Synopsis: Lectures 5-10

5. **Charged particle in an electromagnetic field:**
   Classical and quantum mechanics of particle in a field; normal Zeeman effect; gauge invariance and the Aharonov-Bohm effect; Landau levels.
6. **Spin:**
   Stern-Gerlach experiment; spinors, spin operators and Pauli matrices; spin precession in a magnetic field; parametric resonance; addition of angular momenta.
7. **Time-independent perturbation theory:**
   Perturbation series; first and second order expansion; degenerate perturbation theory; Stark effect; nearly free electron model.
8. **Variational and WKB method:**
   Variational method: ground state energy and eigenfunctions; application to helium; Semiclassics and the WKB method.

Lecture 8

Approximation methods for stationary states

Approximation methods: outline

- We have succeeded in developing formal analytical solutions for stationary states of Schrödinger operator, $\hat{H}$ in variety of settings.

- But majority of "real-life" applications are formally intractable!

  e.g. the "three-body problem" already non-integrable – rules out exact solution for non-hydrogenic atoms!

- It is therefore essential to develop approximation schemes: In the following, we wil develop three complementary approaches:

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  2. Variational method
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Time-independent perturbation theory

- In the perturbative series expansion, states of $\hat{H}$ obtained through sequence of corrections to some reference, $\hat{H}_0$, for which states are known.

- Although perturbative scheme is effective, there are – typically very interesting – problems which cannot be solved using this approach.

  e.g. in 1d, arbitrarily weak attractive potential causes $k = 0$ free particle state to drop below continuum and become bound.

- **Adiabatic continuity:** In general, perturbation theory useful (valid) when states of unperturbed system, $\hat{H}_0$, flow smoothly into states of $\hat{H}$ – viz. symmetries, node structures, etc.

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Perturbation series expansion

- Consider unperturbed Hamiltonian, $\hat{H}^{(0)}$, having known eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$,

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

- How are the eigenstates and eigenenergies modified by small perturbation, $\hat{H}^{(1)}$?

$$(\hat{H}^{(0)} + \hat{H}^{(1)})|n\rangle = E_n|n\rangle$$

e.g. external electric or magnetic field applied to charged particle

- If perturbation small, $\langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \ll E_n^{(0)}$, on "turning on" $\hat{H}^{(1)}$, expect eigenfunctions and eigenvalues to change adiabatically:

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Perturbation series expansion

- Basic assumption: for $\hat{H}^{(1)}$ small, leading corrections are $O(\hat{H}^{(1)})$
- Perturbed eigenfunctions and eigenvalues obtained by successive series of corrections, each $O(\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle)$ compared with previous.
- To identify terms of same order in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$, convenient to extract from $\hat{H}^{(1)}$ a dimensionless parameter λ characterising relative magnitude of perturbation and then expand:

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots = \sum_{m=0}^{\infty} \lambda^m |n^{(m)}\rangle$$

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- Applied to Schrödinger equation, $(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})|n\rangle = E_n|n\rangle$

$$\begin{aligned}&(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) \\ &= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots)\end{aligned}$$

and then relate terms of equal order in λ, e.g. to $O(\lambda)$

$$\hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle$$

First order perturbation theory

- To $O(\lambda)$, taking inner product with $\langle n^{(0)}|$

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- and we assume choose normalization $\langle n^{(0)}|n^{(1)}\rangle = 0$ (see later)

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For $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$,

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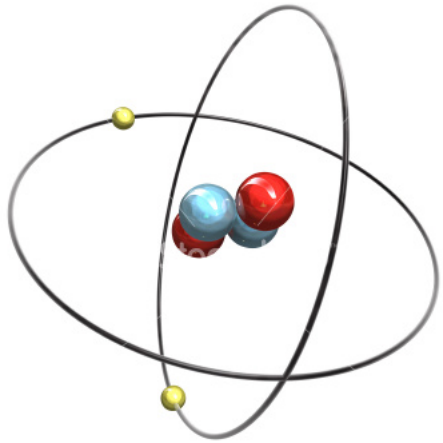
Example: Ground state energy of Helium atom

- Helium atom, two electrons bound to nucleus of two protons and two neutrons ($Z = 2$)



- To leading order in electron-electron interaction, what is ground state energy?

- Without Coulomb interaction between electrons, ground state:

$$|\text{g.s.}^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|100,\uparrow\rangle \otimes |100,\downarrow\rangle - |100,\downarrow\rangle \otimes |100,\uparrow\rangle\right)$$

where $E^{(0)} = -2 \times Z^2 \times \text{Ry}$, with $\text{Ry} = \dfrac{e^2}{4\pi\epsilon_0}\dfrac{1}{2a_0}$, $a_0 = \dfrac{4\pi\epsilon_0}{e^2}\dfrac{\hbar^2}{m_e}$ and

$$\psi_{100}(\mathbf{r}) \equiv \langle \mathbf{r}|n=1,\ell=0,m=0\rangle = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$

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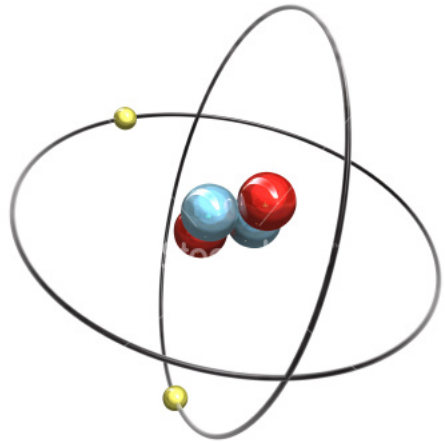

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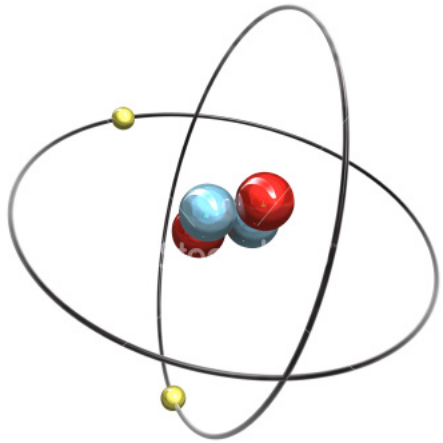
$$\hat{H}^{(1)} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$



- To first order, energy shift: $E^{(1)} = \langle \text{g.s.}^{(0)}|\hat{H}^{(1)}|\text{g.s.}^{(0)}\rangle$

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1 d^3r_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{e^2}{4\pi\epsilon_0}\frac{Z}{2a_0} \times C_0$$

with $C_0 = \frac{1}{(4\pi)^2}\int d^3z_1 d^3z_2 \frac{e^{-(z_1+z_2)}}{|\mathbf{z}_1 - \mathbf{z}_2|} = \frac{5}{4}$, $E^{(1)} = \frac{5}{4} Z\,\text{Ry}$

- $E \simeq (2Z^2 - \frac{5}{4}Z)\,\text{Ry} = -5.5\,\text{Ry}$ (cf. experiment: -5.807Ry)

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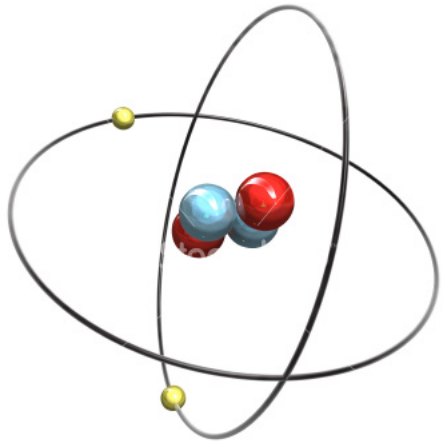

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- Recall expansion: $(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})|n\rangle = E_n|n\rangle$

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots)$$
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- To $O(\lambda^2)$, taking inner product with $\langle n^{(0)}|$

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$$E_n^{(2)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle - E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle$$

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Remarks:

- For ground state, second order energy shift always negative.
- If matrix elements of $\hat{H}^{(1)}$ are of comparable magnitude, neighbouring levels make larger contribution in second order perturbation theory than distant levels.
- If portion of states belong to continuum, sum replaced by intergral.
- Levels that lie in close proximity tend to be pushed apart – degeneracies are never accidental!

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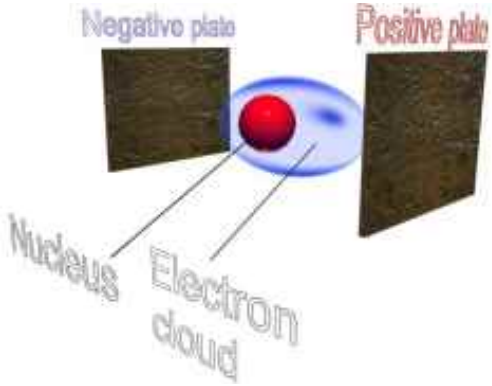
Example: Quadratic Stark Effect

- What is influence of external electric field on ground state of hydrogen atom?



- Electron and proton drawn in different directions by field
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- Unperturbed energy spectrum: $E^{(0)}_{n\ell m} \equiv E^{(0)}_n = -\frac{\mathrm{Ry}}{n^2}$,
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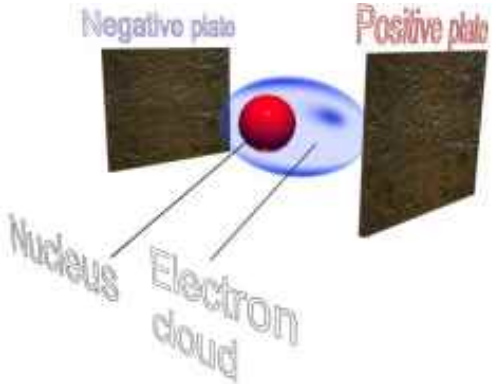
Example: Quadratic Stark Effect

- What is influence of external electric field on ground state of hydrogen atom?



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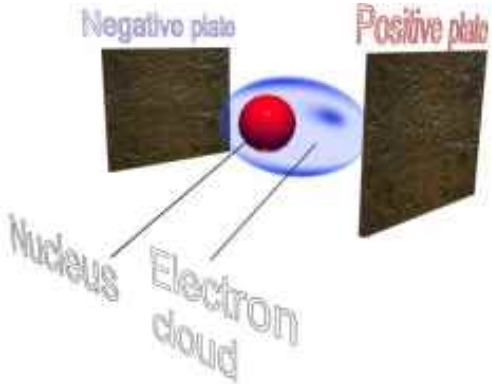

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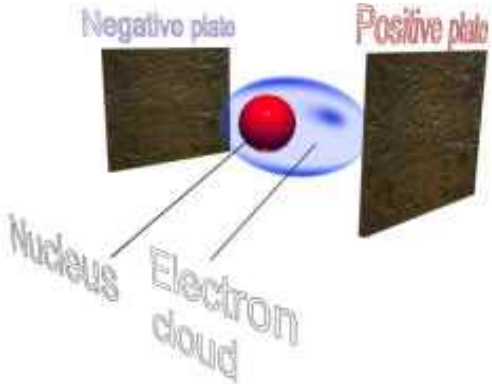

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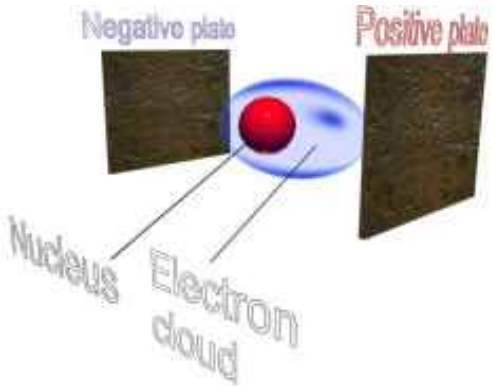
- At second order of perturbation theory, (neglecting continuum of unbound states),

$$E_1^{(2)} = \sum_{n\neq 1,\ell,m} \frac{|\langle n\ell m|e\mathcal{E}z|100\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

where $|n\ell m\rangle$ denote hydrogen bound states.



