

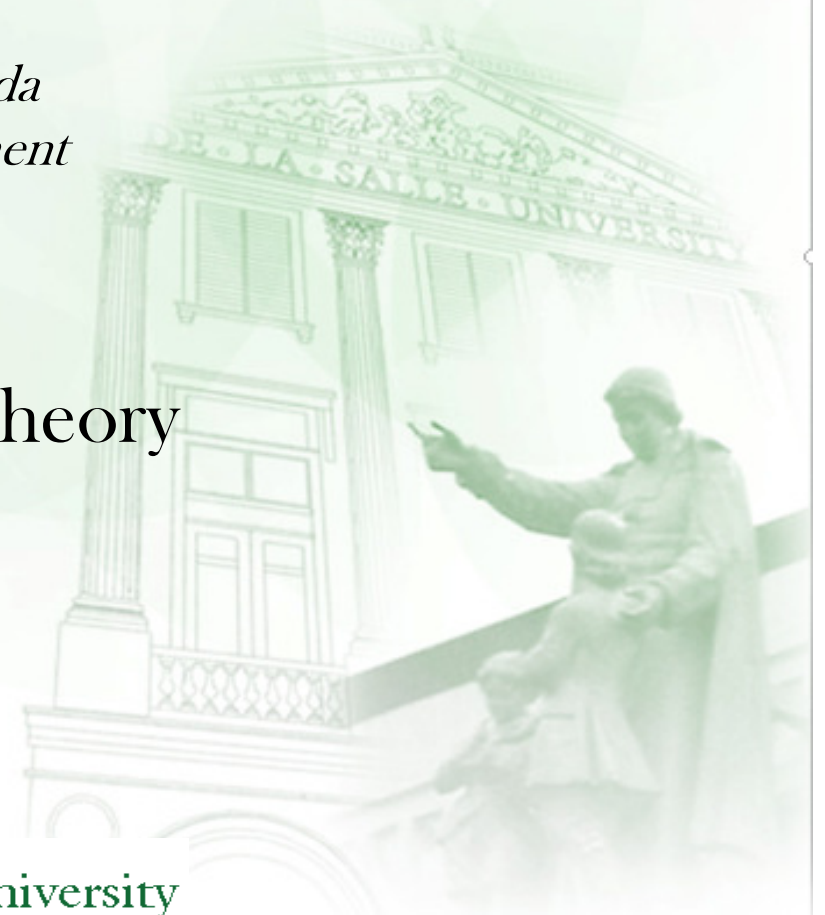
# Quantum Mechanics 2

*Robert C. Roleda*  
*Physics Department*

Perturbation Theory  
Formalism



De La Salle University



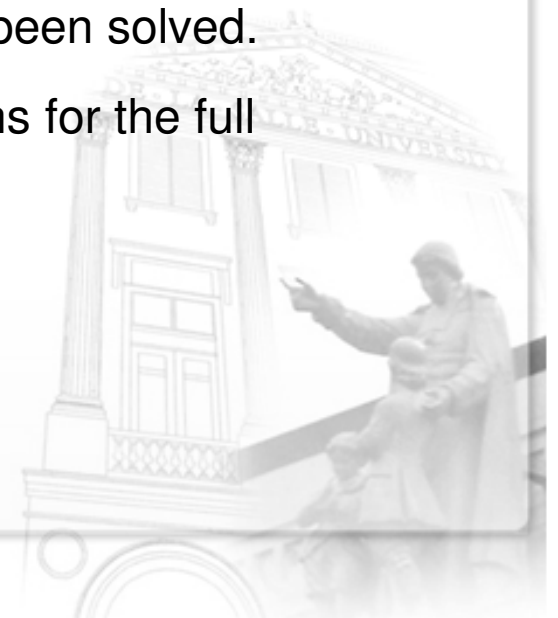
# Perturbation

Perturbations are small influences “on top” of a dominant force. There are very few quantum mechanical systems that are exactly solvable. However, there are a good number of cases in which the Hamiltonian may be expressed as

$$H = H_0 + H_I$$

where (a) the effects of  $H_I$  are much weaker than that of  $H_0$ , and (b) The eigenfunctions and eigenvalues of  $H_0$  are exact, and have been solved.

