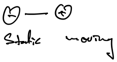
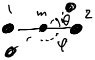
Vibrations and harmonic oscillator

Idea of the dipole:



Electron or molecule



1) translation (T)
   in particle in the box
2) rotation (R)
   θ, φ
3) bond length (V)
   vibration

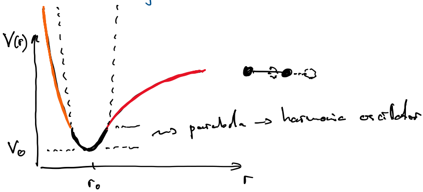
Quantum mechanics recepie!

$V(r) \to \Psi \to E$

1) establish energy potential
2) Solve Shrödinger equation
3) Find E.

V(r) can be zero for T and R, but not for V

why?



1) repulsion
2) attraction

When it can happen? Let's first see what field the proton have:

$e = 1.6 \cdot 10^{-19}\,C$

$r_0 = 5.3 \cdot 10^{-11}\,m$ (Bohr radius)

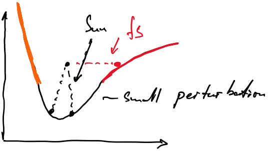
$\varepsilon_0 = 9 \cdot 10^{-12}\,\frac{S}{V \cdot m}$

$$E = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e}{r_0^2} \sim 10^{12}\,\frac{V}{m}$$

① Sun or HeNe ② fs pulse

$I = 0.15 \frac{W}{cm^2}$ $I = 10^9 \frac{W}{cm^2}$ why?

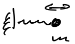
$E = \sqrt{\frac{2I}{\varepsilon_0 c}} = 3 \frac{V}{m}$ $E = \sqrt{\frac{2I}{\varepsilon_0 c}} = 10^9 \frac{V}{m}$



That is small perturbation and described by simple perturbation theory. Electron behaves like a ball on spring or pendulum.

Why it is parabola?

We take simple model of ball on a string:



$F = -kr$ (Hook's force)

r^1 => linear optics.

$V(r) = \frac{1}{2} \cdot k r^2$ – harmonic oscillator

Since potential is established, we can solve Shrödinger equation!

$$\hat{H}\psi = E\psi$$

$$\underbrace{-\frac{h^2}{8\pi^2 m} \cdot \frac{\partial^2}{\partial^2 x}\psi}_{\text{kinetic}} + \underbrace{V(x)\psi}_{\text{potential}} = E\psi$$

(Shrödinger equation is energy conservation law)

$$\boxed{-\frac{h^2}{8\pi^2 m} \cdot \frac{\partial^2}{\partial^2 x}\psi + \frac{1}{2}kx^2\psi = E\psi}$$

Shrödinger equation for harmonic oscillator

$\psi(x) \to$ one dimensional wavefunction

Let's see what function $\psi(x)$ can be:

① Polynom?

$$\left.\begin{aligned}\psi(x) &= a x^3\\ \psi'(x) &= 3ax^2\\ \psi''(x) &= 6ax\end{aligned}\right\} \Rightarrow Ax + Bx^5 = Cx^3$$

not possible

② Exponential (trigonometric)?

$$\left.\begin{aligned}\psi &= a e^{bx}\\ \psi'' &= ab^2 e^{bx}\end{aligned}\right\} \Rightarrow Ae^{bx} + Bx^2 e^{bx} = ce^{bx}$$

better, but not yet there

③ Combination

$$\left.\begin{aligned}\psi &= ae^{bx^2}\\ \psi' &= 2abxe^{bx^2}\\ \psi'' &= 4abe^{bx^2} + 4ab^2xe^{bx^2}\end{aligned}\right\} \text{can work!}$$

$$Ae^{bx^2} + \underline{Bx^2e^{bx^2}} + \underline{Cx^2e^{bx^2}} = De^{bx^2}$$

Now, it is all about how we choose the coefficients.

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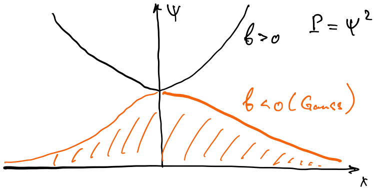
How $\psi(x)$ will look like?



1) Since $P = \psi^2$ (probability to find particle)

$b>0 \Rightarrow \lim\limits_{x\to\infty} P = \infty$

2) $b<0 \Rightarrow$ Gauss $\Rightarrow \psi(x) = Ne^{-\alpha \frac{x^2}{2}}$ why?

