Chapter 16

Time Independent Perturbation Theory

P. J. Grandinetti

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Finding Approximate Eigenvalues and Eigenstates

Imagine you have Hamiltonian

$$\hat{\mathcal{H}}\psi_m = E_m\psi_m$$

but cannot find exact analytical solutions for eigenstates and eigenvalues.

Use *static perturbation theory* (SPT) to find approximation solutions to time-independent Schrödinger equation.

SPT works if

- you can separate $\hat{\mathcal{H}}$ into 2 parts

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \hat{\mathcal{H}}^{(1)}$$

  $\hat{\mathcal{H}}^{(1)}$ is small compared to $\hat{\mathcal{H}}^{(0)}$

- you know exact eigenstates and eigenvalues for $\hat{\mathcal{H}}^{(0)}$

$$\hat{\mathcal{H}}^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}$$

Finding Approximate Eigenvalues and Eigenstates

To understand SPT rewrite the problem as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \lambda \hat{H}^{(1)}$$

where $\hat{\mathcal{H}}^{(1)} = \lambda \hat{H}^{(1)}$.

Find some real scalar that gives size of $\hat{\mathcal{H}}^{(1)}$ relative to $\hat{\mathcal{H}}^{(0)}$

$$\lambda = \frac{||\hat{\mathcal{H}}^{(1)}||}{||\hat{\mathcal{H}}^{(0)}||}$$

Here, $||\hat{\mathcal{H}}||$ is largest eigenvalue of Hamiltonian.

In limit that $\lambda \to 0$, we know that $\hat{\mathcal{H}} \to \hat{\mathcal{H}}^{(0)}$.

$$\lim_{\lambda \to 0} \psi_m = \psi_m^{(0)} \quad \text{and} \quad \lim_{\lambda \to 0} E_m = E_m^{(0)}$$

Finding Approximate Eigenvalues and Eigenstates

Next, expand ψ_m and E_m in Taylor series expansion about $\lambda = 0$

$$\psi_m(\lambda) = \psi_m(0) + \lambda \frac{d\psi_m(0)}{d\lambda} + \frac{\lambda^2}{2!}\frac{d^2\psi_m(0)}{d\lambda^2} + \frac{\lambda^3}{3!}\frac{d^3\psi(0)}{d\lambda^3} + \cdots + \frac{\lambda^k}{k!}\frac{d^k\psi(0)}{d\lambda^k}$$

and

$$E_m(\lambda) = E_m(0) + \lambda \frac{dE_m(0)}{d\lambda} + \frac{\lambda^2}{2!}\frac{d^2E_m(0)}{d\lambda^2} + \frac{\lambda^3}{3!}\frac{d^3E(0)}{d\lambda^3} + \cdots + \frac{\lambda^k}{k!}\frac{d^kE(0)}{d\lambda^k}$$

Finding Approximate Eigenvalues and Eigenstates

We have already defined $\psi_m(0) = \psi_m^{(0)}$ and $E_m(0) = E_m^{(0)}$. Let's further define

$$\varphi_m^{(k)} = \frac{1}{k!}\frac{d^k\psi_m(0)}{d\lambda^k} \text{ and } \varepsilon_m^{(k)} = \frac{1}{k!}\frac{d^k E_m(0)}{d\lambda^k},$$

and write

$$\psi_m(\lambda) = \psi_m^{(0)} + \underbrace{\lambda\varphi_m^{(1)}}_{\psi_m^{(1)}} + \underbrace{\lambda^2\varphi_m^{(2)}}_{\psi_m^{(2)}} + \underbrace{\lambda^3\varphi_m^{(3)}}_{\psi_m^{(3)}} + \cdots + \underbrace{\lambda^k\varphi_m^{(k)}}_{\psi_m^{(k)}}$$

and

$$E_m(\lambda) = E_m^{(0)} + \underbrace{\lambda\varepsilon_m^{(1)}}_{E_m^{(1)}} + \underbrace{\lambda^2\varepsilon_m^{(2)}}_{E_m^{(2)}} + \underbrace{\lambda^3\varepsilon_m^{(3)}}_{E_m^{(3)}} + \cdots + \underbrace{\lambda^k\varepsilon_m^{(k)}}_{E_m^{(k)}}$$

If its true that $|\lambda| \ll 1$, then we should be able to truncate this series after 1st or 2nd order correction.

