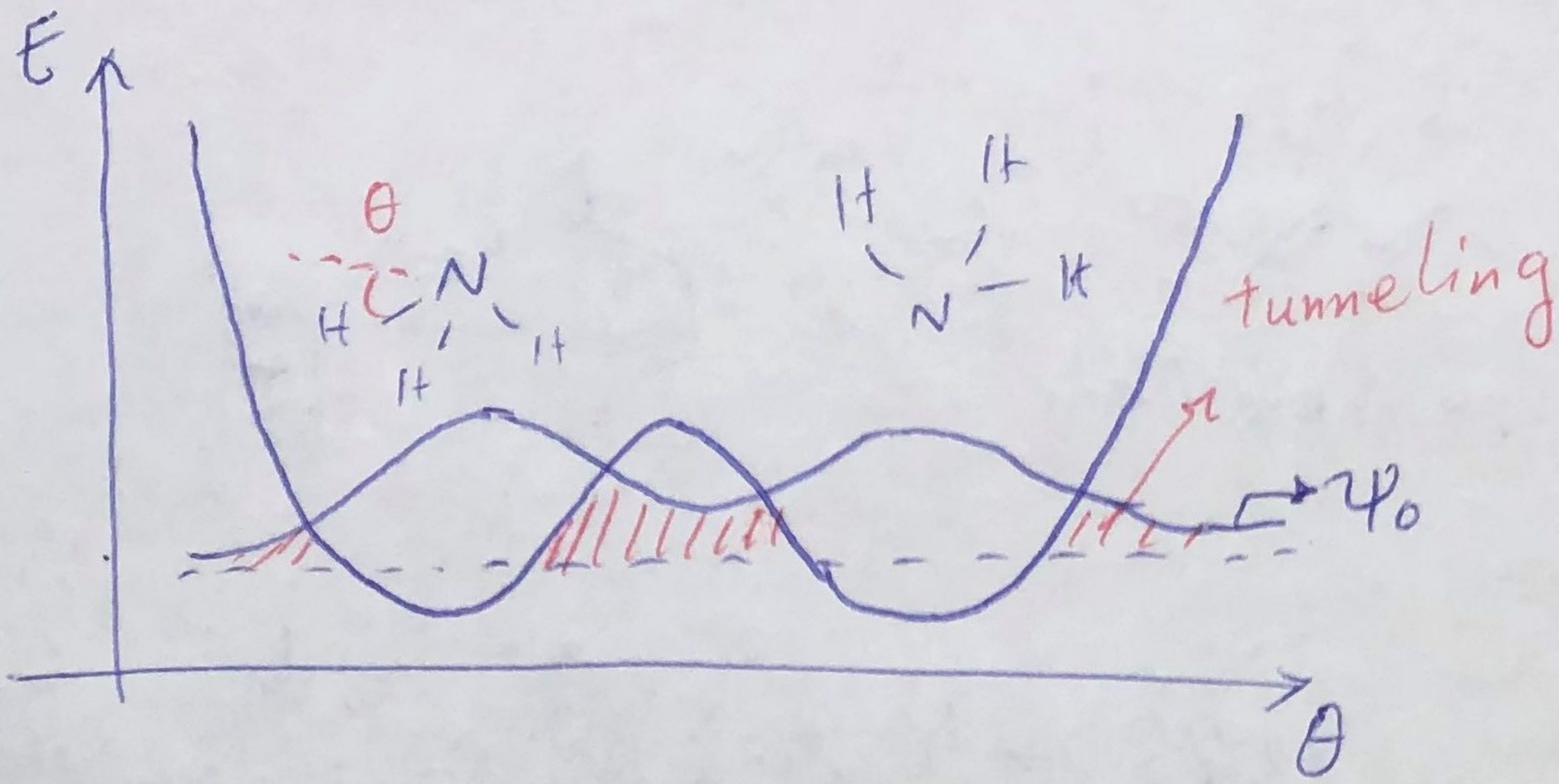
