6. Quantum Mechanics 2, 5
and
7. Hydrogen Atoms, 1

lecture 25, October 25, 2017

housekeeping

Exam 2

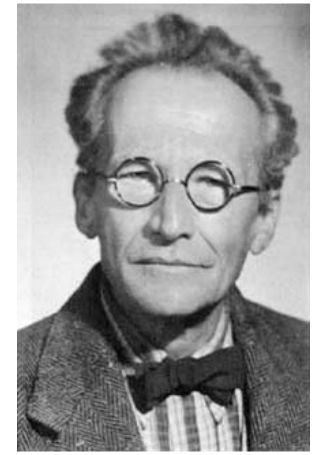
- Next Friday, October 27
- Thornton and Rex, Chapters 3,4,5, 6.1-6.3

today

Simple Harmonic Oscillator

Hydrogen atom

Schroedinger



move much?

1914 Vienna Habilitation, WWI, 1920 Jena, 1920 Stuttgart, 1921 Breslau, 1921 Zurich, (TB treatment 1923), 1927 Berlin, 1934 Oxford, 1933 Nobel, 1934 Princeton? nope, Edinburgh? nope, 1936 Graz…nope, 1933 Oxford, Ghent, Dublin, 1955 Vienna, 1961 died.

1925

learned of deBroglie's work

1926:

January: Quantization as an Eigenvalue Problem: Hydrogen

February: harmonic oscillator, rigid rotator, diatomic molecules

May: equivalence with Heisenberg and Stark Effect

Quantum Oscillator

aka Simple Harmonic oscillator, SHO

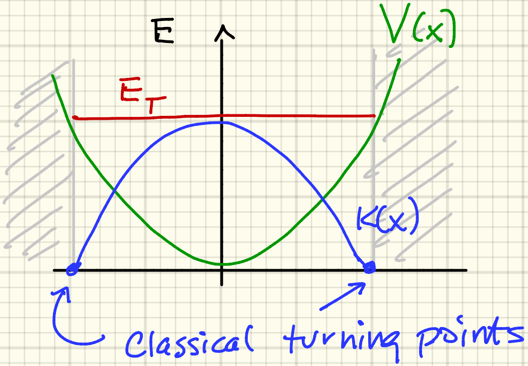
In general: $F = -kx$ classically.

quantum mechanics?

not "forces" but potentials, right? okay: $\vec{F} = -\vec{\nabla} V$ →

$$F = -\frac{dV}{dx}$$

integrating: $V(x) = \frac{1}{2} k x^2$



$$V(x) \xrightarrow{\text{recipe}} \hat{V}(x) \longrightarrow \text{S.E.}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) = \left(\frac{m}{\hbar^2}kx^2 - \frac{2m}{\hbar^2}E\right)\psi x)$$

Series solution:

variable substitution..

$$y = \sqrt[4]{\frac{mk}{\hbar^2}}\, x \equiv \alpha x \;;\quad y^2 = \alpha^2 x^2$$

$$\epsilon = \frac{2E}{\hbar}\sqrt{\frac{m}{k}}$$

$$x \to y : \quad dy = \alpha\, dx \,,\quad dy^2 = \alpha^2 dx^2$$

$$\frac{d^2\psi}{dy^2} = (y^2 - \epsilon)\psi$$

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asymtotically: $y^2 \gg \epsilon$

$$\frac{d^2\psi}{dy^2} = y^2\psi$$

$\rightarrow \psi = e^{\pm y^2/2}$

$\Rightarrow$ want only $-$ sign to keep ψ finite as $y \to \infty$

So solution looks like

$$\psi(y) = C\, e^{-y^2/2}\, H(y)$$

substitute

normalization

TB determined

get auxiliary equation for $H(y)$ $\longrightarrow$

$$\frac{d^2H(y)}{dy^2} - 2y\frac{dH}{dy} + (\epsilon - 1)H = 0 \qquad *$$

Standard approach: assume solution

$$① \qquad H(y) = a_0 + a_1 y + a_2 y^2 + \dots = \sum_{n=0}^{\infty} a_n y^n$$

substitute

$$\frac{dH}{dy} = a_1 + 2a_2 y + 3a_3 y^2 + \dots$$

$$\frac{d^2H}{dy^2} = 2a_2 + 6a_3 y + 12a_4 y^2 + \dots = \sum_{n=0}^{\infty}(n+1)(n+2)a_{n+2}\, y^n \qquad ②$$

$$2y\frac{dH}{dy} = 2y a_1 + 4a_2 y^2 + \dots = \sum 2n a_n y^n \qquad ③$$

$$①, ②, ③ \longrightarrow *$$

$$\sum_{n=0}^{\infty} y^n \left[(n+1)(n+2)\, a_{n+2} - 2n a_n + (\epsilon - 1) a_n \right] = 0$$

only true when $[\cdots] = 0 \implies a_{n+2} = \dfrac{2n+1-\epsilon}{(n+1)(n+2)}\, a_n$

a RECURSION FORMULA

write $H(y)$ in terms of a_0 & a_1 --- and generate the rest

normalization: $\displaystyle\int_{-\infty}^{\infty} \psi^* \psi \, dy = 1$ only if series terminates at some n. Conditions:

