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

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

known known known Now known from (ii) unknown

unknown known

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

$$E_q^{(2)} = \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(0)} \,|\, \psi_q^{(2)} \right\rangle - E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(2)} \right\rangle + \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(1)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

$$E_q^{(2)} = \left\langle \hat{H}^{(0)} \psi_q^{(0)} \,|\, \psi_q^{(2)} \right\rangle - E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(2)} \right\rangle + \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(1)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

$\mathbf{H}^{(0)}$ is self-adjoint

$$E_q^{(2)} = \cancel{E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(2)} \right\rangle} - \cancel{E_q^{(0)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(2)} \right\rangle} + \left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(1)} \right\rangle - E_q^{(1)} \left\langle \psi_q^{(0)} \,|\, \psi_q^{(1)} \right\rangle$$

$$\therefore E_q^{(2)} = \left\langle \psi_q^{(0)} \,|\, \left(\hat{H}^{(1)} - E_q^{(1)} \right) \,|\, \psi_q^{(1)} \right\rangle$$

All terms known

Once $E_q^{(2)}$ is known, (iii) can be solved for $\Psi_q^{(2)}$. Then 3rd order problem can be treated, etc.

A subtlety with benefits

The perturbed wave functions are not completely specified by solving differential equations (ii) and (iii).

The $\{\Psi_q^{(n)}\}$ are arbitrary within $\pm c\Psi_q^{(0)}$ where c is a constant. While $\Psi_q^{(1)}$ is a solution of (ii), $\Psi_q^{(1)} \pm c\Psi_q^{(0)}$ is also a solution.

$$\left(\hat{H}^{(0)} - E_q^{(0)}\right)\left(\psi_q^{(1)} \pm c\,\psi_q^{(0)}\right) = \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(1)} \pm c\left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(0)}$$

$$= \left(\hat{H}^{(0)} - E_q^{(0)}\right)\left(\psi_q^{(1)} \pm c\,\psi_q^{(0)}\right) = \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_q^{(1)} \pm c\cancel{\left(E_q^{(0)} - E_q^{(0)}\right)}\psi_q^{(0)}$$

However, the perturbed energies are independent of $c\Psi_q^{(0)}$

For example: $$E_q^{(2)} = \left\langle \psi_q^{(0)} \,|\, \left(\hat{H}^{(1)} - E_q^{(1)}\right) | \,\psi_q^{(1)} \pm c\,\psi_q^{(0)} \right\rangle$$

$$= \left\langle \psi_q^{(0)} \,|\, \left(\hat{H}^{(1)} - E_q^{(1)}\right) | \,\psi_q^{(1)} \right\rangle \pm c\left[\cancel{\underbrace{\left\langle \psi_q^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_q^{(0)} \right\rangle}_{= E_q^{(1)}}} - \cancel{E_q^{(1)}\left\langle \psi_q^{(0)} \,|\, \psi_q^{(0)} \right\rangle}\right]$$

This arbitrary feature of $\Psi_q^{(1)}$ can be removed by requiring that $\Psi_q^{(1)}$ be orthogonal to $\Psi_q^{(0)}$

$$\Rightarrow \left\langle \psi_q^{(0)} \mid \psi_q^{(1)} \right\rangle = 0$$

This simplifies $E_q^{(2)}$

$$E_q^{(2)} = \left\langle \psi_q^{(0)} \mid \left(\hat{H}^{(1)} - E_q^{(1)}\right) \mid \psi_q^{(1)} \right\rangle = \left\langle \psi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(1)} \right\rangle - \cancel{E_q^{(1)} \left\langle \psi_q^{(0)} \mid \psi_q^{(1)} \right\rangle}$$

$$\boxed{\therefore E_q^{(2)} = \left\langle \psi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(1)} \right\rangle}$$

2nd order correction to the energy depends on first order perturbation acting on 1st order wave function.

Solving the Differential Equation (ii) to find $\Psi_q^{(1)}$

Do we know $\Psi_q^{(1)}$? **Yes** (in principle)

Examine (ii) again:

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

Problem: Getting $\Psi_q^{(1)}$ from differential equation is not trivial!

