The second order correction to the energy-shift is computed from $E_n^{(2)} = -\sum_{m\neq n} \frac{|V_{mn}|^2}{E_{mn}}$, which yields

$$E_n^{(2)} = -\frac{8\hbar^2}{\pi^2 ML^2}\sum_{\substack{m,n=1\\ m\neq n}}^{\infty}\frac{1}{(2m-1)^2 - (2n-1)^2}. \tag{61}$$

Here the sum can be computed exactly, giving

$$E_n^{(2)} = -\frac{2\hbar^2}{\pi^2 ML^2}\frac{1}{n^2}. \tag{62}$$

The resulting energy eigenvalue accurate to second order is

$$E_n \approx \frac{\hbar^2\pi^2}{2ML^2}n^2 + \lambda\frac{\hbar^2}{ML^2} - \lambda^2\frac{2\hbar^2}{\pi^2 ML^2}\frac{1}{n^2}; \qquad n \text{ odd}, \tag{63}$$

and

$$E_n = \frac{\hbar^2\pi^2}{2ML^2}n^2; \qquad n \text{ even}. \tag{64}$$

3 The degenerate case

We now consider the case where some, but not all, of the unperturbed eigenvalues are the same. In this situation, the non-degenerate formulas (22), (23), and (24) cannot be used because the E_{mn} terms in the denominator go to zero when levels m and n are degenerate. Our goal is still to find the eigenvalues and eigenstates of the full Hamiltonian

$$H = H_0 + V, \tag{65}$$

where the bare eigenstates of H_0 are now given two quantum numbers, one which labels the energy level, and the other which takes into account the degeneracy. Our bare basis is thus $\{|nm^{(0)}\rangle\}$, where m labels the degenerate sub-levels. They satisfy

$$H_0|nm^{(0)}\rangle = E_n^{(0)}|nm^{(0)}\rangle. \tag{66}$$

In the case of degeneracy, the choice of basis which satisfied (59) is not unique. Provided that the perturbation lifts the degeneracy, then a unique unperturbed basis is defined by

$$|nm^{(0)}\rangle = \lim_{\lambda\to 0} |nm\rangle. \tag{67}$$

To see why this defines a unique basis, let's look at a very simple example. Consider a two-level Rabi system, governed by the bare Hamiltonian $H_0 = \delta S_z$ and the perturbation $V = S_x$. For the case $\delta = 0$, the eigenstates of H_0 become degenerate, so that for every complex number z, we can define a unique possible basis choice via

$$|1^{(0)}\rangle = \frac{z|\uparrow_z\rangle + |\downarrow_z\rangle}{\sqrt{1+|z|^2}}, \tag{68}$$

$$|2^{(0)}\rangle = \frac{|\uparrow_z\rangle - z^*|\downarrow_z\rangle}{\sqrt{1+|z|^2}}. \tag{69}$$

On the other hand, for any non-zero λ, the eigenstates of $H = H_0 + \lambda V$ are the S_x eigenstates, given by

$$|1\rangle = \frac{|\uparrow_z\rangle - |\downarrow_z\rangle}{\sqrt{2}}, \tag{70}$$

$$|2\rangle = \frac{|\uparrow_z\rangle + |\downarrow_z\rangle}{\sqrt{2}}. \tag{71}$$

Thus if we use $|1^{(0)}\rangle = \lim_{\lambda\to 0}|1\rangle = |1\rangle$, and $|2^{(0)}\rangle = \lim_{\lambda\to 0}|2\rangle = |2\rangle$, we have specified a unique bare basis.

In fact, the 'good' eigenstates will always be the eigenstates of V in the degenerate subspace. To prove this, we start by introducing the projector into the degenerate subspace, I_n, which clearly satisfies $I_n|nm^{(0)}\rangle = |nm^{(0)}\rangle$, $I_nH_0 = H_0I_n = I_nH_0I_n = E_n^{(0)}I_n$, and $I_n^2 = I_n$, while for $n' \neq n$, we have $I_n|n'm\rangle = \langle n'm|I_n = 0$. The energy eigenvalue equation is

$$(H_0 + \lambda V - E_{nm})|nm\rangle = 0. \tag{72}$$

Since $\lim_{\lambda\to 0}|nm\rangle = |nm^{(0)}\rangle$, we can therefore write

$$\lim_{\lambda\to 0}(H_0 + \lambda V - E_{nm})|nm^{(0)}\rangle = 0. \tag{73}$$

Hitting this equation from the left with I_n, and using $|nm^{(0)}\rangle = I_n|nm^{(0)}\rangle$ allows us to write the equation as

$$\lim_{\lambda\to 0}(\lambda I_n V I_n - (E_{nm} - E_n^{(0)}))I_n|nm^{(0)}\rangle = 0. \tag{74}$$