1. For some specific n, $a_{n+2} = 0$ which happens
$$2n+1 = \epsilon = \frac{2E}{\hbar}\sqrt{\frac{m}{k}}$$

2. If that n is odd, $a_0 = 0$; if even $a_1 = 0$

condition 1.

$$2n+1 = \epsilon = \frac{2E}{\hbar}\sqrt{\frac{m}{k}}$$

$$E_n = \left(n+\tfrac{1}{2}\right)\hbar\sqrt{\frac{k}{m}}$$

quantize

for an oscillator... $\underline{\underline{f}} = \sqrt{\frac{k}{m}}\,\frac{1}{2\pi}$

$$E_n = \left(n+\tfrac{1}{2}\right)hf$$

VERY!

VERY ^ BIG DEAL

condition 2. $\Rightarrow$ particular set of polynomials, $H_n(y)$

Hermite Polynomials

even functions if n even

odd " " " odd

very familiar throughout physics

such polynomial sets are produced from "generating functions"

Hermite

$$S(y,s) = e^{-s^2+2sy} = \sum_{n=0}^{\infty} \frac{H_n(y)}{n!} s^n$$

or

$$H(y) = (-1)^n e^{-y^2} \frac{d^n(e^{-y^2})}{dy^n}$$

Restore constants:

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}\, 2^n n!}\right)^{\frac{1}{2}} e^{-\alpha^2 x^2/2} \underbrace{H_n(\alpha x)}_{\text{Hermite Polynomials}}$$

Here are some:

$$\alpha = \sqrt[4]{\frac{mk}{\hbar^2}}$$

$$H_0(\alpha x) = 1$$

$$H_1(\alpha x) = 2\alpha x$$

$$H_2(\alpha x) = 4\alpha^2 x^2 - 2$$

$$H_3(\alpha x) = 8\alpha^3 x^3 - 12\alpha x$$

$$H_4(\alpha x) = 16\alpha^4 x^4 - 48\alpha^2 x^2 + 12$$

$$E_n = (n + \tfrac{1}{2}) h f$$

$$E_n = (n + 1/2)\hbar\omega$$

So fn first 2:

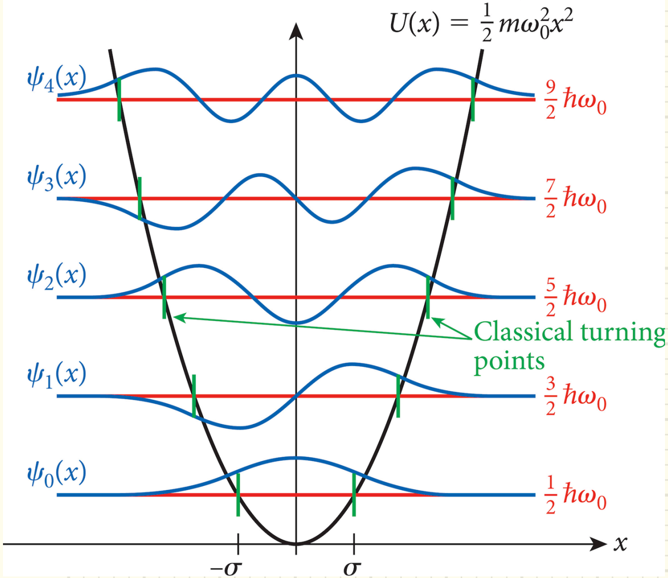
$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2}$$

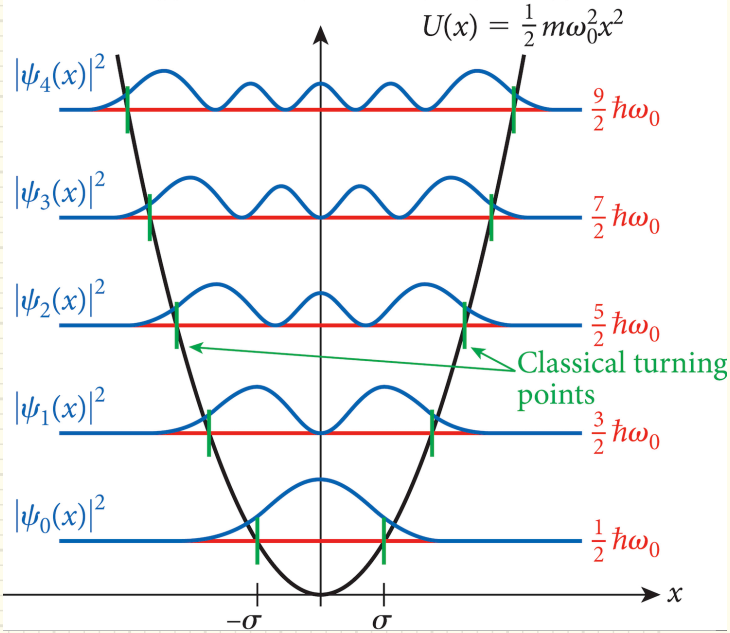
$$E_0 = \tfrac{1}{2}\hbar\omega \leftarrow$$ zero point energy...again