Solution: Try a different method. ***Spectral Approach***

Remember: we know

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

Since $H^{(0)}$ is self-adjoint, $\{\Psi_q^{(0)}\}$ provides a complete orthonormal set of wave functions

Let $$\psi_q^{(1)} = \sum_n a_n \psi_n^{(0)}$$ Solve for a_n to get $\Psi_q^{(1)}$

First: $\left\langle \psi_q^{(0)} \mid \psi_q^{(1)} \right\rangle = 0$ This means $a_q = 0$

Therefore: $\psi_q^{(1)} = \sum_n a_n \psi_n^{(0)} \qquad n \neq q$

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

but $\psi_q^{(1)} = \sum_n a_n \psi_n^{(0)}$

$$\therefore \left(\hat{H}^{(1)} - E_q^{(1)}\right)\psi_q^{(0)} + \left(\hat{H}^{(0)} - E_q^{(0)}\right)\sum_n a_n \psi_n^{(0)} = 0$$

Premultiply by $\Psi_k^{(0)\star}$ and integrate

$$0 = \left\langle \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} \right\rangle - E_q^{(1)} \left\langle \psi_k^{(0)} \mid \psi_q^{(0)} \right\rangle + \sum_n a_n \left\{ \left\langle \psi_k^{(0)} \mid \hat{H}^{(0)} \mid \psi_n^{(0)} \right\rangle - E_q^{(0)} \left\langle \psi_k^{(0)} \mid \psi_n^{(0)} \right\rangle \right\}$$

$$\therefore 0 = \left\langle \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} \right\rangle - E_q^{(1)} \delta_{kq} + \sum_n a_n \left\{ E_n^{(0)} \delta_{kn} - E_q^{(0)} \delta_{kn} \right\}$$

So $$0 = \left\langle \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} \right\rangle - E_q^{(1)} \delta_{kq} + a_k \left\{ E_k^{(0)} - E_q^{(0)} \right\}$$ with a_q=0

A: when k = q, δ_{kq}=1 $$E_q^{(1)} - E_q^{(1)} + a_q (0)$$ Therefore, no information on a_q

B: when k ≠ q, δ_{kq}=0

$$a_k = -\frac{\left\langle \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} \right\rangle}{E_k^{(0)} - E_q^{(0)}}$$

For simplicity introduce the symbol $$H_{kq}^{(1)} = \left\langle \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} \right\rangle$$

Called a **matrix element** (MORE LATER)

$$\boxed{\therefore a_k = -\frac{H_{kq}^{(1)}}{E_k^{(0)} - E_q^{(0)}} \qquad k \neq q}$$

$$\boxed{\psi_q^{(1)} = \sum_{k \neq q} a_k \psi_k^{(0)} = \sum_{k \neq q} \frac{H_{kq}^{(1)}}{E_q^{(0)} - E_k^{(0)}} \psi_k^{(0)}}$$

= an infinite sum

If we are dealing with the ground state: q = 1, then the total wave function is given by:

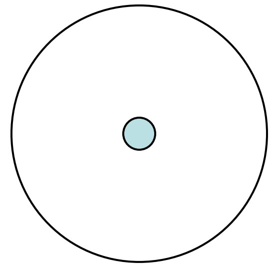
$$\approx \psi_1^{(0)} + \underbrace{a_2\psi_2^{(0)} + a_3\psi_3^{(0)} + a_4\psi_4^{(0)} + a_5\psi_5^{(0)} + a_6\psi_6^{(0)}}....$$

Please note that the changing subscript refers to the quantum number, not the order of the correction. This summation, combined is the first order correction.