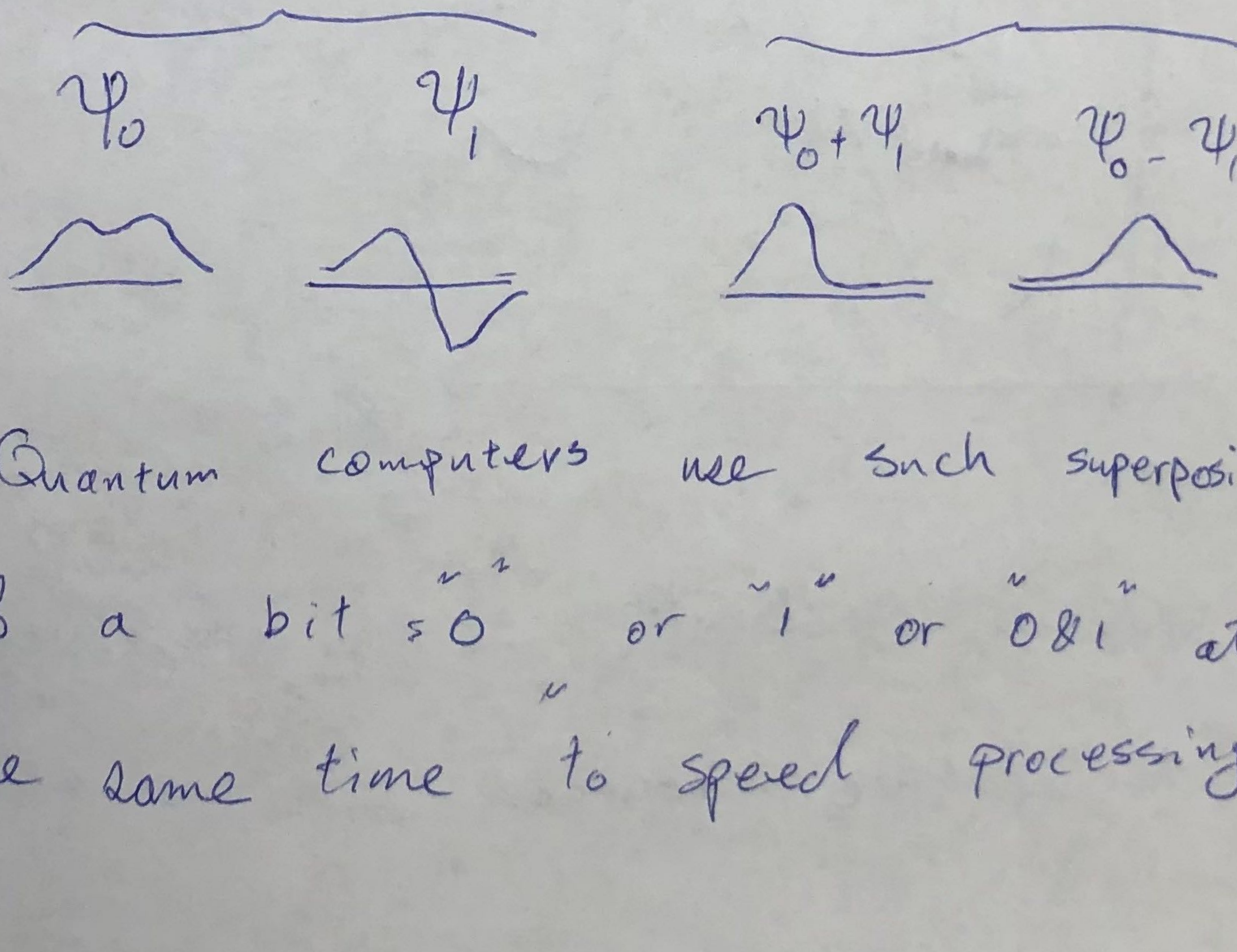
L16: review