Introducing $V_n = I_n V I_n$, noting that $\lim_{\lambda\to 0}(E_{nm} - E_n^{(0)}) = \lim_{\lambda\to 0}\lambda E_{nm}^{(1)}$, and dividing both sides by λ before taking $\lambda \to 0$ gives

$$(V_n - E_{nm}^{(1)})|nm^{(0)}\rangle = 0, \tag{75}$$

which tells us that the correct bare eigenstates are the eigenstates of V_n, which satisfy $V_n|nm^{(0)}\rangle = v_{nm}|nm^{(0)}\rangle$. Furthermore, we see that the first-order energy shifts are just the corresponding eigenvalues, $E_{nm}^{(1)} = v_{nm}$.

At this point, there are two ways to proceed. The first is the straightforward method, we just take this 'good' basis and proceed with expanding the energy eigenvalue equation in powers of λ, and then solve the equations associated with each power. The other method is conceptually 'trickier', but allows us to map the degenerate problem onto the non-degenerate problem, and therefore use the previously derived results.

3.1 Approach #1

First, we will just approach the equations directly, one order at a time. The basic equation is now:

$$(H_0 - E_n^{(0)})|nm^{(j)}\rangle = -V|nm^{(j-1)}\rangle + \sum_{k=1}^{j} E_{nm}^{(k)}|nm^{(j-k)}\rangle, \tag{76}$$

which together with the normalization constraint:

$$\langle nm^{(0)}|nm^{(j)}\rangle = -\frac{1}{2}\sum_{k=1}^{j-1}\langle nm^{(k)}|nm^{(j-k)}\rangle \tag{77}$$

and the 'good basis' condition:

$$\langle nm'^{(0)}|V|nm^{(0)}\rangle = v_{nm}\delta_{m'm}, \tag{78}$$

allow us to compute the perturbed eigenstates and eigenvectors, defined via

$$E_{nm} = E_n^{(0)} + \sum_{j=1}^{\infty}\lambda^j E_{nm}^{(j)} \tag{79}$$

and

$$|nm\rangle = \sum_{j=0}^{\infty}\lambda^j|nm^{(j)}\rangle. \tag{80}$$

In the degenerate case, there are three possible actions we can perform on (76) to generate useable equations, as opposed to two for the non-degenerate case. They are

I Hit with $\langle nm^{(0)}|$ from the left

II Hit with $\langle nm'^{(0)}|$ from the left, where $m' \neq m$.

III Hit with $\langle n'm'^{(0)}|$ from the left, where $n' \neq n$.

The main thing we hope to prove is that the 'good basis' condition is sufficient to remove any singularities due to vanishing energy denominators when degenerate levels are mixed.

3.1.1 First-order terms

With $j = 1$ we can start by computing $\langle nm^{(0)}|nm^{(1)}\rangle$, giving

$$\langle nm^{(0)}|nm^{(1)}\rangle = -\frac{1}{2}\sum_{k=1}^{0}\langle nm^{(k)}|nm^{(j-k)}\rangle = 0. \tag{81}$$

The energy equation is then

$$(H_0 - E_n^{(0)})|nm^{(1)}\rangle = -V|nm^{(0)}\rangle + E_{nm}^{(1)}|nm^{(0)}\rangle. \tag{82}$$

From action I, we get

$$0 = -\langle nm^{(0)}|V|nm^{(0)}\rangle + E_{nm}^{(1)}, \tag{83}$$

which gives

$$E_{nm}^{(1)} = v_{nm}. \tag{84}$$

as expected.
From II, we get

$$0 = -\langle nm'^{(0)}|V|nm^{(0)}\rangle \tag{85}$$

which is just a re-statement of the 'good basis' constraint (78).
From III, we find

$$(E_{n'}^{(0)} - E_n^{(0)})\langle n'm'^{(0)}|nm^{(1)}\rangle = -\langle nm'^{(0)}|V|nm^{(0)}\rangle. \tag{86}$$

Solving for $\langle n'm'^{(0)}|nm^{(1)}\rangle$ gives

$$\langle n'm'^{(0)}|nm^{(1)}\rangle = -\frac{V_{n'm'nm}}{\Delta_{n'n}}, \tag{87}$$

where we have introduced the new notation $\Delta_{n'n} = E_{n'}^{(0)} - E_n^{(0)}$ to avoid confusing the energy denominator with the full energy level E_{nm}.

