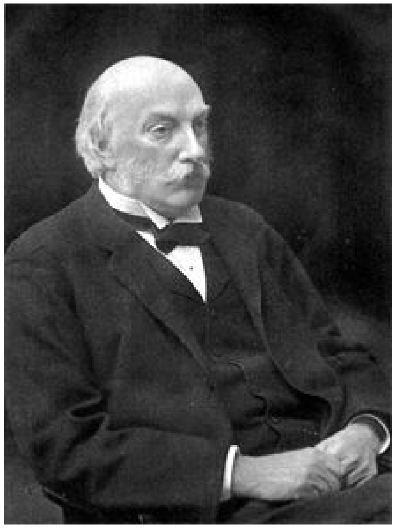
Lecture 20

Time-Independent Perturbation Theory – I
Rayleigh-Schrodinger Perturbation Theory

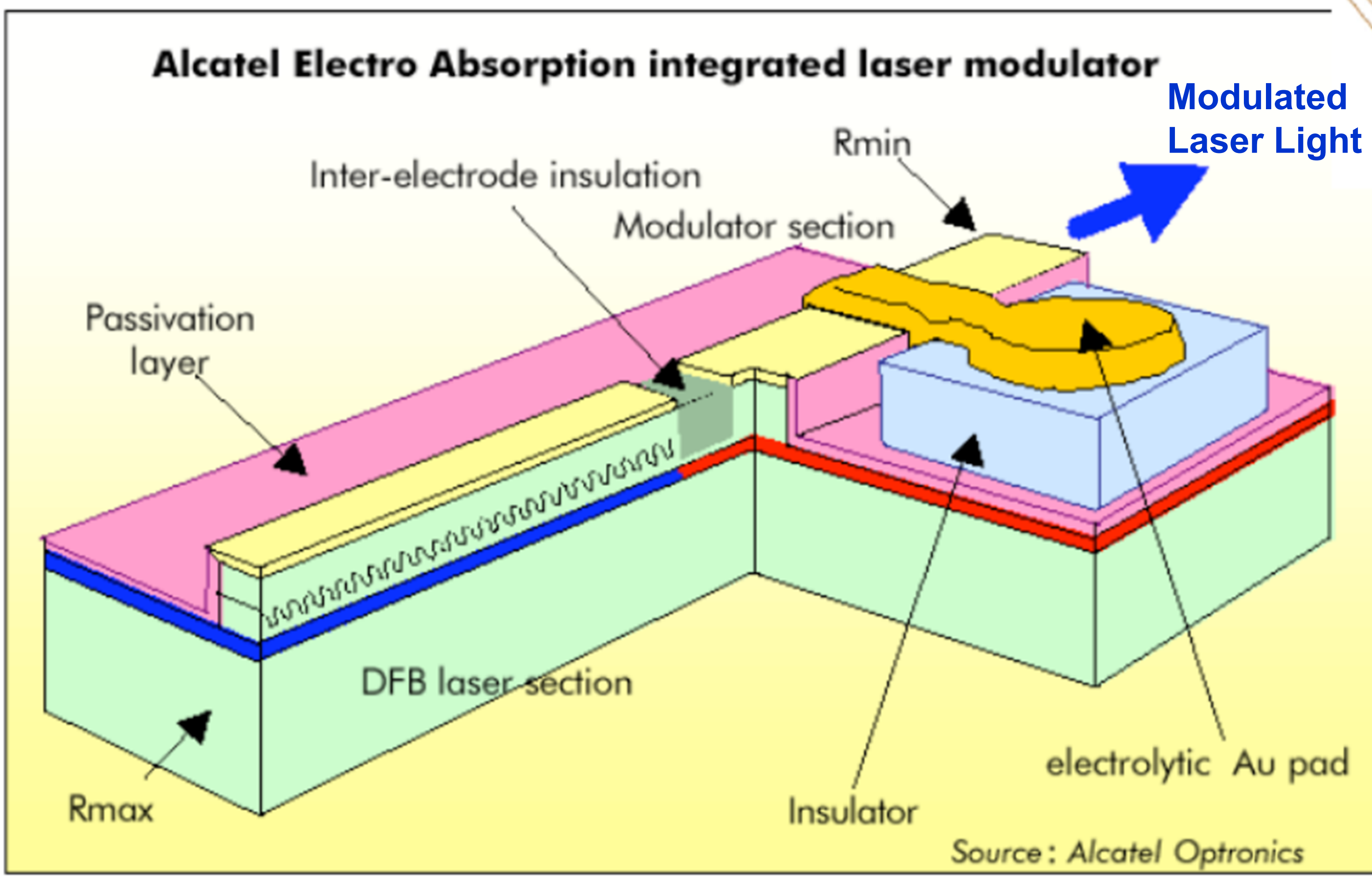
In this lecture you will learn:

- Time independent perturbation theory
- Controlled expansions for changes in eigenenergies and eigenstates
- Quantum Stark Effect



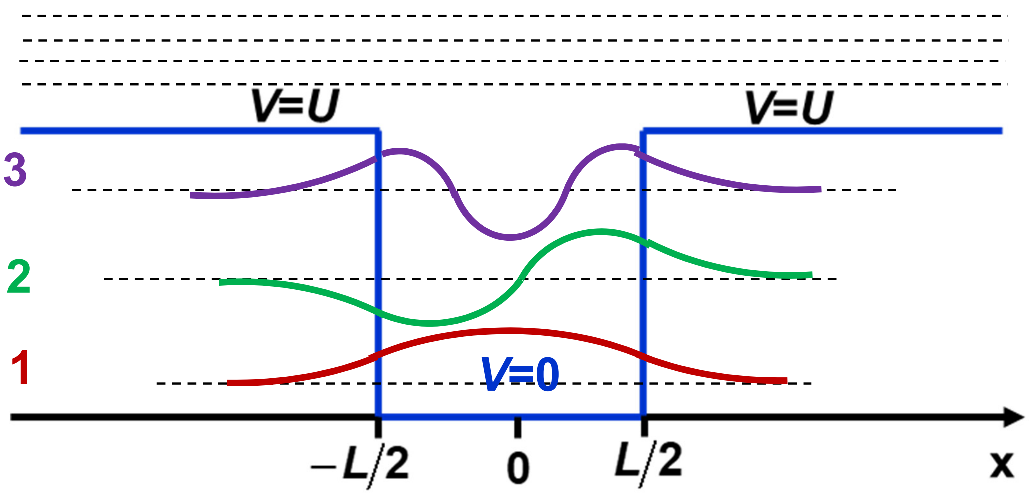
Lord Rayleigh
(1842-1919)
Nobel Prize 1904