$$\psi_1(x) = \left(\frac{\alpha}{2\sqrt{\pi}}\right)^{1/2} 2\alpha x e^{-\alpha^2 x^2/2}$$

$$E_1 = \tfrac{3}{2}\hbar\omega$$

MATHEMATICA $\longrightarrow$

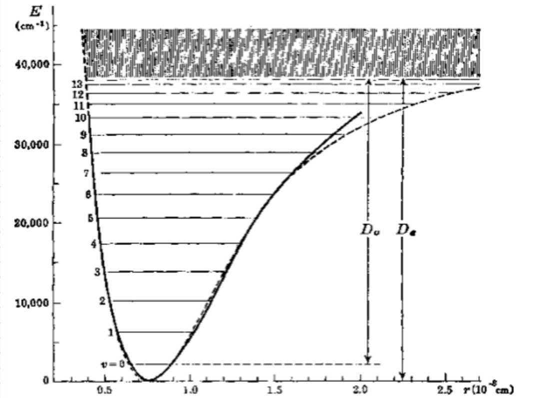




$$\sigma = \sqrt{\frac{\hbar}{m\omega_0}}$$

VERY USEFUL...

Many potentials are nearly parabolic



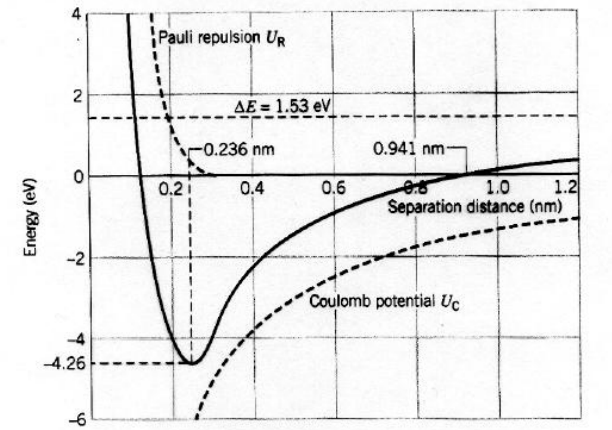
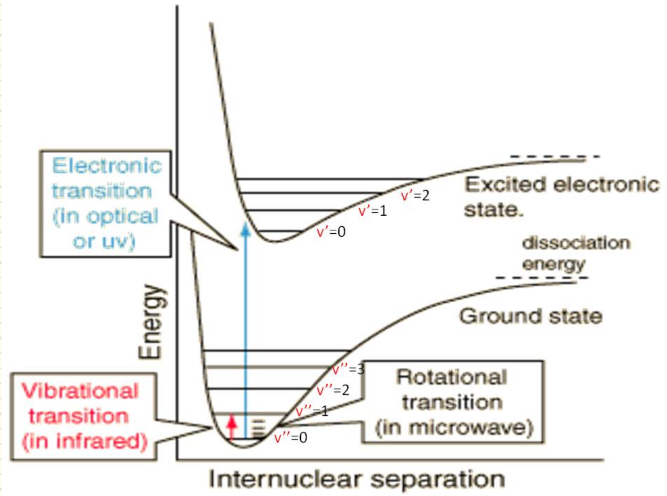


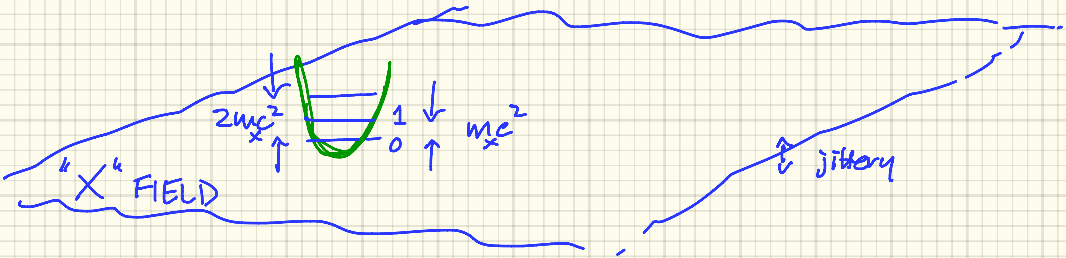
FIGURE 9.19 Molecular energy in NaCl. The "zero" of the energy scale represents neutral Na and Cl atoms. The solid curve is the sum of the three contributions to the molecular energy.