At this point, we note that we have exhausted all of our equations, but have not found the components $\langle nm'^{(0)}|nm^{(1)}\rangle$. We will, however, proceed to the case $(j = 2)$, and hope for the best.

3.1.2 Second-order terms

With $j = 2$, we find

$$\langle nm^{(0)}|nm^{(2)}\rangle = -\frac{1}{2}\langle nm^{(1)}|nm^{(1)}\rangle$$

$$
\begin{aligned}
&= -\frac{1}{2}\sum_{n'm'}\left|\langle n'm'^{(0)}|nm^{(1)}\rangle\right|^2 \\
&= -\frac{1}{2}\sum_{m'\neq m}\left|\langle nm'^{(0)}|nm^{(1)}\rangle\right|^2 - \frac{1}{2}\sum_{\substack{n'\neq n\\ m'}}\left|\langle n'm'^{(0)}|nm^{(1)}\rangle\right|^2 \\
&= -\frac{1}{2}\sum_{m'\neq m}\left|\langle nm'^{(0)}|nm^{(1)}\rangle\right|^2 - \frac{1}{2}\sum_{\substack{n'\neq n\\ m'}}\frac{|V_{n'm'nm}|^2}{\Delta_{n'n}^2}, \qquad (88)
\end{aligned}
$$

which we cannot evaluate further because the remaining coefficients have not been determined.

The second-order eigenvalue equation is

$$(H_0 - E_n^{(0)})|nm^{(2)}\rangle = -V|nm^{(1)}\rangle + E_{nm}^{(1)}|nm^{(1)}\rangle + E_{nm}^{(2)}|nm^{(0)}\rangle \qquad (89)$$

From I, we obtain

$$0 = -\langle nm^{(0)}|V|nm^{(1)}\rangle + E_{nm}^{(2)}, \qquad (90)$$

which leads to

$$
\begin{aligned}
E_{nm}^{(2)} &= \sum_{\substack{n'\neq n\\ m'}} V_{nmn'm'}\langle n'm'^{(0)}|nm^{(1)}\rangle + \sum_{m'} V_{nmnm'}\langle nm'^{(0)}|nm^{(1)}\rangle \\
&= -\sum_{\substack{n'\neq n\\ m'}}\frac{V_{nmn'm'}V_{n'm'nm}}{\Delta_{n'n}} \qquad (91)
\end{aligned}
$$

where we have made use of (78) and (81) to eliminate the second term. This is essentially the same result as that from non-degenerate perturbation theory, but with the singular terms excluded from the summation. From action II on Eq. (89), we find

$$0 = -\langle nm'^{(0)}|V|nm^{(1)}\rangle + E_{nm}^{(1)}\langle nm'^{(0)}|nm^{(1)}\rangle. \qquad (92)$$

Notice that this equation contains no second-order unknown quantities, but it does contain the remaining first-order unknown, $\langle nm'^{(0)}|nm^{(1)}\rangle$. Solving for this variable gives

$$
\begin{aligned}
v_{nm}\langle nm'^{(0)}|nm^{(1)}\rangle &= \sum_{\substack{n''\neq n\\ m''}} V_{nm'n''m''}\langle n''m''^{(0)}|nm^{(1)}\rangle + \sum_{m''} V_{nm'nm''}\langle nm''^{(0)}|nm^{(1)}\rangle \\
&= -\sum_{\substack{n''\neq n\\ m''}}\frac{V_{nm'n''m''}V_{n''m''nm}}{\Delta_{n''n}} + v_{nm'}\langle nm'^{(0)}|nm^{(1)}\rangle \qquad (93)
\end{aligned}
$$

This then leads to

$$\langle nm'^{(0)}|nm^{(1)}\rangle = \sum_{\substack{n''\neq n\\ m''}}\frac{V_{nm'n''m''}V_{n''m''nm}}{v_{nm'm}\Delta_{n''n}}, \qquad (94)$$

where we have introduced

$$v_{nm'm} = v_{nm'} - v_{nm}. \qquad (95)$$

Intriguingly, we have obtained our remaining first-order term by solving a second-order equation. That the equation is second-order can be seen by the fact that there are two V's in the numerator. That the

resulting term is first-order can be seen by the fact that there is a v in the denominator, so that the term scales as $\frac{\lambda^2}{\lambda} = \lambda$.
This allows us to complete our expression for $\langle nm^{(0)}|nm^{(2)}\rangle$, yielding

$$\langle nm^{(0)}|nm^{(2)}\rangle = -\frac{1}{2}\sum_{m'\neq m}\sum_{\substack{n''\neq n\\ m''}}\sum_{\substack{n'''\neq n\\ m'''}}\frac{V_{nmn''m''}V_{n''m''nm'}V_{nm'n'''m'''}V_{n'''m'''nm}}{\Delta_{n''n}v_{nm'm}^2\Delta_{n'''n}} - \frac{1}{2}\sum_{\substack{n'\neq n\\ m'}}\frac{V_{nmn'm'}V_{n'm'nm}}{\Delta_{n'n}^2} \tag{96}$$