- Although $E_1^{(2)}$ can be evaluated exactly (using various tricks), we can place a strong bound by a simpler argument.
- Since, for $n > 2$, $|E_1^{(0)} - E_n^{(0)}| > |E_1^{(0)} - E_2^{(0)}|$,

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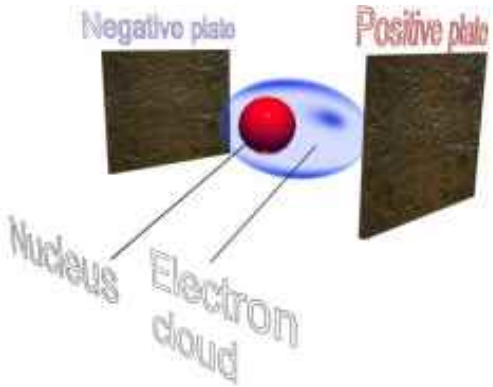

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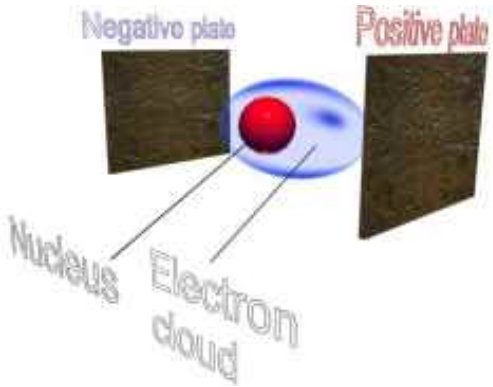

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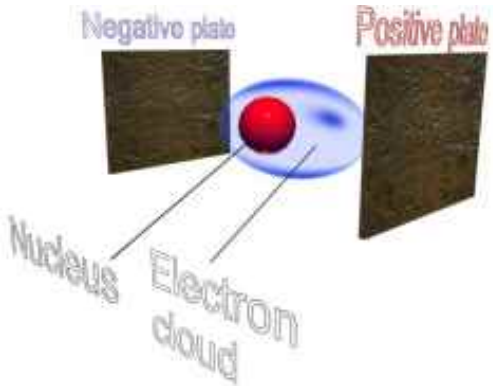

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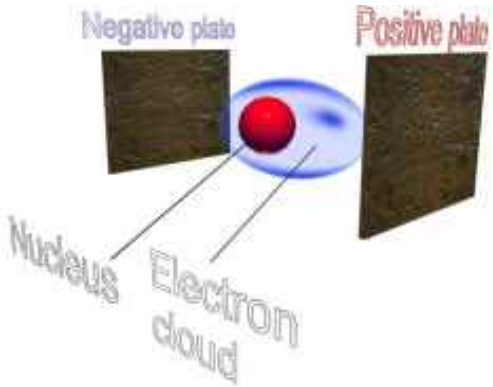

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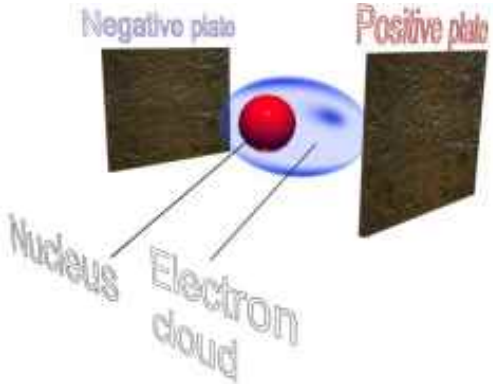

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$$|E_1^{(2)}| > \frac{|\langle 210|e\mathcal{E}z|100\rangle|^2}{E_2^{(0)} - E_1^{(0)}}$$

- Leads to $0.55 \times \dfrac{8}{3}4\pi\epsilon_0\mathcal{E}^2 a_0^3 < |E_1^{(2)}| < \dfrac{8}{3}4\pi\epsilon_0\mathcal{E}^2 a_0^3$

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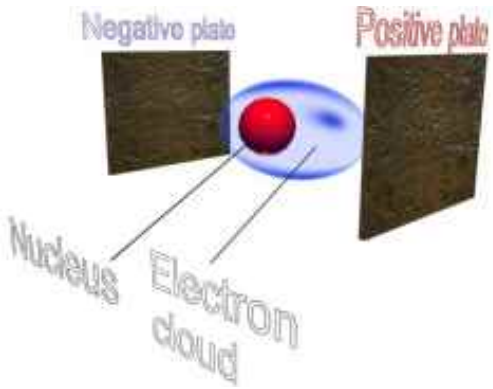

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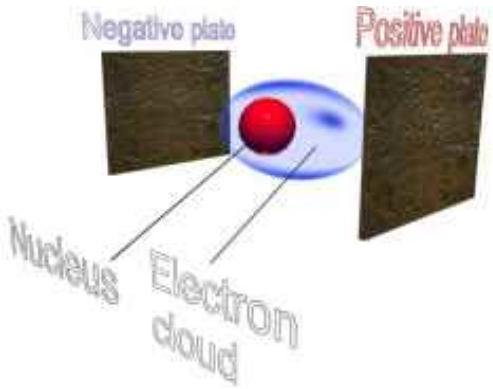

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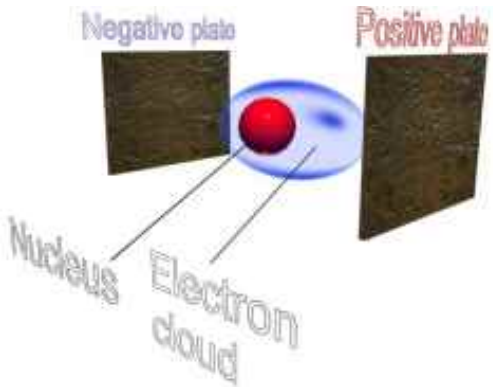

- In general, the induced electric dipole moment in an electric field is given by $\mathbf{d} = \alpha\epsilon_0\mathbf{E}$ where α is the polarizability (generally a tensor).
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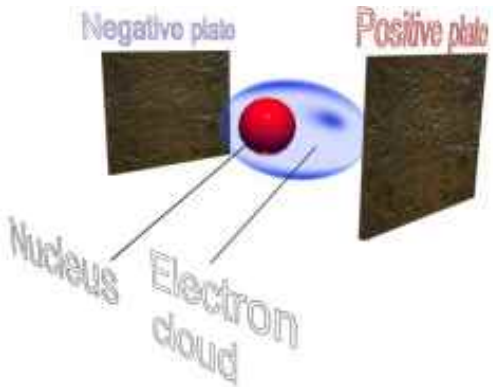

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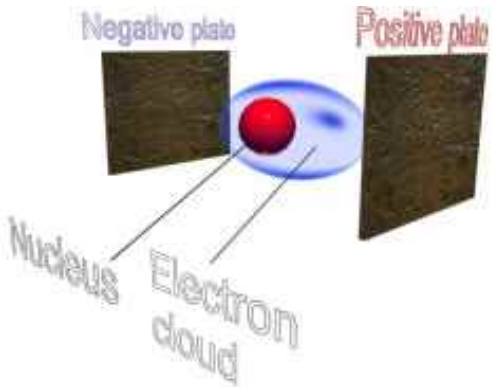

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How are states of a quantum system modified by the action of a small perturbation $\hat{H}^{(1)}$?

$$(\hat{H}^{(0)} + \hat{H}^{(1)})|n\rangle = E_n|n\rangle$$

- If perturbed states are "adiabatically" connected to unperturbed, corrections can be treated through series expansion in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$.
- At first order in perturbation theory, we have shown that

$$E_n \simeq E_n^{(0)} + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle$$

$$|n\rangle \simeq |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

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- At second order,

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Degenerate Perturbation Theory

- Validity of perturbation series expansion relies upon matrix elements being smaller than corresponding energy level differences, e.g.

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

- If unperturbed states $|m^{(0)}\rangle$ and $|n^{(0)}\rangle$ are degenerate, and $\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \neq 0$, perturbation theory fails!

- However, problem is easily fixed...

Degenerate Perturbation Theory

- ... to understand how, consider two-dimensional oscillator,

$$\hat{H}^{(0)} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2)$$

wavefunctions are separable into two one-dimensional oscillators.

- Setting $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ and $\eta = \sqrt{\frac{m\omega}{\hbar}}y$, ground state given by $|0,0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(\xi^2+\eta^2)/2}$, and two *degenerate* first excited states,

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- By symmetry, $\langle 0,0|\hat{H}^{(1)}|0,0\rangle = \langle 1,0|\hat{H}^{(1)}|1,0\rangle = \langle 0,1|\hat{H}^{(1)}|0,1\rangle = 0$
  $\therefore$ according to a naïve perturbation theory, no first-order correction.

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

- However, second-order correction appears to diverge!

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

since $\langle 1,0|\hat{H}^{(1)}|0,1\rangle \neq 0$, but $|0,1\rangle$ and $|1,0\rangle$ are degenerate

- Yet we know that perturbation will not spoil two-dimensional harmonic oscillator – so what's gone wrong with approach?

Degenerate Perturbation Theory

$$\hat{H}^{(0)} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2), \qquad \hat{H}^{(1)} = \alpha m\omega^2 xy$$

- By symmetry, $\langle 0,0|\hat{H}^{(1)}|0,0\rangle = \langle 1,0|\hat{H}^{(1)}|1,0\rangle = \langle 0,1|\hat{H}^{(1)}|0,1\rangle = 0$
  $\therefore$ according to a naïve perturbation theory, no first-order correction.

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

- However, second-order correction appears to diverge!