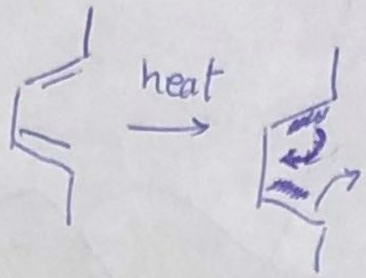
Some possible states:

eigenstates of $\hat{H}$ not eigenstates of $\hat{H}$

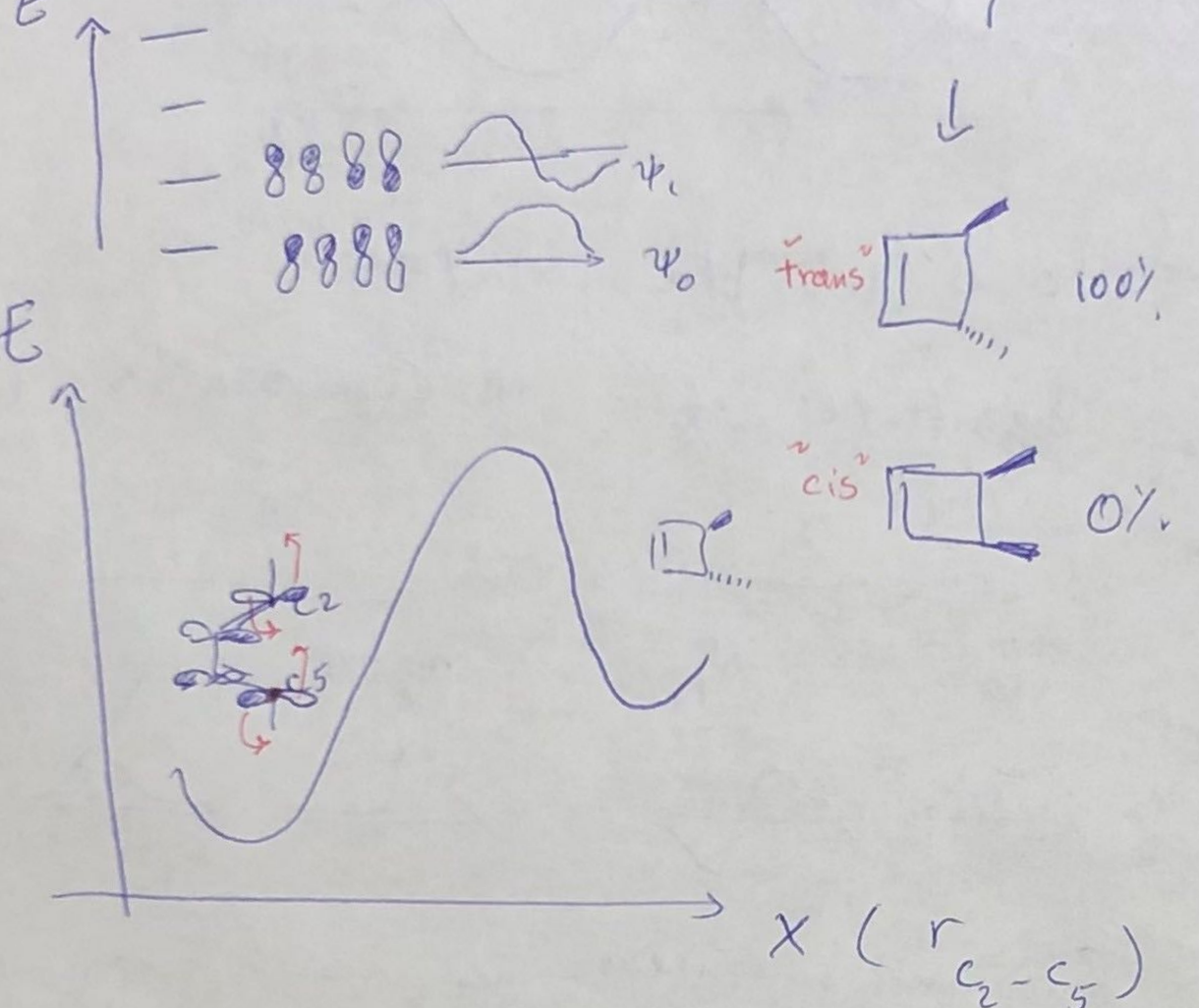


Quantum computers use such superpositions of a bit "0" or "1" or "0 & 1" at the same time to speed processing".

