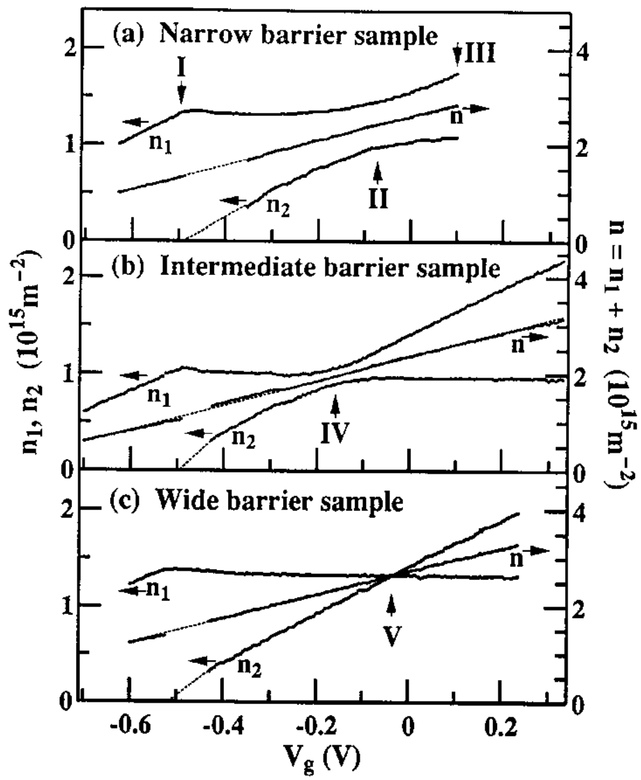
Advanced Quantum Physics

Lecture 8



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Section 2 –Methods of Approximation

•Very few problems in Quantum Mechanics can be solved analytically.

•For many situations we must resort to approximate techniques.

2.4 Degenerate Perturbation theory (1)

- There is a problem when different stationary states of the unperturbed Hamiltonian have the same energy i.e. degenerate states.
- If $E_k^{(0)} = E_n^{(0)}$ for $k \neq n$ then

$$\left|\phi_n\right\rangle = \left|\psi_n\right\rangle + \sum_{k\neq n} \frac{\left\langle\psi_k\left|\hat{H}'\right|\psi_n\right\rangle}{E_n^{(0)} - E_k^{(0)}}\left|\psi_k\right\rangle$$

and

$$E_n^{(2)} = \sum_{k\neq n} \frac{\left|\left\langle\psi_k\left|\hat{H}'\right|\psi_n\right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} \frac{\left|\hat{H}'_{nk}\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

give meaningless results.

- To get over this replace the set of degenerate basis states $\{\left|\psi_k\right\rangle\}$ by linear combinations of the same states.
- Choose linear combinations so that for a new degenerate basis $\{\left|\chi_k\right\rangle\}$ all the matrix elements with $k \neq n$:

$$\left\langle\chi_k\left|\hat{H}'\right|\chi_n\right\rangle = 0$$

- This means that the second order energy shift gives $0^2/0 = 0$.

Degenerate Perturbation theory (2)

- Choosing a set of degenerate states so $\langle \chi_k | \hat{H}' | \chi_n \rangle = 0, \quad k \neq n$ corresponds to diagonalizing the matrix $[H'_{kn}] = \langle \psi_k | \hat{H}' | \psi_n \rangle$.
- New basis states $\{ | \chi_k \rangle \}$ are eigenvectors of this matrix - new estimates of energy levels will be it's eigenvalues.
- Suppose we have two states $|\psi_1\rangle$ & $|\psi_2\rangle$ with energies $E_1^{(0)} = E_2^{(0)}$.
- In L7 we derived an exact result for new energy levels due to perturbation:

$$E_{1,2} = \tfrac{1}{2}\left(E_1^{(0)} + E_2^{(0)} + H'_{11} + H'_{22} \pm \sqrt{(E_1^{(0)} - E_2^{(0)} + H'_{11} - H'_{22})^2 + 4H'_{12}H'_{21}} \right)$$

- So in this case:

$$E_{1,2} = E_1^{(0)} + \tfrac{1}{2}\left[H'_{11} + H'_{22} \pm \sqrt{(H'_{11} - H'_{22})^2 + 4H'_{12}H'_{21}} \right]$$

- Which is $E_1^{(0)}$ plus the eigenvalues of the 2x2 matrix $[H'_{ij}]$ (below) .

$$\begin{vmatrix} H'_{11} - \alpha & H'_{12} \\ H'_{21} & H'_{22} - \alpha \end{vmatrix} = 0$$

$$\Rightarrow \alpha = \tfrac{1}{2}\left(H'_{11} + H'_{22} \pm \sqrt{(H'_{11} + H'_{22})^2 - 4(H'_{11}H'_{22} - H'_{12}H'_{21})} \right) \Rightarrow$$ Eq. above

