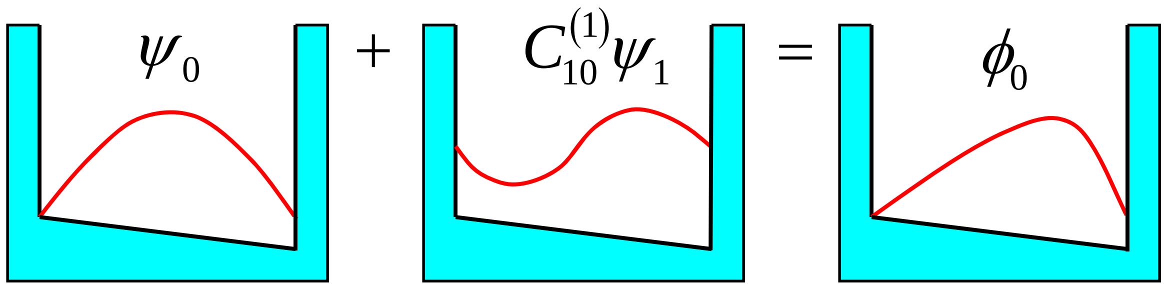
Advanced Quantum Physics

Lecture 7



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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.

2.3 Perturbation theory: Two state problem (1)

- Few problems in quantum mechanics can be exactly solved.
- But problems are often soluble if we neglect small terms in $\hat{H}$.
- We use pertubation theory to estimate the effect of these terms.
- Consider a simple two state problem with a Hamiltonian; $\hat{H} = \hat{H}_0 + \hat{H}'$ where $\hat{H}_0$ is the unperturbed Hamiltonian and $\hat{H}'$ is a small perturbation
- If the solutions to Schrodinger's equation for $\hat{H}_0$ are known to be;

$$\hat{H}_0\psi_1 = E_1\psi_1 \quad ; \quad \hat{H}_0\psi_2 = E_2\psi_2$$

and we assume $E_1 \neq E_2$, the exact solution, $\left|\phi\right\rangle$, for $\hat{H}\left|\phi\right\rangle = E\left|\phi\right\rangle$ can be expanded;

$$\left|\phi\right\rangle = c_1\left|\psi_1\right\rangle + c_2\left|\psi_2\right\rangle .$$

- Substituting into Schrodinger's equation; $\left(\hat{H}_0 + \hat{H}'\right)\left|\phi\right\rangle = E\left|\phi\right\rangle$ we obtain;

$$c_1\left(E_1 + \hat{H}'\right)\left|\psi_1\right\rangle + c_2\left(E_2 + \hat{H}'\right)\left|\psi_2\right\rangle = E(c_1\left|\psi_1\right\rangle + c_2\left|\psi_2\right\rangle) .$$

Two state problem (2)

- From the previous slide:

$$c_1\left(E_1+\hat{H}'\right)|\psi_1\rangle + c_2\left(E_2+\hat{H}'\right)|\psi_2\rangle = E(c_1|\psi_1\rangle + c_2|\psi_2\rangle)\ .$$

- Taking the inner product with $\langle\psi_1|$ and $\langle\psi_2|$ in turn gives:

$$c_1(E_1+H'_{11}-E)+c_2H'_{12}=0, \quad c_1H'_{21}+c_2(E_2+H'_{22}-E)=0.$$

- Elimination of c_1 and c_2 ; $(E_1+H'_{11}-E)(E_2+H'_{22}-E)=H'_{12}H'_{21}$

$$\Rightarrow E^2 - E\left(E_1+E_2+H'_{11}+H'_{22}\right) - H'_{12}H'_{21} + \left(E_1+H'_{11}\right)\left(E_2+H'_{22}\right) = 0$$

which is quadratic in E with solution;

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

- So far this is exact – it doesn't require $\hat{H}'$ to be small.

