1 Module 8 Lecture 1: First-Order Perturbation Theory and the Feynman-Hellman Theorem

All problems in quantum mechanics cannot be solved exactly, and thus we need approximation methods, such as the variational method and perturbation theory.

1.1 Example: Simple Harmonic Oscillator

We perturb the spring constant of the Simple Harmonic Oscillator (SHO) by δ.

Definition 1. The perturbed Hamiltonian for a Simple Harmonic Oscillator with a perturbed spring constant is given by:

$$\hat{H}(\delta) = \frac{\hat{p}^2}{2m} + \frac{1}{2}k(1+\delta)\hat{x}^2 \tag{1.1}$$

where the unperturbed Hamiltonian is $\hat{H}(0) = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2$.

We know the exact energy to be:

$$\begin{aligned} E_n(\delta) &= \hbar\omega\sqrt{1+\delta}\left(n+\frac{1}{2}\right) \\ &= E_n(0)\left(1+\frac{1}{2}\delta - \frac{1}{8}\delta^2 + \frac{1}{16}\delta^3 + \cdots\right) \\ \text{with } \omega &= \sqrt{\frac{k}{m}} \end{aligned} \tag{1.2}$$

We claim that the first order term of this expansion, $\frac{1}{2}\delta$, can be calculated using the variational method. This is computed with respect to the eigenstates of the unperturbed $\hat{H}$.

Example. Applying the variational method to find the first-order correction for the SHO:

$$\begin{aligned} E_n(\delta) &\approx \langle \psi_n^0 | \hat{H}(\delta) | \psi_n^0 \rangle \\ &= \langle \psi_n^0 | \hat{H}(0) + \frac{1}{2}k\delta\hat{x}^2 | \psi_n^0 \rangle \\ &= E_n(0) + \delta \langle \psi_n^0 | \frac{1}{2}k\hat{x}^2 | \psi_n^0 \rangle \end{aligned} \tag{1.3}$$

By the Virial theorem, for a harmonic oscillator, $\left\langle \hat{K} \right\rangle = \left\langle \hat{V} \right\rangle = \frac{1}{2}E$. So, $\langle \psi_n^0 | \frac{1}{2}k\hat{x}^2 | \psi_n^0 \rangle = \frac{1}{2}E_n(0)$. Thus, using the variational method, we have:

$$E_n(\delta) \approx E_n(0)\left(1+\frac{\delta}{2}\right) \tag{1.4}$$

This result agrees with the first-order term in the Taylor series expansion shown in (1.2).

1.2 Feynman-Hellman Theorem

We aim to compute the derivative of an energy with respect to some parameter λ.

Theorem 1 (Feynman-Hellman Theorem). Given a Hamiltonian $\hat{H}(\lambda)$ that depends on a parameter λ, and its corresponding normalized eigenstate $|\psi(\lambda)\rangle$ with eigenvalue $E(\lambda)$, the derivative of the energy with respect to λ is given by:

$$\frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda} = \langle\psi(\lambda)| \frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda} |\psi(\lambda)\rangle \tag{1.5}$$

Proof. We start with the time-independent Schrödinger equation and the normalization condition:

$$\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \tag{1.6}$$
$$\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$$

We want to compute $\frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda}$. We can express $E(\lambda)$ as the expectation value of $\hat{H}(\lambda)$:

$$E(\lambda) = \langle\psi(\lambda)| \hat{H}(\lambda) |\psi(\lambda)\rangle \tag{1.7}$$

Now, we take the derivative with respect to λ:

$$\begin{aligned}\frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda} &= \frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi(\lambda)| \hat{H}(\lambda) |\psi(\lambda)\rangle \\ &= \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi(\lambda)|\right)\hat{H}(\lambda)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle + \langle\psi(\lambda)|\hat{H}(\lambda)\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi(\lambda)\rangle\right)\end{aligned} \tag{1.8}$$

In the first and third terms, we can substitute $\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$ and $\langle\psi(\lambda)|\hat{H}(\lambda) = E(\lambda)\langle\psi(\lambda)|$:

$$\begin{aligned}&= \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi(\lambda)|\right)E(\lambda)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle + \langle\psi(\lambda)|E(\lambda)\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi(\lambda)\rangle\right) \\ &= \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle + E(\lambda)\left(\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi(\lambda)|\right)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi(\lambda)\rangle\right)\right)\end{aligned} \tag{1.9}$$

The terms inside the parenthesis for $E(\lambda)$ can be recognized as the derivative of the normalization condition:

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\langle\psi(\lambda)|\psi(\lambda)\rangle\right) = \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi(\lambda)|\right)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi(\lambda)\rangle\right) \tag{1.10}$$

Since $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$, its derivative with respect to λ is 0.

$$\begin{aligned}&= \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle + E(\lambda)\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}1\right) \\ &= \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle + E(\lambda)\cdot 0 \\ &= \langle\psi(\lambda)|\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi(\lambda)\rangle\end{aligned} \tag{1.11}$$

This completes the proof. □

Example. Using the Feynman-Hellman equation, we can show that the variational form of the first-order energy correction is equivalent to the first-order Taylor expansion derived earlier. Let $\hat{H}(\delta) = \hat{H}(0) + \delta\hat{V}$. Then $E_n(\delta)$ can be expanded as a Taylor series around $\delta = 0$:

$$\begin{aligned} E_n(\delta) &\approx E_n(0) + \delta \left.\frac{\mathrm{d}E_n(\delta)}{\mathrm{d}\delta}\right|_{\delta=0} \\ &= E_n(0) + \delta \left\langle \psi_n^0 \right| \left.\frac{\mathrm{d}\hat{H}(\delta)}{\mathrm{d}\delta}\right|_{\delta=0} \left|\psi_n^0\right\rangle \\ &= E_n(0) + \delta \left\langle \psi_n^0 \right| \frac{\mathrm{d}}{\mathrm{d}\delta}\left(\hat{H}(0) + \delta\hat{V}\right) \left|\psi_n^0\right\rangle \\ &= E_n(0) + \delta \left\langle \psi_n^0 \right| \hat{V} \left|\psi_n^0\right\rangle \end{aligned} \tag{1.12}$$

This result, $E_n(0) + \delta \left\langle \psi_n^0 \right| \hat{V} \left|\psi_n^0\right\rangle$, is precisely the first-order energy correction from perturbation theory, which we saw earlier also matched the variational method's result for the SHO.

1.3 Application: Hyperfine Structure of Hydrogen

1.4 Application: Calculating $\langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$ by Feynman-Hellman

Problem. For hydrogen, the radial Hamiltonian is given by:

$$\hat{H}_l = \frac{\hat{p}_r^2}{2M} + \frac{\hbar^2 l(l+1)}{2M\hat{r}^2} - \frac{e^2}{\hat{r}} \tag{1.13}$$

and $\hat{H}_l |n, l\rangle = E_n |n, l\rangle$. We are also given the energy for the m-th excited state for a generalized parameter λ:

$$E_m(\lambda) = -\frac{e^2}{2a_0(m+\lambda+1)^2} \tag{1.14}$$

Calculate the expectation value $\langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$ using the Feynman-Hellman Theorem.

Solution. We generalize the Hamiltonian by replacing l with a continuous parameter λ:

$$\hat{H}(\lambda) = \frac{\hat{p}_r^2}{2M} + \frac{\hbar^2 \lambda(\lambda+1)}{2M\hat{r}^2} - \frac{e^2}{\hat{r}} \tag{1.15}$$

Although l is an integer, making derivatives with respect to l seem invalid, the Feynman-Hellman theorem still applies by considering λ as a formal continuous parameter for the purpose of differentiation, and then setting $\lambda = l$ at the end.

Applying the Feynman-Hellman theorem:

$$\begin{aligned} \frac{\mathrm{d}E_m(\lambda)}{\mathrm{d}\lambda} &= \langle n, l| \frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda} |n, l\rangle \\ \frac{\mathrm{d}}{\mathrm{d}\lambda}\left(-\frac{e^2}{2a_0(m+\lambda+1)^2}\right) &= \langle n, l| \frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{\hat{p}_r^2}{2M} + \frac{\hbar^2\lambda(\lambda+1)}{2M\hat{r}^2} - \frac{e^2}{\hat{r}}\right) |n, l\rangle \\ -\frac{e^2}{2a_0}(-2)(m+\lambda+1)^{-3}(1) &= \langle n, l| \frac{\hbar^2(2\lambda+1)}{2M\hat{r}^2} |n, l\rangle \\ \frac{e^2}{a_0(m+\lambda+1)^3} &= \langle n, l| \frac{\hbar^2(2\lambda+1)}{2M\hat{r}^2} |n, l\rangle \end{aligned} \tag{1.16}$$

Now we set $m + \lambda + 1 = n$ (where n is the principal quantum number for hydrogen, $n = l+1, l+2, \ldots$ and also $\lambda = l$) and substitute into the equation:

$$\frac{e^2}{a_0 n^3} = \langle n, l| \frac{\hbar^2(2l+1)}{2M\hat{r}^2} |n, l\rangle \tag{1.17}$$
$$\frac{e^2}{a_0 n^3} = \frac{\hbar^2(2l+1)}{2M} \langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$$

Recalling that the Bohr radius $a_0 = \frac{\hbar^2}{Me^2}$, we can substitute $M = \frac{\hbar^2}{a_0 e^2}$:

$$\frac{e^2}{a_0 n^3} = \frac{\hbar^2(2l+1)}{2(\frac{\hbar^2}{a_0 e^2})\hat{r}^2} \langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$$
$$\frac{e^2}{a_0 n^3} = \frac{a_0 e^2(2l+1)}{2} \langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$$

Solving for $\langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle$:

$$\boxed{\langle n, l| \frac{1}{\hat{r}^2} |n, l\rangle = \frac{1}{a_0^2 n^3 (l + \frac{1}{2})}} \tag{1.18}$$

□

2 Module 8 Lecture 2: Second Order Perturbation Theory (via derivatives)

There is a general formal technique to determine perturbation theory to an arbitrary order. However, it is complicated so this lecture only covers the second order-derivation.