Stark Effect in Telecom: Quantum Well Electro-Absorption Modulators



A Practical Problem: Quantum Stark Effect

Consider a potential well



The Hamiltonian is:

$$\hat{H}_o = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

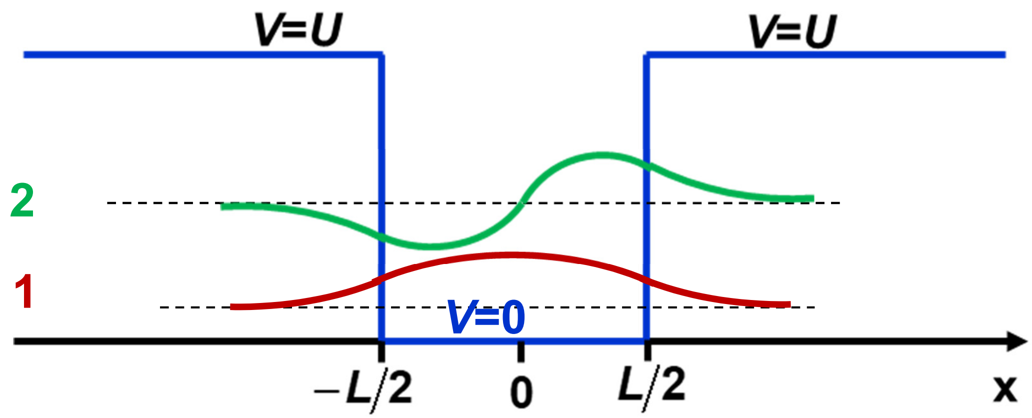
The eigenstates are:

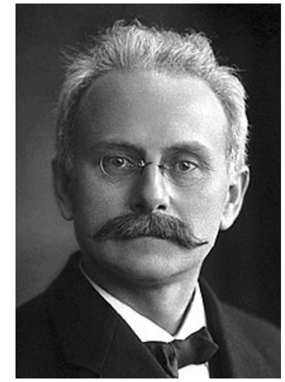
$$\hat{H}_o |e_j\rangle = E_j |e_j\rangle$$

The eigenstates form a complete orthonormal set:

$$\sum_j |e_j\rangle\langle e_j| = \hat{1} \qquad \langle e_j|e_k\rangle = \delta_{jk}$$

A Practical Problem: Quantum Stark Effect





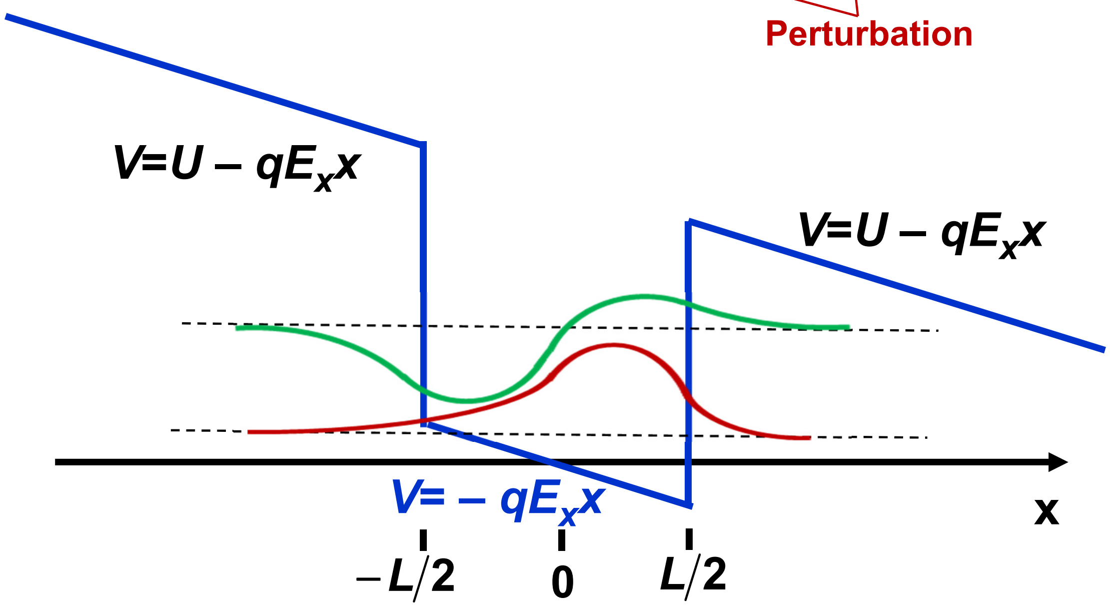
Johannes Stark (1874-1957) Nobel Prize

Now suppose a small DC electric field is applied and the Hamiltonian becomes:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V\left(\hat{x}\right) - qE_x\hat{x} = \hat{H} + \hat{O}$$

Perturbation

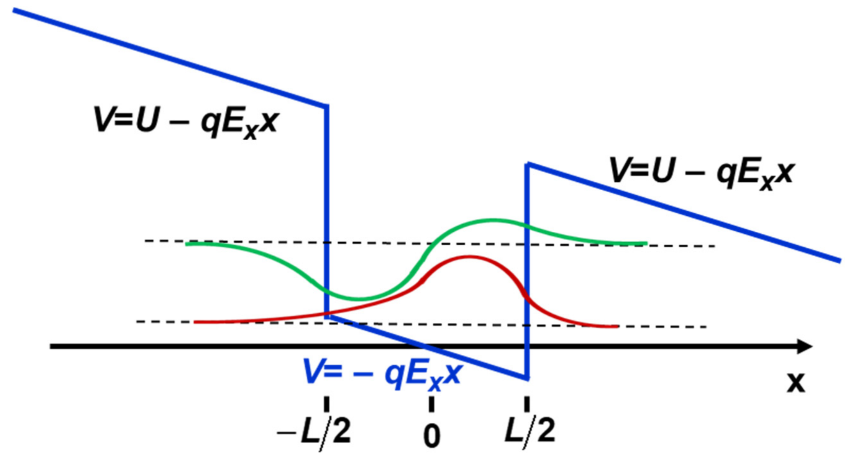
The shift in energy levels due to an applied DC electric field is called quantum stark effect



How do we find the shift in the energy levels and the new energy eigenstates?

