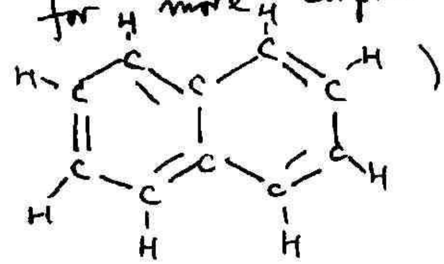
Lecture VIII Complex numbers & waves

① We have drawn the MO diagrams of N_2, O_2 & HF. At this point we are stuck. What we want to derive are the MO diagrams for more complicated molecules (molecules like napthalene



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To do that we'll need the actual equation which underlie the pictures we derived for N_2 & HF.

② On the other hand, the course so far has raised more questions than it has answered.

Questions (partial list)

(i) Why should e^- be thought of as waves?

(ii) Why are rules ①-④ of MO theory correct?

(iii) Why is there an Aufbau principle?

(iv) Why are there principal, total angular momentum, directional orbital angular momentum & directional spin quantum numbers?

③ We will start by answering question (i). In answering this question we will develop the math to make more complex MO diagrams. For reading Zumdahl is a little help but not much. [see Zumdahl pp510-519] Much more useful are Chapters 1-3 of Feynman's Lectures in Physics Vol. 3. These are (hopefully) attached to the end of week 3's lecture notes.

④ To answer ⓘ we are going to have to learn the basics of quantum mechanics. The physics of quantum mechanics is embedded in math which you may be somewhat familiar with : complex numbers, vectors and matrices. If you are not familiar with these things don't worry. We'll teach you everything you need to know in this course.

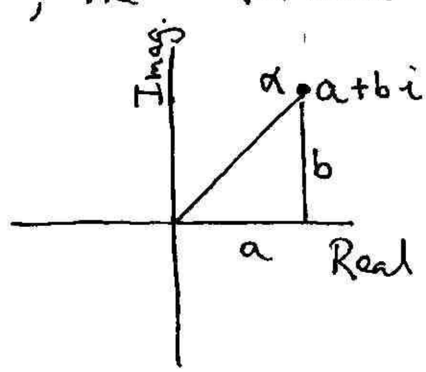
⑤ Complex numbers : i is defined $i\,i = i^2 = -1$
A complex number is made of two parts, a real part and an imaginary part.

$$6 + 2i$$

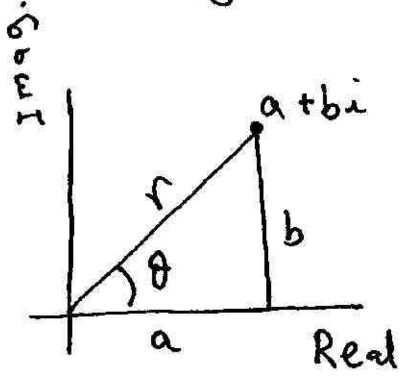
6 is the real part ; 2 is the imaginary part. A lot of people use the letters a, b, c to represent real numbers & α, β, γ to represent complex numbers.

$$\alpha = a + bi$$

⑥ Visually complex #'s can be thought of as points on a plane. The horizontal axis is the real axis, the vertical axis is the imaginary axis.



⑦ With this picture we can set up a "polar" type of coordinate system:



$$a = r\cos\theta \qquad b = r\sin\theta$$

$$\alpha = a + bi = r\cos\theta + ir\sin\theta$$
$$= r(\cos\theta + i\sin\theta)$$

⑧. In calculus you will (or have) learned:

$$\sin\theta = \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \frac{\theta^7}{7!} + \dots$$

$$\cos\theta = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \frac{\theta^6}{6!} + \dots$$

$$e^{\alpha} = 1 + \alpha + \frac{\alpha^2}{2!} + \frac{\alpha^3}{3!} + \frac{\alpha^4}{4!} + \dots$$

$$\cos\theta + i\sin\theta = 1 + i\theta - \frac{\theta^2}{2!} - i\frac{\theta^3}{3!} + \frac{\theta^4}{4!} + i\frac{\theta^5}{5!} - \frac{\theta^6}{6!} - \dots$$

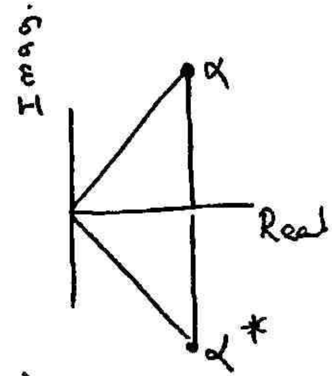
$$e^{i\theta} = 1 + i\theta - \frac{\theta^2}{2!} - i\frac{\theta^3}{3!} + \frac{\theta^4}{4!} + \dots$$

Conclusion

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$\boxed{\therefore\ \alpha = re^{i\theta}}$$