2.1 Derivation

Using λ as the small parameter, we write $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$. The wavefunction is denoted $|\psi_n(\lambda)\rangle$ and the energy $E_n(\lambda)$. We then perform a Taylor series expansion on the energy:

$$E_n(\lambda) = E_n(0) + \lambda \left.\frac{\mathrm{d}E_n(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=0} + \frac{\lambda^2}{2} \left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0} + \cdots \tag{2.1}$$

We recall the basic properties:

$$E_n(0) = \langle\psi_n| \hat{H}_0 |\psi_n\rangle, \qquad \hat{H}(\lambda) |\psi_n(\lambda)\rangle = E_n(\lambda) |\psi_n(\lambda)\rangle, \qquad \langle\psi_n(\lambda)|\psi_n(\lambda)\rangle = 1 \tag{2.2}$$

From the Feynman-Hellman theorem, we derived the first derivative:

$$\left.\frac{\mathrm{d}E_n(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=0} = \langle\psi_n| \left.\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=0} |\psi_n\rangle = \langle\psi_n| \hat{V} |\psi_n\rangle = V_{nn} \tag{2.3}$$

We now aim to calculate the second derivative, $\left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0}$.

Theorem 2 (Second-Order Perturbation Energy Correction). The second-order energy correction for a non-degenerate eigenvalue E_n due to a perturbation $\lambda\hat{V}$ is given by:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m| \hat{V} |\psi_n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \tag{2.4}$$

where $E_n^{(0)}$ and $|\psi_n\rangle$ are the unperturbed energy and wavefunction respectively.

Proof. We start by differentiating the Feynman-Hellman result (2.3) with respect to λ:

$$\begin{aligned} \left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0} &= \frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\langle \psi_n(\lambda)| \frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda} |\psi_n(\lambda)\rangle\right)\Bigg|_{\lambda=0} \\ &= \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle \psi_n(\lambda)|\right)\left(\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}\right)|\psi_n(\lambda)\rangle\Bigg|_{\lambda=0} \\ &\quad + \langle \psi_n(\lambda)|\left(\frac{\mathrm{d}^2\hat{H}(\lambda)}{\mathrm{d}\lambda^2}\right)|\psi_n(\lambda)\rangle\Bigg|_{\lambda=0} \\ &\quad + \langle \psi_n(\lambda)|\left(\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}\right)\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)\Bigg|_{\lambda=0} \end{aligned} \tag{2.5}$$

Since $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$, we have $\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda} = \hat{V}$ and $\frac{\mathrm{d}^2\hat{H}(\lambda)}{\mathrm{d}\lambda^2} = 0$. Evaluating at $\lambda = 0$ and replacing $|\psi_n(\lambda)\rangle$ with $|\psi_n\rangle$, we get:

$$\begin{aligned} \left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0} &= \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle \psi_n(\lambda)|\right)_{\lambda=0}\hat{V}|\psi_n\rangle + \langle \psi_n|\hat{V}\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} \\ &= 2\,\mathrm{Re}\left(\langle \psi_n|\hat{V}\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0}\right) \end{aligned} \tag{2.6}$$

To compute $\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0}$, we differentiate the Schrödinger equation $\hat{H}(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle$ with respect to λ:

$$\frac{\mathrm{d}\hat{H}(\lambda)}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle + \hat{H}(\lambda)\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle = \frac{\mathrm{d}E_n(\lambda)}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle + E_n(\lambda)\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle \tag{2.7}$$

At $\lambda = 0$:

$$\hat{V}|\psi_n\rangle + \hat{H}_0\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} = V_{nn}|\psi_n\rangle + E_n(0)\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} \tag{2.8}$$

Rearranging the terms, we get:

$$(\hat{H}_0 - E_n(0))\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} = (V_{nn} - \hat{V})|\psi_n\rangle \tag{2.9}$$

Since $|\psi_n(\lambda)\rangle$ is normalized, $\langle\psi_n(\lambda)|\psi_n(\lambda)\rangle = 1$. Differentiating gives $\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_n(\lambda)|\right)|\psi_n(\lambda)\rangle + \langle\psi_n(\lambda)|\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right) = 0$. At $\lambda = 0$:

$$\langle\psi_n|\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} + \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_n(\lambda)|\right)_{\lambda=0}|\psi_n\rangle = 0 \tag{2.10}$$

This means $\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0}$ is orthogonal to $|\psi_n\rangle$. Let $\left|\psi_n^{(1)}\right\rangle = \left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0}$.

For non-degenerate energy eigenvalues, we can express $\left|\psi_n^{(1)}\right\rangle$ as a linear combination of other unperturbed eigenstates $|\psi_m\rangle$ (where $m \neq n$):

$$\left|\psi_n^{(1)}\right\rangle = \sum_{m\neq n} c_m |\psi_m\rangle \tag{2.11}$$

Applying $\langle\psi_k|$ (for $k \neq n$) to (2.9):

$$\begin{aligned} \langle\psi_k|(\hat{H}_0 - E_n(0))\left|\psi_n^{(1)}\right\rangle &= \langle\psi_k|(V_{nn} - \hat{V})|\psi_n\rangle \qquad (2.12)\\ (E_k(0) - E_n(0))\left\langle\psi_k\middle|\psi_n^{(1)}\right\rangle &= \langle\psi_k|V_{nn}|\psi_n\rangle - \langle\psi_k|\hat{V}|\psi_n\rangle \\ (E_k(0) - E_n(0))c_k &= V_{nn}\langle\psi_k|\psi_n\rangle - V_{kn} \end{aligned}$$

Since $\langle\psi_k|\psi_n\rangle = 0$ for $k \neq n$, this simplifies to:

$$\begin{aligned} (E_k(0) - E_n(0))c_k &= -V_{kn} \qquad (2.13)\\ c_k &= \frac{V_{kn}}{E_n(0) - E_k(0)} \end{aligned}$$

So, the first-order correction to the wavefunction is:

$$\left|\psi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{V_{mn}}{E_n(0) - E_m(0)}|\psi_m\rangle \tag{2.14}$$

Now substitute this back into (2.6):

$$\begin{aligned} \left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0} &= \langle\psi_n|\hat{V}\sum_{m\neq n}\frac{V_{mn}}{E_n(0) - E_m(0)}|\psi_m\rangle + \sum_{m\neq n}\frac{V_{nm}}{E_n(0) - E_m(0)}\langle\psi_m|\hat{V}|\psi_n\rangle \qquad (2.15)\\ &= \sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n(0) - E_m(0)} + \sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n(0) - E_m(0)} \\ &= 2\sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n(0) - E_m(0)} \\ &= 2\sum_{m\neq n}\frac{|V_{mn}|^2}{E_n(0) - E_m(0)} \end{aligned}$$

Therefore, the second-order energy correction term in the Taylor expansion ($E_n^{(2)} = \frac{\lambda^2}{2}\left.\frac{\mathrm{d}^2 E_n(\lambda)}{\mathrm{d}\lambda^2}\right|_{\lambda=0}$) is:

$$E_n^{(2)} = \frac{\lambda^2}{2}\left(2\sum_{m\neq n}\frac{|V_{mn}|^2}{E_n(0)-E_m(0)}\right) = \lambda^2\sum_{m\neq n}\frac{|V_{mn}|^2}{E_n(0)-E_m(0)} \tag{2.16}$$

And the total energy up to second order is:

$$E_n(\lambda) = E_n^{(0)} + \lambda V_{nn} + \lambda^2\sum_{m\neq n}\frac{|V_{mn}|^2}{E_n^{(0)}-E_m^{(0)}} + \cdots \tag{2.17}$$

The wavefunction to first order is:

$$\begin{aligned} |\psi_n(\lambda)\rangle &= |\psi_n\rangle + \lambda\left(\frac{\mathrm{d}}{\mathrm{d}\lambda}|\psi_n(\lambda)\rangle\right)_{\lambda=0} + \cdots \\ &= |\psi_n\rangle + \lambda\sum_{m\neq n}\frac{V_{mn}}{E_n(0)-E_m(0)}|\psi_m\rangle + \cdots \end{aligned} \tag{2.18}$$

□

2.2 Example: Simple Harmonic Oscillator

Example. We apply the second-order perturbation theory to the perturbed Hamiltonian operator from Section 1.1:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 + \lambda\left(\frac{1}{2}k\hat{x}^2\right) \tag{2.19}$$

Here, the perturbation is $\hat{V} = \frac{1}{2}k\hat{x}^2$.