Degenerate Perturbation theory (3)

$$H'_{12} = H'^{*}_{21}$$
Since $\hat{H}'$ is Hermitian

- From the last slide, the new eigenvalues are given by:

$$E_{1,2} = E_1^{(0)} + \tfrac{1}{2}\left[H'_{11} + H'_{22} \pm \sqrt{(H'_{11} - H'_{22})^2 + 4\,|H'_{12}|^2} \right]$$

- Note: even when $H'_{11} = H'_{22} = 0$ we get $E_{1,2} = E_1^{(0)} \pm |H'_{12}|$

- an energy shift of first order in $\hat{H}'$- only happens with degenerate states.

- Reason for this; we have for eigenstates of the matrix $[H'_{ij}]$.

$$|\chi_1\rangle = \tfrac{1}{\sqrt{2}}\left(|\psi_1\rangle + |\psi_2\rangle\right), \qquad |\chi_2\rangle = \tfrac{1}{\sqrt{2}}\left(|\psi_1\rangle - |\psi_2\rangle\right)$$

- Using these states instead of $|\psi_1\rangle$ and $|\psi_2\rangle$ and with $H'_{11} = H'_{22} = 0$ we get a first order shift of :

$$\langle\chi_1|\hat{H}'|\chi_1\rangle = \tfrac{1}{2}\left\langle\left(\langle\psi_1| + \langle\psi_2|\right)\middle|\hat{H}'\middle|\left(|\psi_1\rangle + |\psi_2\rangle\right)\right\rangle = \tfrac{1}{2}\left(\langle\psi_2|\hat{H}'|\psi_1\rangle + \langle\psi_1|\hat{H}'|\psi_2\rangle\right)$$

$$\langle\chi_2|\hat{H}'|\chi_2\rangle = \tfrac{1}{2}\left\langle\left(\langle\psi_1| - \langle\psi_2|\right)\middle|\hat{H}'\middle|\left(|\psi_1\rangle - |\psi_2\rangle\right)\right\rangle = -\tfrac{1}{2}\left(\langle\psi_2|\hat{H}'|\psi_1\rangle + \langle\psi_1|\hat{H}'|\psi_2\rangle\right)$$

- Hence:

$$\langle\chi_1|\hat{H}'|\chi_1\rangle = -\langle\chi_2|\hat{H}'|\chi_2\rangle = H'_{12} = H'_{21}.$$

Remember

$$H'_{kn} = \langle\psi_k|\hat{H}'|\psi_n\rangle$$
$$= \langle\psi_n|\hat{H}'|\psi_k\rangle^* = H'^{*}_{nk}$$

Example – Linear Stark effect in Hydrogen (1)

- Consider an atom in a uniform electric field $\boldsymbol{\varepsilon} = \begin{pmatrix} 0 & 0 & \varepsilon \end{pmatrix}$.
- Electron acquires potential energy, $\hat{H}' = -e\mathcal{E}Z$ (e negative).
- First order perturbation theory: $\Delta E = -e\mathcal{E}\langle\psi|z|\psi\rangle$
- But atomic potential in $\hat{H}_0$ is spherically symmetric hence $\hat{H}_0$ commutes with parity operator*.
- So: ψ is an eigenstate of parity $\Rightarrow \psi^* z \psi$ is odd under reflection about $z = 0$

hence $\Delta E = -e\mathcal{E}\langle\psi|z|\psi\rangle = 0$ - which does not depend on details of ψ.

- We expect leading contribution to come from 2nd order perturbation theory $\Rightarrow \Delta E \propto \mathcal{E}^2$ - which we expect classically from induced dipoles.
- But this argument collapses for hydrogen atom because we have degenerate states of different parity e.g. $2s$ and $2p$ states.

$$\hat{P}\psi_{2s} = \psi_{2s}, \qquad \hat{P}\psi_{2p} = -\psi_{2p}$$

$$\boxed{\text{*Parity operator: } \hat{P}\psi(\mathbf{r}) = \pm\psi(-\mathbf{r})}$$

Linear Stark effect in Hydrogen (2)

- Use degenerate perturbation theory procedure.
- Find matrix elements of $\hat{H}' = -e\mathcal{E}z$ between all (16) pairs of states.
- Label states: $2s : |nlm\rangle = |200\rangle$ $\quad 2p : |nlm\rangle = |210\rangle, |211\rangle, |21-1\rangle$

