2.1 Approximation Methods

General approach to perturbation theory

$\hat{H}$ is complicated and difficult to solve. Therefore write

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

Major portion which can be solved by itself ($\hat{H}^{(0)}$)

Minor part which is treated as a perturbation ($\hat{H}_p$)

Use solutions to $\mathbf{H}^{(0)}$ in $\mathbf{H}$ to get approximate solutions to $\mathbf{H}$

Approximations differ mathematically depending on whether solutions to $\mathbf{H}^{(0)}$ give states with degenerate (equal) energies or not, or if the perturbation is time dependent

Three cases

I: non-degenerate, time independent perturbation theory

II: degenerate, time-independent perturbation theory

Yields approximate Φ_i

III: time-dependent perturbation theory

Yields $|c_i(t)|^2$

2.2: Non-degenerate Time Independent Perturbation Theory

Let: $\hat{H}\psi(\vec{r}) = \left(\hat{H}^{(o)} + \hat{H}_p\right)\psi(\vec{r})$

Here $\mathbf{H}_p$ is independent of time

Assume we know solutions to the **unperturbed problem**

$$\hat{H}^{(0)}\psi_q^{(0)} = E_q^{(0)}\psi_q^{(0)}$$

Eigenvalue problem → quantum numbers = q's

Require that each $\Psi_q^{(0)}$ has a different $E_q^{(0)}$

This implies we are dealing with non-degenerate energy levels; for example,
A 1-D particle in a box or a 1-D simple harmonic oscillator.

To get approximate solution to $$\hat{H}\psi_q = E_q\psi_q$$

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

and $$\left[\left(\hat{H}^{(0)} + \lambda\hat{H}^{(1)}\right) - E_q\right]\psi_q = 0 \qquad (1)$$

Here λ is an arbitrary counting parameter which keeps track of where the perturbation is in the result. Will set λ = 1 later.

Note: $$\lim_{\lambda\to 0} E_q = E_q^{(0)}$$ = non-degenerate energy for $\mathbf{H}^{(o)}$

and $$\lim_{\lambda\to 0}\psi_q = \psi_q^{(0)}$$ = eigenfunction of $\mathbf{H}^{(0)}$ for $E_q^{(0)}$

Will get Ψ_q and E_q as Taylor series

$$\psi_q = \psi_q^{(0)} + \lambda \psi_q^{(1)} + \lambda^2 \psi_q^{(2)} + \lambda^3 \psi_q^{(3)} + \ldots$$

$$E_q = E_q^{(0)} + \lambda E_q^{(1)} + \lambda^2 E_q^{(2)} + \lambda^3 E_q^{(3)} + \ldots$$

$\Psi_q^{(n)}$ and $E_q^{(n)}$ are the n^{th}-order corrections to $\Psi_q^{(0)}$ and $E_q^{(0)}$, respectively.

Derivation ahead

Substitute expansions into Eq. (1) and collect terms proportional to λ^n

$$\left(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}\right)\left(\psi_q^{(0)} + \lambda \psi_q^{(1)} + \lambda^2 \psi_q^{(2)} + \lambda^3 \psi_q^{(3)} + \ldots\right)$$
$$= \left(E_q^{(0)} + \lambda E_q^{(1)} + \lambda^2 E_q^{(2)} + \lambda^3 E_q^{(3)} + \ldots\right)\left(\psi_q^{(0)} + \lambda \psi_q^{(1)} + \lambda^2 \psi_q^{(2)} + \lambda^3 \psi_q^{(3)} + \ldots\right)$$

Collect terms in λ

$$\lambda^0\left[\hat{H}^{(0)}\psi_q^{(0)} - E_q^{(0)}\psi_q^{(0)}\right]$$
$$+\lambda^1\left[\hat{H}^{(1)}\psi_q^{(0)} + \hat{H}^{(0)}\psi_q^{(1)} - E_q^{(1)}\psi_q^{(0)} - E_q^{(0)}\psi_q^{(1)}\right]$$
$$+\lambda^2\left[\hat{H}^{(0)}\psi_q^{(2)} + \hat{H}^{(1)}\psi_q^{(1)} - E_q^{(2)}\psi_q^{(0)} - E_q^{(1)}\psi_q^{(1)} - E_q^{(0)}\psi_q^{(2)}\right]$$
$$+\ldots.$$
$$= 0$$

or

$$\lambda^0\left[\left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(0)}\right]$$
$$+\lambda^1\left[\left(\hat{H}^{(1)} - E_q^{(1)}\right)\psi_q^{(0)} + \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(1)}\right]$$
$$+\lambda^2\left[\left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(2)} + \left(\hat{H}^{(1)} - E_q^{(1)}\right)\psi_q^{(1)} - E_q^{(2)}\psi_q^{(0)}\right]$$
$$+\ldots$$
$$= 0$$

Set λ = 1 and each term in the expansion =0;
that is, define the nth order perturbed Ψ as the solution to the differential equation obtained by setting the coefficient of each power of λ=0.

$$(i)\quad \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(0)} = 0$$

Defines $\Psi_q^{(0)}$ and $E_q^{(0)}$

= zeroth order problem = unperturbed problem. **known**

$$(ii)\quad \left(\hat{H}^{(1)} - E_q^{(1)}\right)\psi_q^{(0)} + \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(1)} = 0$$

Defines $\Psi_q^{(1)}$ and $E_q^{(1)}$

known **unknown** **known** **known** **known** **unknown**

Since (i) is known, use (ii) to get $E_q^{(1)}$

Premultiply (ii) $\Psi_q^{(0)\star}$ and integrate.

$$\Rightarrow \left\langle \psi_q^{(0)} \,|\, \left(\hat{H}^{(0)} - E_q^{(1)}\right) | \, \psi_q^{(0)} \right\rangle + \left\langle \psi_q^{(0)} \,|\, (\hat{H}^{(0)} - E_q^{(0)}) \,|\, \psi_q^{(1)} \right\rangle = 0$$

$$0 = \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(0)} \right\rangle - E_q^{(1)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(0)} \right\rangle + \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(0)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

$$0 = \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(0)} \right\rangle - E_q^{(1)} + \left\langle \hat{H}^{(0)} \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

Self-adjoint

$$0 = \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(0)} \right\rangle - E_q^{(1)} + E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

$$\therefore E_q^{(1)} = \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(0)} \right\rangle$$

1^{st} order correction to the energy is given by first order perturbation of **H** operating on 0^{th} order wave function.

Now, everything in (ii) is known except for $\Psi_q^{(1)}$.
Solution of differential equation (ii) gives $\Psi_q^{(1)}$.
LATER

To get 2^{nd} order correction to the energy, examine term to 2^{nd} order in λ; that is λ^2

$$(iii) \quad \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(2)} + \left(\hat{H}^{(1)} - E_q^{(1)}\right)\psi_q^{(1)} - E_q^{(2)}\psi_q^{(0)} = 0$$

$\hat{H}^{(0)}$: known; $E_q^{(0)}$: known; $\psi_q^{(2)}$: unknown; $\hat{H}^{(1)}$: known; $E_q^{(1)}$ and $\psi_q^{(1)}$: Now known from (ii); $E_q^{(2)}$: unknown; $\psi_q^{(0)}$: known