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

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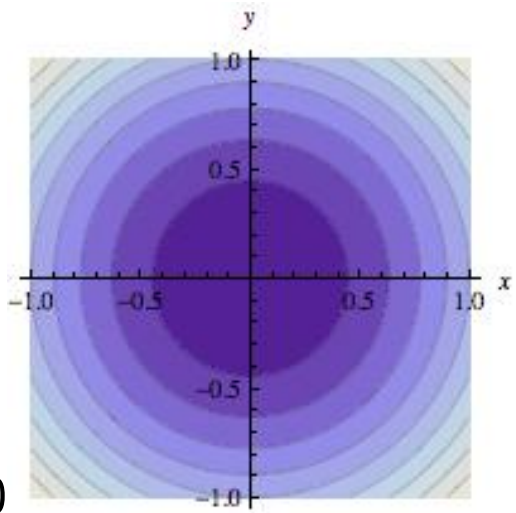
- Consider contours of constant potential energy:

$\alpha = 0$



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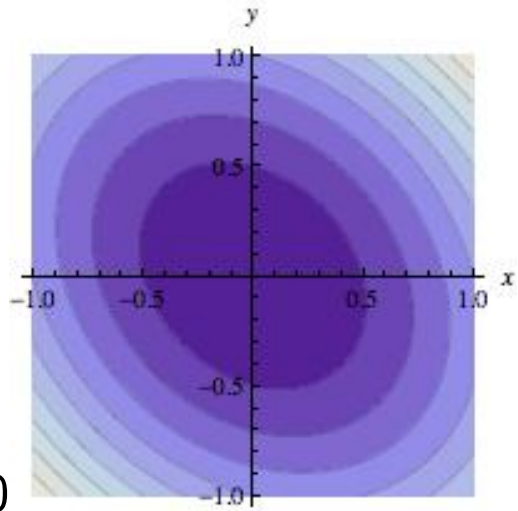

- For $\alpha \neq 0$, circles of constant potential become ellipses, with axes aligned along $x = \pm y$.
- As soon as perturbation is introduced, eigenstates lie in direction of the new elliptic axes – switch not proportional to α.

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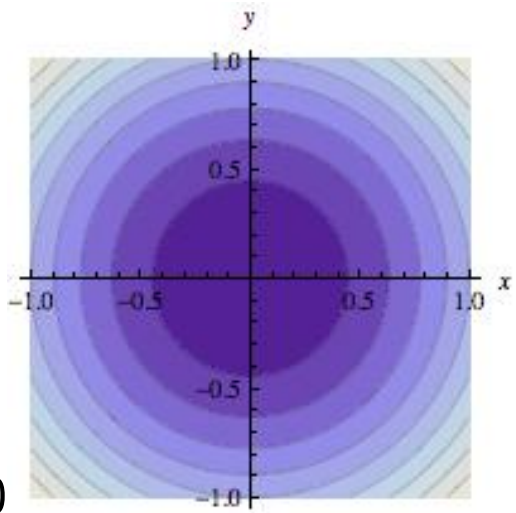

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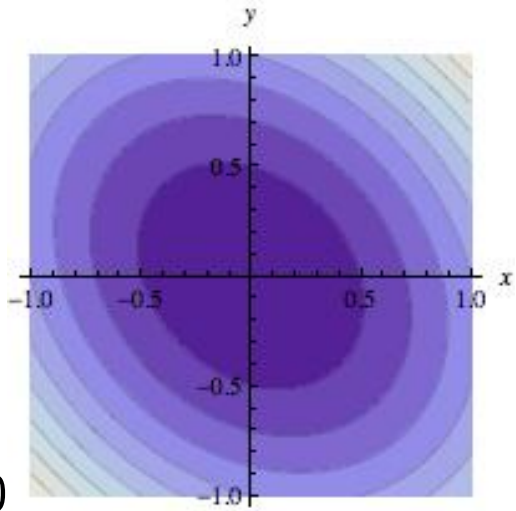

- For $\alpha \neq 0$, circles of constant potential become ellipses, with axes aligned along $x = \pm y$.
- But original unperturbed problem had circular symmetry, and there was no particular reason to choose axes along x and y.

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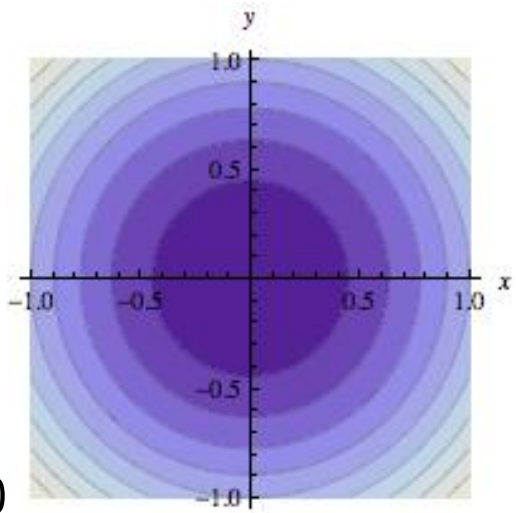

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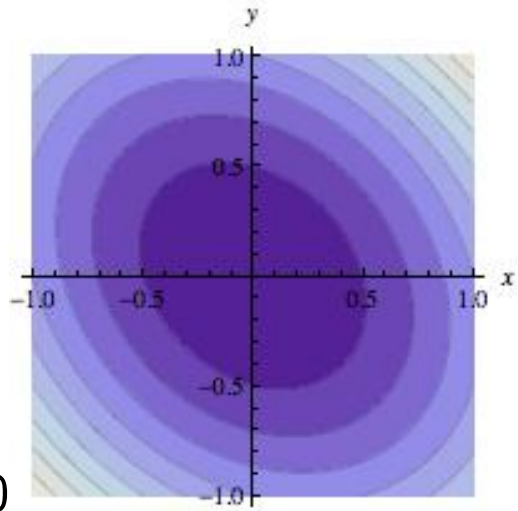

- For $\alpha \neq 0$, circles of constant potential become ellipses, with axes aligned along $x = \pm y$.
- If we had chosen axes along $x = \pm y$, basis states would not have undergone large changes on switching on perturbation.

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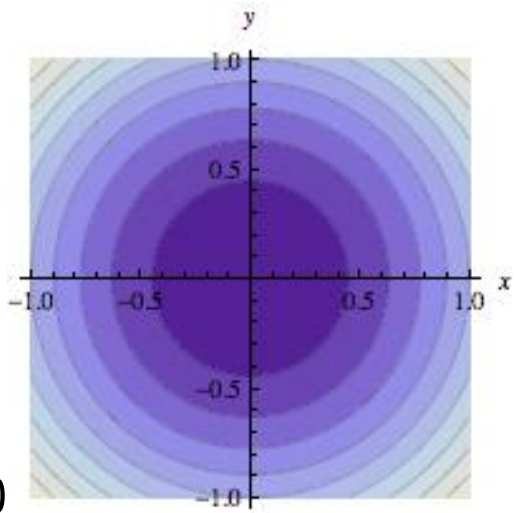

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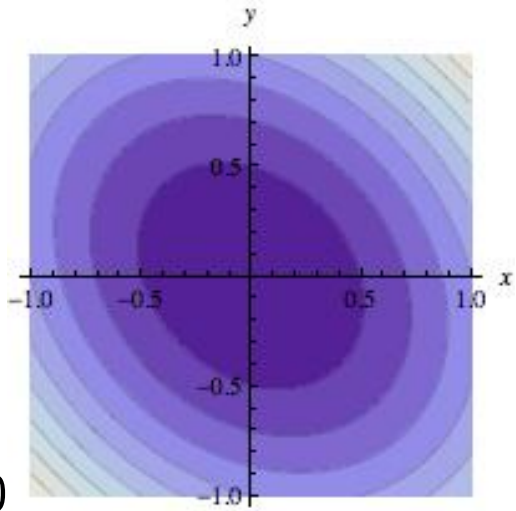

- For $\alpha \neq 0$, circles of constant potential become ellipses, with axes aligned along $x = \pm y$.
- Lesson: *before* switching on perturbation, *choose basis states in degenerate subspace in which perturbation is diagonal.*

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- By rearranging the coordinates along the principle axes,

$$\frac{1}{2}m\omega^2(x^2 + y^2) + \alpha m\omega^2 xy$$
$$= \frac{1}{2}m\omega^2\left[(1+\alpha)\left(\frac{x+y}{\sqrt{2}}\right)^2 + (1-\alpha)\left(\frac{x-y}{\sqrt{2}}\right)^2\right]$$

despite the results of naïve first order perturbation theory, there is indeed a first order energy shift:

$$\hbar\omega \to \hbar\omega\sqrt{1 \pm \alpha} \approx \hbar\omega(1 \pm \alpha/2)$$

Degenerate Perturbation Theory: formal

- So, generally, suppose we have a Hamiltonian, $\hat{H}^{(0)}$ in which the following states $|n_a^{(0)}\rangle, |n_b^{(0)}\rangle, \cdots |n_k^{(0)}\rangle$ are degenerate,

$$\hat{H}^{(0)}|n_i^{(0)}\rangle = \epsilon|n_i^{(0)}\rangle$$

- Since perturbation theory is an expansion in

$$\frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

the theory will fail. Instead we can proceed by transforming basis states of the degenerate subspace, $|n_i^{(0)}\rangle$, to eigenstates of $\hat{H}^{(1)}$, $|n_\alpha^{(0)}\rangle$

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$$\langle n_\alpha^{(0)} | \hat{H}^{(1)} | n_\beta^{(0)} \rangle = H_\alpha^{(1)} \delta_{\alpha\beta}$$

- The eigenvalues $H_\alpha^{(1)}$ are determined by the **secular equation**,

$$\det(H_{ij}^{(1)} - H_\alpha^{(1)}) = 0$$

  where the matrix elements $H_{ij}^{(1)} = \langle n_i^{(0)} | \hat{H}^{(1)} | n_j^{(0)} \rangle$ involve *only the degenerate states in the original basis.*

- N.B. of course, in general, one wont be able to find a basis in which both $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$ are diagonal, i.e. $[\hat{H}^{(0)}, \hat{H}^{(1)}] \neq 0$.

  However, it is always possible to find such a basis in the degenerate subspace of $\hat{H}^{(0)}$ since the matrix elements $\langle n_i^{(0)} | \hat{H}^{(0)} | n_j^{(0)} \rangle = \epsilon \delta_{ij}$.

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- The new states $|n_\alpha^{(0)}\rangle = \sum_i c_{i\alpha} |n_i^{(0)}\rangle$, defined by the eigenstates $c_{i\alpha}$ of $H_{ij}^{(1)}$ now define a non-degenerate basis in which one can develop a perturbative series expansion involving all states.
- In practice, this change of basis is often sufficient.

Example I: Two-dimensional oscillator

$$\hat{H}^{(0)} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2), \qquad \hat{H}^{(1)} = \alpha m\omega^2 xy$$

- Working in the degenerate subspace of the first excited states, $|1,0\rangle$ and $|0,1\rangle$, the diagonal matrix elements of $\hat{H}^{(1)}$ vanish, $\langle 1,0|\hat{H}^{(1)}|1,0\rangle = \langle 0,1|\hat{H}^{(1)}|0,1\rangle = 0$.
- However, off-diagonal matrix elements are non-zero,

$$\langle 1,0|\hat{H}^{(1)}|0,1\rangle = \langle 0,1|\hat{H}^{(1)}|1,0\rangle = \hbar\omega\frac{\alpha}{2}$$

- In *two*-dimensional degenerate subspace spanned by $|1,0\rangle$ and $|0,1\rangle$,

$$H_{ij}^{(1)} = \hbar\omega\frac{\alpha}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

- Eigenstates $(|1,0\rangle \pm |0,1\rangle)/\sqrt{2}$ have eigenvalue $E_1^{(1)} = \pm\hbar\omega\frac{\alpha}{2}$, i.e. $E_1 = E_1^{(0)} + E_1^{(1)} = \hbar\omega(1 \pm \alpha/2)$ as expected from exact solution.