First, calculate the first-order energy correction V_{nn}:

$$V_{nn} = \langle n|\frac{1}{2}k\hat{x}^2|n\rangle = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) \tag{2.20}$$

So, the energy to first order is:

$$E_n(\lambda) = \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \cdots \tag{2.21}$$

Next, we need the matrix elements $V_{mn} = \langle m|\hat{V}|n\rangle$:

$$\begin{aligned} V_{mn} &= \langle m|\frac{1}{2}k\hat{x}^2|n\rangle \\ &= \frac{1}{2}m\omega^2\frac{\hbar}{2m\omega}\langle m|(\hat{a}+\hat{a}^\dagger)^2|n\rangle \\ &= \frac{\hbar\omega}{4}\langle m|\hat{a}^2+\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a}+(\hat{a}^\dagger)^2|n\rangle \\ &= \frac{\hbar\omega}{4}\left(\sqrt{n(n-1)}\delta_{m,n-2}+(2n+1)\delta_{m,n}+\sqrt{(n+1)(n+2)}\delta_{m,n+2}\right) \end{aligned} \tag{2.22}$$

Note that the $\delta_{m,n}$ term corresponds to V_{nn} and does not contribute to the second-order sum since $m \neq n$. The terms that contribute to the second-order sum are for $m = n-2$ and $m = n+2$.

The second-order energy correction is $\lambda^2 \sum_{m\neq n} \frac{|V_{mn}|^2}{E_n(0)-E_m(0)}$. For $m = n-2$: $V_{n,n-2} = \frac{\hbar\omega}{4}\sqrt{n(n-1)}$. $E_n(0) - E_{n-2}(0) = \hbar\omega(n+\frac{1}{2}) - \hbar\omega(n-2+\frac{1}{2}) = 2\hbar\omega$. For $m = n+2$: $V_{n,n+2} = \frac{\hbar\omega}{4}\sqrt{(n+1)(n+2)}$. $E_n(0) - E_{n+2}(0) = \hbar\omega(n+\frac{1}{2}) - \hbar\omega(n+2+\frac{1}{2}) = -2\hbar\omega$.

Substituting these into the second-order formula:

$$E_n(\lambda) = \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \lambda^2\left(\frac{|V_{n,n-2}|^2}{E_n(0)-E_{n-2}(0)} + \frac{|V_{n,n+2}|^2}{E_n(0)-E_{n+2}(0)}\right) + \cdots \tag{2.23}$$

$$\begin{aligned}
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \lambda^2\left(\frac{\left(\frac{\hbar\omega}{4}\right)^2 n(n-1)}{2\hbar\omega} + \frac{\left(\frac{\hbar\omega}{4}\right)^2 (n+1)(n+2)}{-2\hbar\omega}\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \lambda^2\frac{(\hbar\omega)^2}{16\cdot 2\hbar\omega}\left(n(n-1)-(n+1)(n+2)\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \lambda^2\frac{\hbar\omega}{32}\left(n^2-n-(n^2+3n+2)\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) + \lambda^2\frac{\hbar\omega}{32}\left(-4n-2\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) - \lambda^2\frac{\hbar\omega}{16}\left(2n+1\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right) + \lambda\frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right) - \lambda^2\frac{\hbar\omega}{8}\left(n+\frac{1}{2}\right) + \cdots \\
&= \hbar\omega\left(n+\frac{1}{2}\right)\left(1+\frac{\lambda}{2}-\frac{\lambda^2}{8}+\cdots\right)
\end{aligned}$$

This result precisely matches the Taylor expansion of the exact energy $E_n(\delta) = \hbar\omega\left(n+\frac{1}{2}\right)\sqrt{1+\lambda}$ from (1.2), confirming the validity of the perturbation theory derivation.

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3 Messiah Chapter XVI

3.1 §15 The Hamiltonian and its Resolvent

Note. A convenient way to organize stationary perturbation theory to all orders is to use the resolvent of the Hamiltonian. For a complex parameter z, the resolvent is defined as:

$$\hat{G}(z) := \frac{1}{z-\hat{H}} \tag{3.1}$$

As a function of z, $\hat{G}(z)$ is analytic everywhere except when $z - \hat{H} = 0$, namely at the eigenvalues of $\hat{H}$. For now, we assume the spectrum is discrete.

Let $\{E_i\}$ be the eigenvalues and let $\hat{P}_i$ denote the projector onto the eigenspace associated with E_i. We know that $\hat{P}_i = |E_i\rangle\langle E_i|$ for a nondegenerate eigenvalue E_i and normalized eigenvectors $|E_i\rangle$. We assume that all eigenvalues are non-degenerate. These projectors satisfy orthogonality and completeness.

Lemma 1 (Orthogonality of Projectors). For distinct eigenvalues E_i and E_j, the projectors $\hat{P}_i$ and $\hat{P}_j$ are orthogonal:

$$\hat{P}_i\hat{P}_j = \delta_{ij}\hat{P}_i \tag{3.2}$$

Proof. For normalized eigenvectors $|E_i\rangle$, $\hat{P}_i = |E_i\rangle\langle E_i|$.

$$\begin{aligned} \hat{P}_i\hat{P}_j &= (|E_i\rangle\langle E_i|)(|E_j\rangle\langle E_j|) && (3.3) \\ &= |E_i\rangle \langle E_i|E_j\rangle \langle E_j| && (3.4) \\ &= \langle E_j|E_i\rangle |E_i\rangle\langle E_j| && (3.5) \\ &= \delta_{ij} |E_i\rangle\langle E_i| && (3.6) \\ &= \delta_{ij}\hat{P}_i && (3.7) \end{aligned}$$

□

Definition 2 (Completeness Relation). The sum of all projectors onto the eigenspaces of a complete set of eigenvalues forms the identity operator:

$$\sum_i \hat{P}_i = \hat{I} \tag{3.8}$$

Lemma 2. The Hamiltonian operator acts on a projector $\hat{P}_i$ such that:

$$\hat{H}\hat{P}_i = E_i\hat{P}_i \tag{3.9}$$

Proof. Let $\psi \in \mathcal{H}$. $\hat{P}_i |\psi\rangle = c\,|E_i\rangle$ for some scalar c, as $\hat{P}_i$ projects onto the eigenspace of E_i. Now, apply $\hat{H}$ to $\hat{P}_i |\psi\rangle$:

$$\begin{aligned} \hat{H}\hat{P}_i |\psi\rangle &= \hat{H}(c\,|E_i\rangle) && (3.10) \\ &= c(\hat{H}\,|E_i\rangle) \\ &= c(E_i\,|E_i\rangle) && \text{(since } |E_i\rangle \text{ is an eigenstate of } \hat{H}) \\ &= E_i(c\,|E_i\rangle) \\ &= E_i(\hat{P}_i\,|\psi\rangle) \end{aligned}$$

Since this relationship holds for every $|\psi\rangle$ in the Hilbert space, we can conclude that $\hat{H}\hat{P}_i = E_i\hat{P}_i$. □

Proposition 1 (Spectral Decomposition of the Resolvent). The resolvent operator $\hat{G}(z)$ can be expressed as a sum over the projectors of the Hamiltonian's eigenspaces:

$$\hat{G}(z) = \sum_i \frac{\hat{P}_i}{z - E_i} \tag{3.11}$$

Proof. From (3.9), we have $\hat{H}\hat{P}_i = E_i\hat{P}_i$. Rearranging this, we get $(z - \hat{H})\hat{P}_i = (z - E_i)\hat{P}_i$.

Left-multiplying by $\hat{G}(z) = (z - \hat{H})^{-1}$:

$$\begin{aligned} \hat{G}(z)(z - \hat{H})\hat{P}_i &= \hat{G}(z)(z - E_i)\hat{P}_i \\ \hat{I}\hat{P}_i &= \hat{G}(z)(z - E_i)\hat{P}_i \\ \hat{P}_i &= (z - E_i)\hat{G}(z)\hat{P}_i \end{aligned} \tag{3.12}$$

This implies that $\hat{G}(z)\hat{P}_i = \frac{\hat{P}_i}{z-E_i}$. Summing over all i and using the completeness relation (3.8):

$$\begin{aligned} \sum_i \hat{G}(z)\hat{P}_i &= \sum_i \frac{\hat{P}_i}{z - E_i} \\ \hat{G}(z)\sum_i \hat{P}_i &= \sum_i \frac{\hat{P}_i}{z - E_i} \\ \hat{G}(z)\hat{I} &= \sum_i \frac{\hat{P}_i}{z - E_i} \\ \hat{G}(z) &= \sum_i \frac{\hat{P}_i}{z - E_i} \end{aligned} \tag{3.13}$$

This formula shows that each discrete eigenvalue E_i is a simple pole of $\hat{G}(z)$. □

Theorem 3 (Residue of the Resolvent)**.** The residue of the resolvent $\hat{G}(z)$ at a simple pole E_i is the corresponding projector $\hat{P}_i$.

$$\frac{1}{2\pi i}\oint_{\Gamma_i} \hat{G}(z)\mathrm{d}z = \hat{P}_i \tag{3.14}$$

where Γ_i is a small contour enclosing only E_i.