RELATIVISTIC QUANTUM FIELD THEORY

It's all fields... "particles" are harmonic excitations of the parent quantum field

cartoon of X field



HYDROGEN ATOM

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \longrightarrow \hat{V} \longrightarrow \text{S.E.}$$

Need spherical coordinates:

$$\theta = \cos^{-1}\left(\frac{z}{r}\right) \quad \text{"polar angle"}$$

$$\varphi = \phi = \tan^{-1}\left(\frac{y}{x}\right) \quad \text{"azimuthal angle"}$$

$$z = r\cos\theta$$

$\psi(\vec{r}) = \psi(x,y,z)$ $\mu \to$ electron reduced mass $= \left(\frac{M_p}{m_e + M_p}\right) m_e$

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

Laplacian Operator (cartesian)

Need spherical coordinates! $\longrightarrow$ Laplacian changes... transforms

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

S.E.

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Need to solve this...

In spherical coordinates, solution is separable:

$$\psi(\vec{r}) = \psi(r, \theta, \phi) = R(r)\,T(\theta)\,\Phi(\varphi)$$

separation of variables technique to solving (many!) differential equations in physics

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(\vec{r})\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi(\vec{r})\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi(\vec{r})\right]$$

$$-\frac{e^2}{4\pi\epsilon_0 r}\psi(\vec{r}) = E\,\psi(\vec{r})$$

substitute and calculate

$\psi(\vec{r}) = \psi(r, \theta, \phi) = R(r)T(\theta)P(\varphi)$

$$-\frac{\hbar^2}{2\mu}\left[\underline{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(\vec{r})\right)} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi(\vec{r})\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi(\vec{r})\right] - \frac{e^2}{4\pi\epsilon_0 r}\psi(\vec{r}) = E\psi(\vec{r})$$

substitute.. the $\frac{\partial}{\partial r}$'s act only on $R(r)$

$\frac{\partial}{\partial\theta}$'s " $T(\theta)$

$\frac{\partial}{\partial\varphi}$'s " $P(\varphi)$

So, substitute and divide by $R(r)T(\theta)P(\varphi)$, multiply by $-\frac{2\mu}{\hbar^2}r^2\sin^2\theta$

look at <u>first term</u> to see:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(\vec{r})\right)\right] \longrightarrow -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\left[R(r)T(\theta)P(\varphi)\right]\right)\right)$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}T(\theta)P(\varphi)\frac{d}{dr}r^2\left[\frac{d}{dr}R(r)\right]\right]$$

now divide:

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{T(\theta)P(\varphi)R(r)}\,\frac{T(\theta)P(\varphi)}{}\,\frac{1}{r^2}\frac{d}{dr}r^2\left[\frac{d}{dr}R(r)\right]\right]$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{R}\frac{1}{r^2}\frac{d}{dr}r^2\left[\frac{d}{dr}R\right]\right]$$

now multiply:

$$= \frac{\sin^2\theta}{R}\frac{d}{dr}r^2\left[\frac{dR}{dr}\right]$$

$$\underbrace{\left[\frac{\sin^2\theta}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\frac{\sin\theta}{T(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)\right]}+\underbrace{\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}}$$

$$\underbrace{\left[+\frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)\right]}=0$$

ϕ is only in the 3rd term So this can be written

$$\underbrace{-[\quad]-[\quad]}_{\text{no } \varphi \text{ dependence}}=\underbrace{\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}}_{\text{no } r,\theta \text{ dependence}}$$

$=$ a constant. ("separation constant")

$\equiv -m^2$ (NOT a mass!)

$$\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}=-m^2 \xrightarrow{\text{solution:}} \Phi(\varphi)=e^{im\varphi}$$

$$\left[\frac{\sin^2\theta}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\frac{\sin\theta}{T(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)\right]+\underbrace{\frac{1}{P(\varphi)}\frac{d^2P(\varphi)}{d\varphi^2}}_{-m^2}$$

$$\left[+\frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)\right]=0$$

only θ dependence in r-land → divide out

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)}_{\text{only } r \text{ dependence}}=\underbrace{\frac{m^2}{\sin^2\theta}-\frac{1}{T(\theta)\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT(\theta)}{d\theta}\right)}_{\text{only } \theta \text{ dependence}}$$

so, same song, different verse: set = a common constant

$$= \frac{\lambda}{\hbar^2}$$

Result: 2 equations.