Today: How reactions go over barriers

ex  bond rotation 

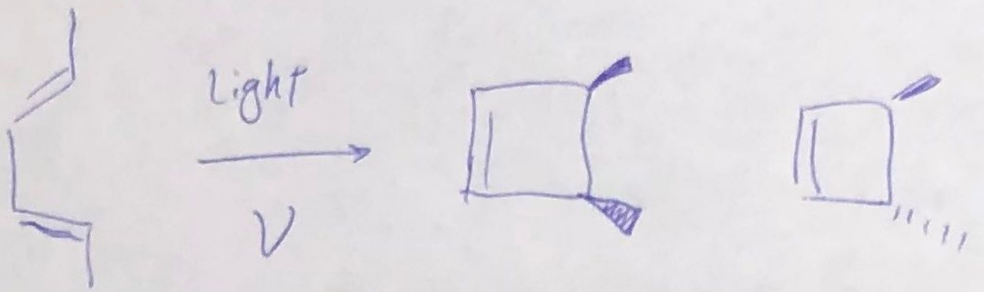
2,4-hexadiene

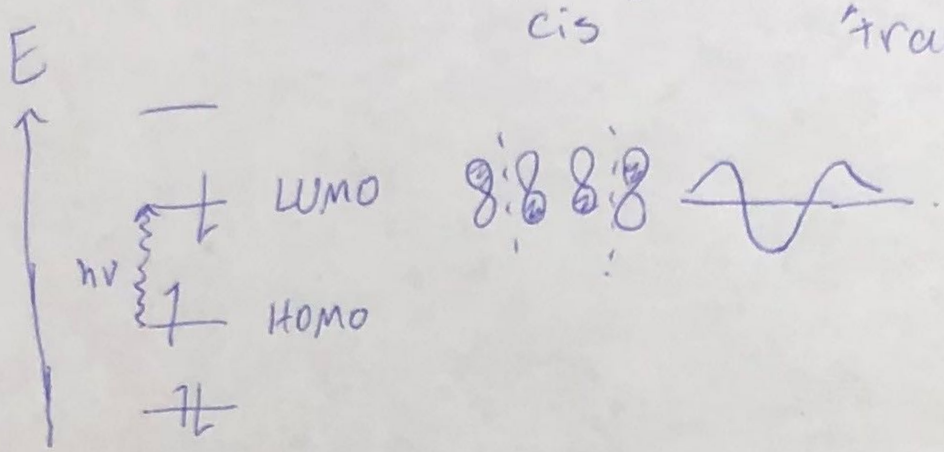


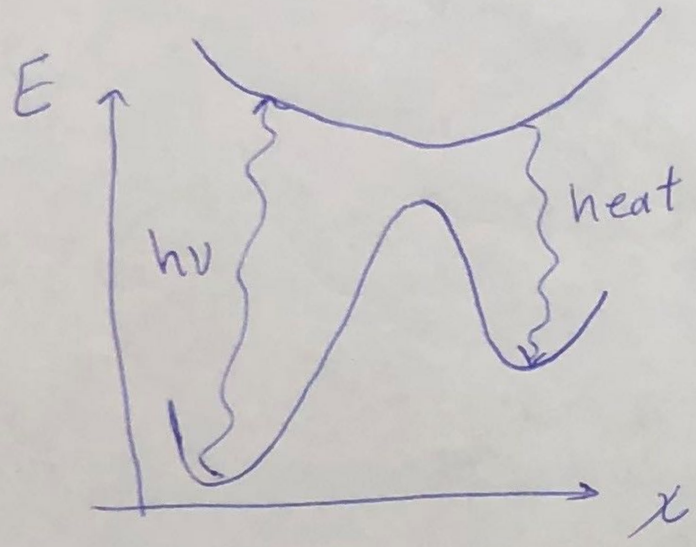
* reaction coordinate is the (negative of) the distance between C2 and C5.

* It was puzzling for some time why the only product is  and no  is formed. The phase of molecular orbitals (+/- of Ψ) gives a plausible explanation: for optimal bond overlap, p orbitals with similar sign overlapping, the methyl groups have to rotate in the same direction. Thus only the trans product will form.

* The trick to get the cis product is using light instead of heat.





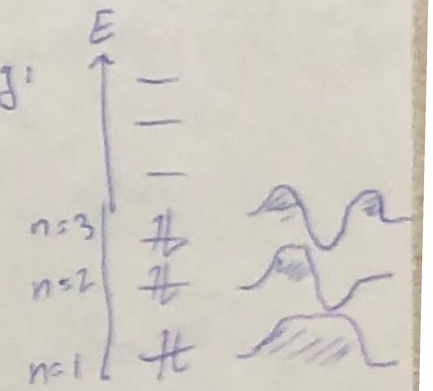


* exciting the electron into LUMO, sends the electron into an orbital with opposite p-orbitals having similar phase, i.e. ~~8 8 8 8~~. Therefor, (next page)

(cont'd) for optimal overlap the methyl groups have to rotate in opposite direction, giving rise to the cis product. The system eventually comes back to the ground state by dissipating heat.