Proof. Using the spectral decomposition (3.11), we can calculate the residue directly:

$$\begin{aligned} \frac{1}{2\pi i}\oint_{\Gamma_i} \hat{G}(z)\mathrm{d}z &= \frac{1}{2\pi i}\oint_{\Gamma_i} \sum_j \frac{\hat{P}_j}{z - E_j}\mathrm{d}z \\ &= \sum_j \frac{1}{2\pi i}\oint_{\Gamma_i} \frac{\hat{P}_j}{z - E_j}\mathrm{d}z \end{aligned} \tag{3.15}$$

By Cauchy's residue theorem, only the term where E_j is inside Γ_i contributes. Since Γ_i only encloses E_i:

$$\begin{aligned} &= \frac{1}{2\pi i}\oint_{\Gamma_i} \frac{\hat{P}_i}{z - E_i}\mathrm{d}z \\ &= \hat{P}_i \cdot 1 \\ &= \hat{P}_i \end{aligned} \tag{3.16}$$

This result is significant as it provides a way to extract projectors using contour integrals. □

Theorem 4 (Projector for a Set of Eigenvalues). For any closed contour Γ that encloses a set of eigenvalues $\{E_j\}$ and excludes all others, the sum of the associated projectors, $\hat{P}_\Gamma$, is given by:

$$\hat{P}_\Gamma = \frac{1}{2\pi i}\oint_\Gamma \hat{G}(z)\mathrm{d}z \tag{3.17}$$

Furthermore, multiplying by $\hat{H}$:

$$\hat{H}\hat{P}_\Gamma = \frac{1}{2\pi i}\oint_\Gamma z\hat{G}(z)\mathrm{d}z \tag{3.18}$$

Proof. The first part follows directly from summing the residues for all E_j inside Γ. For the second part, using $(z-\hat{H})\hat{G}(z) = \hat{I}$:

$$\begin{aligned}
\hat{H}\hat{P}_\Gamma &= \hat{H}\left(\frac{1}{2\pi i}\oint_\Gamma \hat{G}(z)\mathrm{d}z\right) && (3.19)\\
&= \frac{1}{2\pi i}\oint_\Gamma \hat{H}\hat{G}(z)\mathrm{d}z \\
&= \frac{1}{2\pi i}\oint_\Gamma (z\hat{G}(z)-\hat{I})\mathrm{d}z && (\text{since } \hat{H}\hat{G}(z) = z\hat{G}(z)-\hat{I})\\
&= \frac{1}{2\pi i}\oint_\Gamma z\hat{G}(z)\mathrm{d}z - \frac{1}{2\pi i}\oint_\Gamma \hat{I}\mathrm{d}z \\
&= \frac{1}{2\pi i}\oint_\Gamma z\hat{G}(z)\mathrm{d}z - 0 \\
&= \frac{1}{2\pi i}\oint_\Gamma z\hat{G}(z)\mathrm{d}z
\end{aligned}$$

The integral of $\hat{I}$ over a closed contour is zero, assuming the contour is finite and well-behaved. □

Theorem 5 (Norm of the Resolvent). The norm of the resolvent operator is given by the reciprocal of the distance from z to the closest eigenvalue:

$$\|\hat{G}(z)\| = \frac{1}{\Delta(z)} \tag{3.20}$$

where $\Delta(z) = \min_i |z-E_i|$ is the distance from z to the closest eigenvalue E_i.

Proof. For any state $|\psi\rangle = \sum_i |\psi_i\rangle$ with $|\psi_i\rangle = \hat{P}_i|\psi\rangle$, we can write:

$$\begin{aligned}
\|\hat{G}(z)|\psi\rangle\|^2 &= \left\|\sum_i \frac{\hat{P}_i|\psi\rangle}{z-E_i}\right\|^2 && (3.21)\\
&= \left\|\sum_i \frac{|\psi_i\rangle}{z-E_i}\right\|^2
\end{aligned}$$

Since the $|\psi_i\rangle$ components are orthogonal (as they lie in orthogonal eigenspaces), the norm squared is:

$$
\begin{aligned}
&= \sum_i \left\| \frac{|\psi_i\rangle}{z - E_i} \right\|^2 \\
&= \sum_i \frac{\| \, |\psi_i\rangle \, \|^2}{|z - E_i|^2} \\
&\leq \left(\max_i \frac{1}{|z - E_i|^2} \right) \sum_i \| \, |\psi_i\rangle \, \|^2 \\
&= \left(\max_i \frac{1}{|z - E_i|^2} \right) \| \, |\psi\rangle \, \|^2
\end{aligned}
$$

Taking the square root, we get $\|\hat{G}(z)\| \leq \max_i \frac{1}{|z-E_i|} = \frac{1}{\min_i |z-E_i|} = \frac{1}{\Delta(z)}$.

To show equality, choose a state $|\psi\rangle$ that lies entirely within an eigenspace corresponding to an eigenvalue E_k such that $|z - E_k| = \Delta(z)$. For such a state, $\hat{G}(z) |\psi\rangle = \frac{1}{z-E_k} |\psi\rangle$. Then, $\|\hat{G}(z) |\psi\rangle \| = \left| \frac{1}{z-E_k} \right| \| \, |\psi\rangle \, \| = \frac{1}{\Delta(z)} \| \, |\psi\rangle \, \|$. Therefore, the operator norm is exactly $\frac{1}{\Delta(z)}$. □

3.2 §16 Expansion of $\hat{G}(z)$, $\hat{P}$ and $\hat{H}\hat{P}$ in powers of $\lambda\hat{V}$

Definition 3 (Perturbed and Unperturbed Resolvents). We write the perturbed Hamiltonian as $\hat{H} = \hat{H}_0 + \lambda\hat{V}$, where λ is a bookkeeping parameter. The unperturbed and full resolvents are defined as:

$$\hat{G}_0(z) = \frac{1}{z - \hat{H}_0} \tag{3.22}$$

$$\hat{G}(z) = \frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \tag{3.23}$$

Proposition 2 (Equation for Resolvents). The full resolvent $\hat{G}(z)$ can be expressed in terms of the unperturbed resolvent $\hat{G}_0(z)$ and the perturbation $\hat{V}$ as:

$$\hat{G} = \hat{G}_0(z)(1 + \lambda\hat{V}\hat{G}(z)) \tag{3.24}$$

Proof. We start with the definition of $\hat{G}(z)$:

$$\begin{aligned}
\hat{G}(z) &= \frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \\
&= \frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \\
&= \frac{1}{z - \hat{H}_0}(z - \hat{H}_0)\frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \\
&= \frac{1}{z - \hat{H}_0}[(z - \hat{H}_0 - \lambda\hat{V}) + \lambda\hat{V}]\frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \\
&= \frac{1}{z - \hat{H}_0}(z - \hat{H}_0 - \lambda\hat{V})\frac{1}{z - \hat{H}_0 - \lambda\hat{V}} + \frac{1}{z - \hat{H}_0}\lambda\hat{V}\frac{1}{z - \hat{H}_0 - \lambda\hat{V}} \\
&= \frac{1}{z - \hat{H}_0}\hat{I} + \frac{1}{z - \hat{H}_0}\lambda\hat{V}\hat{G}(z) \\
&= \hat{G}_0(z) + \hat{G}_0(z)\lambda\hat{V}\hat{G}(z) \\
&= \hat{G}_0(z)(\hat{I} + \lambda\hat{V}\hat{G}(z))
\end{aligned} \tag{3.25}$$

□

Theorem 6 (Neumann Series Expansion of the Resolvent). The full resolvent $\hat{G}(z)$ can be expressed as a Neumann series:

$$\hat{G}(z) = \sum_{n=0}^{\infty} \lambda^n \hat{G}_0(z)(\hat{V}\hat{G}_0(z))^n \tag{3.26}$$

This series converges when $\|\lambda\hat{V}\hat{G}_0(z)\| < 1$.

Proof. From Proposition 2, we have $\hat{G} = \hat{G}_0 + \hat{G}_0\lambda\hat{V}\hat{G}$. We can rearrange this to isolate $\hat{G}$:

$$\begin{aligned}
\hat{G} - \hat{G}_0\lambda\hat{V}\hat{G} &= \hat{G}_0 \\
(\hat{I} - \hat{G}_0\lambda\hat{V})\hat{G} &= \hat{G}_0 \\
\hat{G} &= (\hat{I} - \hat{G}_0\lambda\hat{V})^{-1}\hat{G}_0
\end{aligned} \tag{3.27}$$

Using the geometric series expansion for operators, $(\hat{I} - \hat{X})^{-1} = \sum_{n=0}^{\infty} \hat{X}^n$, which converges if the operator norm $\|\hat{X}\| < 1$. Here, $\hat{X} = \hat{G}_0\lambda\hat{V}$. So, the series converges if $\|\hat{G}_0\lambda\hat{V}\| < 1$.

$$\begin{aligned}
\hat{G} &= \left(\sum_{n=0}^{\infty}(\hat{G}_0\lambda\hat{V})^n\right)\hat{G}_0 \\
&= \sum_{n=0}^{\infty} \lambda^n (\hat{G}_0\hat{V})^n \hat{G}_0 \\
&= \sum_{n=0}^{\infty} \lambda^n \hat{G}_0(\hat{V}\hat{G}_0)^n
\end{aligned} \tag{3.28}$$

The convergence condition is $\|\lambda \hat{V} \hat{G}_0\| < 1$. Since $\|\hat{G}_0(z)\| = 1/\Delta_0(z)$ (where $\Delta_0(z)$ is the distance from z to the nearest eigenvalue of $\hat{H}_0$), a sufficient condition for convergence is $\|\lambda \hat{V}\| < \Delta_0(z)$. This means that the perturbation must be sufficiently small. □

Proposition 3 (Expansion of the Projector $\hat{P}$). The projector $\hat{P}$ onto an eigenspace of the perturbed Hamiltonian can be expanded as a power series in the perturbation parameter λ:

$$\hat{P} = \hat{P}_a + \sum_{n=1}^{\infty} \lambda^n \hat{A}^{(n)} \tag{3.29}$$

where $\hat{P}_a$ is the unperturbed projector and $\hat{A}^{(n)} = \frac{1}{2\pi i} \oint_{\Gamma_a} \hat{G}_0(\hat{V}\hat{G}_0)^n \mathrm{d}z$.