Two state problem (3)

- For systems with more than two states, not usually possible to obtain an exact analytic solution – but a computational approach may be viable.
- From the previous slide:

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

- We can simplify this when $H'_{ij} \ll | E_1 - E_2 |$ - the perturbation matrix elements are much smaller than the energy level spacing.
- Expanding the square root:

$$E = E_1 + H'_{11} + \frac{H'_{12}H'_{21}}{E_1 - E_2} + O\left(H'^3_{ij}\right) \text{ or } E = E_2 + H'_{22} - \frac{H'_{12}H'_{21}}{E_1 - E_2} + O\left(H'^3_{ij}\right)$$

- This is a power series in the matrix elements of $\hat{H}'$. To first order the shift in the energy levels is:

$$\Delta E_i = \left\langle \psi_i \middle| \hat{H}' \middle| \psi_i \right\rangle = H'_{ii} \ .$$

General case (1)

- The general case: suppose energy levels $E_n^{(0)}$ & stationary states $|\psi_n\rangle$ of unperturbed Hamiltonian $\hat{H}_0$ are known.
- We have a small perturbation $\lambda\hat{H}'$* so:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

- We want to find new eigenvalues E_n and eigenstates $|\phi_n\rangle$ where

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle .$$

- Make a power series expansion in λ :

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

$$|\phi_n\rangle = |\psi_n\rangle + \lambda\sum_{k\neq n} C_{nk}^{(1)}|\psi_k\rangle + \lambda^2\sum_{k\neq n} C_{nk}^{(2)}|\psi_k\rangle + \ldots.$$

- Completeness of set of unperturbed $\{|\psi_k\rangle\}$ means we can expand each term in power series for $|\phi_n\rangle$.

* λ Is simply a device to keep track of terms in the equation - when we want to get rid of it we let $\lambda \rightarrow 1$.

General case (2)

- Substitute power series: $E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$

$$\left|\phi_n\right\rangle = \left|\psi_n\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} \left|\psi_k\right\rangle + \lambda^2 \sum_{k\neq n} C_{nk}^{(2)} \left|\psi_k\right\rangle + \ldots.$$

- into Schrodinger's equation: $(\hat{H}_0 + \lambda \hat{H}')\left|\phi_n\right\rangle = E_n \left|\phi_n\right\rangle$ to give…..

$$E_n^{(0)}\left|\psi_n\right\rangle + \lambda \hat{H}'\left|\psi_n\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \left|\psi_k\right\rangle + \lambda^2 \sum_{k\neq n} (C_{nk}^{(1)} \hat{H}' + C_{nk}^{(2)} E_k^{(0)})\left|\psi_k\right\rangle + O(\lambda^3) =$$

$$E_n^{(0)}\left|\psi_n\right\rangle + \lambda E_n^{(1)}\left|\psi_n\right\rangle + \lambda E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \left|\psi_k\right\rangle$$

$$+\lambda^2 E_n^{(2)}\left|\psi_n\right\rangle + \lambda^2 \sum_{k\neq n} (E_n^{(1)} C_{nk}^{(1)} + E_n^{(0)} C_{nk}^{(2)})\left|\psi_k\right\rangle + O(\lambda^3)\,.$$

- Equating coefficients of λ :

$$\hat{H}'\left|\psi_n\right\rangle + \sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \left|\psi_k\right\rangle = E_n^{(1)} \left|\psi_n\right\rangle + E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \left|\psi_k\right\rangle\,.$$

General case (3)

- From last slide: $\hat{H}'\left|\psi_n\right\rangle + \sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)}\left|\psi_k\right\rangle = E_n^{(1)}\left|\psi_n\right\rangle + E_n^{(0)}\sum_{k\neq n} C_{nk}^{(1)}\left|\psi_k\right\rangle$
- Taking the inner product with $\left\langle\psi_n\right|$ and using orthonormality, $\left\langle\psi_m \mid \psi_k\right\rangle = \delta_{mk}$ we obtain:

$$E_n^{(1)} = \left\langle\psi_n\right|\hat{H}'\left|\psi_n\right\rangle$$

- So the first order energy shift is the expectation value of the perturbation – the same result as for the two state system.
- To obtain the wavefunction - take inner product with $\left\langle\psi_k\right|$ where $k \neq n$:

$$C_{nk}^{(1)} = \frac{\left\langle\psi_k\right|\hat{H}'\left|\psi_n\right\rangle}{E_n^{(0)} - E_k^{(0)}} \Rightarrow \quad \left|\phi_n\right\rangle = \left|\psi_n\right\rangle + \sum_{k\neq n}\frac{\left\langle\psi_k\right|\hat{H}'\left|\psi_n\right\rangle}{E_n^{(0)} - E_k^{(0)}}\left|\psi_k\right\rangle \qquad (\lambda \to 1)$$