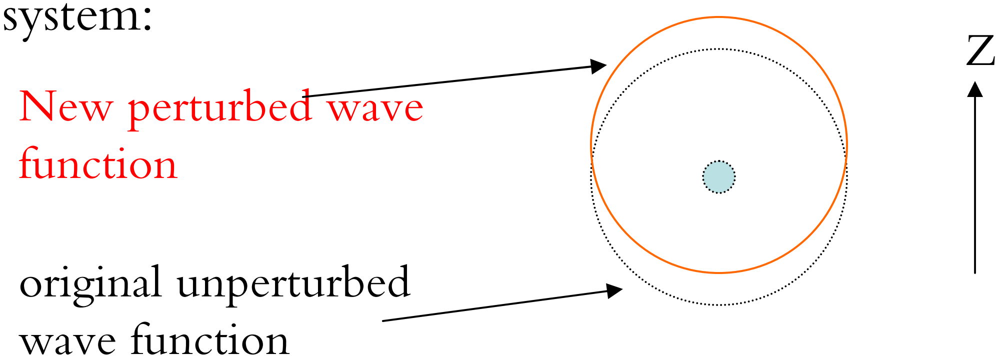
The perturbed wave function ψ becomes the unperturbed wave function plus contributions from excited states.

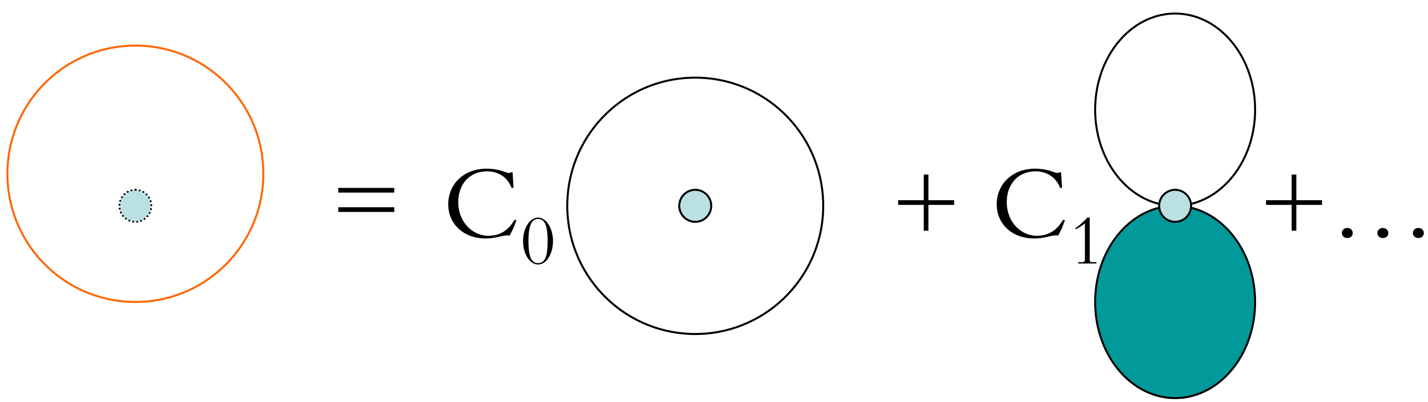
The effect of the perturbation is to 'mix-in' contributions from other states!

Pictorial Example: Let us consider the hydrogen atom in the ground state with a spherical charge distribution.



Let us now add a uniform electric field in the z-direction as to perturb the system:





Let us look at the correction term again:

$$\psi_q \approx \psi_q^{(0)} + \sum_{k \neq q} \underbrace{\frac{<\psi_{\mathrm{k}}^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_{\mathrm{q}}^{(0)}>}{E_{\mathrm{q}}^{(0)} - E_{\mathrm{k}}^{(0)}}}_{\mathrm{a_k}} \psi_{\mathrm{k}}^{(0)}$$

The larger the magnitude of $\mathrm{a_k}$ the more that state contributes.

$$E_{\mathrm{q}}^{(0)} - E_{\mathrm{k}}^{(0)}$$

The denominator tells us that the greater the energy separation, the smaller the contribution. In other words, the most important contributions come from the states nearest in energy.

Thus, for the ground state, the first few excited states will 'mix-in' the most.

$$\psi_1 \approx \psi_1^{(0)} + a_2\psi_2^{(0)} + a_3\psi_3^{(0)} + a_4\psi_4^{(0)} + a_5\psi_5^{(0)} + a_6\psi_6^{(0)} \ldots.$$

Diminishing contribution