- Because of parity $\langle \psi_i | z | \psi_j \rangle = 0$

if ψ_i & ψ_j are both $2s$ or both $2p$ so:

$$H'_{ij} = \begin{array}{cc} \begin{array}{cccc} |200\rangle & |210\rangle & |211\rangle & |21-1\rangle \end{array} & \\ \begin{pmatrix} 0 & ? & ? & ? \\ ? & 0 & 0 & 0 \\ ? & 0 & 0 & 0 \\ ? & 0 & 0 & 0 \end{pmatrix} & \begin{array}{c} |200\rangle \\ |210\rangle \\ |211\rangle \\ |21-1\rangle \end{array} \end{array}$$

- Several others also zero, the ϕ dependence of wavefunction $e^{im\phi}$

$$\Rightarrow \langle ...m' | z | ...m \rangle = \iint .... \underbrace{r\cos\theta}_{=z} \, dr d\theta \underbrace{\int_0^{2\pi} e^{im\phi} e^{im'\phi} d\phi}_{=0,\, m \neq -m'}$$

- So the only non-zero matrix elements are:

$$\langle 200 | z | 210 \rangle = \langle 210 | z | 200 \rangle = -3a_0$$

An exercise for the reader!

Linear Stark effect in Hydrogen (3)

- From previous slide: $$\langle 200|z|210\rangle = \langle 210|z|200\rangle = -3a_0$$
- Hence:

$$\begin{array}{ccccc} & |200\rangle & |210\rangle & |211\rangle & |21{-1}\rangle \\ H'_{ij} = -e\mathcal{E} & \left(\begin{array}{c} 0 \\ -3a_0 \\ 0 \\ 0 \end{array}\right. & \begin{array}{c} -3a_0 \\ 0 \\ 0 \\ 0 \end{array} & \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} & \left.\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array}\right) \begin{array}{l} |200\rangle \\ |210\rangle \\ |211\rangle \\ |21{-1}\rangle \end{array} \end{array}$$

- Find eigenvalues and eigenvectors:

$$\begin{vmatrix} -E_0^{(1)} & 3ea_0\mathcal{E} & 0 & 0 \\ 3ea_0\mathcal{E} & -E_0^{(1)} & 0 & 0 \\ 0 & 0 & -E_0^{(1)} & 0 \\ 0 & 0 & 0 & -E_0^{(1)} \end{vmatrix} = 0$$

- Evaluating determinent: $\left[E_0^{(1)}\right]^4 - \left[E_0^{(1)}\right]^2 \left[3ea_0\mathcal{E}\right]^2 = 0$
- Eigenvalues $\quad 0 \quad 0 \quad +3ea_0\mathcal{E} \quad -3ea_0\mathcal{E}$
- Eigenvectors

$$\underbrace{\begin{pmatrix}0\\0\\1\\0\end{pmatrix} \quad \begin{pmatrix}0\\0\\0\\1\end{pmatrix}}_{\text{Unperturbed, still degenerate}} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\\0\end{pmatrix} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\\0\end{pmatrix}$$

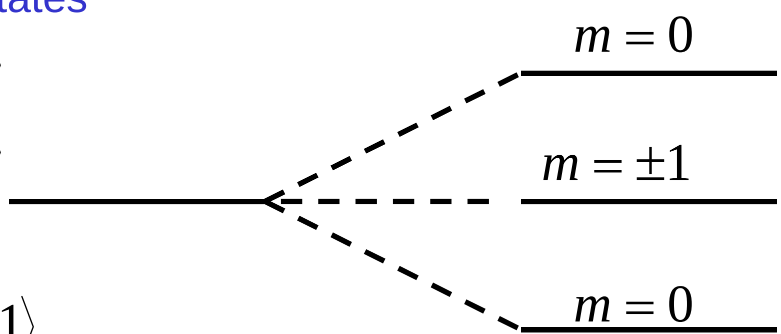
- In this case we have a linear dependence on $\mathcal{E}$
- H atom behaves as if it had a permanent dipole moment of $\pm 3ea_0$

Linear Stark effect in Hydrogen (4)

Pattern of Stark splitting of hydrogen:

4 degenerate states

$$|nlm\rangle = \begin{cases} |200\rangle \\ |210\rangle \\ |211\rangle \\ |21-1\rangle \end{cases}$$