- So the admixture of $\left|\psi_k\right\rangle$ in the n^{th} perturbed eigenstate is the matrix element of the perturbation divided by the energy difference.
- The main contribution to the perturbed wavefunction comes from states nearby in energy.
- If $E_n^{(0)} = E_k^{(0)}$ we need degenerate perturbation theory.

Perturbation theory: second order

- As previously:

$$E_n^{(0)}|\psi_n\rangle+\lambda\hat{H}'|\psi_n\rangle+\lambda\sum_{k\neq n}C_{nk}^{(1)}E_k^{(0)}|\psi_k\rangle+\lambda^2\sum_{k\neq n}(C_{nk}^{(1)}\hat{H}'+C_{nk}^{(2)}E_k^{(0)})|\psi_k\rangle+O(\lambda^3)=$$

$$E_n^{(0)}|\psi_n\rangle+\lambda E_n^{(1)}|\psi_n\rangle+\lambda E_n^{(0)}\sum_{k\neq n}C_{nk}^{(1)}|\psi_k\rangle+\lambda^2E_n^{(2)}|\psi_n\rangle+\lambda^2\sum_{k\neq n}(E_n^{(1)}C_{nk}^{(1)}+E_n^{(0)}C_{nk}^{(2)})|\psi_k\rangle+O(\lambda^3)\,.$$

- Equating coefficients of λ^2 and taking inner product with $\langle\psi_n|$:

$$E_n^{(2)}=\sum_{k\neq n}C_{nk}^{(1)}\langle\psi_n|\hat{H}'|\psi_k\rangle,$$

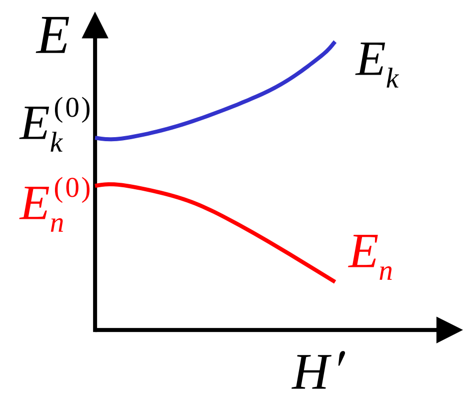
Hermitian

- Last slide: $C_{nk}^{(1)}=\dfrac{\langle\psi_k|\hat{H}'|\psi_n\rangle}{E_n^{(0)}-E_k^{(0)}}$ & since: $\langle\psi_n|\hat{H}'|\psi_k\rangle=\langle\psi_k|\hat{H}'|\psi_n\rangle^*$
- Energy to 2nd order:

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

- Symmetry $\Rightarrow$ first order shift often vanishes.
- Nearby states contribute most to 2nd order energy shift.
- Nearby states 'repel' when perturbation applied

-If $E_k^{(0)}>E_n^{(0)}$ state k moves up and n down.



Example: 1D Harmonic Oscillator (1)

- A 1D harmonic oscillator with linear perturbation

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \tfrac{1}{2}m\omega^2\hat{x}^2 + \lambda\hat{x}\,.$$

- To evaluate matrix elements of the perturbation express $\hat{x}$ in terms of harmonic oscillator ladder operators $\hat{a}$ and $\hat{a}^\dagger$,

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)\,.$$

- Since $\hat{a}\left|\phi_n\right\rangle = \sqrt{n}\left|\phi_{n-1}\right\rangle, \quad \hat{a}^\dagger\left|\phi_n\right\rangle = \sqrt{n+1}\left|\phi_{n+1}\right\rangle,$
- The first order energy shift:

$$E = \left\langle\phi_n\right|\lambda\hat{x}\left|\phi_n\right\rangle = \lambda\sqrt{\frac{\hbar}{2m\omega}}\left\langle\phi_n\right|\hat{a} + \hat{a}^\dagger\left|\phi_n\right\rangle$$

$$= \lambda\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\left\langle\phi_n\middle|\phi_{n-1}\right\rangle + \sqrt{n+1}\left\langle\phi_n\middle|\phi_{n+1}\right\rangle\right) = 0$$ For all n.