Problem: predict the product of octa triene ( ) under i) heat and ii) light excitation.

Hint: the phase of the molecular orbitals are the following:

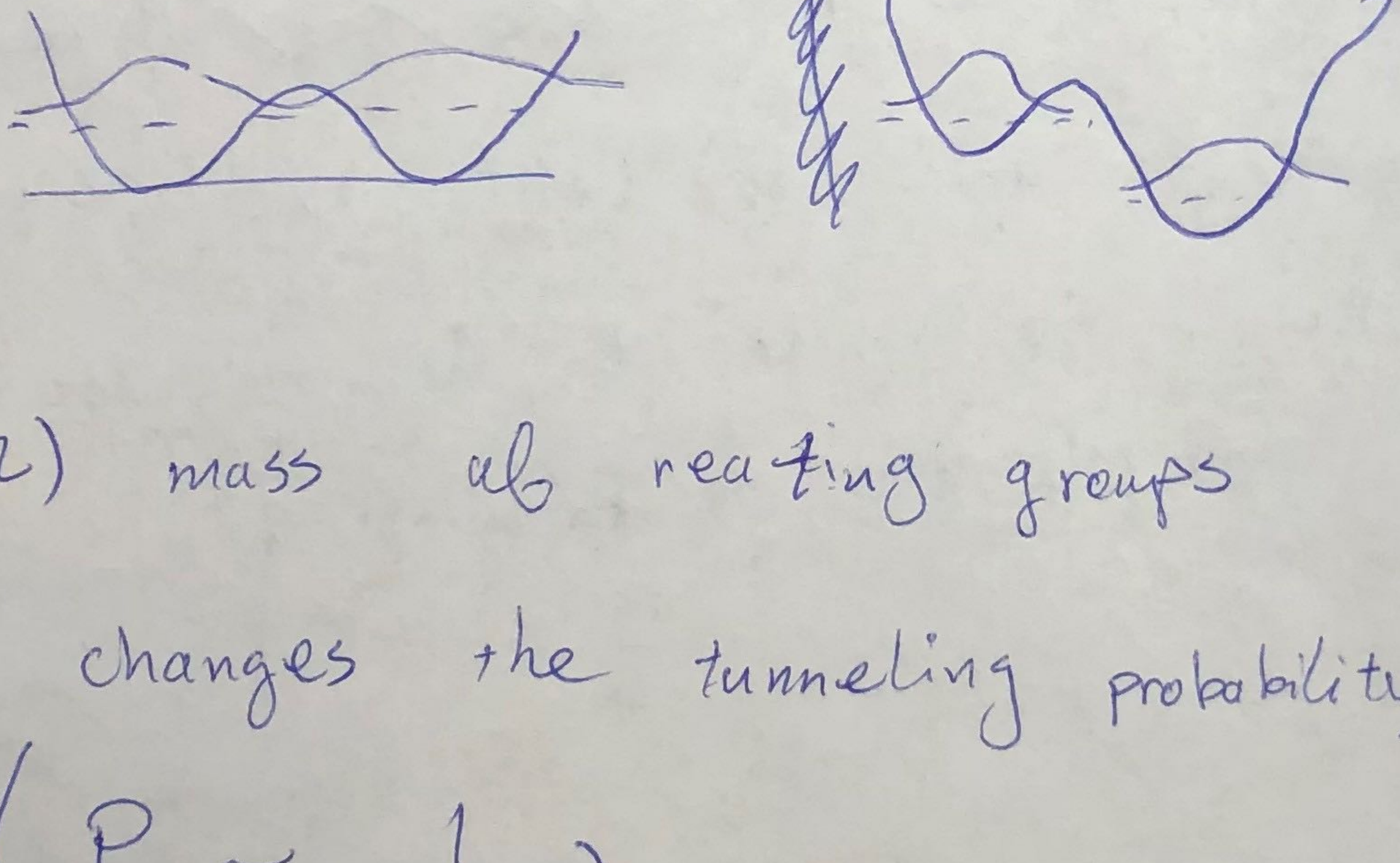


why not tunnel for chem rx?

* note that by using light or heat a lot of energy is wasted, so it will save considerable amount of energy if tunneling were to occur.

Problems wit tunneling:

1) mismatch of E levels



2) mass of reating groups changes the tunneling probability:

$\left(P \sim \frac{1}{m^n}\right)$