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Example II: Linear Stark Effect

- Previously, we used second order perturbation theory to explore influence of a static electric field on the polarizability of the hydrogen atom ground state. There we showed that the leading correction to the energy scaled quadratically with field, $\mathcal{E}^2$.
- But how does the electric field influence the excited states?
- For atomic hydrogen, the four unperturbed $n = 2$ states are all degenerate with $E_2^{(0)} = -\frac{1}{4}\mathrm{Ry}$.
- How are these states influenced by a weak electric field?

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- From the structure of the four $n = 2$ states,

$$\begin{Bmatrix} \psi_{200}(\mathbf{r}) \\ \psi_{210}(\mathbf{r}) \\ \psi_{21,\pm1}(\mathbf{r}) \end{Bmatrix} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} e^{-r/2a_0} \begin{Bmatrix} \left(2 - \frac{r}{a_0}\right) \\ \frac{r}{a_0}\cos\theta \\ \frac{r}{a_0} e^{\pm i\phi}\sin\theta \end{Bmatrix} .$$

  and the symmetry of $\hat{H}^{(1)}$, it is clear that only the matrix element $\Delta = \langle 200|\hat{H}^{(1)}|210\rangle$ is non-vanishing (and given by $\Delta = 3e\mathcal{E}a_0$).
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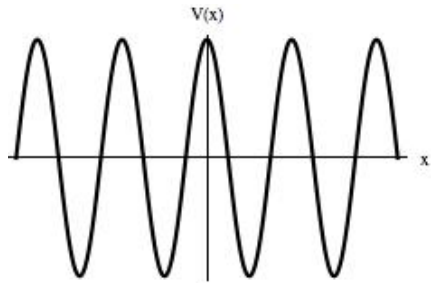
- How is free quantum particle influenced by weak periodic potential, $V(x) = 2V\cos(2\pi x/a)$?

  cf. conduction electrons in simple crystalline solid



- If $V \ll E$, $V(x)$ may be treated as a perturbation of $\hat{H}_0 = \dfrac{\hat{\mathbf{p}}^2}{2m}$
- With periodic b.c., $L = Na$, free particle states are plane waves $\psi_k(x) = \langle x|k\rangle = \dfrac{1}{\sqrt{L}}e^{ikx}$, with $k = 2\pi n/L$, n integer, $E_k^{(0)} = \dfrac{\hbar^2 k^2}{2m}$.
- Matrix elements of $V(x)$:

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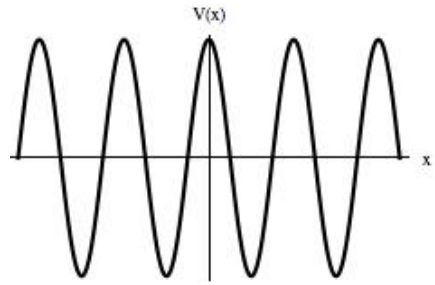

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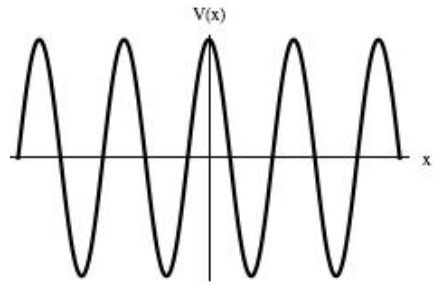

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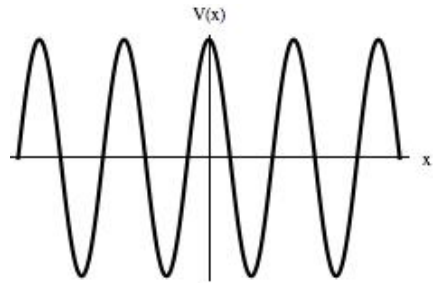

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- Matrix elements of $V(x)$:

$$\boxed{\langle k|V|k'\rangle = V\delta_{k'-k,\pm 2\pi/a}}$$

i.e. only states separated by $G \equiv 2\pi/a$ coupled by perturbation.

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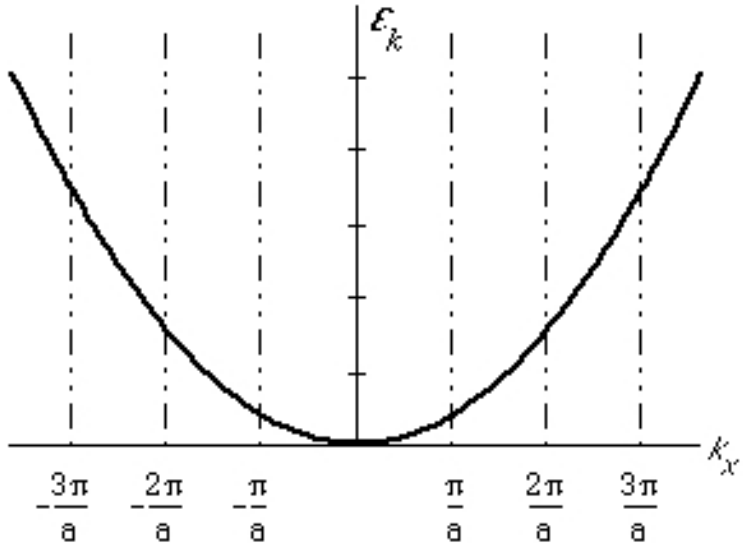
$$\langle k|V|k'\rangle = V\delta_{k'-k,\pm G}, \qquad G = 2\pi/a$$



- In particular, the degenerate states with $k = \pm\pi/a$ are coupled by $V(x)$ – demands application of degenerate perturbation theory.
- Taking all pairs of coupled states, $|k = G/2 + q\rangle$, $|k = -G/2 + q\rangle$, in neighbourhood of $k = \pm G/2$ (i.e. q small), the matrix elements of the total Hamiltonian $\hat{H} = \hat{H}^{(0)} + V(x)$ are given by

$$H_q = \begin{pmatrix} E^{(0)}_{G/2+q} & V \\ V & E^{(0)}_{-G/2+q} \end{pmatrix}$$

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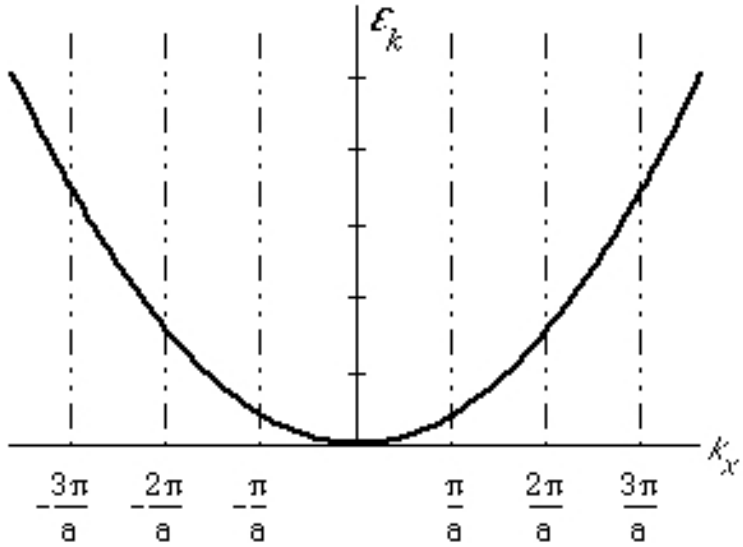

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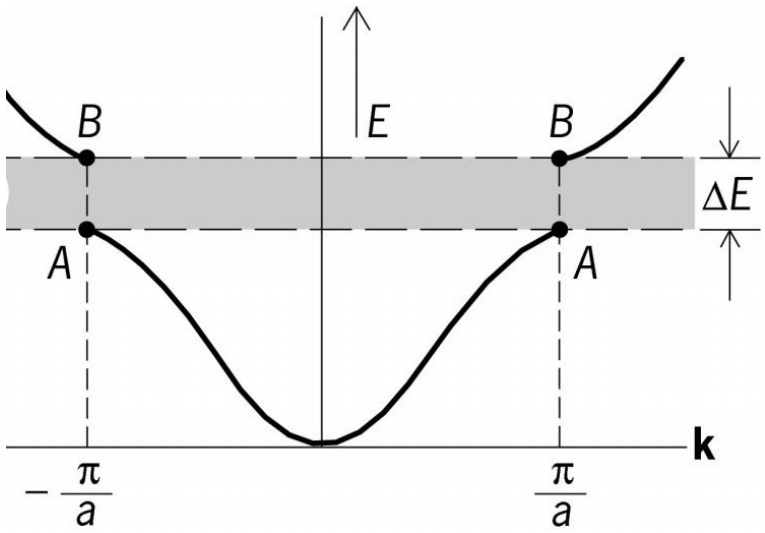

- Solving secular equation $\det(H_q - E_q \mathbb{I}) = 0$, obtain

$$E^{\pm}_q = \frac{E^{(0)}_{G/2+q} + E^{(0)}_{-G/2+q}}{2} \pm \left[\left(\frac{E^{(0)}_{G/2+q} - E^{(0)}_{-G/2+q}}{2} \right)^2 + V^2 \right]^{1/2}$$

- i.e. for $k = \pm G/2$ ($q = 0$), degeneracy lifted by potential. For $|q| \ll G$, spectrum has a gap of size $\Delta E = 2V$, cf. Kronig-Penney.