Perturbation Theory: The Basic Idea

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) - qE_x\hat{x}$$
$$= \hat{H}_o + \hat{O}$$



Suppose:

$$\hat{H}_o\left|e_j\right\rangle = E_j\left|e_j\right\rangle$$

$$\hat{H}\left|e_j^{new}\right\rangle = E_j^{new}\left|e_j^{new}\right\rangle$$

Perturbation theory idea:

If $\hat{O}$ represents a small perturbation then it may be possible to express the new energy as a series expansion in the perturbation:

$$E_j^{new} = E_j + \Delta E_j = E_j + \underbrace{a_1 E_x + a_2 E_x^2 + a_3 E_x^3 + \ldots\ldots}$$

A power series in the perturbation strength

Similarly:

$$\left|e_j^{new}\right\rangle = \left|e_j\right\rangle + \left|\Delta e_j\right\rangle = \left|e_j\right\rangle + \sum_{n \neq j} c_n \left|e_n\right\rangle$$

$$c_n = \underbrace{b_1 E_x + b_2 E_x^2 + b_3 E_x^3 + \ldots\ldots}$$

A power series in the perturbation strength

Perturbation Theory: Statement of the Problem

Consider a problem for which the Hamiltonian is:

$$\hat{H}_o$$

The eigenstates are:

$$\hat{H}_o \left| e_j \right\rangle = E_j \left| e_j \right\rangle$$

The eigenstates form a complete orthonormal set:

$$\sum_j \left| e_j \right\rangle \left\langle e_j \right| = \hat{1} \qquad \left\langle e_j \middle| e_k \right\rangle = \delta_{jk}$$

Now suppose a small <u>perturbation</u> $\hat{O}$ is added to the Hamiltonian:

$$\hat{H} = \hat{H}_o + \hat{O}$$

Then new energy eigenstates and eigenvalues are given by:

$$\hat{H} \left| e_j^{new} \right\rangle = E_j^{new} \left| e_j^{new} \right\rangle$$

We write:

$$E_j^{new} = E_j + \Delta E_j$$

$$\left| e_j^{new} \right\rangle = \left| e_j \right\rangle + \left| \Delta e_j \right\rangle$$

How do we find: ΔE_j

How do we find: $\left| \Delta e_j \right\rangle$

Perturbation Theory: Change in Energy Eigenstates

$$\left|e_j^{new}\right\rangle = \left|e_j\right\rangle + \left|\Delta e_j\right\rangle$$

$$\left\{ \begin{array}{l} \sum_j \left|e_j\right\rangle\left\langle e_j\right| = \hat{1} \\ \left\langle e_j \middle| e_k\right\rangle = \delta_{jk} \end{array} \right.$$

The change is (without loosing generality) orthogonal to the original state:

$$\left\langle e_j \middle| \Delta e_j\right\rangle = 0$$

We write:

$$\left|\Delta e_j\right\rangle = \hat{1}\left|\Delta e_j\right\rangle = \left(\sum_m \left|e_m\right\rangle\left\langle e_m\right|\right)\left|\Delta e_j\right\rangle$$

$$= \sum_m \left\langle e_m \middle| \Delta e_j\right\rangle \left|e_m\right\rangle = \sum_{m \neq j} c_m \left|e_m\right\rangle$$

Finding $\left|\Delta e_j\right\rangle$ **amounts to finding the coefficients** c_m

$$\left|e_j^{new}\right\rangle = \left|e_j\right\rangle + \left|\Delta e_j\right\rangle$$

$$= \left|e_j\right\rangle + \sum_{m \neq j} c_m \left|e_m\right\rangle$$

Perturbation Theory: The Smallness Parameter

We write the perturbation term $\hat{O}$ as:

$$\hat{H} = \hat{H}_o + \lambda \hat{O}$$

Here λ is a "smallness" parameter that will help us do a controlled perturbation expansion in powers of λ and we will set λ equal to unity when we are done with the calculations

Eigenenergies:

$$E_j^{new} = E_j + \Delta E_j = E_j + \underbrace{\lambda \Delta E_j^{(1)} + \lambda^2 \Delta E_j^{(2)} + \lambda^3 \Delta E_j^{(3)} + ...}_{\text{A power series in the perturbation strength}}$$

Eigenstates:

$$\left| e_j^{new} \right\rangle = \left| e_j \right\rangle + \left| \Delta e_j \right\rangle$$

$$= \left| e_j \right\rangle + \sum_{m \neq j} c_m \left| e_m \right\rangle$$

$$= \left| e_j \right\rangle + \sum_{m \neq j} \underbrace{\left[\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + ... \right]}_{\text{A power series in the perturbation strength}} \left| e_m \right\rangle$$

Perturbation Theory

We start from:

$$\hat{H}\left|e_j^{new}\right\rangle = E_j^{new}\left|e_j^{new}\right\rangle$$

$$\Rightarrow \left(\hat{H}_o + \lambda\hat{O}\right)\left|e_j^{new}\right\rangle = E_j^{new}\left|e_j^{new}\right\rangle$$