- The same is true for any odd function of x.

1D Harmonic Oscillator (2)

- To second order:

$$E_n^{(2)} = \sum_{k\neq n} \frac{|\langle \phi_k | \hat{H}' | \phi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} \frac{\left| \lambda \sqrt{\frac{\hbar}{2m\omega}} \langle \phi_k | \hat{a} + \hat{a}^\dagger | \phi_n \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$= \sum_{k\neq n} \frac{\left| \lambda \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n} \langle \phi_k | \phi_{n-1} \rangle + \sqrt{n+1} \langle \phi_k | \phi_{n+1} \rangle \right) \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

- $\langle \phi_k | \phi_m \rangle = \delta_{km} \Rightarrow E_n^{(2)}$ only has terms from adjacent levels $k = n \pm 1$
- Since $E_n^{(0)} = (n + \frac{1}{2})\hbar\omega$ we find:

$$E_n = E_n^{(0)} + \frac{\hbar\lambda^2}{2m\omega} \left(\frac{n}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{n+1}{E_n^{(0)} - E_{n+1}^{(0)}} \right) = (n + \tfrac{1}{2})\hbar\omega - \frac{\lambda^2}{2m\omega^2}$$

- This is the *exact* solution !!! – because we can re-write the potential as:

$$\tfrac{1}{2} m\omega^2 x^2 + \lambda x = \tfrac{1}{2} m\omega^2 \left(x + \frac{\lambda}{m\omega^2} \right)^2 - \frac{\lambda^2}{2m\omega^2} .$$

- So a harmonic Oscillator with a linear Perturbation is the same as a harmonic Oscillator with a shifted centre of oscillation and reduced energy

Example – the He atom (again)

- Lecture 5:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_1} - \frac{Z}{r_2}\right)}_{\hat{H}_0} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}}_{\hat{H}'} \quad \begin{cases} \nabla_1^2 \text{ w.r.t. } \mathrm{r}_1 \\ \nabla_2^2 \text{ w.r.t. } \mathrm{r}_2 \\ r_{12} = \left|r_1 - r_2\right| \end{cases}$$

- For $\hat{H}_0$ ground state energy $E_0^{(0)} = -2Z^2 R_\infty, \qquad \psi_0 = \psi_{1s}(r_1)\psi_{1s}(r_2),$

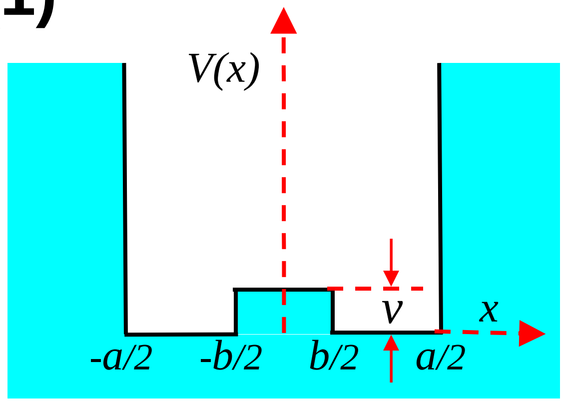
where $\psi_{1s}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}, Z = 2, a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}.$

So:

$$E_0^{(1)} = \left\langle \psi_{1s}(r_1)\psi_{1s}(r_2) \right| \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}} \left| \psi_{1s}(r_1)\psi_{1s}(r_2) \right\rangle = \frac{5}{8}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = \frac{5}{4} Z R_\infty$$

- This is the same integral as the variational calculation with $Z' \to Z$.
- Total energy= $\left(\frac{5}{4}Z - 2Z^2\right)R_\infty = -74.7eV.$
- C/w variational value $-77.4eV$, experimental value $-79.0eV$.
- In this case $\hat{H}'$ is not small!