Lastly, from III, we obtain

$$\Delta_{n'n}\langle n'm'^{(0)}|nm^{(2)}\rangle = -\langle n'm'^{(0)}|V|nm^{(1)}\rangle + E_{nm}^{(1)}\langle n'm'^{(0)}|nm^{(1)}\rangle, \tag{97}$$

which gives us

$$\langle n'm'^{(0)}|nm^{(2)}\rangle = \sum_{\substack{n''\neq n\\ m''}}\frac{V_{n'm'n''m''}V_{n''m''nm}}{\Delta_{n'n}\Delta_{n''n}} - \sum_{m''\neq m}\sum_{\substack{n'''\neq n\\ m'''}}\frac{V_{n'm'nm''}V_{nm''n'''m'''}V_{n'''m'''nm}}{\Delta_{n'n}v_{nm''m}\Delta_{n'''n}} - \frac{V_{n'm'nm}v_{nm}}{\Delta_{n'n}^2} \tag{98}$$

At this point we see that we have run out of second-order equations, yet have not obtained an expression for the components $\langle nm'^{(0)}|nm^{(2)}\rangle$. It is logical at this point to assume that we can obtain these coefficients by solving a third-order equation, which is left as an exercise.

3.1.3 Results to second-order (almost)

Thus we have found

$$E_{nm} = E_n^{(0)} + \lambda v_{nm} - \sum_{\substack{n'\neq n\\ m'}}\frac{V_{nmn'm'}V_{n'm'nm}}{\Delta_{n'n}} + O(\lambda^3) \tag{99}$$

as well as

$$\begin{aligned}
|nm\rangle &= |nm^{(0)}\rangle\left[1 - \frac{\lambda^2}{2}\sum_{\substack{n'\neq n\\ m'}}\frac{V_{nmn'm'}}{\Delta_{n'n}}\left(\sum_{m''\neq m}\sum_{\substack{n'''\neq n\\ m'''}}\frac{V_{n'm'nm''}V_{nm''n'''m'''}V_{n'''m'''nm}}{v_{nm''m}^2\Delta_{n'''n}} + \frac{V_{n'm'nm}}{\Delta_{n'n}}\right) + O(\lambda^3)\right] \\
&+ \sum_{m'\neq m}|nm'^{(0)}\rangle\left[\lambda\sum_{\substack{n''\neq n\\ m''}}\frac{V_{nm'n''m''}V_{n''m''nm}}{v_{nm'm}\Delta_{n''n}} + O(\lambda^2)\right] \\
&+ \sum_{\substack{n'\neq n\\ m'}}|n'm'^{(0)}\rangle\left[-\lambda\frac{V_{n'm'nm}}{\Delta_{n'n}}\left(1 + \lambda\frac{v_{nm}}{\Delta_{n'n}}\right)\right. \\
&\qquad \left. + \lambda^2\sum_{\substack{n''\neq n\\ m''}}\left(V_{n'm'n''m''} - \sum_{m'''\neq m}\frac{V_{n'm'nm'''}V_{nm'''n''m''}}{v_{nm'''m}}\right)\frac{V_{n''m''nm}}{\Delta_{n'n}\Delta_{n''n}} + O(\lambda^3)\right]
\end{aligned} \tag{100}$$

Note, in going from Eq. (98) to (100) it was necessary to make the change of dummy variables $n''' \to n''$. $m''' \to m''$, and $m'' \to m'''$.