And we substitute the expressions:

$$E_j^{new} = E_j + \Delta E_j = E_j + \lambda\Delta E_j^{(1)} + \lambda^2\Delta E_j^{(2)} + \lambda^3\Delta E_j^{(3)} + ...$$

$$\left|e_j^{new}\right\rangle = \left|e_j\right\rangle + \sum_{m\neq j}\left[\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + ...\right]\left|e_m\right\rangle$$

To get:

$$\left(\hat{H}_o + \lambda\hat{O}\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + ...\right)\left|e_m\right\rangle\right]$$

$$= \left(E_j + \lambda\Delta E_j^{(1)} + \lambda^2\Delta E_j^{(2)} + \lambda^3\Delta E_j^{(3)} + ...\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + ...\right)\left|e_m\right\rangle\right]$$

Perturbation Theory: First Order Eigenenergy Change

$$\left(\hat{H}_o + \lambda \hat{O}\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

$$= \left(E_j + \lambda \Delta E_j^{(1)} + \lambda^2 \Delta E_j^{(2)} + \lambda^3 \Delta E_j^{(3)} + \ldots\ldots\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

STEP 1:

Multiply by the bra $\left\langle e_j\right|$ from the left side and keep only the terms that are of zero-order in the parameter λ (i.e. that are independent of λ)

$$\left\langle e_j\left|\hat{H}_o\right|e_j\right\rangle = E_j\left\langle e_j | e_j\right\rangle$$

Nothing new here

STEP 2:

Multiply by the bra $\left\langle e_j\right|$ from the left side and keep only the terms that are of first-order in the parameter λ

$$\left\langle e_j\left|\lambda\hat{O}\right|e_j\right\rangle + \sum_{m\neq j}\lambda c_m^{(1)}\underbrace{\left\langle e_j\left|\hat{H}_o\right|e_m\right\rangle}_{0} = \lambda\Delta E_j^{(1)}\left\langle e_j | e_j\right\rangle + E_j\sum_{m\neq j}\lambda c_m^{(1)}\underbrace{\left\langle e_j | e_m\right\rangle}_{0}$$

$$\Rightarrow \Delta E_j^{(1)} = \left\langle e_j\left|\hat{O}\right|e_j\right\rangle$$

This means that the first order energy change of an eigenstate is just the mean value of the perturbation operator with respect to that eigenstate

$$E_j^{new} \approx E_j + \Delta E_j^{(1)} = E_j + \left\langle e_j\left|\hat{O}\right|e_j\right\rangle + \ldots\ldots$$

Perturbation Theory: First Order Energy Eigenstate Change

$$\left(\hat{H}_o + \lambda\hat{O}\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

$$= \left(E_j + \lambda\Delta E_j^{(1)} + \lambda^2\Delta E_j^{(2)} + \lambda^3\Delta E_j^{(3)} + \ldots\ldots\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

STEP 3:

Multiply by the bra $\left\langle e_p\right|$ (where $p \neq j$) from the left side and keep only the terms that are of first-order in the parameter λ

$$\left\langle e_p\middle|\lambda\hat{O}\middle|e_j\right\rangle + \sum_{m\neq j}\lambda c_m^{(1)}\left\langle e_p\middle|\hat{H}_o\middle|e_m\right\rangle = \lambda\Delta E_j^{(1)}\underbrace{\left\langle e_p\middle|e_j\right\rangle}_{0} + E_j\sum_{m\neq j}\lambda c_m^{(1)}\left\langle e_p\middle|e_m\right\rangle$$

$$\Rightarrow \left\langle e_p\middle|\hat{O}\middle|e_j\right\rangle + c_p^{(1)}E_p = E_j c_p^{(1)}$$

$$\Rightarrow c_p^{(1)} = \frac{\left\langle e_p\middle|\hat{O}\middle|e_j\right\rangle}{E_j - E_p}$$

This means the first order change in the eigenstate is:

$$\left|e_j^{new}\right\rangle \approx \left|e_j\right\rangle + \sum_{m\neq j}c_m^{(1)}\left|e_m\right\rangle + \ldots\ldots = \left|e_j\right\rangle + \sum_{m\neq j}\frac{\left\langle e_m\middle|\hat{O}\middle|e_j\right\rangle}{E_j - E_m}\left|e_m\right\rangle + \ldots\ldots$$

Perturbation Theory: Second Order Eigenenergy Change

$$\left(\hat{H}_o + \lambda\hat{O}\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

$$= \left(E_j + \lambda\Delta E_j^{(1)} + \lambda^2\Delta E_j^{(2)} + \lambda^3\Delta E_j^{(3)} + \ldots\right)\left[\left|e_j\right\rangle + \sum_{m\neq j}\left(\lambda c_m^{(1)} + \lambda^2 c_m^{(2)} + \lambda^3 c_m^{(3)} + \ldots\ldots\ldots\right)\left|e_m\right\rangle\right]$$

STEP 4:

Multiply by the bra $\left\langle e_j\right|$ from the left side and keep only the terms that are of second-order in the parameter λ

$$\sum_{m\neq j}\lambda c_m^{(1)}\left\langle e_j\right|\lambda\hat{O}\left|e_m\right\rangle + \sum_{m\neq j}\lambda^2 c_m^{(2)}\underbrace{\left\langle e_j\middle|e_m\right\rangle}_{0}$$

$$= \lambda^2\Delta E_j^{(2)}\left\langle e_j\middle|e_j\right\rangle + \lambda\Delta E_j^{(1)}\sum_{m\neq j}\lambda c_m^{(1)}\underbrace{\left\langle e_j\middle|e_m\right\rangle}_{0} + E_j\sum_{m\neq j}\lambda^2 c_m^{(2)}\underbrace{\left\langle e_j\middle|e_m\right\rangle}_{0}$$

$$\Rightarrow \Delta E_j^{(2)} = \sum_{m\neq j} c_m^{(1)}\left\langle e_j\right|\hat{O}\left|e_m\right\rangle = \sum_{m\neq j}\frac{\left|\left\langle e_j\right|\hat{O}\left|e_m\right\rangle\right|^2}{E_j - E_m}$$

$$\left\{ c_m^{(1)} = \frac{\left\langle e_m\right|\hat{O}\left|e_j\right\rangle}{E_j - E_m} \right.$$