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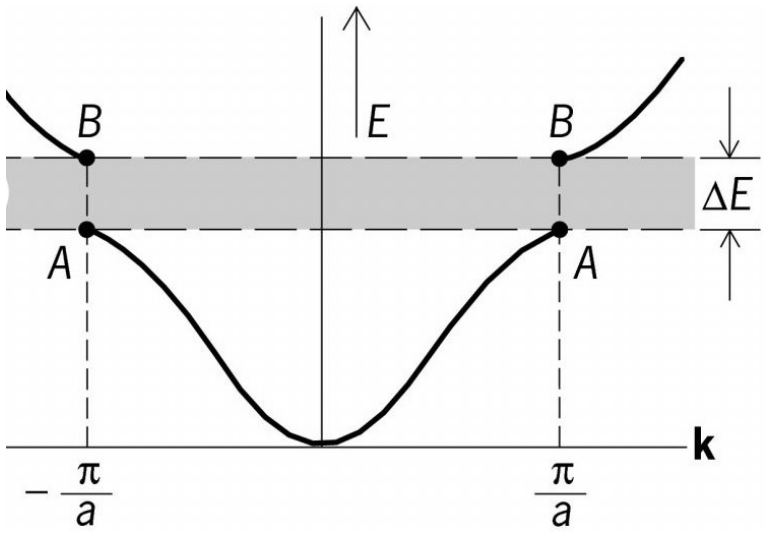

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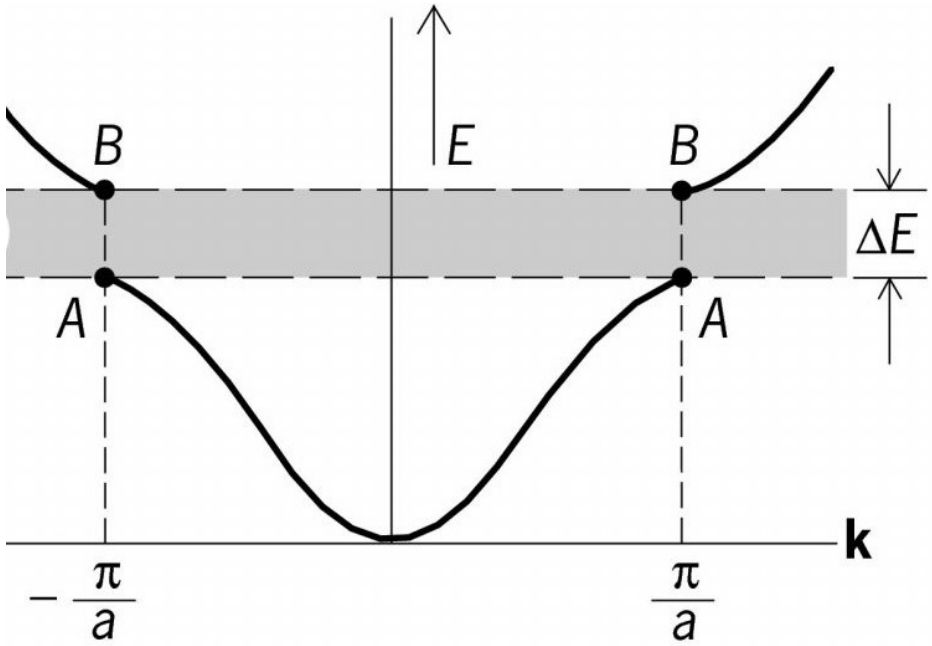
Example III: Nearly free electron model

- Appearance of gap has important consequences in theory of solids.



- Electrons are fermions and have to obey Pauli's exclusion principle.
- **Metal:** electrons occupy states up to "Fermi" energy; low-energy excitations allows current flow in electric field.
- **Band insulator:** When Fermi energy lies in gap, electric field is unable to create excitations and induce current flow.

Summary: perturbation series

How are states of a quantum system modified by the action of a small perturbation $\hat{H}^{(1)}$?

$$(\hat{H}^{(0)} + \hat{H}^{(1)})|n\rangle = E_n|n\rangle$$

- If perturbed states are "adiabatically" connected to unperturbed, corrections can be treated through series expansion in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$.
- At first order in perturbation theory, we have shown that

$$E_n \simeq E_n^{(0)} + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle$$

$$|n\rangle \simeq |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

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- If perturbed states are "adiabatically" connected to unperturbed, corrections can be treated through series expansion in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$.
- At second order,

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

- When the perturbation acts on system with degeneracies, perturbation theory must be developed using basis of degenerate subspace in which perturbation is diagonal.

Lecture 9

Approximation methods: Variational method

Variational method

- So far, we have focused on perturbative scheme in which states of non-perturbed system provid platform, i.e. unperturbed states mirror those of new Hamiltonian – adiabatic contunity.

  e.g. anharmonic oscillator

- However, often new states may not be adiabatically connected.

  e.g. nucleation of bound states, or strongly interacting quantum systems where many-particle correlations can effect transitions to new states such as superfluid or fractional quantum Hall fluid – typically associated with breaking of fundamental symmetry.

- To address such systems it is often extremely effective to "guess" and then optimize a trial ground state wavefunction
  – the variational method.

Variational method

- Method involves optimization of some trial wavefunction, $|\psi_{\text{trial}}\rangle$, on the basis of one or more adjustable "variational" parameters.
- Achieved by minimizing expectation value of the energy,

$$E = \langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle$$

  of the trial wavefunction.
- Seemingly crude approach can provide a (surprisingly) good approximation to the ground state energy (but not quite so good for wavefunction).

- Crucially, the method can be extended to many-particle quantum, and to problems for which a perturbative expansion is invalid.

Variational method

- Consider Hamiltonian $\hat{H}$ with (unknown) eigenstates, $|n\rangle$ and energy E_n. A normalized trial state $|\psi(\alpha)\rangle$ (a function of some set of parameters α) can be expanded as

$$|\psi(\alpha)\rangle = \sum_n a_n(\alpha)|n\rangle$$

with the normalization $\sum_n |a_n|^2 = 1$.

- Therefore, for *any* $|\psi(\alpha)\rangle$,

$$E(\alpha) \equiv \langle\psi(\alpha)|\hat{H}|\psi(\alpha)\rangle = \sum_n |a_n|^2 E_n$$

- Then, since the ground state energy $E_0 \leq E_n$, we have

$$E(\alpha) \geq E_0 \sum_n |a_n|^2 = E_0$$

showing that $E(\alpha)$ places an upper bound on E_0.

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$$E(\alpha) \equiv \langle \psi(\alpha) | \hat{H} | \psi(\alpha) \rangle \geq E_0$$

- The variational method entails minimizing the function $E(\alpha)$ with respect to α from which follows an upper bound on ground state energy, E_0.
- Generally, the approach provides a good approximation to the energy, while the estimate of the wavefunction is less effective.
- e.g. if optimum state includes ca. 20% admixtue of first excited state $|\alpha_{\min}\rangle = \frac{1}{\sqrt{1+0.2^2}}(|0\rangle + 0.2|1\rangle)$, energy estimate will be too high by only,

$$\frac{1}{1+0.2^2}(E_0 + 0.2^2 E_1) - E_0 = \frac{0.2^2}{1+0.2^2}(E_1 - E_0)$$

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- Previously, we have shown that the radial Schrödinger equation for atomic hydrogen is given by

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2+\frac{2}{r}\partial_r\right)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]R(r)=ER(r)$$

- Setting $R(r)=u(r)/r$,

$$\left[-\frac{\hbar^2\partial_r^2}{2m}+\frac{\hbar^2}{2mr^2}\ell(\ell+1)-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]u(r)=uR(r)$$

- Finally,

$$\left[-\partial_r^2+\frac{1}{r^2}\ell(\ell+1)-\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2}\frac{1}{r}\right]u(r)=\frac{2mE}{\hbar^2}u(r)$$

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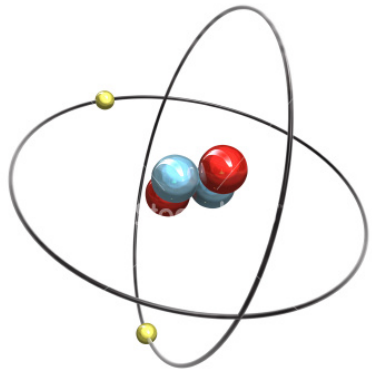
Example II: Helium atom by variational method

- For atomic hydrogen, ground state energy is $-1\,\mathrm{Ry}$
- He^+ ion (with just a single electron) has nuclear charge $Z = 2$, so $E_{\mathrm{g.s.}} = -2^2\,\mathrm{Ry}$.
- For Helium atom, if we negect Coulomb interaction between electrons, $E_{\mathrm{g.s.}} = -2 \times 2^2\,\mathrm{Ry}$



- To get better estimate, retain form of ionic wavefunction, $(\frac{Z^3}{\pi a_0^3})^{1/2} e^{-Zr/a_0}$, but treat Z as variational parameter.

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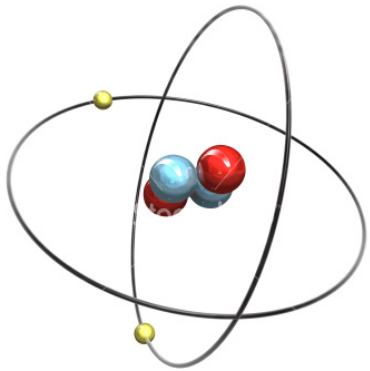

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- To find **potential energy** from interaction with nucleus, must use the actual nuclear charge $Z = 2$, but impose a variable Z for wavefunction,

$$\text{p.e.} = -2 \times \frac{2e^2}{4\pi\epsilon_0} \int_0^\infty 4\pi r^2 dr \frac{Z^3}{\pi a_0^3} \frac{e^{-2Zr/a_0}}{r} = -8Z\,\text{Ry}$$

- **Kinetic energy** determined solely by trial function and translates to $Z^2\,\text{Ry}$ per electron, i.e. total $\text{k.e.} = 2Z^2\,\text{Ry}$.

- Contribution from **electron-electron interaction**,

$$\frac{e^2}{4\pi\epsilon_0} \frac{Z^3}{(\pi a_0^3)^2} \int d^3r_1 d^3r_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5}{4} \frac{e^2}{4\pi\epsilon_0} \frac{Z}{2a_0} = \frac{5}{4} Z\,\text{Ry}$$

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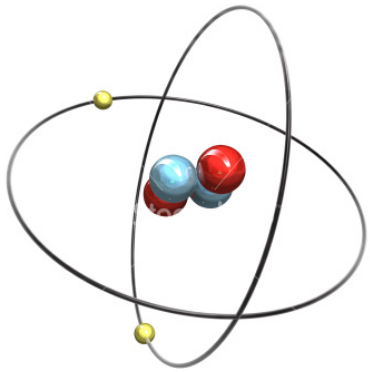
- Altogether, variational state energy:

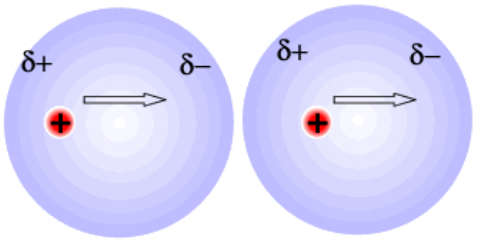
$$E(Z) = -2\left(4Z - Z^2 - \frac{5}{8}Z\right)\,\mathrm{Ry}$$



  - Minimization of $E(Z)$ w.r.t. $Z \rightsquigarrow Z = 2 - \frac{5}{16}$ which translates to energy 77.5 eV ca. 1 eV smaller than true ground state energy.
  - So electron-electron interaction leads effectively to a shielding of nuclear charge by an amount of ca. $(5/16)e$.

Example III: Van der Waals interaction

How do electric dipole fluctuations influence interaction between neutral atoms?



- For two hydrogen atoms, if we ignore dynamics of the nuclei A and B, the total Hamiltonian for the two electrons 1 and 2 is given by $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$ where

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right)$$

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- Since $\langle r_{1A}\rangle \sim \langle r_{2B}\rangle \sim a_0$, if the atomic separation is large, $|r_{AB}| \gg a_0$, we can treat $\hat{H}^{(1)}$ as a small perturbation which can be expanded in r_{AB}.