3.2 Approach #2

We begin by noting that the 'good' bare eigenstates are eigenstates of $H_0 + \lambda V_n$, with eigenvalues $E_n^{(0)} + \lambda v_{nm}$. Armed with this, we can re-define our bare Hamiltonian as $\tilde{H}_0 = H_0 + \lambda V_n$, and introduce the new perturbation $\tilde{V} = \lambda(V - V_n)$. We will then use non-degenerate perturbation theory to solve

$$(\tilde{H} + \mu\tilde{V})|nm\rangle = E_{nm}|nm\rangle, \tag{101}$$

taking as our bare basis $\{|nm^{(0)}\rangle\}$, with bare energies now given by $E_{nm}^{(0)} = E_n^{(0)} + \lambda v_{nm}$. By setting $\mu = 1$ at the end, we will recover the eigenstates of $H = H_0 + \lambda V$. Note that even if some of the eigenvalues of V_n are degenerate, we can still use the non-degenerate theory, as the fact that $\langle nm^{(0)}|\tilde{V}|nm'^{(0)}\rangle = 0$ will kill all singular terms.

In using perturbation theory, we have to replace n with n, m, and the condition $n' \neq n$ will go to $n' \neq n$ & $m' \neq m$. This is because we are elevating each $|nm^{(0)}\rangle$ state to the level of a non-degenerate state. After transforming the indices in this manner, the second-order energy formula (32) become:

$$E_{nm} = E_{nm}^{(0)} + \mu\tilde{V}_{nmnm} - \mu^2 \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{|\tilde{V}_{n'm'nm}|^2}{E_{n'm'nm}} - \mu^2 \sum_{\substack{m'=1 \\ m' \neq m}}^{d_n} \frac{|\tilde{V}_{nm'nm}|^2}{E_{nm'nm}} + O(\mu^3), \tag{102}$$

where $E_{n'm'nm} = E_{n'm'}^{(0)} - E_{nm}^{(0)}$, and $\tilde{V}_{n'm'nm} = \langle n'm'^{(0)}|\tilde{V}|nm^{(0)}\rangle$. Taking into account $\tilde{V}_{nm'nm} = 0$, this simplifies to

$$E_{nm} = E_{nm}^{(0)} - \mu^2 \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{|\tilde{V}_{n'm'nm}|^2}{E_{n'm'nm}} + O(\mu^2) \tag{103}$$

The next step is to set $\mu = 1$, and express everything in terms of our original $E_n^{(0)}$ and V, giving

$$E_{nm} = E_n^{(0)} + \lambda v_{nm} - \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{\lambda^2 |V_{n'm'nm}|^2}{\Delta_{n'n} + \lambda v_{n'm'nm}}, \tag{104}$$

where $\Delta_{n'n} = E_{n'}^{(0)} - E_n^{(0)}$ and $v_{n'm'nm} = v_{n'm'} - v_{nm}$. As we only want the correct energies up to $O(\lambda^2)$, we need to expand this expression in powers of λ and throw away terms of $O(\lambda^3)$ or higher. Since $(a + \lambda b)^{-1} = \frac{1}{a}(1 - \lambda\frac{b}{a} + \lambda^2\frac{b^2}{a^2} - \ldots)$, we see that keeping only terms up to second-order gives

$$E_{nm} = E_n^{(0)} + \lambda v_{nm} - \lambda^2 \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{|V_{n'm'nm}|^2}{\Delta_{n'n}} + O(\lambda^3). \tag{105}$$

Thus Eq. (73) is the correct second-order expression for the energies in degenerate perturbation theory.

Similarly, translating the indices on the second-order state formulas (33) gives:

$$\begin{aligned}
|nm\rangle &= |nm^{(0)}\rangle \left(1 - \frac{\mu^2}{2} \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{|\tilde{V}_{n'm'nm}|^2}{E_{n'm'nm}^2} + O(\mu^3)\right) \\
&+ \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} |n'm'^{(0)}\rangle \left(-\mu \frac{\tilde{V}_{n'm'nm}}{E_{n'm'nm}} + \mu^2 \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{\tilde{V}_{n'm'n''m''}\tilde{V}_{n''m''nm}}{E_{n'm'nm}E_{n''m''nm}} + O(\mu^3)\right)
\end{aligned}$$

$$+ \quad \sum_{\substack{m'=1 \\ m' \neq m}}^{d_n} |nm'^{(0)}\rangle \left(\mu^2 \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{V_{nm'n''m''} V_{n''m''nm}}{E_{nm'nm} E_{n''m''nm}} + O(\mu^3) \right) \tag{106}$$

where we have again relied on $\tilde{V}_{nm'nm} = 0$ for simplifications. Setting $\mu = 1$ and expressing everything in terms of V and $E_n^{(0)}$ gives