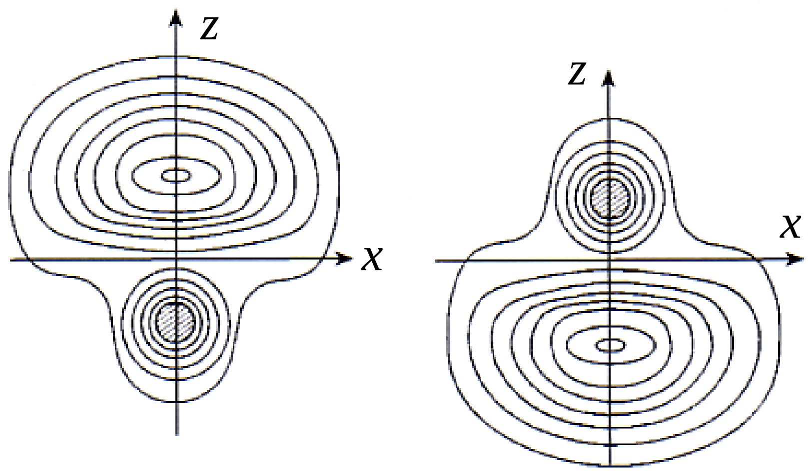
$\frac{1}{\sqrt{2}}\left[|200\rangle - |210\rangle\right]$

$|211\rangle, |21-1\rangle$ 2 degenerate states

$\frac{1}{\sqrt{2}}\left[|200\rangle + |210\rangle\right]$

- Contour maps of the electron density:

Diagram: "Quantum mechanics" - Rae



$\frac{1}{\sqrt{2}}\left[|200\rangle - |210\rangle\right]$ $\frac{1}{\sqrt{2}}\left[|200\rangle + |210\rangle\right]$

- The mixing of the degenerate states gives rise to a dipole moment of size $3ea_0$ which can align parallel or anti-parallel to $\mathcal{E}$

- Stark effect observed in optical spectra from the transition $n = 2 \rightarrow n = 1$

Electrons in a one-dimensional solid (1)

- Here we develop a 1D model of a solid where free electrons move in a periodic potential.
- This is similar to the potential arising in a crystalline solid due to the nuclei and other electrons.
- Assume the potential is weak enough to be treated as a perturbation.
- If we have a crystal lattice constant a assume we have a periodic potential in the x direction of the form

$$V(x) = 2V\cos(2\pi x/a)$$

where $2V$ is assumed small so that $V(x)$ is a perturbation.

- The unperturbed wavefunctions and energy for free electrons in a sample of length L are:

$$\psi_k = |k\rangle = \frac{1}{\sqrt{L}}e^{ikx}, \quad E_k^{(0)} = \frac{\hbar^2k^2}{2m}$$

Electrons in a one-dimensional solid (2)

- The matrix elements between states of different wavevector i.e. k_1 and k_2 can be written as follows:

$$\hat{H}'_{12} = \langle k_1 | \hat{H}' | k_2 \rangle = \frac{1}{L}\int_0^L e^{-ik_1x} 2V\cos(2\pi x/a) e^{ik_2x} dx$$

$$= \frac{V}{L}\int_0^L e^{i(k_2-k_1+2\pi/a)x} + e^{i(k_2-k_1-2\pi/a)x} dx \quad = V, \text{ if } k_2 - k_1 = \pm\frac{2\pi}{a}$$

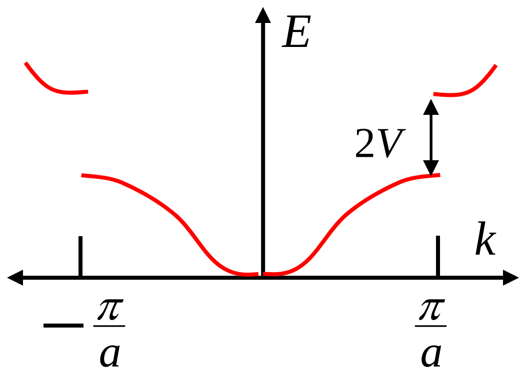
$$= 0 \text{ otherwise (osc. functions)}$$

- Note that the diagonal elements of the matrix $\hat{H}'$ are all zero.
- If states $|k_1\rangle$ and $|k_2\rangle$ are degenerate then $E_k^{(0)} = \frac{\hbar^2 k^2}{2m} \Rightarrow k_1 = -k_2$ the matrix element between these states is non-zero if $k = \pm\pi/a$.
- So to first order we have:

$$\hat{H}' = \begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} = \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} \quad \text{Hence} \quad \begin{vmatrix} -E & V \\ V & -E \end{vmatrix} = 0$$

Electrons in a one-dimensional solid (3)