In these cases, approximate eigenvalues and eigenfunctions for the full Hamiltonian  $H$  can be solved using Perturbation Theory.



# Eigenenergy

Let  $|n^{(0)}\rangle$  be the (known and exact) eigenkets of  $H_0$ , then

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$$

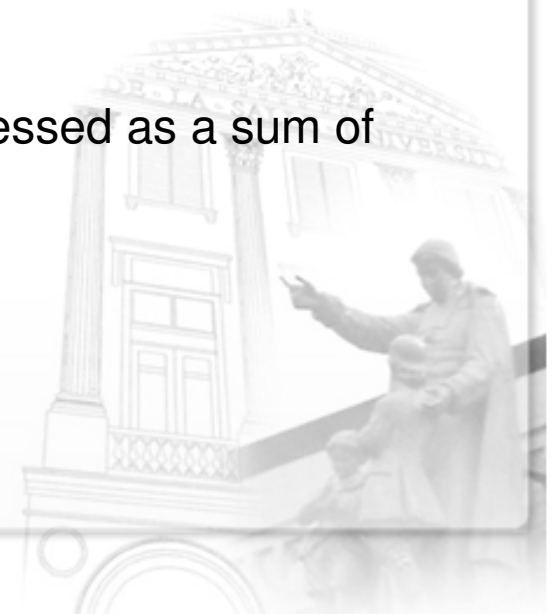
$E_n^{(0)}$  are called the unperturbed eigenenergies, and  $|n^{(0)}\rangle$  are the unperturbed states.

In order to keep track of the order of approximation, let us put a marker  $\lambda$  (or a parameter) beside the perturbation Hamiltonian  $H_I$ .

$$H = H_0 + \lambda H_I$$

We now make an ansatz that the eigenenergy can be expressed as a sum of successive correction terms of decreasing values

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$



# Eigenkets

Since the eigenkets  $|n^{(0)}\rangle$  of  $H_0$  are complete, we may use the expansion postulate to express the eigenkets  $|n\rangle$  of  $H$  as linear combinations of the former

$$|n\rangle = N(\lambda) \left[ |n^{(0)}\rangle + \sum_{k \neq n} C_{nk}(\lambda) |k^{(0)}\rangle \right]$$

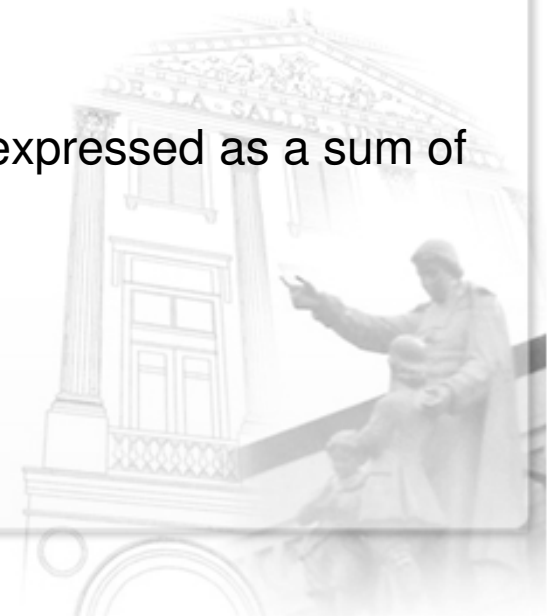
If  $\lambda = 0$ , the Hamiltonian  $H$  reduces to the unperturbed Hamiltonian  $H_0$ . Thus, for consistency

$$N(\lambda = 0) = 1$$

$$C_{nk}(\lambda = 0) = 0$$

We likewise assume that the expansion coefficient can be expressed as a sum of correction terms