$$\begin{aligned} |nm\rangle &= |nm^{(0)}\rangle \left(1 - \frac{1}{2} \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{\lambda^2 |V_{n'm'nm}|^2}{\Delta E_{n'n} + \lambda(v_{n'm'} - v_{nm})} \right) \\ &+ \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} |n'm'^{(0)}\rangle \left(-\frac{\lambda V_{n'm'nm}}{\Delta_{n'n} + \lambda v_{n'm'nm}} + \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{\lambda^2 V_{n'm'n''m''} V_{n''m''nm}}{(\Delta_{n'n} + \lambda v_{n'm'nm})(\Delta_{n''n} + \lambda v_{n''m''nm})} \right) \\ &+ \sum_{\substack{m'=1 \\ m' \neq m}}^{d_n} |nm'^{(0)}\rangle \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{\lambda^2 V_{nm'n''m''} V_{n''m''nm}}{\lambda v_{nm'nm} (\Delta_{n''n} + \lambda v_{n''m''nm})}. \end{aligned} \tag{107}$$

The next step is to expand in powers of λ and keep only terms up to $O(\lambda^2)$, which gives

$$\begin{aligned} |nm\rangle &= |nm^{(0)}\rangle \left(1 - \frac{1}{2} \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} \frac{\lambda^2 |V_{n'm'nm}|^2}{\Delta_{n'n}} \right) \\ &+ \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} |n'm'^{(0)}\rangle \left(-\frac{\lambda V_{n'm'nm}}{\Delta_{n'n}} + \frac{\lambda^2 V_{n'm'nm} v_{n'm'nm}}{\Delta_{n'n}^2} + \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{\lambda^2 V_{n'm'n''m''} V_{n''m''nm}}{\Delta_{n'n} \Delta_{n''n}} \right) \\ &+ \sum_{\substack{m'=1 \\ m' \neq m}}^{d_n} |nm'^{(0)}\rangle \lambda \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{V_{nm'n''m''} V_{n''m''nm}}{v_{nm'm} \Delta_{n''n}}. \end{aligned} \tag{108}$$

Notice that something very strange has occurred with the final term. This term, which was originally second order in μ, has become first-order in λ. This means that a second-order calculation was necessary to obtain the correct state to first-order. Thus we can predict that a third-order calculation will similarly yield second-order terms. This means that we can actually only trust our states (76) up to first-order. Dropping all terms greater than first-order gives

$$\begin{aligned} |nm\rangle &= |nm^{(0)}\rangle \left(1 + O(\lambda^2) \right) \\ &+ \sum_{n' \neq n} \sum_{m'=1}^{d_{n'}} |n'm'^{(0)}\rangle \left(-\frac{\lambda V_{n'm'nm}}{\Delta_{n'n}} + O(\lambda^2) \right) \\ &+ \sum_{\substack{m'=1 \\ m' \neq m}}^{d_n} |nm'^{(0)}\rangle \left(\lambda \sum_{n'' \neq n} \sum_{m''=1}^{d_{n''}} \frac{V_{nm'n''m''} V_{n''m''nm}}{v_{nm'm} \Delta_{n''n}} + O(\lambda^2) \right). \end{aligned} \tag{109}$$

Equations (73) and (77) are the main results of this section, giving the energies to second-order and the states to first-order.

3.3 Examples

A three level system: The simplest quantum system which can require degenerate perturbation theory is the three-state system. If a two-state system is degenerate, it must first be diagonalized in the degenerate subspace, after which the problem is solved exactly. Let us consider, therefore, a three-level system with

$$H_0 \to E_0 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{110}$$

and

$$V \to V_0 \begin{pmatrix} 0 & \sqrt{2} & 2\sqrt{2} \\ \sqrt{2} & 0 & 2 \\ 2\sqrt{2} & 2 & 0 \end{pmatrix}, \tag{111}$$

both defined in the 'physical' basis $\{|1\rangle, |2\rangle, |3\rangle\}$. The bare Hamiltonian has two energy eigenvalues $E_1^{(0)} = 0$ and $E_2^{(0)} = E_0$. The first eigenvalue is non-degenerate, with eigenvector $|1, 1^{(0)}\rangle = |1\rangle$, while the second is doubly degenerate, with a degenerate subspace spanned by $|2\rangle$ and $|3\rangle$. The projection operator for the degenerate subspace is

$$I_2 = |2\rangle\langle 2| + |3\rangle\langle 3| \to \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{112}$$

This leads to the projection

$$V_2 = I_2 V I_2 = V_0 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 2 \\ 0 & 2 & 0 \end{pmatrix}. \tag{113}$$

This operator has eigenvalues 0, $-2V_0$, and $2V_0$, with corresponding eigenvectors $|1\rangle$, $\frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$, and $\frac{1}{\sqrt{2}}(|2\rangle + 3\rangle)$. To determine which two eigenvectors live in the degenerate subspace (pretending for the moment that it is not completely obvious), we can apply I_2 to each, and discard any states which give zero. Applying this test, we find that the two 'good' basis states for the degenerate subspace are $|2, 1^{(0)}\rangle = \frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$ and $|2, 2^{(0)}\rangle = \frac{1}{\sqrt{2}}(|2\rangle + |3\rangle)$.