Proof. Let Γ_a be a contour that encloses the unperturbed eigenvalue E_a^0 and the eigenvalues of $\hat{H}$ that tend to E_a^0 for small λ. From the residue formula (3.17), the projector $\hat{P}$ is:

$$\hat{P} = \frac{1}{2\pi i} \oint_{\Gamma_a} \hat{G}(z) \mathrm{d}z \tag{3.30}$$

Substituting the Neumann series for $\hat{G}(z)$ from (3.26):

$$\begin{aligned}
\hat{P} &= \frac{1}{2\pi i} \oint_{\Gamma_a} \sum_{n=0}^{\infty} \lambda^n \hat{G}_0(z) (\hat{V} \hat{G}_0(z))^n \mathrm{d}z \qquad (3.31)\\
&= \frac{1}{2\pi i} \oint_{\Gamma_a} \hat{G}_0(z) \mathrm{d}z + \sum_{n=1}^{\infty} \lambda^n \left(\frac{1}{2\pi i} \oint_{\Gamma_a} \hat{G}_0(z) (\hat{V} \hat{G}_0(z))^n \mathrm{d}z \right)
\end{aligned}$$

The first term is the projector onto the unperturbed eigenspace corresponding to E_a^0, denoted $\hat{P}_0$. The remaining terms define $\hat{A}^{(n)}$:

$$\hat{P} = \hat{P}_a + \sum_{n=1}^{\infty} \lambda^n \hat{A}^{(n)} \tag{3.32}$$

□

To evaluate the residues for $\hat{A}^{(n)}$, we expand $\hat{G}_0(z)$ about E_a^0 in a Laurent series. Let $\hat{Q}_a := \hat{I} - \hat{P}_a = \sum_{i \neq a} \hat{P}_i$, which is the projector onto the subspace orthogonal to the unperturbed eigenspace of E_a^0.

Definition 4 (Laurent Series of Unperturbed Resolvent). The unperturbed resolvent $\hat{G}_0(z)$ can be written in terms of projectors:

$$\hat{G}_0(z) = \frac{\hat{P}_a}{z - E_a^0} + \sum_{i \neq a} \frac{\hat{P}_i}{z - E_i^0} \tag{3.33}$$

For $|z - E_a^0| < \min_{i \neq a} |E_i^0 - E_a^0|$, we can expand the second term as a geometric series.

Expanding a single term $\frac{1}{z-E_i^0}$:

$$\frac{1}{z-E_i^0} = \frac{1}{(z-E_a^0)-(E_i^0-E_a^0)} \tag{3.34}$$
$$= \frac{1}{E_i^0-E_a^0}\frac{E_i^0-E_a^0}{(z-E_a^0)-(E_i^0-E_a^0)} \tag{3.35}$$
$$= -\frac{1}{E_i^0-E_a^0}\frac{1}{1-\frac{z-E_a^0}{E_i^0-E_a^0}} \tag{3.36}$$
$$= -\sum_{k=0}^{\infty}\frac{(z-E_a^0)^k}{(E_i^0-E_a^0)^{k+1}} \tag{3.37}$$

The convergence condition for this geometric series is $\left|\frac{z-E_a^0}{E_i^0-E_a^0}\right| < 1$. Summing over $i \neq a$:

$$\sum_{i\neq a}\frac{\hat{P}_i}{z-E_i^0} = \sum_{k=0}^{\infty}(-1)^k(z-E_a^0)^k\sum_{i\neq a}\frac{\hat{P}_i}{(E_a^0-E_i^0)^{k+1}} \tag{3.38}$$

Definition 5 (Operator $\hat{O}_a$)**.** Define the operator $\hat{O}_a$, which is the inverse of $(E_a^0-\hat{H}_0)$ on the $\hat{Q}_a$ subspace:

$$\hat{O}_a := \hat{Q}_a(E_a^0-\hat{H}_0)^{-1}\hat{Q}_a \tag{3.39}$$

Lemma 3 (Explicit Form of $\hat{O}_a$)**.** The operator $\hat{O}_a$ can be explicitly written as:

$$\hat{O}_a = \sum_{i\neq a}\frac{1}{E_a^0-E_i^0}\hat{P}_i \tag{3.40}$$

Proof. Consider the operator $\hat{X} = \sum_{i\neq a}\frac{1}{E_a^0-E_i^0}\hat{P}_i$. We need to show that this is the inverse of $(E_a^0-\hat{H}_0)$ on the $\hat{Q}_a$ subspace. This means we need to show $(E_a^0-\hat{H}_0)\hat{X} = \hat{Q}_a$ and $\hat{X}(E_a^0-\hat{H}_0) = \hat{Q}_a$.

First, consider $(E_a^0-\hat{H}_0)\hat{X}$:

$$(E_a^0-\hat{H}_0)\hat{X} = (E_a^0-\hat{H}_0)\left(\sum_{i\neq a}\frac{\hat{P}_i}{E_a^0-E_i^0}\right) \tag{3.41}$$
$$= \left(\sum_j(E_a^0-E_j^0)\hat{P}_j\right)\left(\sum_{i\neq a}\frac{\hat{P}_i}{E_a^0-E_i^0}\right)$$

Using the orthogonality of projectors $\hat{P}_j \hat{P}_i = \delta_{ji} \hat{P}_i$:

$$
\begin{aligned}
&= \sum_j \sum_{i \neq a} \frac{(E_a^0 - E_j^0)}{(E_a^0 - E_i^0)} \hat{P}_j \hat{P}_i \\
&= \sum_{i \neq a} \frac{(E_a^0 - E_i^0)}{(E_a^0 - E_i^0)} \hat{P}_i \\
&= \sum_{i \neq a} \hat{P}_i \\
&= \hat{Q}_a
\end{aligned}
$$

Now, consider $\hat{X}(E_a^0 - \hat{H}_0)$:

$$
\begin{aligned}
\hat{X}(E_a^0 - \hat{H}_0) &= \left(\sum_{i \neq a} \frac{\hat{P}_i}{E_a^0 - E_i^0} \right) \left(\sum_j (E_a^0 - E_j^0) \hat{P}_j \right) \qquad (3.42) \\
&= \sum_{i \neq a} \sum_j \frac{(E_a^0 - E_j^0)}{(E_a^0 - E_i^0)} \hat{P}_i \hat{P}_j \\
&= \sum_{i \neq a} \frac{(E_a^0 - E_i^0)}{(E_a^0 - E_i^0)} \hat{P}_i \\
&= \sum_{i \neq a} \hat{P}_i \\
&= \hat{Q}_a
\end{aligned}
$$

Thus, we have shown that $\hat{X}$ is the left and right inverse of $(E_a^0 - \hat{H}_0)$ in the $\hat{Q}_a$ subspace, which is precisely the definition of $\hat{O}_a$. Therefore, $\hat{O}_a = \sum_{i \neq a} \frac{1}{E_a^0 - E_i^0} \hat{P}_i$. □

Lemma 4 (Powers of $\hat{O}_a$)**.** The k-th power of $\hat{O}_a$ is given by:

$$
(\hat{O}_a)^k = \sum_{i \neq a} \frac{\hat{P}_i}{(E_a^0 - E_i^0)^k} \qquad (3.43)
$$

Proof. This can be shown by induction. For $k = 1$, it is the definition of $\hat{O}_a$. Assuming it holds for k, we show for $k+1$:

$$\begin{aligned}
(\hat{O}_a)^{k+1} &= (\hat{O}_a)^k \hat{O}_a \\
&= \left(\sum_{j\neq a} \frac{\hat{P}_j}{(E_a^0 - E_j^0)^k}\right)\left(\sum_{i\neq a} \frac{\hat{P}_i}{E_a^0 - E_i^0}\right) \\
&= \sum_{j\neq a}\sum_{i\neq a} \frac{\hat{P}_j \hat{P}_i}{(E_a^0 - E_j^0)^k (E_a^0 - E_i^0)} \\
&= \sum_{i\neq a} \frac{\hat{P}_i}{(E_a^0 - E_i^0)^k (E_a^0 - E_i^0)} \qquad (\text{since } \hat{P}_j \hat{P}_i = \delta_{ji}\hat{P}_i) \\
&= \sum_{i\neq a} \frac{\hat{P}_i}{(E_a^0 - E_i^0)^{k+1}}
\end{aligned} \tag{3.44}$$

This completes the proof. □

Substituting (3.43) into (3.38), we can simplify the Laurent series for the unperturbed resolvent:

$$\begin{aligned}
\hat{G}_0(z) &= \frac{\hat{P}_a}{z - E_a^0} + \sum_{k=0}^{\infty}(-1)^k (z - E_a^0)^k \sum_{i\neq a} \frac{\hat{P}_i}{(E_a^0 - E_i^0)^{k+1}} \\
&= \frac{\hat{P}_a}{z - E_a^0} + \sum_{k=0}^{\infty}(-1)^k (z - E_a^0)^k (\hat{O}_a)^{k+1} \\
&= \frac{\hat{P}_a}{z - E_a^0} - \sum_{k=1}^{\infty}(-1)^{k-1} (z - E_a^0)^{k-1} (\hat{O}_a)^k \\
&= \frac{\hat{P}_a}{z - E_a^0} + \sum_{k=1}^{\infty}(-1)^{k-1} (z - E_a^0)^{k-1} \hat{O}_a^k
\end{aligned} \tag{3.45}$$

This expression is a Laurent series where the principal part corresponds to the projector $\hat{P}_a$ and the analytic part involves powers of $\hat{O}_a$.