$$C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \dots$$



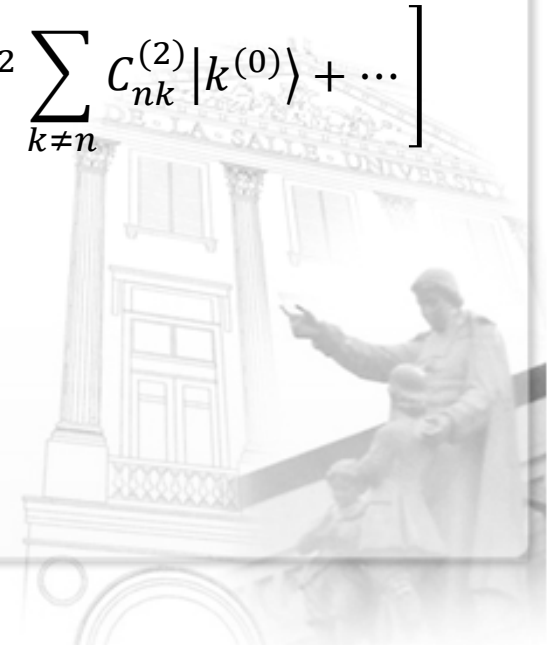
# Expansion

The eigenvalue equation

$$H|n\rangle = E_n|n\rangle$$

may then be expressed as

$$\begin{aligned} & (H_0 + \lambda H_I) \left[ |n^{(0)}\rangle + \lambda \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle + \lambda^2 \sum_{k \neq n} C_{nk}^{(2)} |k^{(0)}\rangle + \dots \right] \\ &= \left( E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right) \left[ |n^{(0)}\rangle + \lambda \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle + \lambda^2 \sum_{k \neq n} C_{nk}^{(2)} |k^{(0)}\rangle + \dots \right] \end{aligned}$$



# Orders

Equating terms of the same power of  $\lambda$ , we have for order zero,

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

For order one,

$$H_0 \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle + H_I |n^{(0)}\rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle + E_n^{(1)} |n^{(0)}\rangle \quad \star$$

For order two,

$$\begin{aligned} & H_0 \sum_{k \neq n} C_{nk}^{(2)} |k^{(0)}\rangle + H_I \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle \\ &= E_n^{(0)} \sum_{k \neq n} C_{nk}^{(2)} |k^{(0)}\rangle + E_n^{(1)} \sum_{k \neq n} C_{nk}^{(1)} |k^{(0)}\rangle + E_n^{(2)} |n^{(0)}\rangle \end{aligned}$$

and so on

⋮



# First-Order Energy

If we take the inner product of the first-order expression with  $\langle n^{(0)} |$

$$\sum_{k \neq n} C_{nk}^{(1)} \langle n^{(0)} | H_0 | k^{(0)} \rangle + \langle n^{(0)} | H_I | n^{(0)} \rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(1)} \langle n^{(0)} | k^{(0)} \rangle + E_n^{(1)} \langle n^{(0)} | n^{(0)} \rangle$$

we have

$$\sum_{k \neq n} C_{nk}^{(1)} E_k^{(0)} \delta_{nk} + \langle n^{(0)} | H_I | n^{(0)} \rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(1)} \delta_{nk} + E_n^{(1)}$$

which yields the formula for the first-order correction for energy

$$E_n^{(1)} = \langle n^{(0)} | H_I | n^{(0)} \rangle$$



# First-Order Eigenkets

If we take the inner product of the first-order expression with  $\langle m^{(0)} |$ , for  $m \neq n$ ,

$$\sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | H_0 | k^{(0)} \rangle + \langle m^{(0)} | H_I | n^{(0)} \rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | k^{(0)} \rangle + E_n^{(1)} \langle m^{(0)} | n^{(0)} \rangle$$

we have

$$\sum_{k \neq n} C_{nk}^{(1)} E_k^{(0)} \delta_{mk} + \langle m^{(0)} | H_I | n^{(0)} \rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(1)} \delta_{mk} + E_n^{(1)} \delta_{mn}$$

which reduces to

$$C_{nm}^{(1)} E_m^{(0)} + \langle m^{(0)} | H_I | n^{(0)} \rangle = E_n^{(0)} C_{nm}^{(1)}$$

Rearranging, we get the first order coefficient for the eigenkets

$$C_{nm}^{(1)} = \frac{\langle m^{(0)} | H_I | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$





