Idea of the dipole:

⊖ — ⊕

Static moving

Electron or molecule

1) translation (T) ~ particle in the box

2) rotation (R) θ, φ

3) bond length (V) vibration

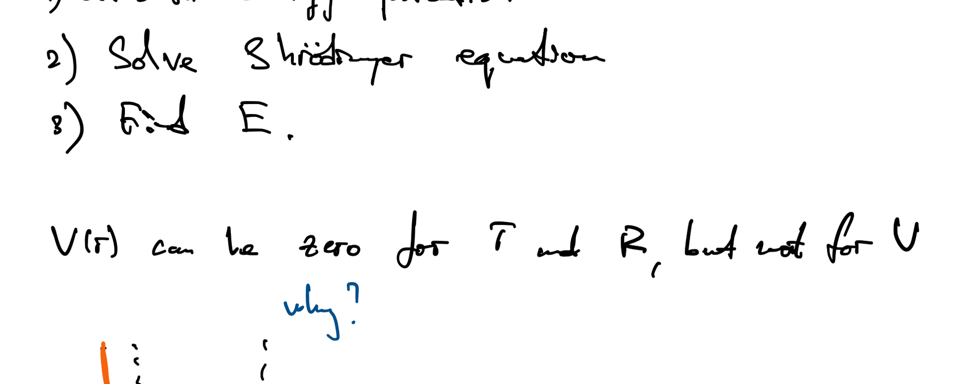
Quantum mechanics recepie!

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

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)

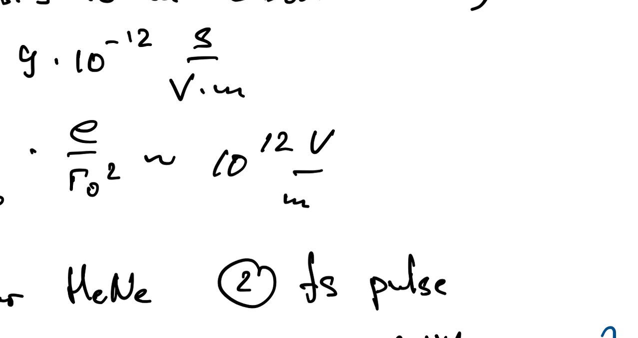
$\varepsilon_0 = 9 \cdot 10^{-12}\,\frac{s}{V \cdot m}$

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

① Sun or HeNe ② fs pulse

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

$E = \sqrt{\frac{2I}{\varepsilon_0 c}} = 3\,\frac{V}{m}$ $\qquad$ $E = \sqrt{\frac{2I}{\varepsilon_0 c}} = 10^5\,\frac{V}{m}$



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:

$F = -k\bar{r}$ (Hook's force)

$\bar{r}' \Rightarrow$ linear optics.

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

Since potential is established, we can solve Shrödinger equation!

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

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

(Shrödinger equation is energy conservation law)

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

Shrödinger equation for harmonic oscillator

$\Psi(x) \rightarrow$ one dimensional wavefunction

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

① Polynom?

$\Psi(x) = ax^3$

$\Psi'(x) = 3ax^2$

$\Psi''(x) = 6ax$

$\Rightarrow Ax + Bx^5 = Cx^3$ not possible

② Exponential (trigonometric)?