In the new basis $\{|1, 1^{(0)}\rangle, |2, 1^{(0)}\rangle, |2, 2^{(0)}\rangle\}$, the bare Hamiltonian matrix is unchanged, and the perturbation is diagonalized in the degenerate subspace giving

$$V \to \begin{pmatrix} V_{1111} & V_{1121} & V_{1122} \\ V_{1121}^* & -2V_0 & 0 \\ V_{1122}^* & 0 & 2V_0 \end{pmatrix}. \tag{114}$$

Computing the necessary matrix elements, we find

$$V_{1111} = \langle 1, 1^{(0)}|V|1, 1^{(0)}\rangle = \langle 1|V|1\rangle = 0, \tag{115}$$

$$V_{1121} = \langle 1, 1^{(0)}|V|2, 1^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(\langle 1|V|2\rangle - \langle 1|V|3\rangle\right) = -V_0, \tag{116}$$

and

$$V_{1122} = \langle 1, 1^{(0)}|V|2, 2^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(\langle 1|V|2\rangle + \langle 1|V|3\rangle\right) = 3V_0, \tag{117}$$

so that in the new basis,

$$V \to V_0 \begin{pmatrix} 0 & -1 & 3 \\ -1 & -2 & 0 \\ 3 & 0 & 2 \end{pmatrix}. \tag{118}$$

We can now readily evaluate Eqs. (73) and (77), giving

$$\begin{aligned} E_{11} &= E_1^{(0)} + \lambda v_{11} - \lambda^2 \left(\frac{|V_{2111}|^2}{\Delta E_{21}} + \frac{|V_{2211}|^2}{\Delta E_{21}} \right) + O(\lambda^3) \\ &= -\lambda^2 \frac{10V_0}{E_0} + O(\lambda^3), \end{aligned} \tag{119}$$

$$\begin{aligned} E_{21} &= E_2^{(0)} + \lambda v_{21} - \lambda^2 \frac{|V_{1121}|^2}{\Delta E_{12}} + O(\lambda^3) \\ &= E_0 - \lambda 2V_0 + \lambda^2 \frac{V_0^2}{E_0} + O(\lambda^3), \end{aligned} \tag{120}$$

and

$$\begin{aligned} E_{22} &= E - 2^{(0)} + \lambda v_{22} - \lambda^2 \frac{|V_{1122}|^2}{\Delta E_{12}} \\ &= E_0 + \lambda 2V_0 + \lambda^2 \frac{9V_0^2}{E_0}. \end{aligned} \tag{121}$$

For the first-order states, we find

$$\begin{aligned} |1,1\rangle &= |1,1^{(0)}\rangle + \lambda \left(|2,1^{(0)}\rangle \frac{V_{2111}}{\Delta E_{21}} + |2,2^{(0)}\rangle \frac{V_{2211}}{\Delta E_{21}} \right) + O(\lambda^3) \\ &= |1,1^{(0)}\rangle - |2,1^{(0)}\rangle \lambda \frac{V_0}{E_0} + |2,2^{(0)}\rangle \lambda \frac{3V_0}{E_0} + O(\lambda^3) \\ &= |1\rangle + |2\rangle \lambda \frac{\sqrt{2}V_0}{E_0} + |3\rangle \lambda \frac{2\sqrt{2}V_0}{E_0} + O(\lambda^3), \end{aligned} \tag{122}$$

$$\begin{aligned} |2,1\rangle &= |2,1^{(0)}\rangle + |2,2^{(0)}\rangle \lambda \frac{V_{2211}V_{1121}}{\Delta v_{2221}\Delta E_{12}} + |1,1^{(0)}\rangle \lambda \frac{V_{1121}}{\Delta E_{12}} + O(\lambda^3) \\ &= |1,1^{(0)}\rangle \lambda \frac{V_0}{E_0} + |2,1^{(0)}\rangle + |2,2^{(0)}\rangle \lambda \frac{3V_0}{4E_0} + O(\lambda^3) \\ &= |1\rangle \lambda \frac{V_0}{E_0} + |2\rangle \frac{1}{\sqrt{2}} \left(1 + \lambda \frac{3V_0}{4E_0} \right) + |3\rangle \frac{1}{\sqrt{2}} \left(-1 + \lambda \frac{3V_0}{4E_0} \right) + O(\lambda^3), \end{aligned} \tag{123}$$