This means that up to <u>second order</u> the energy change of an eigenstate is:

$$E_j^{new} \approx E_j + \Delta E_j^{(1)} + \Delta E_j^{(2)} + \ldots = E_j + \left\langle e_j\right|\hat{O}\left|e_j\right\rangle + \sum_{m\neq j}\frac{\left|\left\langle e_j\right|\hat{O}\left|e_m\right\rangle\right|^2}{E_j - E_m} + \ldots\ldots$$

Perturbation Theory: Summary

New energies:

$$E_j^{new} \approx E_j + \Delta E_j^{(1)} + \Delta E_j^{(2)} + ... = E_j + \langle e_j | \hat{O} | e_j \rangle + \sum_{m \neq j} \frac{\left| \langle e_j | \hat{O} | e_m \rangle \right|^2}{E_j - E_m} + ...$$

New energy eigenstates:

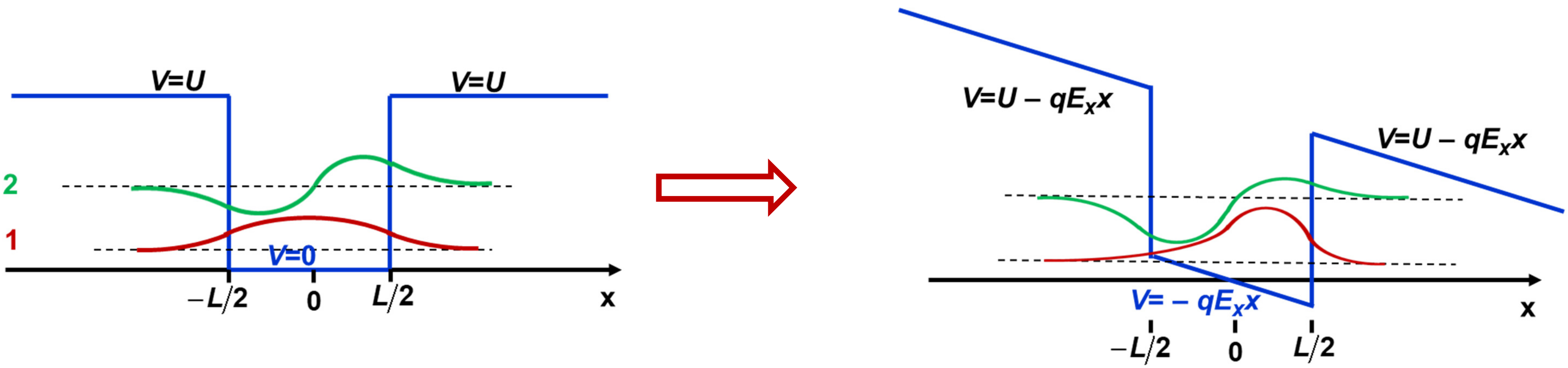
$$\left| e_j^{new} \right\rangle \approx | e_j \rangle + \sum_{m \neq j} c_m^{(1)} | e_m \rangle + ... = | e_j \rangle + \sum_{m \neq j} \frac{\langle e_m | \hat{O} | e_j \rangle}{E_j - E_m} | e_m \rangle + ...$$

Perturbation Theory for the Stark Effect

Now we get back to the Stark Effect problem:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) - qE_x\hat{x} = \hat{H} + \hat{O}$$

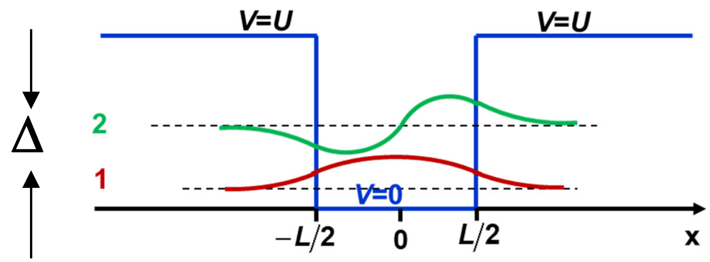
Perturbation

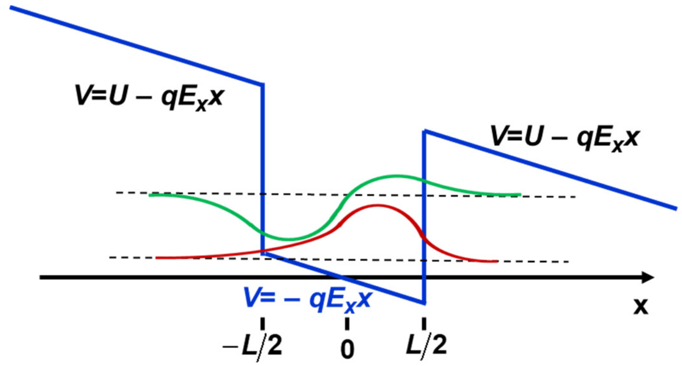


Change in the first quantum state:

$$\left|e_1^{new}\right\rangle \approx \left|e_1\right\rangle + \sum_{m\neq 1} c_m^{(1)}\left|e_m\right\rangle + \ldots.. = \left|e_1\right\rangle + \sum_{m\neq 1} \frac{\left\langle e_m\right|\left(-qE_x\hat{x}\right)\left|e_1\right\rangle}{E_1 - E_m}\left|e_m\right\rangle + \ldots...$$

Perturbation Theory for the Stark Effect





Change in the first quantum state:

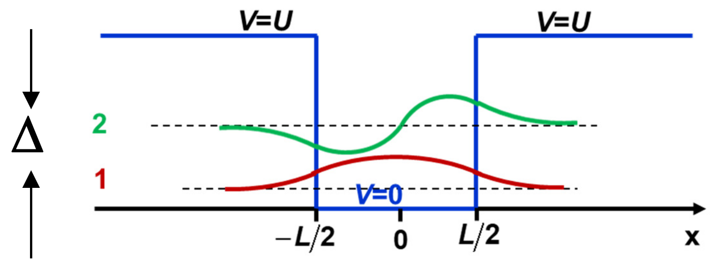
$$\left|e_1^{new}\right\rangle \approx \left|e_1\right\rangle + \sum_{m\neq 1} c_m^{(1)} \left|e_m\right\rangle + \ldots\ldots = \left|e_1\right\rangle + \sum_{m\neq 1} \frac{\left\langle e_m \middle| \left(-qE_x\hat{x}\right) \middle| e_1\right\rangle}{E_1 - E_m}\left|e_m\right\rangle + \ldots\ldots$$