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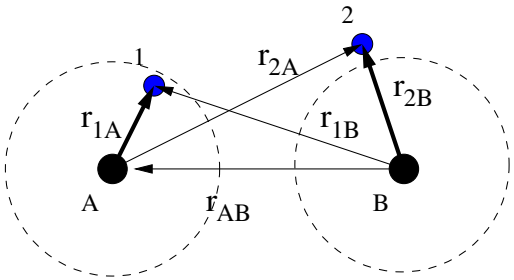

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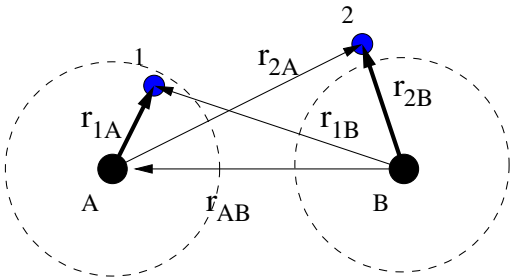

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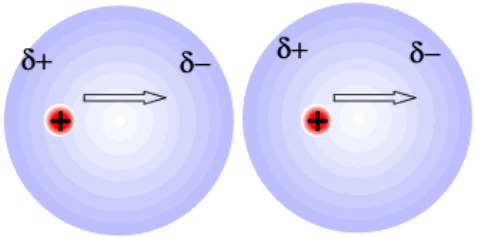

- If we define the z-axis to lie along the direction $\mathbf{r}_{AB}$, an expansion obtains (exercise – cf. multipole expansion)

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{AB}^3}\left[\mathbf{r}_{1A}\cdot\mathbf{r}_{2B} - 3(\mathbf{r}_{1A}\cdot\hat{\mathbf{e}}_z)(\mathbf{r}_{2B}\cdot\hat{\mathbf{e}}_z)\right]$$

- Physically, fluctuations of the electron charge cloud on each hydrogen atom result in an electric dipole moment leading to an instantaneous **dipole-dipole interaction**.
- The unperturbed ground state involves both electrons in the $1s$ orbital, $|0^{(0)}\rangle = |100\rangle \otimes |100\rangle$. Since the matrix element $\langle 0^{(0)}|\hat{H}^{(1)}|0^{(0)}\rangle$ vanishes (by symmetry), we have to turn to higher orders to obtain a non-zero contribution to the energy shift.

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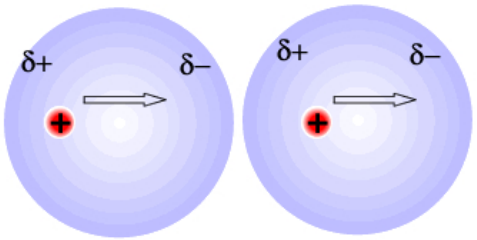

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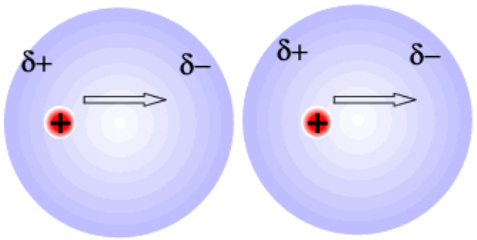

- At second order of **perturbation theory**, energy shift is given by

$$E^{(2)} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{AB}^6}\sum_{n\neq 0}\frac{|\langle 0^{(0)}|\mathbf{r}_{1A}\cdot\mathbf{r}_{2B} - 3z_{1A}z_{2B})|n^{(0)}\rangle|^2}{E_0^{(0)} - E_n^{(0)}} < 0$$

- The instantaneous dipole-dipole interaction always leads to an **attractive** interaction which scales as $1/r_{AB}^6$ – **Van der Waals**.
- Result is valid for any pair of atoms in spherically symmetric states.
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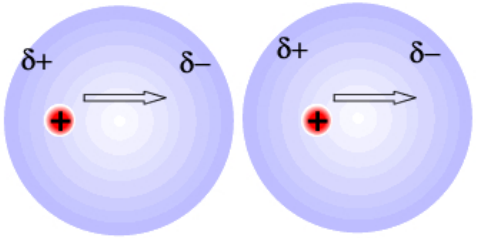

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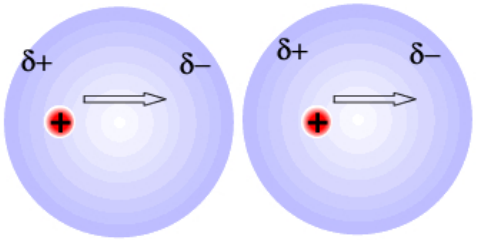

- If $|1^{(0)}\rangle = |21m\rangle \otimes |21m\rangle$ denotes a lowest excited state with non-vanishing dipole matrix element with $|0^{(0)}\rangle$, we may set

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- Then, since the $n = 0$ matrix element in the sum vanishes, we may extend the sum and make use of the identity $\sum_n |n^{(0)}\rangle\langle n^{(0)}| = \mathbb{I}$,

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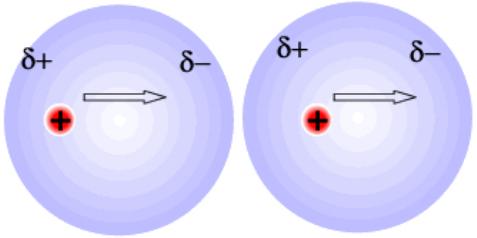

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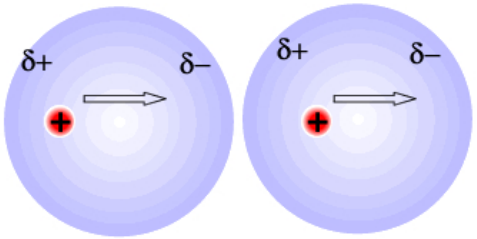

- Noting that the matrix elements of the cross-terms (such as $\langle x_{1A}x_{2B}z_{1A}z_{2B}\rangle$) in the expansion of $(\mathbf{r}_{1A}\cdot\mathbf{r}_{2B}-3z_{1A}z_{2B})^2$ vanish, and using $E_0^{(0)}=-2\times\mathrm{Ry}$ and $E_1^{(0)}=-2\times\frac{\mathrm{Ry}}{4}$, we find

$$E^{(2)} \geq \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{AB}^6}\frac{6\langle 0^{(0)}|z_{1A}^2z_{2B}^2|0^{(0)}\rangle}{-2(1-\frac{1}{4})\mathrm{Ry}}$$

- Evaluating the matrix element, we finally obtain (exercise)

$$E^{(2)} \geq -8\frac{e^2}{4\pi\epsilon_0}\frac{a_0^5}{r_{AB}^6}$$

- However, we can also place an upper limit by making use of the variational method...

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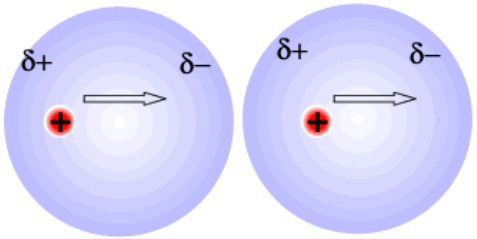

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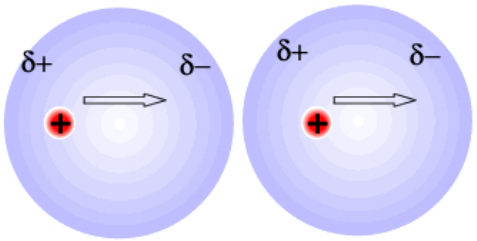

- For reasons that will become clear, consider the (non-normalized) variational state wavefunction,

$$\boxed{|\psi_{\text{trial}}\rangle = (1 + A\hat{H}^{(1)})|0^{(0)}\rangle}$$

  where A is a variational parameter.

- According to the variational principle, the ground state energy is bound by the inequality,

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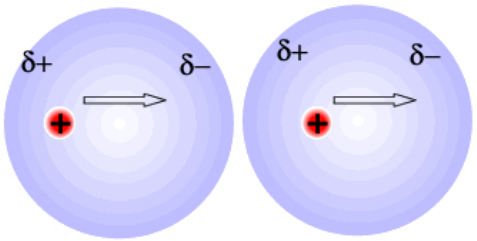

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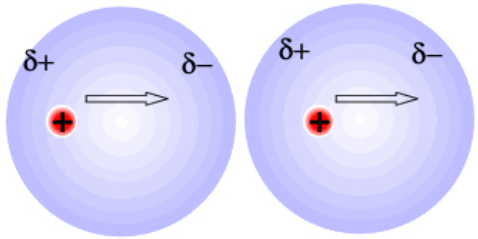

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[N.B. We are more concerned with principle than practice!]

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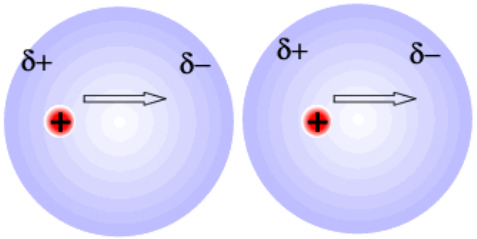

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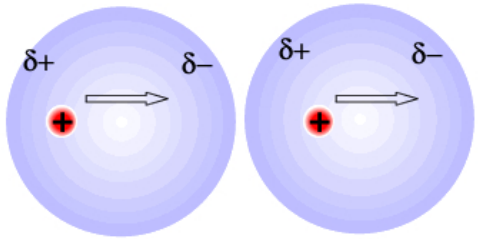

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$$E_0 \leq E_0^{(0)} - 6 \frac{e^2}{4\pi\epsilon_0} \frac{a_0^5}{r_{AB}^6}$$

- Combined with first perturbative result, we therefore find that Van der Waals interaction energy has the following bound:

$$E_0^{(0)} - 8 \frac{e^2}{4\pi\epsilon_0} \frac{a_0^5}{r_{AB}^6} \leq E_0(r_{AB}) \leq E_0^{(0)} - 6 \frac{e^2}{4\pi\epsilon_0} \frac{a_0^5}{r_{AB}^6}$$

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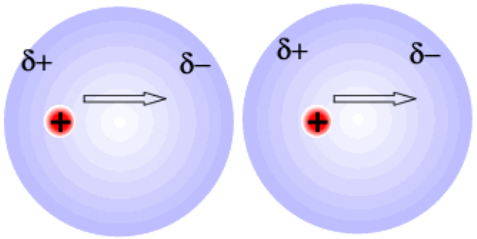

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Perturbation theory: summary

- When a general quantum system is subject to a small perturbation,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

we have two approximation schemes at our disposal:

1. When the perturbed states are, by symmetry, "adiabatically" connected to the unperturbed system, we can adopt a **series expansion** in the small parameter $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$.

2. When states are disconnected – often due to some symmetry breaking (e.g. development of a bound state) – we can implement the **variational approach**.

Variational method: summary

- By introducing a trial wavefunction $|\psi_{\text{trial}}(\alpha)\rangle$, a function of variational parameters α, a minimization of the expectation value,

$$E(\alpha) = \langle \psi_{\text{trial}}(\alpha) | \hat{H} | \psi_{\text{trial}} \rangle$$

  provides an upper bound on the ground state energy.

- The variational method can be very effective – but it demands some insight into the underlying physics of the ground state wavefunction.
- This is rarely a problem when investigating a single-particle Hamiltonian.
- However, in strongly interacting many-particle quantum systems – the arena in which the variational approach has provided ground-breaking discoveries (e.g. fractional quantum Hall effect and superconductivity) – the approach can demand great inspiration.