$\Psi = ae^{bx}$

$\Psi'' = ab^2e^{bx}$

$\Rightarrow Ae^{bx} + Bx^2e^{bx} = Ce^{bx}$ better, but not yet there

③ Combination

$\Psi = ae^{bx^2}$

$\Psi' = 2abxe^{bx^2}$

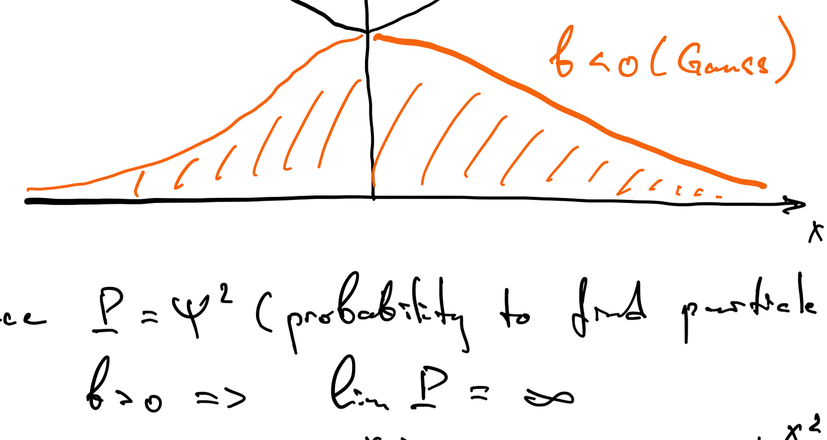
$\Psi'' = 4abe^{bx^2} + 4ab^2xe^{bx^2}$

can work!

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

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

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



1) Since $P = \Psi^2$ (probability to find particle)
$b > 0 \Rightarrow \lim_{x\to\infty} P = \infty$

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

Let's solve it:

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

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

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

$\Psi' = -\alpha Nxe^{-\alpha\frac{x^2}{2}}$

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

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

Hence:

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

Reorganize:

$$\left(-\frac{h^2}{8\pi^2 m}\alpha^2 + \frac{1}{2}k\right)x^2\Psi + \frac{h^2}{8\pi^2 m}\alpha\Psi = E\Psi$$

This will only be possible if

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

$\Downarrow$

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

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 $\Rightarrow$ $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ – 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:

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

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

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

⋮

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

$H_n(\xi)$ – Hermite polynomial

$H_0(\xi) = 1$ even

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

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

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

⋮

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

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 must be 1.

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

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

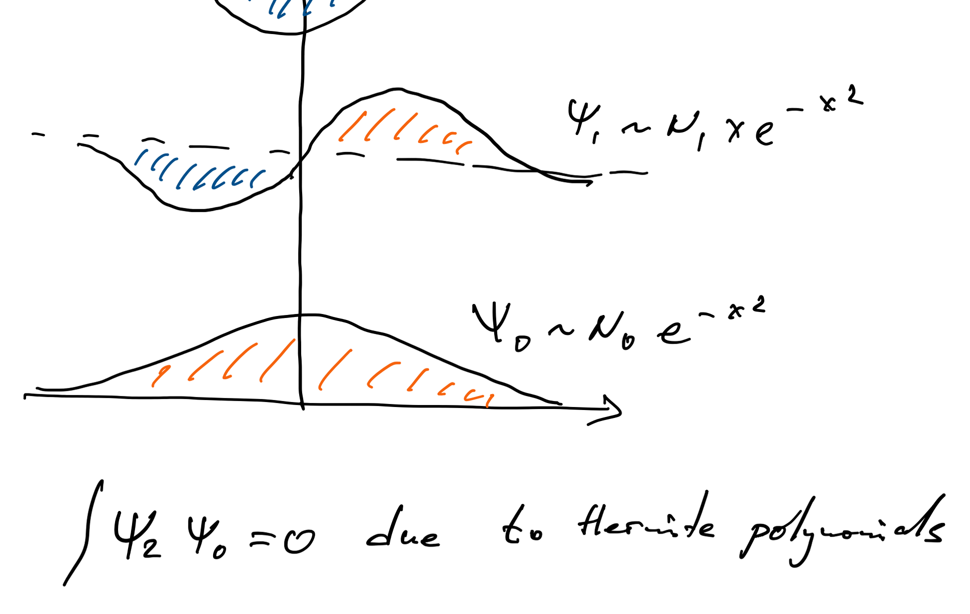
$$I = \int_{-\infty}^{+\infty} N_0^2 e^{-\alpha\frac{x^2}{2}} e^{-\alpha\frac{x^2}{2}} dx = N_0^2\int_{-\infty}^{+\infty} e^{-\alpha x^2}dx =$$

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

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.



$\int \Psi_2\Psi_0 = 0$ due to Hermite polynomials