L7: review

Postulate 2 $\Rightarrow \left\{ \frac{\hat{p}^2}{2m} + V(x) \right\} \psi = i\hbar \frac{\partial}{\partial t} \psi$

P1: $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ ↓ In chemistry we choose x and t as independent variables ↓ P1: $E = -\frac{\hbar}{i} \frac{\partial}{\partial t}$

$$\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right\} \psi = E\psi \quad \text{or} \quad \hat{H}\psi = E\psi$$

solving this differential equation yields either a finite or infinite set of ψs and Es

→ kinetic energy (K): more curvature, more kinetic energy

P4: Pauli exclusion principle

↳ for example, two electrons cannot occupy the same space.

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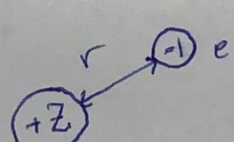
today: How big are atoms and molecules?

$$V(x) = \frac{Ze^2}{4\pi\varepsilon_0 x} ; \quad K = \frac{p^2}{2m_e}$$



$$\Delta V \approx \Delta K \approx E/2$$

As the e^- moves around, energy goes back and forth between potential and kinetic, or

$$\Delta V \approx \frac{Ze^2}{4\pi\varepsilon_0} ; \quad \frac{1}{\Delta x} \approx \Delta K \approx \frac{\Delta p^2}{2m_e}$$

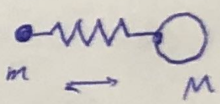
($\Delta p = \frac{\hbar}{2\Delta x}$ from Heisenberg principle)

$$\Rightarrow \Delta x \approx \frac{\pi \varepsilon_0 \hbar^2}{2 m_e Z^2 e^2} \approx 0.06\,\text{Å}$$

So molecules are small!

(assumption is $\Delta x \sim x$)

Vibrating molecules:



As we'll see later, e^- pairs act like a spring holding nuclei together: $V = \frac{1}{2}kx^2$

(How can we get k?)

$$\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \right\} \psi_n = E_n \psi_n$$

could be more than 1 solution

HWK Q2.1: Try $\psi_0 = e^{-ax^2}$

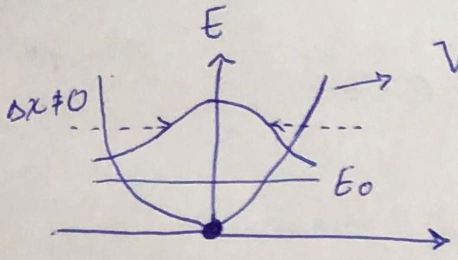
(continued)

$$-\frac{\partial^2}{\partial x^2} e^{-ax^2} = -\frac{\partial}{\partial x}\left(-2axe^{-ax^2}\right) =$$

$$\left(2a - 4a^2x^2\right) e^{-ax^2}$$

$\sim \Psi_0$; $\underbrace{4a^2x^2}$ cancels $\frac{1}{2}kx^2\Psi_0$

A diagram of this solution :



$V(x) = \frac{1}{2}kx^2$

$E_0 = \frac{h}{4\pi}\sqrt{\frac{k}{m}} \Rightarrow E_0 = h\nu \cdot \frac{1}{2}$

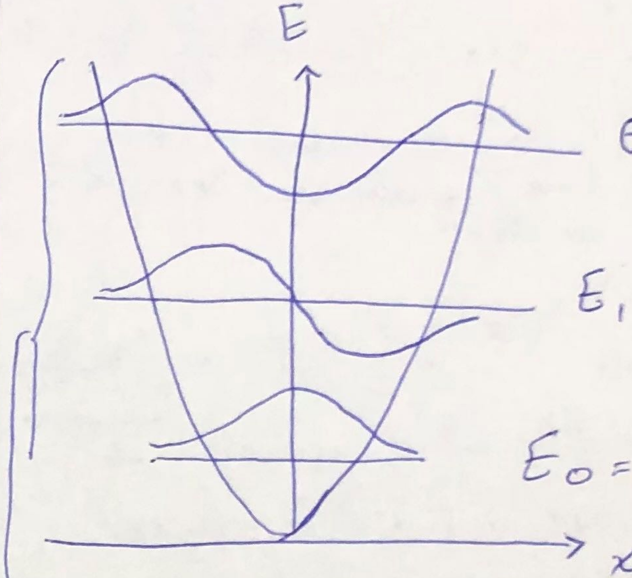
Q : why can the energy not be 0, like a classical spring at • ?

(Ans: $\Delta x = 0$; $\Delta p = 0 \Rightarrow \Delta x \Delta p = 0$ violates Heisenberg's Principle)

E_0 = "zero point energy"

↳ $E_0 > 0$: this is why atoms do not collapse.

HWK Q2.1: $\Psi_1 \sim xe^{-ax^2}$ is also a solution



$E_2 = h\nu \cdot \frac{5}{2}$

$E_1 = h\nu \cdot \frac{3}{2}$

$E_0 = h\nu \cdot \frac{1}{2}$

note that the higher the curvature, the higher the energy of the system.

$E_2 > E_1 > E_0 \Leftrightarrow \left|\frac{\partial^2}{\partial x^2}\Psi_2\right| > \left|\frac{\partial^2}{\partial x^2}\Psi_1\right| > \left|\frac{\partial^2}{\partial x^2}\Psi_0\right|$

$E_n = h\nu(n + \frac{1}{2})$; quantum number (n) ; only certain energies are allowed.

thought: what does it mean if Ψ has more wiggles? / Ψ gets wider ?