and

$$\begin{aligned} |2,2\rangle &= |2,2^{(0)}\rangle + |2,1^{(0)}\rangle \lambda \frac{V_{2111}V_{1122}}{\Delta v_{2122}\Delta E_{12}} + |1,1^{(0)}\rangle \lambda \frac{V_{1122}}{\Delta E_{21}} + O(\lambda^3) \\ &= -|1,1^{(0)}\rangle \lambda \frac{3V_0}{E_0} - |2,1^{(0)}\rangle \lambda \frac{3V_0}{4E_0} + |2,2^{(0)}\rangle + O(\lambda^3) \\ &= -|1\rangle \lambda \frac{3V_0}{E_0} + |2\rangle \frac{1}{\sqrt{2}} \left(1 - \lambda \frac{3V_0}{4E_0} \right) + |3\rangle \frac{1}{\sqrt{2}} \left(1 + \lambda \frac{3V_0}{4E_0} \right) + O(\lambda^3). \end{aligned} \tag{124}$$

4 Practical Iterative Approach

While some energy was spent deriving analytic expressions for second-order and third-order terms, keep in mind that in practice, the terms would be computed iteratively. In other words, instead of expressing the j^{th}-order terms in terms of zeroth order terms, as is customary for terms up to second-order, it is more efficient to express the j^{th}-order terms in terms of $(j-1)^{th}$ order terms only, and just iterate the equations.

4.1 Non-degenerate iterative equations

For the non-degenerate case, the iterative equation (adopting uniform notation) for the energy level shifts is

$$E_n^{(j)} = \sum_{n'} V_{nn'} \langle n'^{(0)} | n^{(j-1)} \rangle - \sum_{k=1}^{j-2} E_n^{(k)} \langle n^{(0)} | n^{(j-k)} \rangle. \tag{125}$$

For the expansion coefficients, the iterative equations are

$$\langle n^{(0)} | n^{(j)} \rangle = -\frac{1}{2} \sum_{k=1}^{j-1} \langle n^{(k)} | n^{(j-k)} \rangle, \tag{126}$$

and for $n' \neq n$,

$$\langle n'^{(0)} | n^{(j)} \rangle = -\sum_{n''} \frac{V_{n'n''}}{\Delta_{n'n}} \langle n''^{(0)} | n^{(j-1)} \rangle + \sum_{k=1}^{j-2} \frac{E_n^{(k)}}{\Delta_{n'n}} \langle n'^{(0)} | n^{(j-k)} \rangle. \tag{127}$$

4.2 Degenerate iterative equations

Assuming that the correct bare eigenstates are in use, we have

$$E_{nm}^{(j)} = v_{nm} \langle nm^{(0)} | nm^{(j-1)} \rangle + \sum_{\substack{n' \neq n \\ m'}} V_{nmn'm'} \langle n'm'^{(0)} | nm^{(j-1)} \rangle - \sum_{k=1}^{j-2} E_{nm}^{(k)} \langle nm^{(0)} | nm^{(j-k)} \rangle, \tag{128}$$

and

$$\langle nm^{(0)} | nm^{(j)} \rangle = -\frac{1}{2} \sum_{k=1}^{j-1} \langle nm^{(k)} | nm^{(j-k)} \rangle, \tag{129}$$

and for $n' \neq n$,

$$\langle n'm'^{(0)} | nm^{(j)} \rangle = -\sum_{n'',m''} \frac{V_{n'm'n''m''}}{\Delta_{n'n}} \langle n''m''^{(0)} | nm^{(j-1)} \rangle + \sum_{k=1}^{j-1} \frac{E_{nm}^{(k)}}{\Delta_{n'n}} \langle n'm'^{(0)} | nm^{(j-k)} \rangle. \tag{130}$$

For $n' = n$, but $m' \neq m$, we have

$$\langle nm'^{(0)} | nm^{(j)} \rangle = -\sum_{\substack{n'' \neq n \\ m''}} \frac{V_{nm'n''m''}}{v_{nm'm}} \langle n''m''^{(0)} | nm^{(j)} \rangle + \sum_{k=2}^{j} \frac{E_{nm}^{(k)}}{v_{nm'm}} \langle nm'^{(0)} | nm^{(j-k+1)} \rangle \tag{131}$$