Definition 6 (Kato's Operators $\hat{S}^k$)**.** Kato's operators $\hat{S}^k$ are defined as:

$$\hat{S}^k = \begin{cases} -\hat{P}_a, & k = 0, \\ \hat{O}_a^k, & k \geq 1. \end{cases} \tag{3.46}$$

Using these operators, the Laurent expansion of $\hat{G}_0(z)$ around E_a^0 can be written compactly as:

$$\hat{G}_0(z) = \sum_{k=0}^{\infty}(-1)^{k-1}(z - E_a^0)^{k-1}\hat{S}^k \tag{3.47}$$

Multiplying both sides by $\hat{V}$,

$$\hat{V}\hat{G}_0 = \sum_{k=0}^{\infty}(-1)^{k-1}(z - E_a^0)^{k-1}\hat{V}\hat{S}^k \tag{3.48}$$

Now we use this compact form to expand $(\hat{V}\hat{G}_0)^n$:

$$
\begin{aligned}
(\hat{V}\hat{G}_0)^n &= \prod_{j=1}^{n} \left(\hat{V} \sum_{k_j \geq 0} (-1)^{k_j - 1} (z - E_a^0)^{k_j - 1} \hat{S}^{k_j} \right) && (3.49) \\
&= \prod_{j=1}^{n} \Big(\hat{V} \big[(-1)^{-1} (z - E_a^0)^{-1} \hat{S}^0 + (-1)^0 (z - E_a^0)^0 \hat{S}^1 + (-1)^1 (z - E_a^0)^1 \hat{S}^2 + \cdots \big] \Big) \\
&= \prod_{j=1}^{n} \Big(-(z - E_a^0)^{-1} \hat{V} + \hat{V}\hat{S} - (z - E_a^0) \hat{V}\hat{S}^2 + \cdots \Big) && (3.50) \\
&= \Big(-(z - E_a^0)^{-1} \hat{V} + \hat{V}\hat{S} - (z - E_a^0) \hat{V}\hat{S}^2 + \cdots \Big) \\
&\quad \times \Big(-(z - E_a^0)^{-1} \hat{V} + \hat{V}\hat{S} - (z - E_a^0) \hat{V}\hat{S}^2 + \cdots \Big) \times \cdots && (3.51)
\end{aligned}
$$

As we can see, each element in the distributed product will contain one element from each sum. We can reorder and combine the scalars since they commute, while the operators must retain their order.

$$
\begin{aligned}
(\hat{V}\hat{G}_0)^n &= \prod_{j=1}^{n} \left(\sum_{k_j \geq 0} (-1)^{k_j - 1} (z - E_a^0)^{k_j - 1} \hat{V}\hat{S}^{k_j} \right) && (3.52) \\
&= \sum_{k_1, \cdots, k_n \geq 0} \left[\prod_{j=1}^{n} (-1)^{k_j - 1} (z - E_a^0)^{k_j - 1} \right] (\hat{V}\hat{S}^{k_1}) \cdots (\hat{V}\hat{S}^{k_n}) && (3.53) \\
&= \sum_{k_1, \cdots, k_n \geq 0} (-1)^{\left(\sum_{j=1}^{n} k_j\right) - n} (z - E_a^0)^{\left(\sum_{j=1}^{n} k_j\right) - n} (\hat{V}\hat{S}^{k_1}) \cdots (\hat{V}\hat{S}^{k_n}) && (3.54)
\end{aligned}
$$

Finally, we combine $\hat{G}_0$ with $(\hat{V}\hat{G}_0)^n$:

$$
\begin{aligned}
\hat{G}_0(\hat{V}\hat{G}_0)^n &= \left[\sum_{k_0 \geq 0} (-1)^{k_0 - 1} (z - E_a^0)^{k_0 - 1} \hat{S}^{k_0} \right] \\
&\quad \times \left[\sum_{k_1, \cdots, k_n \geq 0} (-1)^{\left(\sum_{j=1}^{n} k_j\right) - n} (z - E_a^0)^{\left(\sum_{j=1}^{n} k_j\right) - n} (\hat{V}\hat{S}^{k_1}) \cdots (\hat{V}\hat{S}^{k_n}) \right] && (3.55) \\
&= \Big[-(z - E_a^0)^{-1} \hat{S}^0 + \hat{S}^1 - (z - E_a^0) \hat{S}^2 + \cdots \Big] \\
&\quad \times \left[\sum_{k_1, \cdots, k_n \geq 0} (-1)^{\left(\sum_{j=1}^{n} k_j\right) - n} (z - E_a^0)^{\left(\sum_{j=1}^{n} k_j\right) - n} (\hat{V}\hat{S}^{k_1}) \cdots (\hat{V}\hat{S}^{k_n}) \right] && (3.56)
\end{aligned}
$$

Again, the final product will contain one element from each of the sums. We can reorder the scalars since they commute but the operators retain their initial order, with $\hat{S}^{k_0}$ appearing first.

$$
\hat{G}_0(\hat{V}\hat{G}_0)^n = \sum_{k_0, \cdots, k_n \geq 0} (-1)^{(k_0 - 1) + \left(\sum_{j=1}^{n} k_j\right) - n} (z - E_a^0)^{(k_0 - 1) + \left(\sum_{j=1}^{n} k_j\right) - n} \big(\hat{S}^{k_0} \hat{V}\hat{S}^{k_1} \cdots \hat{V}\hat{S}^{k_n} \big) \tag{3.57}
$$

Let $K = \sum_{j=0}^{n} k_j$. The coefficient of $(z - E_a^0)^{-1}$ (which corresponds to the residue and thus $\hat{A}^{(n)}$) occurs when the exponent $(k_0 - 1) + \left(\sum_{j=1}^{n} k_j\right) - n = K - (n+1)$ equals -1. This implies

$K-(n+1)=-1$, so $K=n$. Therefore, $k_0+\cdots+k_n=n$. Hence, the expression for $\hat{A}^{(n)}$ is $=-\sum_{\substack{k_0,\cdots,k_n\geq 0\\ k_0+\cdots+k_n=n}} \hat{S}^{k_0}\hat{V}\hat{S}^{k_1}\cdots\hat{V}\hat{S}^{k_n}$. We reindex the sum from $k_0,k_1,\cdots k_n$ to $k_1,k_2,\cdots k_{n+1}$ to match the form in the textbook.

Theorem 7 (Explicit Form of $\hat{A}^{(n)}$).

$$\hat{A}^{(n)}=-\sum_{(n)}\hat{S}^{k_1}\hat{V}\hat{S}^{k_2}\cdots\hat{V}\hat{S}^{k_{n+1}}, \quad \text{where } k_1+\cdots+k_{n+1}=n \tag{3.58}$$

Now, we calculate the first few coefficients $\hat{A}_n$. Recall equation (3.46).

$$\hat{A}^{(0)}=-\sum_{0}\hat{S}^{k_1} \tag{3.59}$$
$$=-(-\hat{P}_a)=\hat{P}_a \tag{3.60}$$
$$\hat{A}^{(1)}=-\sum_{1}\hat{S}^{k_1}\hat{V}\hat{S}^{k_2} \tag{3.61}$$
$$=-(\hat{S}_0\hat{V}\hat{S}_1+\hat{S}_1\hat{V}\hat{S}_0) \tag{3.62}$$
$$=-(-\hat{P}_a\hat{V}\hat{O}_a+-\hat{O}_a\hat{V}\hat{P}_a) \tag{3.63}$$
$$=\hat{P}_a\hat{V}\hat{O}_a+\hat{O}_a\hat{V}\hat{P}_a \tag{3.64}$$
$$\hat{A}^{(2)}=-\sum_{2}\hat{S}^{k_1}\hat{V}\hat{S}^{k_2}\hat{V}\hat{S}^{k_3} \tag{3.65}$$
$$=-\Big(\hat{S}_2\hat{V}\hat{S}_0\hat{V}\hat{S}_0+\hat{S}_0\hat{V}\hat{S}_2\hat{V}\hat{S}_0+\hat{S}_0\hat{V}\hat{S}_0\hat{V}\hat{S}_2+\hat{S}_1\hat{V}\hat{S}_1\hat{V}\hat{S}_0+\hat{S}_1\hat{V}\hat{S}_0\hat{V}\hat{S}_1+\hat{S}_0\hat{V}\hat{S}_1\hat{V}\hat{S}_1\Big)$$
$$\begin{aligned}=-\Big(&\hat{O}_a^2\hat{V}(-\hat{P}_a)\hat{V}(-\hat{P}_a)+(-\hat{P}_a)\hat{V}\hat{O}_a^2\hat{V}(-\hat{P}_a)+(-\hat{P}_a)\hat{V}(-\hat{P}_a)\hat{V}\hat{O}_a^2\\ &+\hat{O}_a\hat{V}\hat{O}_a\hat{V}(-\hat{P}_a)+\hat{O}_a\hat{V}(-\hat{P}_a)\hat{V}\hat{O}_a+(-\hat{P}_a)\hat{V}\hat{O}_a\hat{V}\hat{O}_a\Big)\end{aligned} \tag{3.66}$$
$$=\hat{O}_a\hat{V}\hat{O}_a\hat{V}\hat{P}_a+\hat{O}_a\hat{V}\hat{P}_a\hat{V}\hat{O}_a+\hat{P}_a\hat{V}\hat{O}_a\hat{V}\hat{O}_a \tag{3.67}$$
$$-\hat{O}_a^2\hat{V}\hat{P}_a\hat{V}\hat{P}_a-\hat{P}_a\hat{V}\hat{O}_a^2\hat{V}\hat{P}_a-\hat{P}_a\hat{V}\hat{P}_a\hat{V}\hat{O}_a^2 \tag{3.68}$$