(9) Complex conjugates. Every complex number, α, has a complex conjugate, α^* where if



$$\alpha = a + bi$$

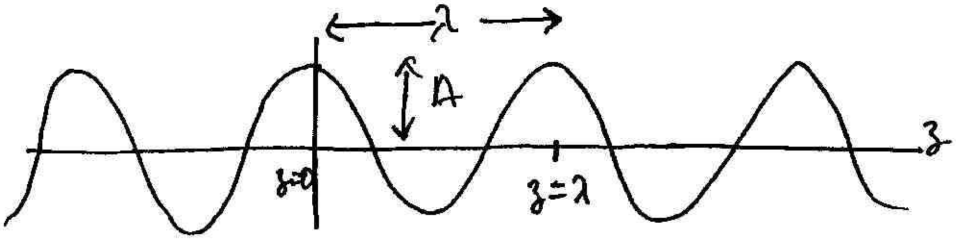
$$\alpha^* = a - bi$$

Note $\alpha\alpha^* = \alpha^*\alpha = (a+bi)(a-bi)$

$$= a^2 + b^2$$

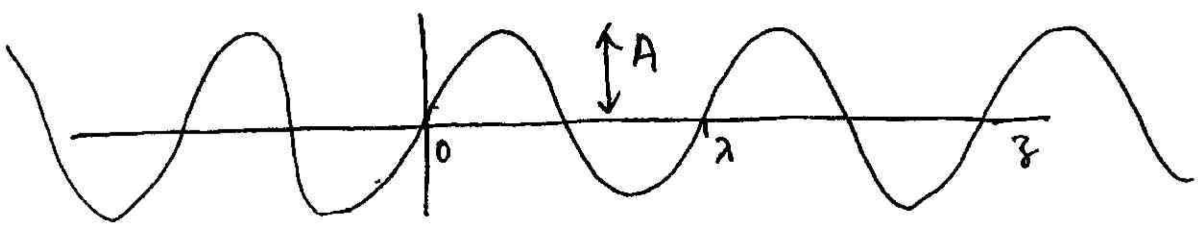
$\alpha\alpha^*$ is always a <u>positive</u> real number

(10) With this introduction, we can begin to look at waves.



$A\cos(kz)$ $\qquad k = \frac{2\pi}{\lambda}$ $\qquad$ at $z=\lambda$: $\therefore \cos k\lambda = \cos 2\pi = 1$

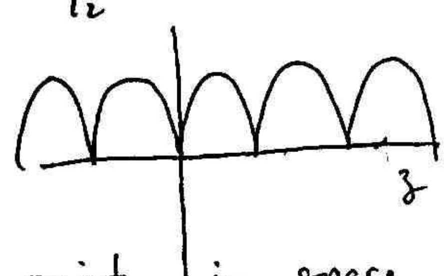
or similarly



$A\sin kz$ $\qquad A\sin k\lambda = A\sin 2\pi = 0$

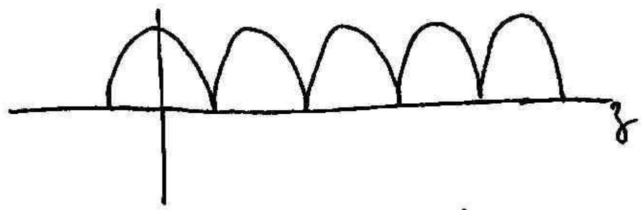
(11) We know from our earlier lectures that we want to represent electrons as waves. Both $\psi_1 = \cos kz$ or $\psi_2 = \sin kz$ correspond to waves, but these are not the waves we want.

<u>Reason</u> ψ_1^2 & ψ_2^2 are supposed to represent the electron density. ψ_1^2 looks like this $\qquad \psi_2^2$



The e^- is never found in a certain point in space.

(12) We want quantum mechanics to apply to all particles, not just e^-. If ψ_1 was a photon of light ψ_1^2



the light would flicker on & off depending on z.

– demonstration –

(13) Expt. shows there is no flickering up to 10^{-11} m (?)

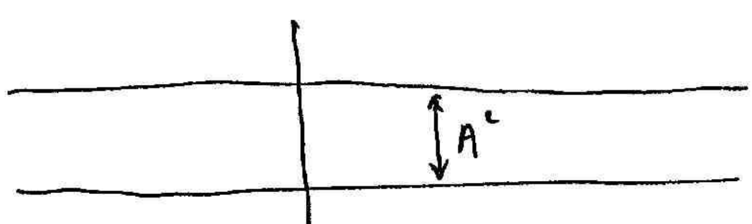
(14) Let's "improve" our math. Let's call the wave $\psi_1 = A[\cos(kz) + i\sin(kz)]$

Let's change ψ^2 into $\psi\psi^*$

$$\psi\psi^* = A[\cos(kz) + i\sin(kz)]A[\cos(kz) - i\sin(kz)]$$

$$= A^2[\cos^2(kz) + \sin^2(kz)] = A^2$$

$\psi\psi^*$ is a constant number for all z.



We call A^2 the light intensity.