Finding Approximate Eigenvalues and Eigenstates

To get these corrections go back to $\hat{\mathcal{H}}\psi_m = E_m\psi_m$ and put in expression

$$\left(\hat{\mathcal{H}}^{(0)} + \lambda\hat{\mathcal{H}}^{(1)}\right)\left(\psi_m^{(0)} + \lambda\varphi_m^{(1)} + \lambda^2\varphi_m^{(2)} + \cdots\right) = \left(E_m^{(0)} + \lambda\varepsilon_m^{(1)} + \lambda^2\varepsilon_m^{(2)} + \cdots\right)\left(\psi_m^{(0)} + \lambda\varphi_m^{(1)} + \lambda^2\varphi_m^{(2)} + \cdots\right)$$

Expanding this out and collecting terms with similar powers of λ gives

$$\hat{\mathcal{H}}^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}$$

$$\lambda\left(\hat{\mathcal{H}}^{(0)}\varphi_m^{(1)} + \hat{H}^{(1)}\psi_m^{(0)}\right) = \lambda\left(\varepsilon_m^{(1)}\psi_m^{(0)} + E_m^{(0)}\varphi_m^{(1)}\right)$$

$$\lambda^2\left(\hat{\mathcal{H}}^{(0)}\varphi_m^{(2)} + \hat{H}^{(1)}\varphi_m^{(1)}\right) = \lambda^2\left(\varepsilon^{(1)}\varphi_m^{(1)} + \varepsilon^{(2)}\psi_m^{(0)} + E_m^{(0)}\varphi_m^{(2)}\right)$$

Solve for energy and wave function corrections in terms of zeroth-order energies and zeroth-order wave functions.

First-order corrections

See notes for full derivation. Final result is...

$$\boxed{E_m^{(1)} = \lambda \varepsilon_m^{(1)} = \int \psi_m^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_m^{(0)} dx}$$

$$\boxed{\psi_m^{(1)} = \lambda \varphi_m^{(1)} = \sum_{\substack{j=1, \\ j \neq m}}^{N} \left[\frac{\int \psi_j^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_m^{(0)} dx}{E_m^{(0)} - E_j^{(0)}} \right] \psi_j^{(0)}}$$

Example

Using harmonic oscillator as unperturbed problem, calculate 1st-order energy correction of $n = 0$ level for oscillator governed by potential

$$V(x) = \frac{1}{2}\kappa_{\rm f}\, x^2 + \frac{1}{6}\gamma_{\rm f}\, x^3 + \frac{1}{24}\beta_{\rm f}\, x^4$$

First, we identify 0th-order Hamiltonian and perturbation as

$$\hat{\mathcal{H}}^{(0)} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\kappa_{\rm f}\,\hat{x}^2, \quad \text{and} \quad \hat{\mathcal{H}}^{(1)} = \frac{1}{6}\gamma_{\rm f}\,\hat{x}^3 + \frac{1}{24}\beta_{\rm f}\, x^4$$

For $\hat{\mathcal{H}}^{(0)}$ we have solutions

$$E_n^{(0)} = \hbar\omega_0(n + 1/2), \quad \text{and} \quad \psi_n^{(0)}(x) = N_n H_n(\alpha x) e^{-(\alpha x)^2/2}$$

Using $\hat{\mathcal{H}}^{(1)}$ and $\psi_n^{(0)}(x)$ we calculate 1st-order correction to energy

$$E_0^{(1)} = \int_{-\infty}^{\infty} \psi_0^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_0^{(0)} dx = \frac{1}{6}\gamma_{\rm f} \int_{-\infty}^{\infty} \psi_0^{*(0)} x^3 \psi_0^{(0)} dx + \frac{1}{24}\beta_{\rm f} \int_{-\infty}^{\infty} \psi_0^{*(0)} x^4 \psi_0^{(0)} dx$$

Example

Using harmonic oscillator as unperturbed problem, calculate 1st-order energy correction of $n = 0$ level for oscillator governed by potential

$$V(x) = \frac{1}{2}\kappa_f x^2 + \frac{1}{6}\gamma_f x^3 + \frac{1}{24}\beta_f x^4$$

$$E_0^{(1)} = \frac{1}{6}\gamma_f \int_{-\infty}^{\infty} \psi_0^{*(0)} x^3 \psi_0^{(0)} dx + \frac{1}{24}\beta_f \int_{-\infty}^{\infty} \psi_0^{*(0)} x^4 \psi_0^{(0)} dx$$