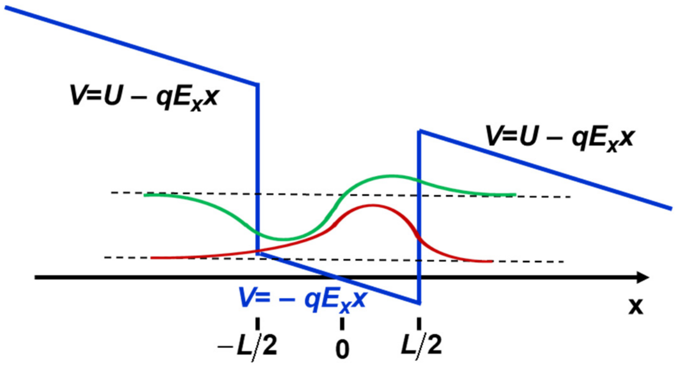
$$\approx \left|e_1\right\rangle + \frac{\left\langle e_2 \middle| \left(-qE_x\hat{x}\right) \middle| e_1\right\rangle}{E_1 - E_2}\left|e_2\right\rangle$$

$$= \left|e_1\right\rangle + \frac{qE_x d_{21}}{\Delta}\left|e_2\right\rangle$$

$$\left\langle e_2 \middle| \hat{x} \middle| e_1\right\rangle = d_{21}$$

Perturbation Theory for the Stark Effect





Change in the second quantum state:

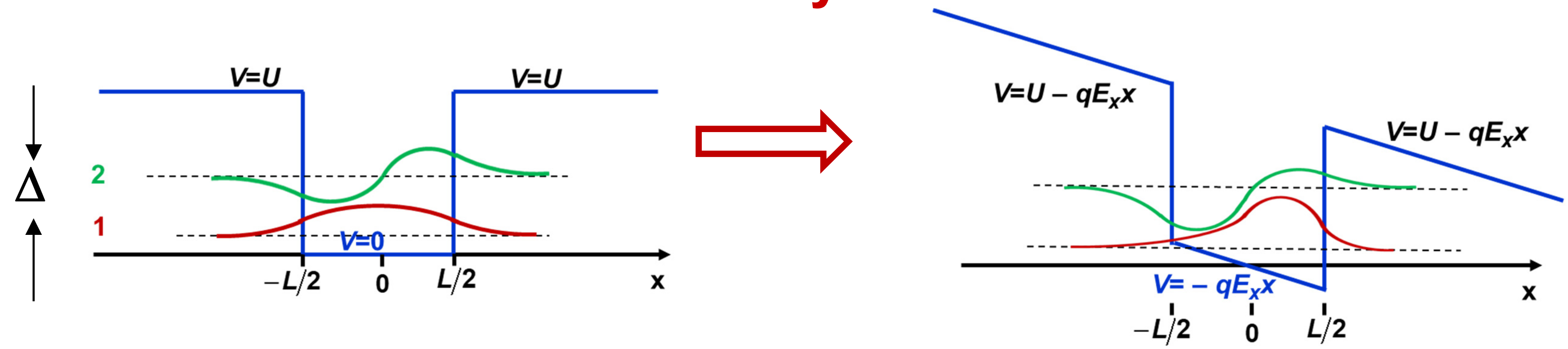
$$\left| e_2^{new} \right\rangle \approx \left| e_2 \right\rangle + \sum_{m \neq 2} c_m^{(1)} \left| e_m \right\rangle + \ldots\ldots = \left| e_2 \right\rangle + \sum_{m \neq 2} \frac{\left\langle e_m \right| \left(-qE_x \hat{x} \right) \left| e_2 \right\rangle}{E_2 - E_m} \left| e_m \right\rangle + \ldots\ldots$$

$$\approx \left| e_2 \right\rangle + \frac{\left\langle e_1 \right| \left(-qE_x \hat{x} \right) \left| e_2 \right\rangle}{E_2 - E_1} \left| e_1 \right\rangle$$

$$= \left| e_2 \right\rangle - \frac{qE_x d_{21}}{\Delta} \left| e_1 \right\rangle$$

$$\left\{ \left\langle e_2 \right| \hat{x} \left| e_1 \right\rangle = d_{21} \right.$$

Perturbation Theory for the Stark Effect



Change in the energy of the first quantum state:

$$E_1^{new} \approx E_1 + \Delta E_1^{(1)} + \Delta E_1^{(2)} + ...$$

$$= E_1 + \langle e_1 | (-qE_x \hat{x}) | e_1 \rangle + \sum_{m \neq 1} \frac{\left| \langle e_1 | (-qE_x \hat{x}) | e_m \rangle \right|^2}{E_1 - E_m} + ...$$