Now, we can write out the expansion $\hat{P}$ to the 2nd order.

$$\begin{aligned}\hat{P}=\hat{P}_a&+\lambda\left(\hat{P}_a\hat{V}\hat{O}_a+\hat{O}_a\hat{V}\hat{P}_a\right)\\ &+\lambda^2\Big(\hat{O}_a\hat{V}\hat{O}_a\hat{V}\hat{P}_a+\hat{O}_a\hat{V}\hat{P}_a\hat{V}\hat{O}_a+\hat{P}_a\hat{V}\hat{O}_a\hat{V}\hat{O}_a\\ &\qquad-\hat{O}_a^2\hat{V}\hat{P}_a\hat{V}\hat{P}_a-\hat{P}_a\hat{V}\hat{O}_a^2\hat{V}\hat{P}_a-\hat{P}_a\hat{V}\hat{P}_a\hat{V}\hat{O}_a^2\Big).\end{aligned} \tag{3.69}$$

Proposition 4 (Expansion of $(\hat{H}-E_a^0)\hat{P}$).

$$(\hat{H}-E_a^0)\hat{P}=\sum_{n=1}^{\infty}\lambda^n\hat{B}^{(n)}, \qquad \hat{B}^{(n)}:=(\hat{H}_0-E_a^0)\hat{A}^{(n)}+\hat{V}\hat{A}^{(n-1)} \quad (n\geq 1). \tag{3.70}$$

Proof. Starting from $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ and the series for $\hat{P}$,

$$\begin{aligned}(\hat{H} - E_a^0)\hat{P} &= \big(\hat{H}_0 - E_a^0\big)\hat{P} + \lambda\hat{V}\hat{P} \\ &= \big(\hat{H}_0 - E_a^0\big)\left(\hat{P}_a + \sum_{n=1}^{\infty}\lambda^n\hat{A}^{(n)}\right) + \lambda\hat{V}\left(\hat{P}_a + \sum_{n=1}^{\infty}\lambda^n\hat{A}^{(n)}\right).\end{aligned}$$

Using $(\hat{H}_0 - E_a^0)\hat{P}_a = 0$ and reindexing the second sum, $\lambda\hat{V}\left(\hat{P}_a + \sum_{n=1}^{\infty}\lambda^n\hat{A}^{(n)}\right) = \lambda\hat{V}\hat{P}_a + \lambda\sum_{n=1}^{\infty}\lambda^{n+1}\hat{V}\hat{A}^{(n)} = \sum_{n=0}^{\infty}\lambda^{n+1}\hat{V}\hat{A}^{(n)}$.

$$\begin{aligned}(\hat{H} - E_a^0)\hat{P} &= \sum_{n=1}^{\infty}\lambda^n(\hat{H}_0 - E_a^0)\hat{A}^{(n)} + \sum_{n=0}^{\infty}\lambda^{n+1}\hat{V}\hat{A}^{(n)} \\ &= \sum_{n=1}^{\infty}\lambda^n(\hat{H}_0 - E_a^0)\hat{A}^{(n)} + \sum_{n=0}^{\infty}\lambda^{n+1}\hat{V}\hat{A}^{(n)} \\ &= \sum_{n=1}^{\infty}\lambda^n\Big[(\hat{H}_0 - E_a^0)\hat{A}^{(n)} + \hat{V}\hat{A}^{(n-1)}\Big].\end{aligned}$$

Defining $\hat{B}^{(n)}$ as stated yields $(\hat{H} - E_a^0)\hat{P} = \sum_{n=1}^{\infty}\lambda^n\hat{B}^{(n)}$. □

With $\hat{A}^{(1)} = \hat{P}_0\hat{V}\hat{O}_a + \hat{O}_a\hat{V}\hat{P}_0$ and $(\hat{H}_0 - E_a^0)\hat{P}_0 = 0$, $(\hat{H}_0 - E_a^0)\hat{O}_a = -\hat{Q}_a$,

$$\hat{B}^{(1)} = (\hat{H}_0 - E_a^0)\hat{A}^{(1)} + \hat{V}\hat{A}^{(0)} = -\hat{Q}_a\hat{V}\hat{P}_0 + \hat{V}\hat{P}_0 = \hat{P}_0\hat{V}\hat{P}_0.$$

---

4 Perturbation Series from the Resolvent Trace

In this section we obtain the (nondegenerate) Rayleigh–Schrödinger energy series directly from the trace of the full resolvent. We assume: (i) $\hat{H}$ is self-adjoint with purely discrete spectrum $\{E_n\}$, and complete orthonormal eigenbases $\{|E_n\rangle\}$ (ii) each eigenspace is 1-dimensional (eigenvalues are non-degenerate).

Definition 7. For $z \in \mathbb{C} \setminus \sigma(\hat{H})$, the resolvent is $\hat{G}(z) := (z - \hat{H})^{-1}$ and we denote

$$F(z) := \operatorname{Tr}\hat{G}(z).$$

Proposition 5 (Spectral trace identity).

$$F(z) = \operatorname{Tr}\Big(z - \hat{H}\Big)^{-1} = \sum_{n=0}^{\infty}\frac{1}{z - E_n}, \qquad z \notin \{E_n\}. \tag{4.1}$$

Proof. Let $\hat{H}\,|E_n\rangle = E_n\,|E_n\rangle$. Therefore, $(z - \hat{H})\,|E_n\rangle = (z - E_n)\,|E_n\rangle$. Therefore, applying $(z - H)^{-1}$ on $|E_n\rangle$ gives

$$\hat{G}(z)\,|E_n\rangle = \frac{1}{z - E_n}\,|E_n\rangle \tag{4.2}$$

Therefore, $\frac{1}{z-E_n}$ is an eigenvalue of $(z-\hat{H})^{-1}$. Since the trace of matrix is given by the sum of its eigenvalues,

$$F(z) = \mathrm{Tr}\Big(z - \hat{H}\Big) = \sum_n \frac{1}{z - E_n} \tag{4.3}$$

□

Perturbed vs. unperturbed traces. Let $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ with unperturbed eigenpairs $\{|m\rangle, E_m^{(0)}\}$. Write $\hat{G}_0(z) = (z-\hat{H}_0)^{-1}$ and expand the full resolvent by the Neumann series (Theorem 3.26):

$$\hat{G}(z) = \sum_{n=0}^{\infty} \lambda^n \hat{G}_0(z)(\hat{V}\hat{G}(z))^n = \hat{G}_0 + \lambda\hat{G}_0\hat{V}\hat{G}_0 + \lambda^2\hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0 + \cdots$$

Taking the trace, we obtain

$$F(z) = \mathrm{Tr}\left(\sum_{n=0}^{\infty} \lambda^n \hat{G}_0(z)(\hat{V}\hat{G}(z))^n\right) = \sum_{n=0}^{\infty} \lambda^n\, \mathrm{Tr}\left(\hat{G}_0(z)(\hat{V}\hat{G}(z))^n\right) \tag{4.4}$$

4.1 Explicit Index Expansion with Inserted Identities

Define

$$\hat{H}_0\,|m\rangle = E_m^{(0)}\,|m\rangle, \qquad g_m(z) := \frac{1}{z - E_m^{(0)}}, \qquad V_{mn} := \langle m|\,\hat{V}\,|n\rangle.$$

We repeatedly insert the identity operator $\hat{I} = \sum_k |k\rangle\langle k|$ between every neighboring pair of operators and use $\langle a|\,\hat{G}_0(z)\,|b\rangle = g_b(z)\delta_{ab}$ and $\langle a|\,\hat{V}\,|b\rangle = V_{ab}$.