Example: potential well (1)



Perturbation:

$\hat{H}' = v, \ |x| \le \frac{b}{2}$

$\hat{H}' = 0, \ \frac{b}{2} \le |x| \le \frac{a}{2}$

- A deep 1D potential well, unperturbed energies, wavefunctions are: $E_n^{(0)} = (n+1)^2 \frac{\hbar^2 \pi^2}{2ma^2}$

$$\psi_n = \sqrt{\tfrac{2}{a}} \cos\left((n+1)\pi x/a\right), \quad n \text{ even}$$

$$\psi_n = \sqrt{\tfrac{2}{a}} \sin\left((n+1)\pi x/a\right), \quad n \text{ odd}$$

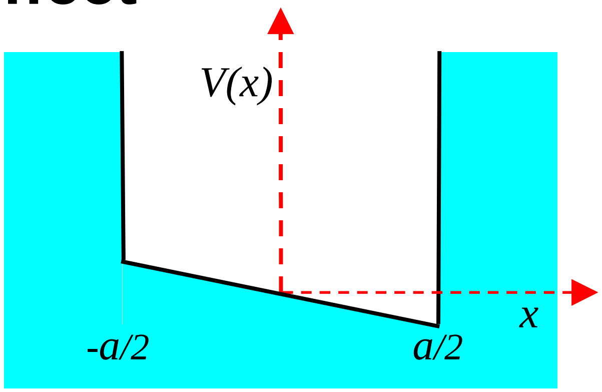
- Hence:

$$E_0^{(1)} = \frac{2v}{a} \int_{\frac{-b}{2}}^{\frac{b}{2}} \cos^2(\pi x/a)\, dx = \frac{v}{a}\left[b + \frac{a}{\pi} \sin(\pi b/a)\right]$$

$$E_1^{(1)} = \frac{2v}{a} \int_{\frac{-b}{2}}^{\frac{b}{2}} \sin^2(2\pi x/a)\, dx = \frac{v}{a}\left[b - \frac{a}{2\pi} \sin(2\pi b/a)\right]$$

- Check: if $b = a$ then $E_0^{(1)} = E_1^{(1)} = v$ as expected.
- For $b \ll a, \ E_0^{(1)} \approx 2vb/a, \ E_1^{(1)} \approx 0$ because $\psi_1 \simeq 0$ in the region of the perturbation whereas ψ_0 is at a maximum.
- For wavefunction; since $V(x)$ symmetrical $C_{kn}^{(1)} = 0$ if $k+n$ odd - no contribution from adjacent level - only a small change in wavefunction.
- Perturbation causes change in energy but not wavefunction to first order.

Potential well (2):Stark effect



•A deep 1D well, apply an electric field $\mathcal{E}$

$$\hat{H}' = -q\mathcal{E}x$$

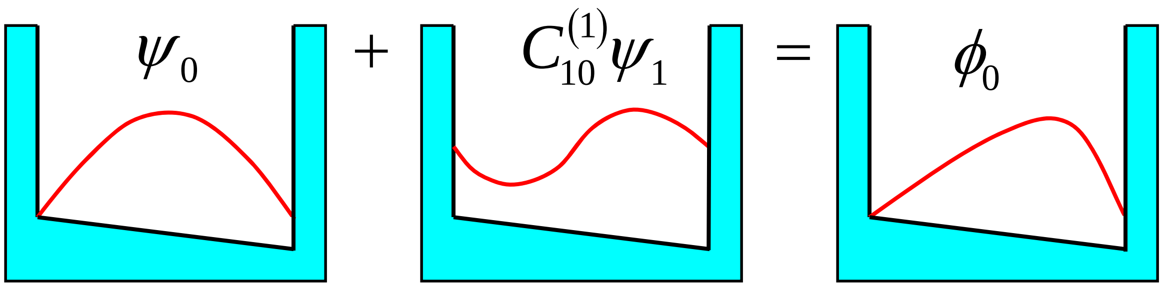
$$\Rightarrow E_0^{(1)} = \frac{-2q\mathcal{E}}{a}\int_{-\frac{a}{2}}^{\frac{a}{2}} x\cos^2\left(\frac{\pi x}{a}\right)dx = 0$$

- since we have an integral of an odd function.