Since $\psi_0^{(0)}$ is even function and x^3 is odd function we know 1st integral is zero, leaving

$$E_0^{(1)} = \frac{1}{24}\beta_f \int_{-\infty}^{\infty} \psi_0^{*(0)} x^4 \psi_0^{(0)} dx$$

Substituting our expression for $\psi_0^{(0)}$ and looking up the integral gives

$$E_0^{(1)} = \frac{1}{24}\beta_f N_0^2 \int_{-\infty}^{\infty} x^4 e^{-(\alpha x)^2} dx = \frac{1}{24}\beta_f N_0^2 \frac{6}{8\alpha^4}\left(\frac{\pi}{\alpha^2}\right)^{1/2} = \frac{\beta_f}{32\alpha^4}$$

Example

Using harmonic oscillator as unperturbed problem, calculate **1st-order correction of $n = 0$ wave function** for oscillator governed by potential

$$V(x) = \frac{1}{2}\kappa_f x^2 + \frac{1}{6}\gamma_f x^3 + \frac{1}{24}\beta_f x^4$$

1st note that indexes for harmonic oscillator begin at $j = 0$. And for $n = 0$ wave function summation skips $j = 0$ leaving

$$\psi_0^{(1)} = \sum_{j=1}^{N-1} \left[\frac{\int \psi_j^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_0^{(0)} dx}{E_0^{(0)} - E_j^{(0)}} \right] \psi_j^{(0)}$$

Substituting in perturbation gives

$$\psi_0^{(1)} = \sum_{j=1}^{N-1} \left[\frac{\int \psi_j^{*(0)} \left(\frac{1}{6}\gamma_f \hat{x}^3 + \frac{1}{24}\beta_f \hat{x}^4 \right) \psi_0^{(0)} dx}{E_0^{(0)} - E_j^{(0)}} \right] \psi_j^{(0)}$$

Example

Using harmonic oscillator as unperturbed problem, calculate **1st-order correction of $n = 0$ wave function** for oscillator governed by potential

$$V(x) = \frac{1}{2}\kappa_{\mathrm{f}}\, x^2 + \frac{1}{6}\gamma_{\mathrm{f}}\, x^3 + \frac{1}{24}\beta_{\mathrm{f}}\, x^4$$

$$\psi_0^{(1)} = \sum_{j=1}^{N-1}\left[\frac{\int \psi_j^{*(0)}\left(\frac{1}{6}\gamma_{\mathrm{f}}\,\hat{x}^3 + \frac{1}{24}\beta_{\mathrm{f}}\,\hat{x}^4\right)\psi_0^{(0)}dx}{E_0^{(0)} - E_j^{(0)}}\right]\psi_j^{(0)}$$

can be split into

$$\psi_0^{(1)} = \frac{1}{6}\gamma_{\mathrm{f}}\sum_{j=1}^{N-1}\left[\frac{\int \psi_j^{*(0)} x^3 \psi_0^{(0)}dx}{E_0^{(0)} - E_j^{(0)}}\right]\psi_j^{(0)} + \frac{1}{24}\beta_{\mathrm{f}}\sum_{j=1}^{N-1}\left[\frac{\int \psi_j^{*(0)} x^4 \psi_0^{(0)}dx}{E_0^{(0)} - E_j^{(0)}}\right]\psi_j^{(0)}$$

From wave function symmetry, 1st integral goes to zero when j are even. Similarly, 2nd integral goes to zero when j are odd.

Second-order corrections

In terms of 1st-order correction to wave function, the 2nd-order correction to energy is

$$\boxed{E_m^{(2)} = \int \psi_m^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_m^{(1)} dx,}$$

Using

$$\psi_m^{(1)} = \lambda \varphi_m^{(1)} = \sum_{\substack{j=1,\\ j\neq m}}^{N} \left[\frac{\int \psi_j^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_m^{(0)} dx}{E_m^{(0)} - E_j^{(0)}} \right] \psi_j^{(0)}$$

$E_m^{(2)}$ is expanded to

$$\boxed{E_m^{(2)} = \lambda \varepsilon_m^{(2)} = \sum_{\substack{j=1,\\ j\neq m}}^{N} \frac{\left| \int \psi_j^{*(0)} \hat{\mathcal{H}}^{(1)} \psi_m^{(0)} dx \right|^2}{E_m^{(0)} - E_j^{(0)}}}$$

Less common to calculate 2nd order correction, to wave function.

