

# Wavefunctions Are Additive

As a way to approximate molecular orbitals (MOs), we simply add or subtract combinations of atomic orbitals. The simplest MO would thus involve taking one wave function centered on the first nucleus ( $\psi_1$ ) and adding it to or subtracting it from another wave function centered on the second nucleus ( $\psi_2$ ). We call this method of constructing molecular orbitals LCAO - linear combination of atomic orbitals. The resulting MO will be designated  $\Psi$ .

Why do we care about  $\psi$ , when  $\psi^2$  is what we observe?

⇒ Because  $\psi$ 's are additive,  $\psi^2$ 's are not.

$$(\psi_1 + \psi_2)^2 \neq \psi_1^2 + \psi_2^2$$

e.g.,  $\psi_1 = -3$  and  $\psi_2 = 3$   
 $(-3 + 3)^2 \neq ((-3)^2 + 3^2)$

The mathematics that describes orbital interactions is addition and subtraction.

The additivity of wavefunctions is the idea behind LCAO (Linear Combination of Atomic Orbitals)