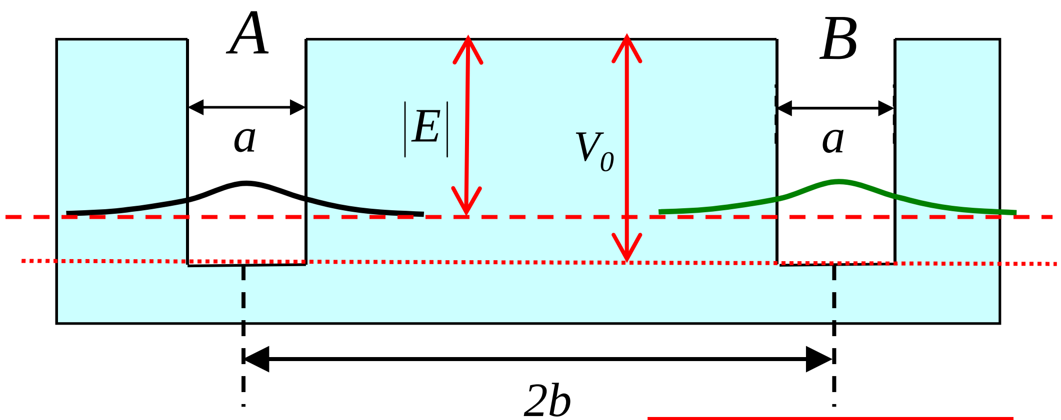
- On the last slide we found that at $k = \pm\pi / a$



$$\begin{vmatrix} -E & V \\ V & -E \end{vmatrix} = 0 \qquad \Rightarrow E = \pm V \Rightarrow E = E^{(0)} \pm V$$

- Degeneracy has been lifted by periodic potential giving two values of energy for the same wavevector.
- Energy gaps have appeared in the energy spectrum at $k = \pm\pi / a$
- This result explains the difference between metals and insulators:
- A metal occurs where there are empty electron states, on application of an electric field, electrons can move into adjacent k states giving a net non-zero k value for all the electrons – hence a current flows.
- An insulator occurs when all the states up to the energy gap are filled. On application of an electric field electrons cannot move into adjacent k states to give a non-zero net k value – therefore no electrons flow.
- A semiconductor is where the temperature is high enough that electrons can move across the energy gap and behave as in a metal.

Example: Coupled quantum wells (1)



- Consider two quantum wells A and B of width a with centres a distance $2b$ apart.

- If $b \gg a$ There is no wave-function over-lap.

$E<0$,-ve total energy, +ve K.E.

- The systems can be described by two Hamiltonians:

$$\hat{H}_A = \frac{\hat{p}_A^2}{2m} + V(x+b), \qquad \hat{H}_B = \frac{\hat{p}_B^2}{2m} + V(x-b)$$

where a function $V(x) = -V_0$ between $x = \pm\frac{a}{2}$ and zero elsewhere.

- These two systems have identical wavefunctions and eigenenergies.

- As $2b$ is reduced and they are brought closer together each system starts to perturb the other.

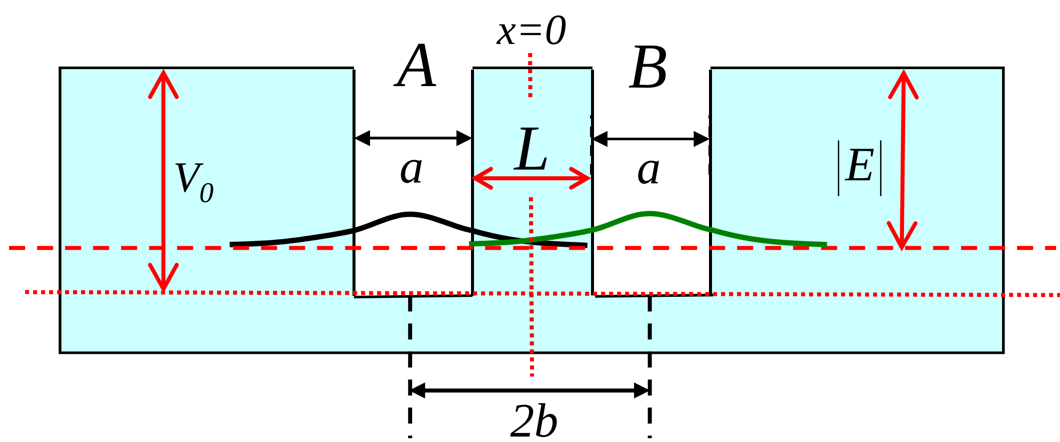
- We introduce a perturbation element to the Hamiltonian, so for system A:

$$\hat{H}'_A = \overbrace{\frac{\hat{p}_A^2}{2m} + V(x+b)}^{\hat{H}_A} + \overbrace{V(x-b)}^{\hat{H}'}$$

- We find the perturbation matrix elements for the degenerate wavefunctions.

Coupled quantum wells (2)

•We reduce the barrier between the two wells to a width $L=2b-a$ so the electron wavefunctions overlap.



•Calculate the perturbation matrix elements from the perturbation potential and the wavefunctions for isolated wells ($b \gg a$).