# Second-Order Energy

If we take the inner product of the second-order expression with  $\langle n^{(0)} |$

$$\begin{aligned} & \sum_{k \neq n} C_{nk}^{(2)} \langle n^{(0)} | H_0 | k^{(0)} \rangle + \sum_{k \neq n} C_{nk}^{(1)} \langle n^{(0)} | H_I | k^{(0)} \rangle \\ &= E_n^{(0)} \sum_{k \neq n} C_{nk}^{(2)} \langle n^{(0)} | k^{(0)} \rangle + E_n^{(1)} \sum_{k \neq n} C_{nk}^{(1)} \langle n^{(0)} | k^{(0)} \rangle + E_n^{(2)} \langle n^{(0)} | n^{(0)} \rangle \end{aligned}$$

we have

$$\sum_{k \neq n} C_{nk}^{(2)} E_k^{(0)} \langle n^{(0)} | k^{(0)} \rangle + \sum_{k \neq n} C_{nk}^{(1)} \langle n^{(0)} | H_I | k^{(0)} \rangle = E_n^{(2)}$$

which yields the second-order correction to the energy

$$E_n^{(2)} = \sum_{k \neq n} \frac{\langle k^{(0)} | H_I | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \langle n^{(0)} | H_I | k^{(0)} \rangle = \sum_{k \neq n} \frac{|\langle n^{(0)} | H_I | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$



# Second-Order Eigenkets

If we take the inner product of the second-order expression with  $\langle m^{(0)} |$ , for  $m \neq n$ ,

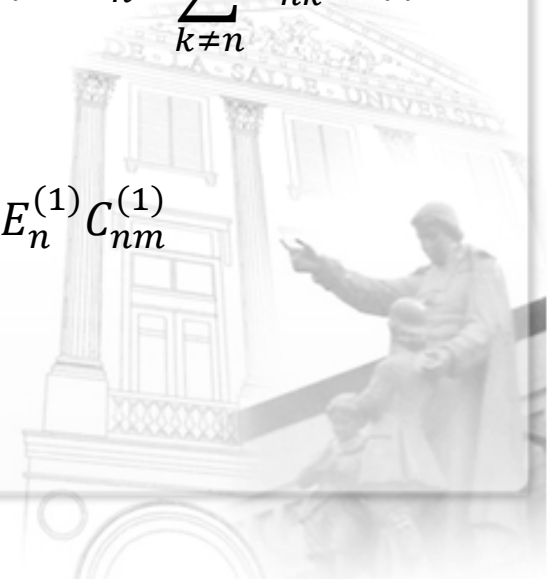
$$\begin{aligned} & \sum_{k \neq n} C_{nk}^{(2)} \langle m^{(0)} | H_0 | k^{(0)} \rangle + \sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | H_I | k^{(0)} \rangle \\ &= E_n^{(0)} \sum_{k \neq n} C_{nk}^{(2)} \langle m^{(0)} | k^{(0)} \rangle + E_n^{(1)} \sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | k^{(0)} \rangle + E_n^{(2)} \langle m^{(0)} | n^{(0)} \rangle \end{aligned}$$

we have

$$\sum_{k \neq n} C_{nk}^{(2)} E_k^{(0)} \delta_{mk} + \sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | H_I | k^{(0)} \rangle = E_n^{(0)} \sum_{k \neq n} C_{nk}^{(2)} \delta_{mk} + E_n^{(1)} \sum_{k \neq n} C_{nk}^{(1)} \delta_{mk}$$

which reduces to

$$C_{nm}^{(2)} E_m^{(0)} + \sum_{k \neq n} C_{nk}^{(1)} \langle m^{(0)} | H_I | k^{(0)} \rangle = E_n^{(0)} C_{nm}^{(2)} + E_n^{(1)} C_{nm}^{(1)}$$



# Second-Order Eigenkets

Rearranging, we have

$$C_{nm}^{(2)} = \sum_{k \neq n} \frac{C_{nk}^{(1)} \langle m^{(0)} | H_I | k^{(0)} \rangle - E_n^{(1)} C_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}}$$

which yields the second-order coefficients for the eigenkets

$$C_{nm}^{(2)} = \sum_{k \neq n} \frac{\langle m^{(0)} | H_I | k^{(0)} \rangle \langle k^{(0)} | H_I | n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)}) (E_n^{(0)} - E_k^{(0)})} - \frac{\langle m^{(0)} | H_I | n^{(0)} \rangle \langle n^{(0)} | H_I | n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})^2}$$