Example - Electric Dipole and Polarizability

Example

(a) Use quantum mechanical operator for electric dipole

$$\vec{\hat{\mu}} = \sum_{k=1}^{N} q_k \vec{\hat{r}}$$

and interaction with external electric field

$$\hat{V}_{\text{dipole}} = -\vec{\hat{\mu}} \cdot \vec{\mathcal{E}}$$

to calculate perturbation expansion for energy to 2nd order in $\mathcal{E}$.

(b) Compare that to energy of classical charge distribution in electric field

$$V = -\vec{\mu}_0 \cdot \vec{\mathcal{E}} - \frac{1}{2}\vec{\mathcal{E}} \cdot \boldsymbol{\alpha} \cdot \vec{\mathcal{E}}$$

Example - Electric Dipole and Polarizability

Hamiltonian with perturbation is

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \hat{V}_{\text{dipole}} = \hat{\mathcal{H}}^{(0)} - \hat{\vec{\mu}} \cdot \vec{\mathcal{E}}$$

$\psi_n^{(0)}$ are eigenstates of $\hat{\mathcal{H}}^{(0)}$ and 1st order correction is

$$E_n^{(1)} = \int_V \psi_m^{*(0)} \hat{V}_{\text{dipole}} \psi_m^{(0)} d\tau = -\underbrace{\left[\int_V \psi_m^{*(0)} \hat{\vec{\mu}}\, \psi_m^{(0)} d\tau\right]}_{\langle \vec{\mu}_0 \rangle_m} \cdot \vec{\mathcal{E}}$$

Identify 1st-order energy correction as associated with expectation value of permanent dipole associated with $\psi_m^{(0)}$ state

$$\boxed{\langle \vec{\mu}_0 \rangle_m = \int_V \psi_m^{*(0)} \hat{\vec{\mu}} \psi_m^{(0)} d\tau}$$

with

$$E_m^{(1)} = -\langle \vec{\mu}_0 \rangle_m \cdot \vec{\mathcal{E}}$$

Example - Electric Dipole and Polarizability

For 2nd-order correction with $\hat{V}_{\text{dipole}} = -\vec{\hat{\mu}} \cdot \vec{\mathcal{E}}$, we obtain

$$E_m^{(2)} = \sum_{\substack{j=1,\\ j\neq m}}^{N} \frac{\left|\int \psi_j^{*(0)} \hat{V}_{\text{dipole}} \psi_m^{(0)} d\tau\right|^2}{E_m^{(0)} - E_j^{(0)}} = \vec{\mathcal{E}} \cdot \underbrace{\left[\sum_{\substack{j=1,\\ j\neq m}}^{N} \frac{\left|\int \psi_j^{*(0)} \vec{\hat{\mu}}\, \psi_m^{(0)} d\tau\right|^2}{E_m^{(0)} - E_j^{(0)}} \right]}_{-\frac{1}{2}\langle \boldsymbol{\alpha} \rangle_m} \cdot \vec{\mathcal{E}} = -\frac{1}{2} \vec{\mathcal{E}} \cdot \langle \boldsymbol{\alpha} \rangle_m \cdot \vec{\mathcal{E}}$$

Identify 2nd-order energy correction as associated with expectation value of polarizability associated with $\psi_m^{(0)}$

$$\langle \boldsymbol{\alpha} \rangle_m = -2 \sum_{\substack{j=1,\\ j\neq m}}^{N} \frac{\left|\int \psi_j^{*(0)} \vec{\hat{\mu}} \psi_m^{(0)} d\tau\right|^2}{E_m^{(0)} - E_j^{(0)}}$$

Example - Electric Dipole and Polarizability

$\boldsymbol{\alpha}$ is a second-rank tensor quantity

$$\langle \boldsymbol{\alpha} \rangle_m = -2 \sum_{\substack{j=1,\\ j \neq m}}^{N} \frac{\left| \int \psi_j^{*(0)} \hat{\vec{\mu}} \psi_m^{(0)} d\tau \right|^2}{E_m^{(0)} - E_j^{(0)}}$$

For example, the $\langle \alpha_{xy} \rangle_m$ element is given by

$$\boxed{\langle \alpha_{xy} \rangle_m = -2 \sum_{\substack{j=1,\\ j \neq m}}^{N} \frac{\left[\int \psi_j^{*(0)} \vec{\mu}_x \psi_m^{(0)} d\tau \right] \left[\int \psi_j^{*(0)} \hat{\mu}_y \psi_m^{(0)} d\tau \right]}{E_m^{(0)} - E_j^{(0)}}}$$