•Solutions of the Schrodinger equation for the wells A & B when $b \gg a$:

$$\psi_A \approx C\cos k\left(x+b\right), \quad -b-\tfrac{a}{2} < x < -b+\tfrac{a}{2}$$

$$\psi_A \approx C\cos(\tfrac{ka}{2})e^{-\kappa\left(x+b-a/2\right)}, \; x > -b+\tfrac{a}{2}$$

$$\psi_B \approx C\cos k\left(x-b\right), \quad b-\tfrac{a}{2} < x < b+\tfrac{a}{2}$$

$$\psi_B \approx C\cos(\tfrac{ka}{2})e^{\kappa\left(x-b+a/2\right)}, \quad x < b-\tfrac{a}{2}$$

$$C = \left[\tfrac{a}{2}+\tfrac{1}{\kappa}\right]^{-\frac{1}{2}}$$ is a constant determined by normalization

k - electron wavevector

$$k^2 = \tfrac{2m}{\hbar^2}\left(E+V_0\right)$$

κ -tunnelling penetration coefficient $\kappa^2 = -\tfrac{2m}{\hbar^2}E$

$$k^2+\kappa^2 = \frac{2mV_0}{\hbar^2}$$

$$k\tan\left(\tfrac{ka}{2}\right) = \kappa$$

See section 5.2 QP course

Coupled quantum wells (3)

- Calculate the matrix elements:

$$H'_{AB} = -V_0 \int_{b-a/2}^{b+a/2} \psi_A \psi_B \, dx = -V_0 C^2 \int_{b-a/2}^{b+a/2} \overbrace{\cos(\tfrac{ka}{2}) e^{-\kappa(x+b-a/2)}}^{\psi_A} \overbrace{\cos k(x-b)}^{\psi_B} dx$$

$$u = x - b \Rightarrow \hat{H}'_{AB} = -V_0 C^2 \cos(\tfrac{ka}{2}) e^{-\kappa(2b-a/2)} \int_{-a/2}^{+a/2} e^{-\kappa u} \cos ku \, du$$

$$= -V_0 C^2 \cos(\tfrac{ka}{2}) e^{-\kappa(2b-a/2)} \left[\tfrac{1}{k^2+\kappa^2} e^{-\kappa u} \left(-\kappa \cos ku + k \sin ku \right) \right]_{-a/2}^{+a/2}$$

$$= -\frac{V_0 C^2}{k^2+\kappa^2} \cos^2(\tfrac{ka}{2}) e^{-\kappa(2b-a/2)} \left[2\kappa e^{+\kappa a/2} \right]$$

$$\boxed{\tan\left(\tfrac{ka}{2}\right) = \tfrac{\kappa}{k}}$$

$$\boxed{H'_{AB} = -4E \frac{1}{a\kappa+2} \left(1 + \frac{E}{V_0}\right) e^{-\kappa L}}$$

$$\boxed{\begin{aligned} &\cos^2(\tfrac{ka}{2}) = \left(1 + \tfrac{E}{V_0}\right) \\ &\tfrac{\kappa^2}{k^2+\kappa^2} = \tfrac{E}{V_0}, C^2 = \tfrac{2\kappa}{\kappa a+2} \\ &L = 2b - a \end{aligned}}$$

Similarly

$$\boxed{H'_{AA} = -\frac{1}{a\kappa+2} (V_0 + E) e^{-2\kappa L} \left[1 - e^{-2\kappa a} \right]}$$

Coupled quantum wells (4)

- From the last slide: $$H'_{AA} = H'_{BB} = -\frac{1}{a\kappa+2}(V_0 + E)e^{-2\kappa L}\left[1-e^{-2\kappa a}\right]$$ $$H'_{AB} = H'_{BA} = -4E\frac{1}{a\kappa+2}\left(1+\frac{E}{V_0}\right)e^{-\kappa L}$$
- As an example let:

$$a = 4nm, L = 5nm, V_0 = 250meV, E = -144meV, \kappa = 0.502nm^{-1}$$

- Giving: $H'_{AA} = 0.1715meV,\qquad H'_{AB} = 4.952meV$

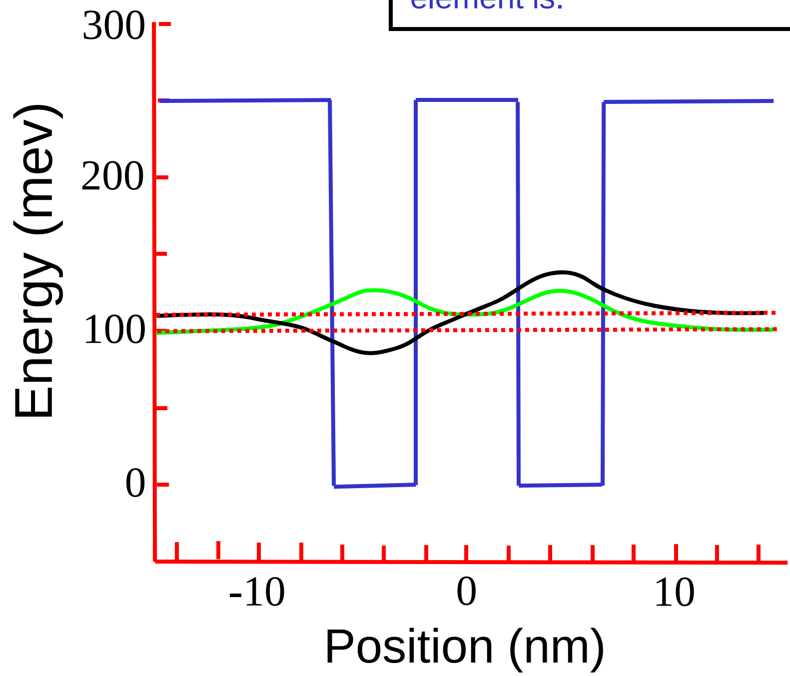
Note: In this case the perturbation to the potential is not small but the perturbation matrix element is.

- So the perturbation Hamiltonian is as follows:

$$\hat{H}' \approx \begin{pmatrix} 0 & H'_{AB} \\ H'_{AB} & 0 \end{pmatrix}$$

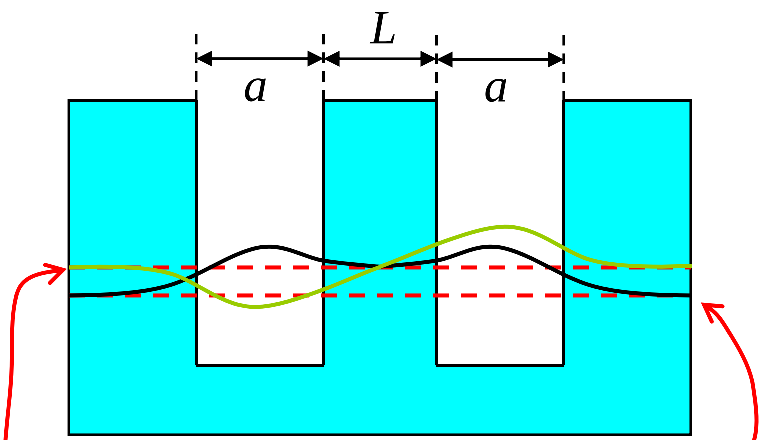
$$\Rightarrow \begin{vmatrix} -E & H'_{AB} \\ H'_{AB} & -E \end{vmatrix} = 0$$

$$\Rightarrow E = \pm H'_{AB} = \pm 4.95meV$$

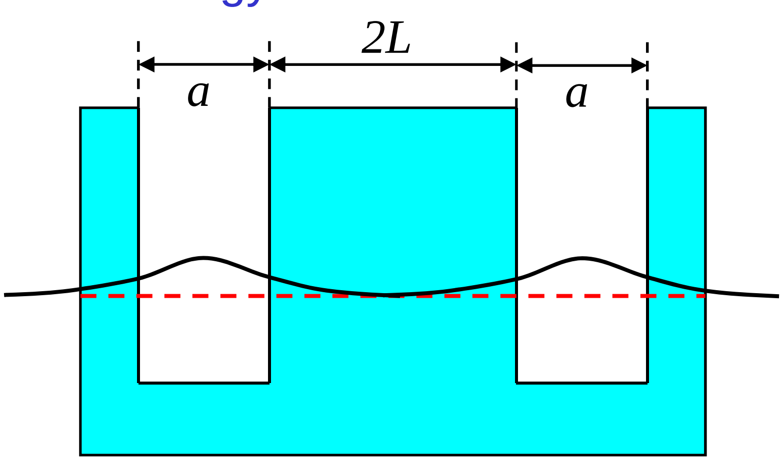


- Wavefunctions form symmetric and anti-symmetric states with energy levels split by: $\Delta E = 2H'_{AB} = 9.90meV$

Coupled quantum wells (5)