•Leading contribution from $E_0^{(2)} \propto \mathcal{E}^2$ since $\langle \psi_k | x | \psi_0 \rangle \neq 0,\ k$ odd.

•Like an induced dipole moment $p \propto \mathcal{E}$ energy $= \frac{1}{2} p\mathcal{E} \propto \mathcal{E}^2$

•In this case $C_{k0}^{(1)} \neq 0$ for odd k – to first order energy unaffected but wavefunction altered:



Asymmetric $\Rightarrow$ dipole moment

Potential well (3):Second order

•If $\hat{H}' = -q\mathcal{E}x$ then 2nd order energy shift : $E_n^{(2)} = q^2\mathcal{E}^2 \sum_{k\neq n} \frac{|\langle\psi_k|x|\psi_n\rangle|^2}{E_n^{(0)} - E_k^{(0)}}$

•If we just consider lowest two levels $n = 0,1$ then:

$$E_0^{(2)} = q^2\mathcal{E}^2 \frac{|\langle\psi_0|x|\psi_1\rangle|^2}{E_0^{(0)} - E_1^{(0)}} = -E_1^{(2)}$$

•Since $E_0^{(2)} < 0, E_1^{(2)} > 0$ the difference between levels increases with electric field:

$$\Delta E = E_1^{(2)} - E_0^{(2)} = -2q^2\mathcal{E}^2 \frac{|\langle\psi_0|x|\psi_1\rangle|^2}{E_0^{(0)} - E_1^{(0)}}$$

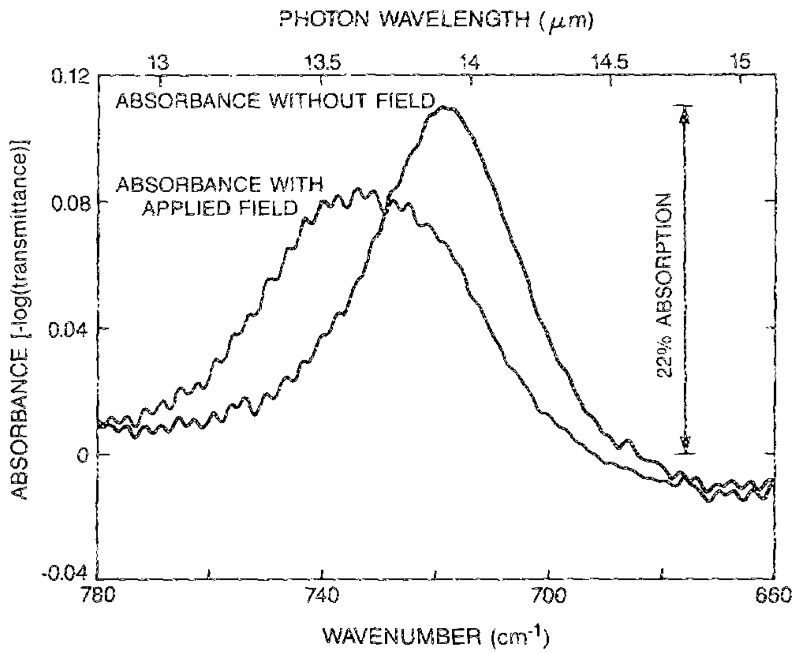
•Given $E_n^{(0)} = (n+1)^2 \frac{\hbar^2\pi^2}{2ma^2}$ on evaluating the matrix element:

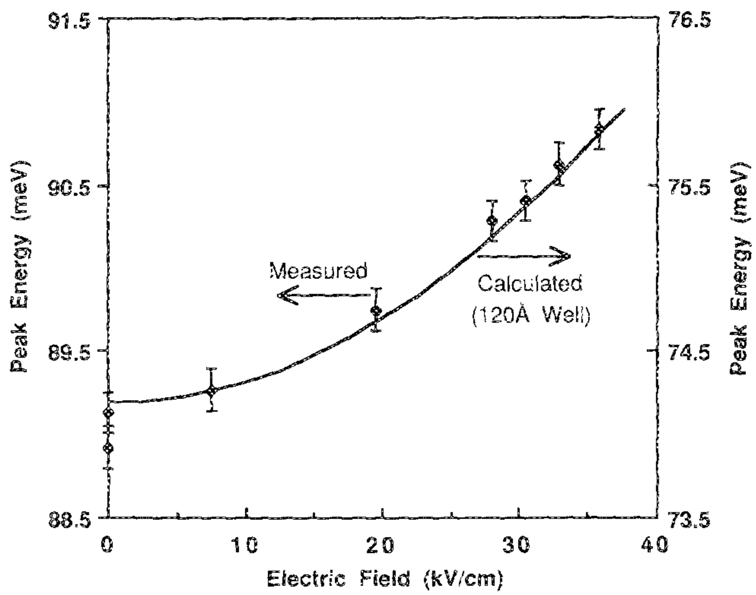
$$\Delta E = \frac{2^{10}}{3^5} \cdot \frac{q^2\mathcal{E}^2 a^4 m}{\hbar^2}$$

•Comparison with experimental results – next slide.

Potential well (4): Experiment:

- •Semiconductor multilayer - 50 off 12nm GaAs quantum wells sandwiched between 35nm AlGaAs barriers.
- •Optical absorbance measured as a function of wavelength, $\psi_0 \rightarrow \psi_1$ transition takes place
- •Apply electric field across structure and observe Stark shift in absorbance peak.
- •Plot peak energy as a function of electric field $\mathcal{E}$.
- •Parabolic variation of energy with $\mathcal{E}$.
- •Reasonable agreement with theory (exact if GaAs wells are actually 10.7nm and not 12.0nm)
- •First observation of Stark effect in QWs – much larger shift than atoms.





A Harwitt and J S Harris Appl Phys Lett **50,** 685-687 (1987)

Lecture 7 - Summary

- Perturbation theory – used to calculate changes in energy levels and wavefunctions due to a small change, $\hat{H}'$ in the Hamiltonian.

- To 1st and 2nd order:

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

- To 1st order:

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

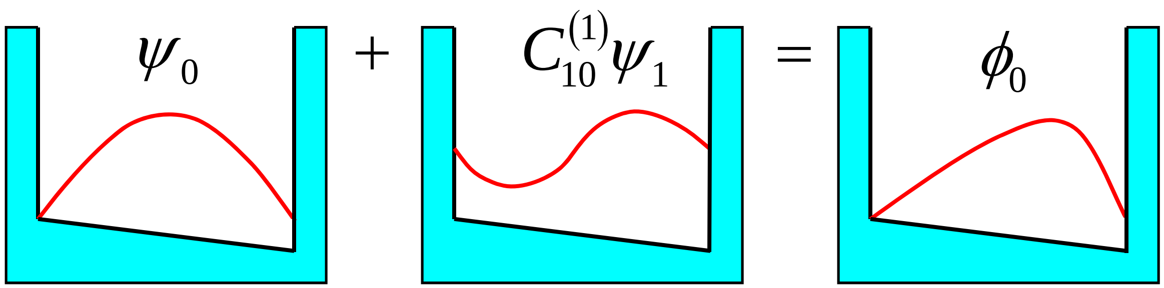
- Example: 1D harmonic oscillator – application of a linear perturbation results in a shifted centre of oscillation and reduced energy.

- Example: Binding energy of He atom – using inter-electron Coulomb energy as perturbation gives $-74.7eV$ c/w $-79.0eV$ from experiment. Not as good an estimate as that from the variational calculation in L5.

- Example: Potential bump in centre of quantum well changes energy but not wavefunction (to first order).

- Example: Electric field applied to quantum well changes wavefunction but not energy to first order. Second order calculation gives a quadratic variation of energy with field – confirmed by experiment (Stark effect).

Lecture 7



The End!!

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