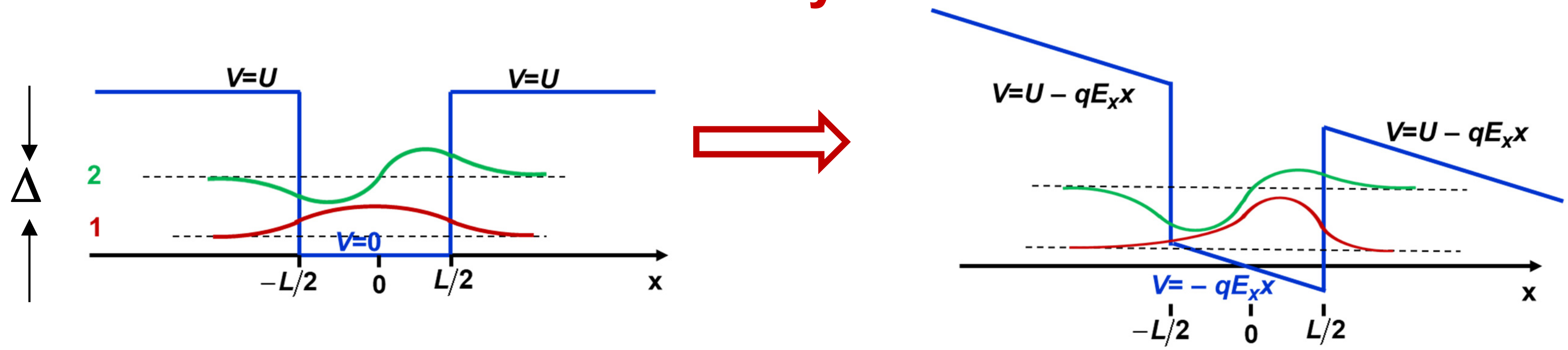
$$= E_1 + \underbrace{\langle e_1 | (-qE_x \hat{x}) | e_1 \rangle}_{0} + \frac{\left| \langle e_1 | (-qE_x \hat{x}) | e_2 \rangle \right|^2}{E_1 - E_2} + ...$$

$$\langle e_2 | \hat{x} | e_1 \rangle = d_{21}$$

$$= E_1 - \frac{(qE_x d_{21})^2}{\Delta} + ...$$

Quadratic dependence on the applied field

Perturbation Theory for the Stark Effect



Change in the energy of the second quantum state:

$$E_2^{new} \approx E_2 + \Delta E_2^{(1)} + \Delta E_2^{(2)} + ...$$

$$= E_2 + \langle e_2 | (-qE_x \hat{x}) | e_2 \rangle + \sum_{m \neq 2} \frac{\left| \langle e_2 | (-qE_x \hat{x}) | e_m \rangle \right|^2}{E_2 - E_m} + ...$$

$$= E_2 + \langle e_2 | (-qE_x \hat{x}) | e_2 \rangle + \frac{\left| \langle e_2 | (-qE_x \hat{x}) | e_1 \rangle \right|^2}{E_2 - E_1} + ...$$

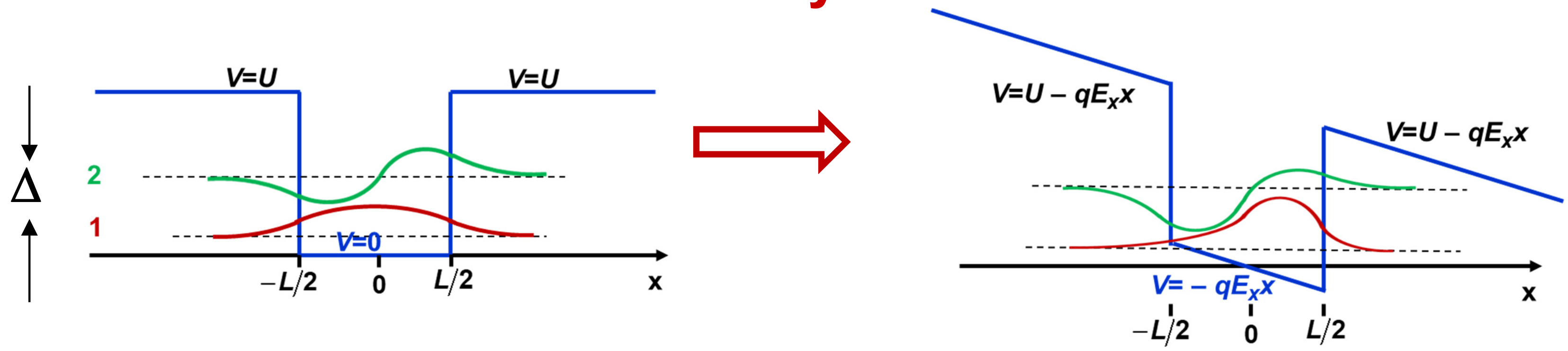
0

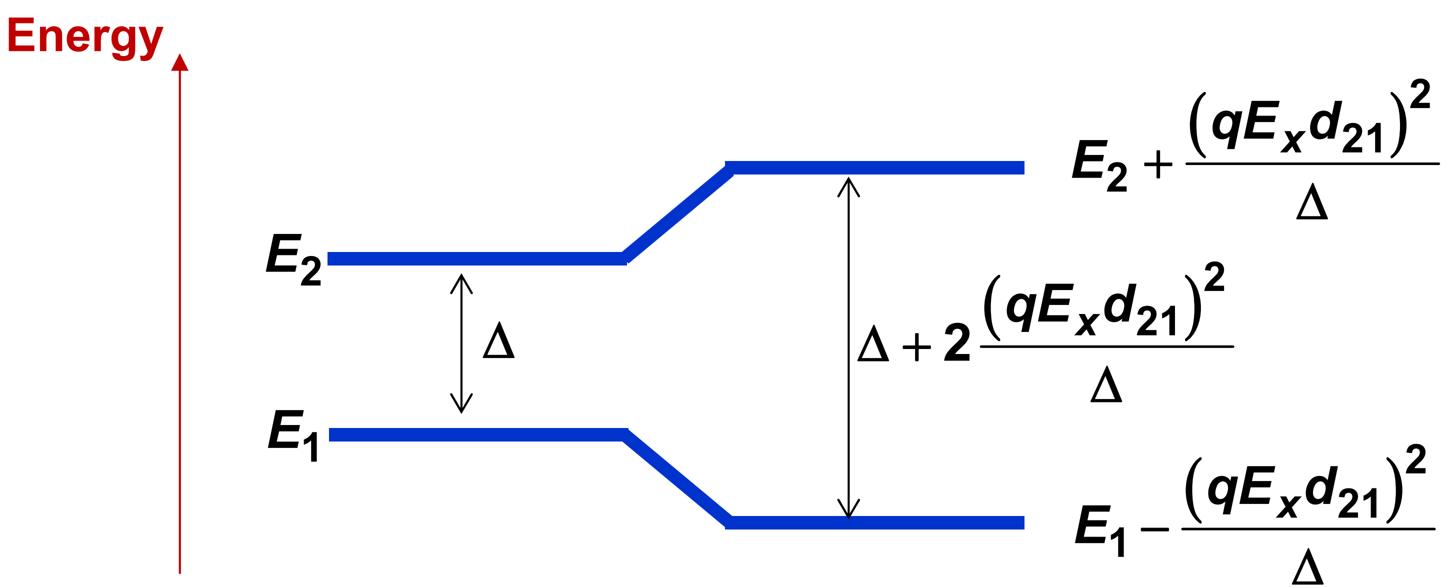
$$\langle e_2 | \hat{x} | e_1 \rangle = d_{21}$$