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Variational method: summary

- By introducing a trial wavefunction $|\psi_{\text{trial}}(\alpha)\rangle$, a function of variational parameters α, a minimization of the expectation value,

$$E(\alpha) = \langle \psi_{\text{trial}}(\alpha) | \hat{H} | \psi_{\text{trial}} \rangle$$

  provides an upper bound on the ground state energy.

- The variational method can be very effective – but it demands some insight into the underlying physics of the ground state wavefunction.

- This is rarely a problem when investigating a single-particle Hamiltonian.

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Looking ahead

- Although the perturbation series expansion and the variational method provide a general approximation scheme, neither exploit the connection between quantum and classical mechanics.
- However, we know that when "$\hbar \to 0$" or, more intuitively, when the energy scales of interest are large as compared to the characteristic energy scales in the problem, we know that the properties become increasing classical.
- Can we develop an approach which exploits this correspondence? In the next lecture, we will introduce such a semiclassical scheme – the **WKB method**.
- Although the method demands some technical ingenuity, its insight and utility mean that it should not be reserved exclusively for TP2!

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Lecture 10

Approximation methods: WKB method

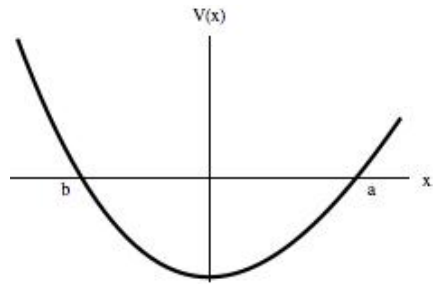
Wentzel, Kramers and Brillouin (WKB) method

- The **WKB method** provides a "semi-classical" approach for solving the one-dimensional time-independent Schrödinger equation.
- History predates Wentzel, Krammers & Brillouin (1926): developed independently by Jeffreys in 1923 and aspects utilized by Liouville and Green a century earlier!
- Provides an effective approach to treating general wave-like systems, e.g. fluids, electromagnetic waves, etc.

  In optics, WKB is known as **eikonal method**, and in general referred to by mathematicians as **short wavelength asymptotics**.
- In quantum mechanics, it provides conceptual framework for understanding the classical limit ($\hbar \to 0$) – hence "semi-classics"

Wentzel, Kramers and Brillouin (WKB) method

- Consider propagation of a quantum particle in a slowly-varying one-dimensional potential, $V(x)$



$$-\frac{\hbar^2}{2m}\partial_x^2\psi(x) + V(x)\psi(x) = E\psi(x)$$

  - For a uniform potential V, solutions are plane waves, $\psi = e^{ikx}$.
  - For a smooth potential, let us parameterize wavefunction as $\psi(x) = e^{i\sigma(x)/\hbar}$, complex $\sigma(x)$ encompasses amplitude and phase.
  - Making use of the identity, $\hbar^2\partial_x^2 e^{i\sigma(x)/\hbar} = e^{i\sigma(x)/\hbar}[i\hbar\,\partial_x^2\sigma - (\partial_x\sigma)^2]$, substitution in the Schrödinger equation leads to nonlinear equation,

$$-i\hbar\,\partial_x^2\sigma(x) + (\partial_x\sigma)^2 = p^2(x), \qquad p(x) \equiv \frac{h}{\lambda(x)} = \sqrt{2m(E - V(x))}$$

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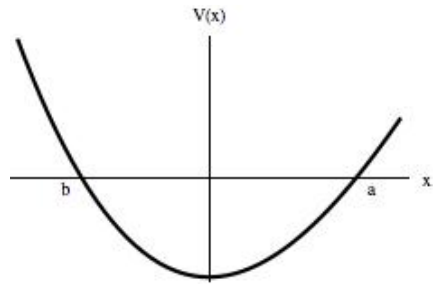

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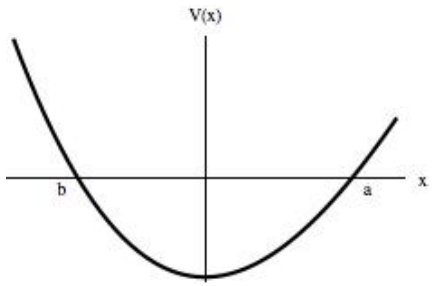

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- Since we're looking for semi-classical approximation, its makes sense to expand $\sigma(x)$ as power series in $\hbar$,

$$\sigma = \sigma_0 + (\hbar/i)\sigma_1 + (\hbar/i)^2\sigma_2 + \cdots$$

- At the leading (zeroth) order of the expansion, can drop the first term in (*),

$$(\partial_x\sigma_0)^2 = p^2(x)$$

- Fixing sign of $p(x) = +\sqrt{2m(E - V(x))}$,

$$\sigma_0(x) = \pm\int p(x)\,dx$$

N.B. for free particle, this is equivalent to classical action.

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$$\left|\frac{\hbar\,\partial_x^2\sigma(x)}{(\partial_x\sigma(x))^2}\right| \equiv \left|\partial_x\left(\frac{\hbar}{\partial_x\sigma}\right)\right| \ll 1$$

- In leading approximation, $\partial_x\sigma \simeq p(x)$ and $p(x) = 2\pi\hbar/\lambda(x)$, so

$$\frac{1}{2\pi}\,|\partial_x\lambda(x)| \ll 1$$

  i.e. change in wavelength over distance of one wavelength must be small.

- Approximation must fail at boundary of classically allowed region, the classical turning points: when $E = V(x)$, $p(x) = 0$ and wavelength infinite – see later!

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$$-i\hbar\,\partial_x^2\sigma_0 + 2\partial_x\sigma_0(\hbar/i)\partial_x\sigma_1 = 0$$

- Rearranging, recalling $\partial_x\sigma_0 = p$, and integrating,

$$\partial_x\sigma_1 = -\frac{\partial_x^2\sigma_0}{2\partial_x\sigma_0} = -\frac{\partial_x p}{2p}, \quad \sigma_1(x) = -\frac{1}{2}\ln p(x), \quad e^{\sigma_1(x)} = \frac{1}{\sqrt{p(x)}}$$

- So, to this order, $$\psi(x) = \frac{C_1}{\sqrt{p(x)}}e^{(i/\hbar)\int p\,dx} + \frac{C_2}{\sqrt{p(x)}}e^{-(i/\hbar)\int p\,dx}$$

  where C_1 and C_2 denote constants of integration.

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- This completes formulation of semi-classical approximation – but to apply it, we have to understand how to deal with regions close to classical turning points $\leftrightarrow$ **energy quantization condition**.

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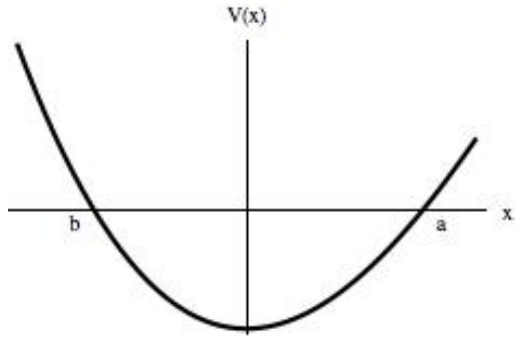

- Consider 1d confining potential where classically allowed region $b \leq x \leq a$.
- How to connect three regions together?
  - Close to turning point at, say, $x = a$, $E - V(x) \simeq F_0(x - a)$, formal solution to Schrödinger equation is an Airy function with

$$\lim_{x \gg a} \psi(x) \simeq \frac{C}{2\sqrt{|p(x)|}} e^{-(1/\hbar)\int_a^x |p|\, dx}$$

translating to decay into classically forbidden region while, to left,

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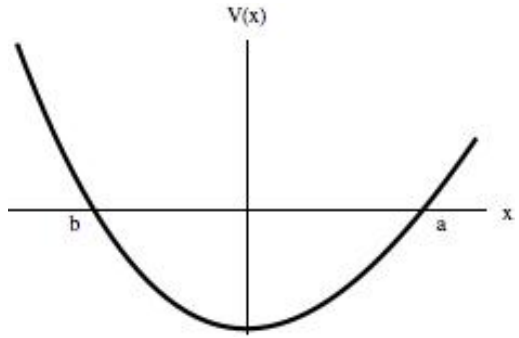

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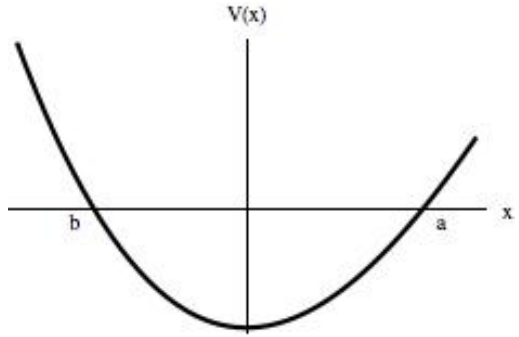

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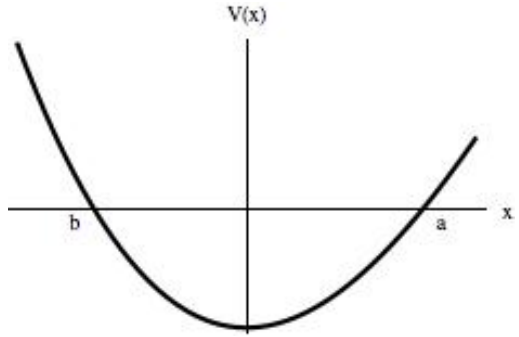

- For expressions to be consistent, we must have $|C'| = |C|$ and

$$\left(\frac{1}{\hbar}\int_b^x p\,dx - \frac{\pi}{4}\right) - \left(\frac{\pi}{4} - \frac{1}{\hbar}\int_x^a p\,dx\right) = n\pi$$

  where, for n even, $C' = C$ and for n odd, $C' = -C$.

- Therefore, $\frac{1}{\hbar}\int_b^a p\,dx = (n + 1/2)\pi$, or when cast in terms of a complete periodic cycle of classical motion,

$$\oint p\,dx = 2\pi\hbar(n + 1/2)$$

n counts nodes, cf. **Bohr-Sommerfeld quantization condition**

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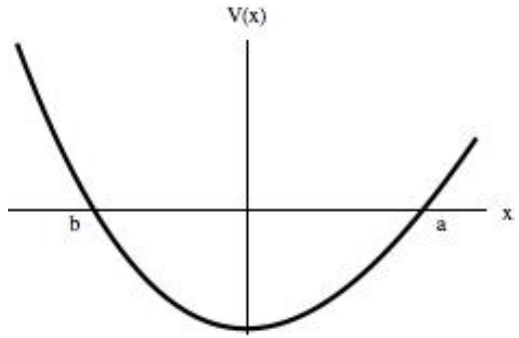

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- What is meant by semi-classics being an $\hbar \to 0$ limit?
  $\hbar$ is a fundamental constant – not easily adjusted!

