

Time Independent Perturbation Theory

Chapter 15

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Chem. 4300

Oct 30, 2017

Finding Approximate Eigenvalues and Eigenstates

Imagine you have Hamiltonian

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

but cannot find exact analytical solution 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{H} into 2 parts

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

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

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

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

Finding Approximate Eigenvalues and Eigenstates

To understand SPT rewrite the problem as

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

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

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

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

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

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

Finding Approximate Eigenvalues and Eigenstates

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

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

and

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

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

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

and write

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

and

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

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 $\hat{H}\psi_m = E_m\psi_m$ and put in expression

$$\begin{aligned} (\hat{H}^{(0)} + \lambda\hat{H}^{(1)}) (\psi_m^{(0)} + \lambda\varphi_m^{(1)} + \lambda^2\varphi_m^{(2)} + \dots) = \\ (E_m^{(0)} + \lambda\varepsilon_m^{(1)} + \lambda^2\varepsilon_m^{(2)} + \dots) (\psi_m^{(0)} + \lambda\varphi_m^{(1)} + \lambda^2\varphi_m^{(2)} + \dots) \end{aligned}$$

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

$$\begin{aligned} \hat{H}^{(0)}\psi_m^{(0)} &= E_m^{(0)}\psi_m^{(0)} \\ \lambda (\hat{H}^{(0)}\varphi_m^{(1)} + \hat{H}^{(1)}\psi_m^{(0)}) &= \lambda (\varepsilon_m^{(1)}\psi_m^{(0)} + E_m^{(0)}\varphi_m^{(1)}) \\ \lambda^2 (\hat{H}^{(0)}\varphi_m^{(2)} + \hat{H}^{(1)}\varphi_m^{(1)}) &= \lambda^2 (\varepsilon_m^{(1)}\varphi_m^{(1)} + \varepsilon_m^{(2)}\psi_m^{(0)} + E_m^{(0)}\varphi_m^{(2)}) \end{aligned}$$

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...

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

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

Example

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

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

First we identify 0th-order Hamiltonian and perturbation as

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\kappa_f \hat{x}^2, \quad \text{and} \quad \hat{H}^{(1)} = \frac{1}{6}\gamma_f \hat{x}^3 + \frac{1}{24}\beta_f \hat{x}^4$$

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

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

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

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

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

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

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

can be split into

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

From symmetry of wave function 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

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

which can be expanded to give

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

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

Example - Electric Dipole and Polarizability

Example

Use quantum mechanical operator for electric dipole

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

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} , and compare that to energy of classical charge distribution in electric field

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

Example - Electric Dipole and Polarizability

Hamiltonian with perturbation is

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

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

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

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

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

with

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

Example - Electric Dipole and Polarizability

For 2nd-order correction we start with

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

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

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

Example - Electric Dipole and Polarizability

α is a tensor quantity

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

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

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