$$= E_2 + \frac{(qE_x d_{21})^2}{\Delta} + ...$$

Quadratic dependence on the applied field

Perturbation Theory for the Stark Effect

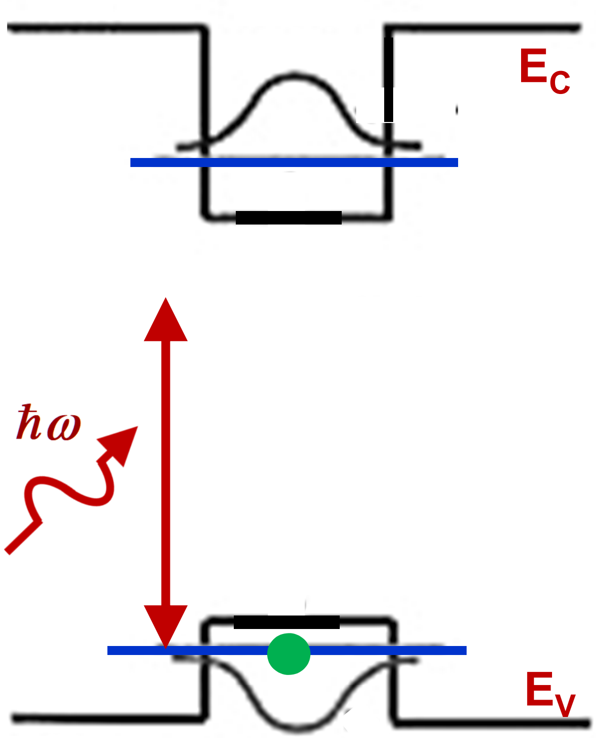




Stark Effect in Telecom: Electro-Absorption Modulators

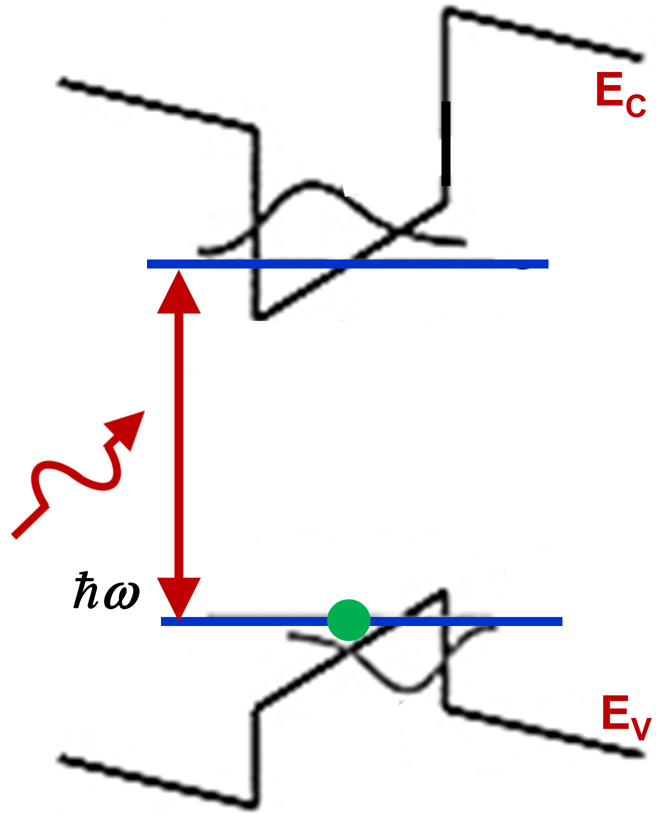
Light absorption can be switched on or off by applying a DC electric field to a semiconductor quantum well

Without Applied Field



Photon energy smaller than the energy level separation – no light absorption

With Applied Field



Photon energy equal to the energy level separation – light absorption

Perturbation Theory: Summary and Problems

New energies:

$$E_j^{new} \approx E_j + \Delta E_j^{(1)} + \Delta E_j^{(2)} + \ldots\ldots = E_j + \langle e_j | \hat{O} | e_j \rangle + \sum_{m \neq j} \frac{\left| \langle e_j | \hat{O} | e_m \rangle \right|^2}{E_j - E_m} + \ldots\ldots$$

New energy eigenstates:

$$\left| e_j^{new} \right\rangle \approx \left| e_j \right\rangle + \sum_{m \neq j} c_m^{(1)} \left| e_m \right\rangle + \ldots\ldots = \left| e_j \right\rangle + \sum_{m \neq j} \frac{\langle e_m | \hat{O} | e_j \rangle}{E_j - E_m} \left| e_m \right\rangle + \ldots\ldots$$

Problems:

1) **What if the perturbation theory does not converge?**

2) **What if the actual new energy eigenstate $\left| e_j^{new} \right\rangle$ is completely orthogonal to the old energy eigenstate $\left| e_j \right\rangle$? Will the perturbation technique work then?**

Exact result: $$\Delta E_j = \frac{\langle e_j | \hat{O} | e_j^{new} \rangle}{\langle e_j | e_j^{new} \rangle}$$ $\langle e_j | e_j^{new} \rangle \rightarrow 0$

3) **What if there are degenerate energy eigenstates $\left| e_j \right\rangle$ in the original problem?**