- Validity of WKB approximation relies upon condition $\lambda/L \ll 1$.
- From de Broglie relation, we may write inequality as $h/pL \ll 1$,
  where p denotes particle momentum.
- Both p and L can be considered as "classical" scales.
- So, formally, we can think of think of accessing the semi-classical limit by adjusting $\hbar$ so that it is small enough to fulfil inequality.
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- For the harmonic oscillator, $H = p^2/2m + m\omega^2 x^2/2$, classical momentum given by

$$p(x) = \sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)}$$

- The classical turning points: set by $E = \frac{1}{2}m\omega^2 x_0^2$, i.e. $x_0 = \pm\frac{2E}{m\omega^2}$
- Over periodic cycle, the classical action is given by

$$\oint p(x)dx = 2\int_{-x_0}^{x_0} dx\sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)} = 2\pi\frac{E}{\omega} \stackrel{!}{=} 2\pi\hbar(n+1/2)$$

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- In WKB approximation, wavefuntions given by

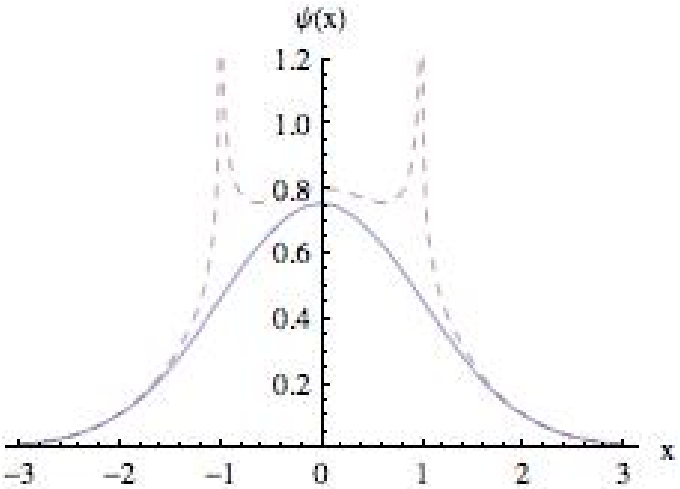
$$\psi(x) = \begin{cases} \frac{C}{\sqrt{p(x)}} \cos\left(\frac{\pi}{4} - \frac{1}{\hbar}\int_x^{x_0} p\,dx\right) & x < x_0 \\ \frac{C}{2\sqrt{p(x)}} \exp\left(-\frac{1}{\hbar}\int_{x_0}^{x} |p|\,dx\right) & x > x_0 \end{cases}$$

Example I: Quantum harmonic oscillator

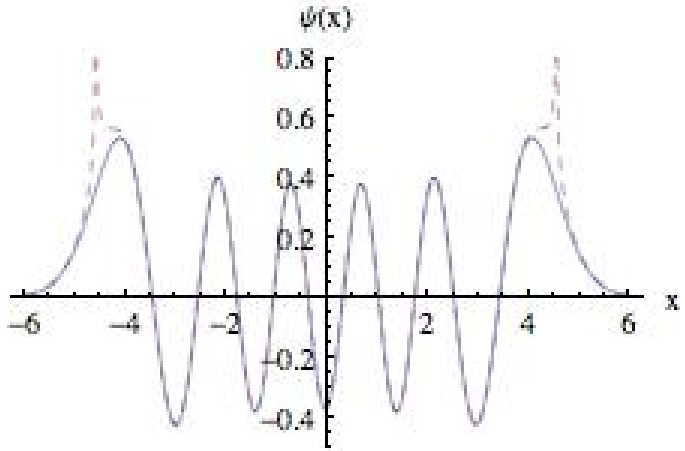
- In WKB approximation, wavefuntions given by

$$\psi(x) = \begin{cases} \frac{C}{\sqrt{p(x)}} \cos\left(\frac{n\pi}{2} + \frac{E}{\hbar\omega}\left[\arcsin\left(\frac{x}{x_0}\right) + \frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}\right]\right) & 0 < x < x_0 \\ \frac{C}{2\sqrt{p(x)}} \exp\left(-\frac{E}{\hbar\omega}\left[\frac{x}{x_0}\sqrt{\frac{x^2}{x_0^2}-1} - \operatorname{arccosh}\left(\frac{x}{x_0}\right)\right]\right) & x > x_0 \end{cases}$$

$n = 0$

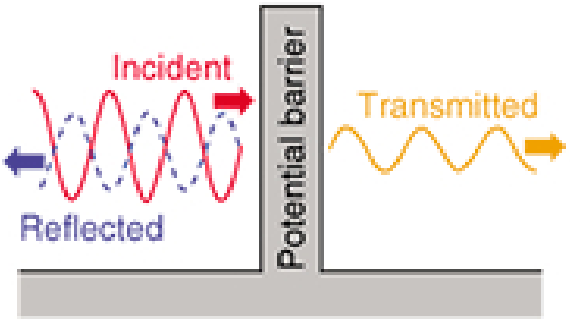


$n = 10$



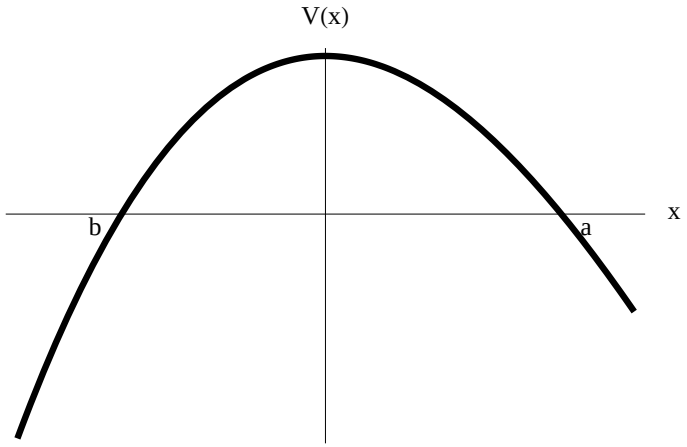
Example II: Quantum tunneling

- Consider beam of particles incident upon a localized potential barrier, $V(x)$.



  - Suppose that, over single continuous region, from b to a, potential rises above incident energy of incoming particles so that, classically, all particles reflected.
  - In quantum system, some particles incident from left may tunnel through the barrier and continue propagating to the right.
  - What is transmission probability?

Example II: Quantum tunneling



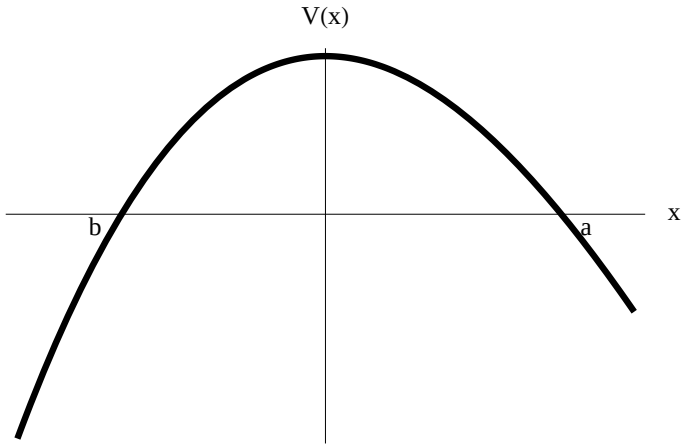
- From WKB, to left of barrier (region 1),

$$\psi_1(x) = \frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar}\int_b^x p\,dx\right] + r(E)\frac{1}{\sqrt{p}} \exp\left[-\frac{i}{\hbar}\int_b^x p\,dx\right]$$

with $p(E) = \sqrt{2m(E - V(x))}$, while, to right (region 3),

$$\psi_3(x) = t(E)\frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar}\int_a^x p\,dx\right]$$

Example II: Quantum tunneling



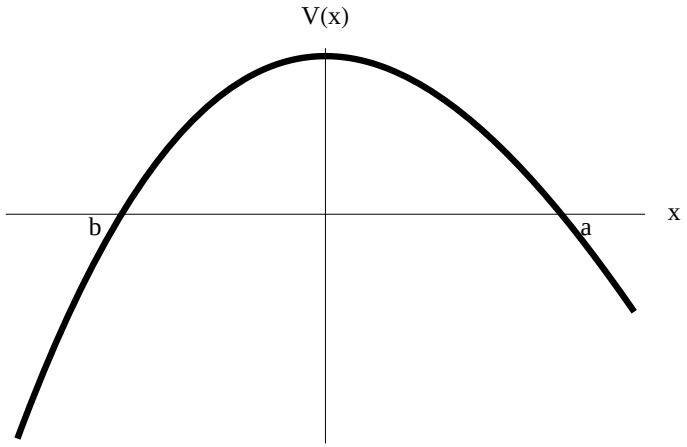
- In barrier region (2),

$$\psi_2(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar}\int_a^x |p|\,dx\right] + \frac{C_2}{\sqrt{|p(x)|}} \exp\left[\frac{1}{\hbar}\int_a^x |p|\,dx\right]$$

- Applying the continuity condition on the wavefunction, one obtains the transmissivity,

$$T(E) = |t(E)|^2 \simeq \exp\left[-\frac{2}{\hbar}\int_a^b |p|\,dx\right]$$

Example II: Quantum tunneling



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$$T(E) = |t(E)|^2 \simeq \exp\left[-\frac{2}{\hbar}\int_a^b |p|\,dx\right]$$

Summary

- Most problems in quantum mechanics are formally intractable. Fortunately, we can draw upon several approximation schemes.
- In cases where a small perturbation conserves the character of the states, we can adopt a **perturbative series expansion**.
- Where a series expansion is invalid, the **variational method** can be deployed – but typically it's application requires some intuition (or prejudice!) about the nature of perturbed states.
- Finally, in systems which are either one-dimensional, or rendered such by symmetry, we can engage the power of the **semi-classical WKB approach**.

Synopsis: Lectures 5-10

5. **Charged particle in an electromagnetic field:**

   Classical and quantum mechanics of particle in a field; normal Zeeman effect; gauge invariance and the Aharonov-Bohm effect; Landau levels.

6. **Spin:**

   Stern-Gerlach experiment; spinors, spin operators and Pauli matrices; spin precession in a magnetic field; parametric resonance; addition of angular momenta.

7. **Time-independent perturbation theory:**

   Perturbation series; first and second order expansion; degenerate perturbation theory; Stark effect; nearly free electron model.

8. **Variational and WKB method:**

   Variational method: ground state energy and eigenfunctions; application to helium; Semiclassics and the WKB method.

Synopsis: Lectures 11-15

9. **Identical particles:**

   Particle indistinguishability and quantum statistics; space and spin wavefunctions; consequences of particle statistics; ideal quantum gases; degeneracy pressure in neutron stars; Bose-Einstein condensation in ultracold atomic gases.

10. **Atomic structure:**

    Relativistic corrections – spin-orbit coupling; Darwin structure; Lamb shift; hyperfine structure. Multi-electron atoms; Helium; Hartree approximation and beyond; Hund's rule; periodic table; coupling schemes LS and jj; atomic spectra; Zeeman effect.

11. **Molecular structure:**

    Born-Oppenheimer approximation; H_2^+ ion; H_2 molecule; ionic and covalent bonding; solids; molecular spectra; rotation and vibrational transitions.