Coupled wells – symmetric and antisymmetric states split in energy

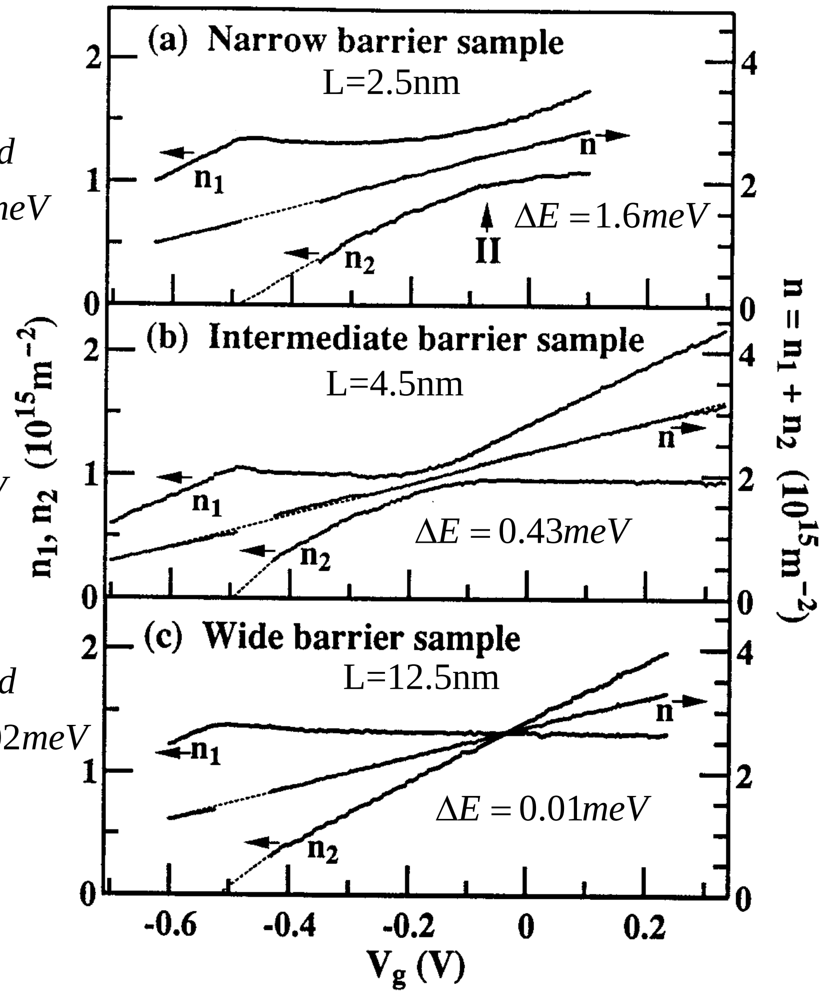


Uncoupled wells - same energies

Calculated
$\Delta E = 2.3meV$

Calc. $\Delta E = 0.32meV$

Calculated
$\Delta E = 0.002meV$



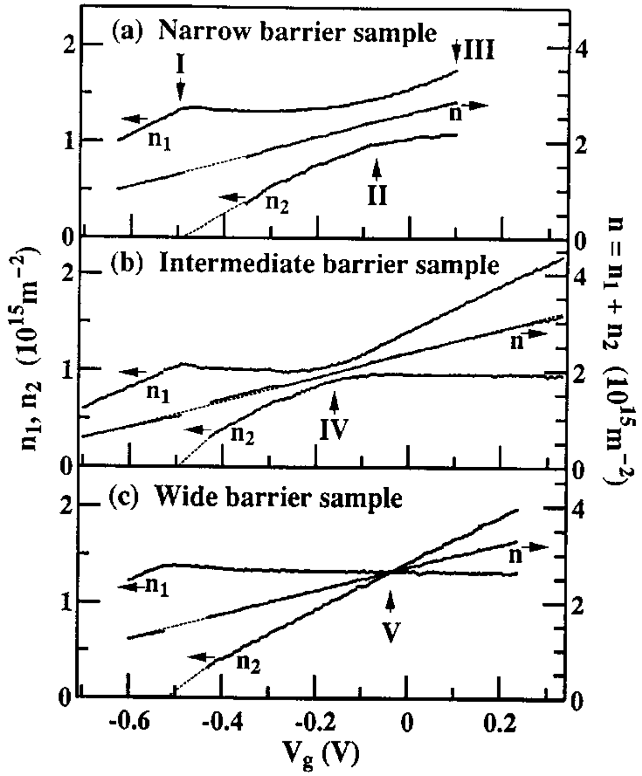
Experimental results of electron densities in uncoupled and coupled wells – energy splitting clearly visible

K R Zolleis PhD Thesis U.Cam. 1999

Lecture 8 - Summary

- Degenerate perturbation theory is required where states of the unperturbed Hamiltonian have the same energy.
- We replace the set of degenerate basis states with linear combinations of the same states.
- These new states are chosen to be eigenstates of the perturbation part of the Hamiltonian and diagonalize the corresponding matrix.
- The energy levels can then be calculated.
- Example: Stark effect in hydrogen – due to different parities of 2s and 2p degenerate states a linear effect is obtained – as opposed to the expected quadratic effect.
- Example: Electrons in a 1D solid – theory predicts forbidden energies which explains the different electrical properties of conductors, insulators and semiconductors.
- Example: Coupled quantum wells – calculation predicts energy splitting between symmetric and anti-symmetric energy levels.

Lecture 8



The End!!

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