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Let's solve it!

$$-\frac{h^2}{8\pi^2 m}\cdot\frac{\partial^2}{\partial x^2}\psi + \frac{1}{2}kx^2\psi = E\psi$$

$$\psi(x) = Ne^{-\alpha\frac{x^2}{2}}$$

$$\psi' = -\alpha N x e^{-\alpha\frac{x^2}{2}}$$

$$\psi'' = -\alpha\underbrace{Ne^{-\alpha\frac{x^2}{2}}}_{\psi} + \alpha^2x^2\underbrace{Ne^{-\alpha\frac{x^2}{2}}}_{\psi} =$$

$$= \alpha^2x^2\psi - \alpha\psi$$

Hence:

$$-\frac{h^2}{8\pi^2 m}(\underline{\underline{\alpha^2x^2}} - \underline{\alpha})\psi + \frac{1}{2}\underline{\underline{kx^2}}\psi = \underline{E}\psi$$

Reorganize:

$$\overset{\to 0}{\left(-\frac{h^2}{8\pi^2 m}\alpha^2 + \frac{1}{2}k\right)}x^2\psi + \underbrace{\frac{h^2}{8\pi^2 m}\alpha}\psi = \underbrace{E}\psi$$

This will only be possible if

$$\frac{1}{2}k - \frac{h^2}{8\pi^2 m}\alpha^2 = 0 \quad !$$

$$\Downarrow$$

$$\alpha = \frac{2\pi}{h}\sqrt{km}$$

That also means:

$$E = \frac{h^2}{8\pi^2 m}\alpha = \frac{h^2}{8\pi^2 m}\cdot\frac{2\pi}{h}\sqrt{km} = \frac{1}{2}\cdot\frac{h}{2\pi}\cdot\sqrt{\frac{k}{m}}$$

But k is a spring constant, m is reduced mass => $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ – classical resonance

$$\boxed{E = \frac{1}{2}h\nu_0}$$ — ta-da!

Is $\psi(x) = Ne^{-\alpha\frac{x^2}{2}}$ the only solution?

You can easily find:

$$\Psi_0 = N e^{-\alpha \frac{x^2}{2}}$$

$$\Psi_1 = N x e^{-\alpha \frac{x^2}{2}}$$

$$\Psi_2 = N(4\alpha x^2 - 2) e^{-\alpha \frac{x^2}{2}}$$

$$\vdots$$

$$\Psi_n(x) = N H_n(\alpha^{1/2} x) e^{-\alpha \frac{x^2}{2}}$$

$H_n(\gamma)$ - Hermite polynomial

$H_0(\gamma) = 1$ even

$H_1(\gamma) = 2\gamma$ odd

$H_2(\gamma) = 4\gamma^2 - 2$ even

$H_3(\gamma) = 8\gamma^3 - 12\gamma$ odd

$\vdots$

$H_n(\gamma) = 2\gamma H_{n+1}(\gamma) - 2nH_{n-1}(\gamma)$

Normalization constants and orthonormality of wavefunctions.

$$\Psi_n(x) = N_n H_n(\alpha^{1/2} x) e^{-\alpha \frac{x^2}{2}}$$

$$\alpha = \frac{2\pi}{h}\sqrt{km}$$

Normalization is needed as total probability needs to be 1.

$$I = \int P(x) = \int_{-\infty}^{+\infty} \psi^* \psi \, dx$$

$$\Psi_0 = N_0 e^{-\alpha \frac{x^2}{2}}$$

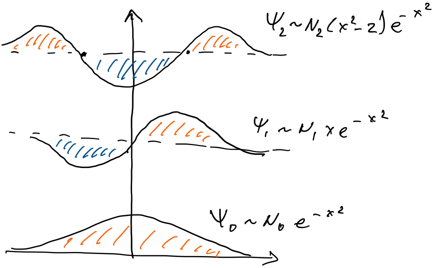
$$I = \int_{-\infty}^{+\infty} N_0^2 e^{-\alpha \frac{x^2}{2}} e^{-\alpha \frac{x^2}{2}} dx = N_0^2 \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx =$$

$$= N_0 \sqrt{\frac{\pi}{\alpha}} \Rightarrow N_0^2 = \sqrt{\frac{\alpha}{\pi}} \Rightarrow N_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

ψ_n and $\psi_{n'}$ have to be orthogonal,

i.e. $\int \psi_n \psi_{n'} \, dx = 0$

That comes from parity of wavefunctions and Hermite polynomials.


$\psi_2 \sim N_2 (x^2 - 2) e^{-x^2}$
$\psi_1 \sim N_1 \, x e^{-x^2}$
$\psi_0 \sim N_0 \, e^{-x^2}$

$\int \psi_2 \psi_0 = 0$ due to Hermite polynomials