$$\begin{aligned}
\mathrm{Tr}\,\hat{G}_0 &= \sum_r \langle r|\,\hat{G}_0\hat{I}\,|r\rangle = \sum_r\sum_m \langle r|\,\hat{G}_0\,|m\rangle\,\langle m|r\rangle \\
&= \sum_r\sum_m g_m(z)\delta_{rm}\delta_{mr} = \sum_r g_r(z) = \sum_{m_1} \frac{1}{z - E_{m_1}^{(0)}}.
\end{aligned} \tag{4.5}$$

$$\begin{aligned}
\mathrm{Tr}\Big(\hat{G}_0\hat{V}\hat{G}_0\Big) &= \sum_r \langle r|\,\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\,|r\rangle \\
&= \sum_r\sum_a\sum_b \langle r|\,\hat{G}_0\,|a\rangle\,\langle a|\,\hat{V}\,|b\rangle\,\langle b|\,\hat{G}_0\,|r\rangle \\
&= \sum_{r,a,b} (g_a\delta_{ra})V_{ab}(g_r\delta_{br}) = \sum_r g_r V_{rr} g_r = \sum_{m_1} \frac{V_{m_1m_1}}{(z - E_{m_1}^{(0)})^2}.
\end{aligned} \tag{4.6}$$

$$\begin{aligned}
\mathrm{Tr}\Big(\hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0\Big) &= \sum_r \langle r|\,\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\,|r\rangle \\
&= \sum_r\sum_a\sum_b\sum_c\sum_d \langle r|\,\hat{G}_0\,|a\rangle\,\langle a|\,\hat{V}\,|b\rangle\,\langle b|\,\hat{G}_0\,|c\rangle\,\langle c|\,\hat{V}\,|d\rangle\,\langle d|\,\hat{G}_0\,|r\rangle \\
&= \sum_{r,a,b,c,d} (g_a\delta_{ra})V_{ab}(g_c\delta_{bc})V_{cd}(g_r\delta_{dr}) \\
&= \sum_{r,b} g_r V_{rb} g_b V_{br} g_r = \sum_{m_1,m_2} g_{m_1}^2 g_{m_2} V_{m_1m_2}V_{m_2m_1} \\
&= \sum_{m_1,m_2} \frac{V_{m_1m_2}V_{m_2m_1}}{(z - E_{m_1}^{(0)})^2(z - E_{m_2}^{(0)})}.
\end{aligned} \tag{4.7}$$

$$
\begin{aligned}
\mathrm{Tr}\Big(\hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0\Big) &= \sum_r \langle r|\,\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\,|r\rangle \\
&= \sum_r \sum_{a,b,c,d,e,f} \langle r|\,\hat{G}_0\,|a\rangle\,\langle a|\,\hat{V}\,|b\rangle\,\langle b|\,\hat{G}_0\,|c\rangle\,\langle c|\,\hat{V}\,|d\rangle\,\langle d|\,\hat{G}_0\,|e\rangle\,\langle e|\,\hat{V}\,|f\rangle\,\langle f|\,\hat{G}_0\,|r\rangle \\
&= \sum_{r,a,b,c,d,e,f} (g_a\delta_{ra})V_{ab}(g_c\delta_{bc})V_{cd}(g_e\delta_{de})V_{ef}(g_r\delta_{fr}) \\
&= \sum_{r,b,d} g_r V_{rb} g_b V_{bd} g_d V_{dr} g_r \\
&= \sum_{m_1,m_2,m_3} \frac{V_{m_1m_2}V_{m_2m_3}V_{m_3m_1}}{(z-E^{(0)}_{m_1})^2(z-E^{(0)}_{m_2})(z-E^{(0)}_{m_3})}.
\end{aligned}
\tag{4.8}
$$

$$
\begin{aligned}
\mathrm{Tr}\big(\hat{G}_0(\hat{V}\hat{G}_0)^N\big) &= \sum_r \langle r|\,\hat{G}_0\hat{I}\hat{V}\hat{I}\hat{G}_0\hat{I}\cdots\hat{V}\hat{I}\hat{G}_0\,|r\rangle \\
&= \sum_r \sum_{m_2,\dots,m_N,m_1} \langle r|\,\hat{G}_0\,|m_1\rangle\,\langle m_1|\,\hat{V}\,|m_2\rangle\,\langle m_2|\,\hat{G}_0\,|m_3\rangle\cdots\langle m_N|\,\hat{V}\,|r\rangle\,\langle r|\,\hat{G}_0\,|r\rangle \\
&= \sum_{r,m_2,\dots,m_N} g_r V_{rm_2} g_{m_2} V_{m_2m_3}\cdots V_{m_Nr} g_r \\
&= \sum_{m_1,\dots,m_N} g^2_{m_1}\prod_{j=2}^{N} g_{m_j}\,\prod_{j=1}^{N} V_{m_jm_{j+1}}, \qquad m_{N+1}\equiv m_1 \\
&= \sum_{m_1,\dots,m_N} \frac{V_{m_1m_2}V_{m_2m_3}\cdots V_{m_Nm_1}}{(z-E^{(0)}_{m_1})^2(z-E^{(0)}_{m_2})\cdots(z-E^{(0)}_{m_N})}.
\end{aligned}
\tag{4.9}
$$

4.2 Extracting energy corrections from residues.

By Proposition 5, the $F(z)$ is a meromorphic function with simple poles at the energies $\{E_n\}$ and unit residues:

$$F(z) = \sum_n \frac{1}{z-E_n}.$$

Fix n and encircle the perturbed eigenvalue with a small contour Γ_n that excludes all other poles. Then

$$\frac{1}{2\pi i}\oint_{\Gamma_n}(z-E^{(0)}_n)F(z)dz = \frac{1}{2\pi i}\sum_i\oint_{\Gamma_n}\frac{z-E^{(0)}_n}{z-E_i}dz \tag{4.10}$$

$$= \frac{1}{2\pi i}\oint_{\Gamma_n}\frac{z-E^{(0)}_n}{z-E_n}dz \tag{4.11}$$

$$= \frac{1}{2\pi i}\oint_{\Gamma_n}\frac{z-E_n+E_n-E^{(0)}_n}{z-E_n}dz \tag{4.12}$$

$$= \frac{1}{2\pi i}\oint_{\Gamma_n}\left(\cancel{1}+\frac{E_n-E^{(0)}_n}{z-E_n}\right)dz \tag{4.13}$$

$$= \frac{E_n-E^{(0)}_n}{2\pi i}\oint_{\Gamma_n}\frac{dz}{z-E_n} \tag{4.14}$$

$$= E_n-E^{(0)}_n = \Delta E_n, \tag{4.15}$$

where $\Delta E_n := E_n - E_n^{(0)}$. Then, we have $E_n = E_n^{(0)} + \frac{1}{2\pi i}\oint_{\Gamma_n}(z - E_n^{(0)})F(z)dz$. Substituting the trace of the Neumann series for the $F(z)$, we get

$$E_n = E_n^{(0)} + \frac{1}{2\pi i}\oint_{\Gamma_n}(z - E_n^{(0)})\sum_{n=0}^{\infty}\lambda^n \operatorname{Tr}\left(\hat{G}_0(z)(\hat{V}\hat{G}(z))^n\right)dz \tag{4.16}$$

$$= E_n^{(0)} + \sum_{N=1}^{\infty}\lambda^n \frac{1}{2\pi i}\oint_{\Gamma_n}(z - E_n^{(0)})\sum_{m_1,\dots,m_N}\frac{V_{m_1m_2}V_{m_2m_3}\cdots V_{m_Nm_1}}{(z - E_{m_1}^{(0)})^2(z - E_{m_2}^{(0)})\cdots(z - E_{m_N}^{(0)})}dz \tag{4.17}$$

4.3 Energy corrections up to fourth order

Define $F_N(z)$ such that

$$F(z) = \operatorname{Tr}\hat{G}(z) = \sum_{N=0}^{\infty}\lambda^N F_N(z), \qquad F_N(z) = \operatorname{Tr}\left(\hat{G}_0(\hat{V}\hat{G}_0)^N\right), \tag{4.18}$$

We derived the explicit form

$$F_N(z) = \sum_{m_1,\dots,m_N}\frac{V_{m_1m_2}V_{m_2m_3}\cdots V_{m_Nm_1}}{(z - E_{m_1}^{(0)})^2\,(z - E_{m_2}^{(0)})\cdots(z - E_{m_N}^{(0)})}. \tag{4.19}$$

As shown earlier,

$$\Delta E_n^{(N)} = \operatorname{Res}_{z=E_n^{(0)}}\left[(z - E_n^{(0)})F_N(z)\right]. \tag{4.20}$$

Write $\Delta_{mn} := E_n^{(0)} - E_m^{(0)}$ and note $g_m(z) = 1/(z - E_m^{(0)})$.

First order.

$$F_1(z) = \sum_{m_1}\frac{V_{m_1m_1}}{(z - E_{m_1}^{(0)})^2}.$$

Only $m_1 = n$ contributes a simple pole to $(z - E_n^{(0)})F_1(z)$:

$$(z - E_n^{(0)})F_1(z) = \frac{V_{nn}}{z - E_n^{(0)}} + \left[\text{holomorphic at } z = E_n^{(0)}\right]$$

Thus

$$\Delta E_n^{(1)} = V_{nn}. \tag{4.21}$$

Second order.

$$F_2(z) = \sum_{m_1,m_2}\frac{V_{m_1m_2}V_{m_2m_1}}{(z - E_{m_1}^{(0)})^2(z - E_{m_2}^{(0)})}.$$

Multiply by $(z - E_n^{(0)})$ and analyze cases:

(i) $m_1 = n$, $m_2 \neq n$. Then

$$(z - E_n^{(0)})\frac{V_{nm_2}V_{m_2n}}{(z - E_n^{(0)})^2(z - E_{m_2}^{(0)})} = \frac{|V_{m_2n}|^2}{(z - E_n^{(0)})(z - E_{m_2}^{(0)})} \xrightarrow[\text{Res at } z=E_n^{(0)}]{} \frac{|V_{m_2n}|^2}{E_n^{(0)} - E_{m_2}^{(0)}}.$$

(ii) $m_1 = n$, $m_2 = n$. Then we have $(z - E_n^{(0)})/(z - E_n^{(0)})^3$ which is of order $(z - E_n^{(0)})^{-2}$ its residue is 0.

No other case yields a pole at $z = E_n^{(0)}$. Hence

$$\Delta E_n^{(2)} = \sum_{m\neq n}\frac{|V_{mn}|^2}{\Delta_{mn}}. \tag{4.22}$$