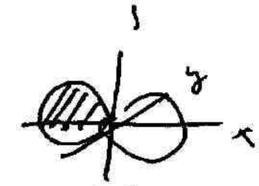
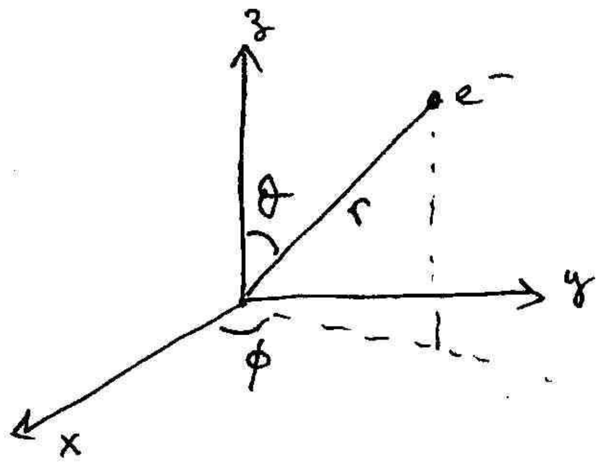
Lecture III + Lecture IV

Radial Functions (Zumdahl p. 542)
Waves (" p. 527)

① All p_x orbitals look like this 

So what is the difference between a $2p_x$ and a $3p_x$ orbital?

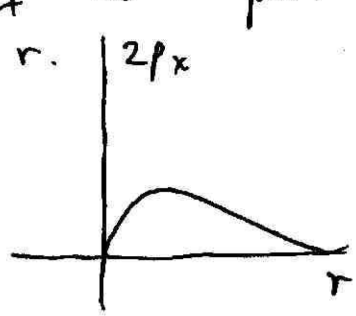
② Answer: the $2p_x$ and $3p_x$ functions differ in their radial component.

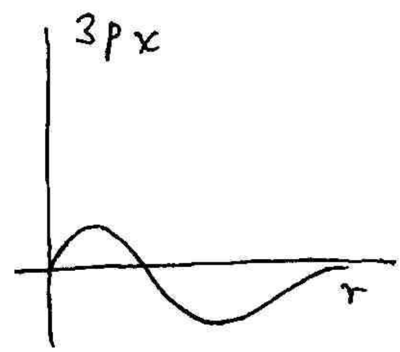


r is the radial component.

[Changing θ & ϕ we remain on the sphere (the unit sphere)].

Let us plot these orbitals as a function of r.





Addenda to Lecture III + Lecture IV

(2a) So when we plot just r portion of the function we are plotting just one part of the orbital.

(2b) Given the mathematical level of this class, perhaps it will help if we look at this as function:

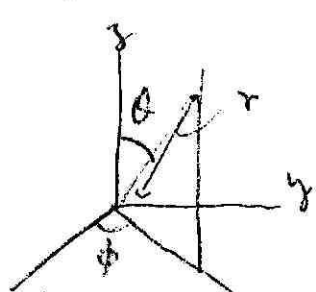
$2p_x$ and $3p_x$ are the functions

$$\psi_{2p_x} = C_{2p_x} r e^{-r/4} \sin\theta \cos\phi$$

$$\psi_{3p_x} = C_{3p_x} r(4 - \tfrac{1}{3}r) e^{-r/6} \sin\theta \cos\phi .$$

where C_{2p_x} and C_{3p_x} are constants & r is a distance variable which depends on Z, the nuclear charge

(2c) As examination of these two functions show both ψ_{2p_x} and ψ_{3p_x} are functions of 3 variables: r, θ & ϕ, the variables shown below.



This leads to a major graphing problem. To portray the ψ function we would need a 4-D sheet of graph paper!

Since such 4-D paper does not exist we plot these functions in the following way.

(2d) We plot separately the r variable from the θ & ϕ variable.

Let's call

$$R_{2px} = r e^{-r/4}$$

$$Y_{2px} = \sin\theta \cos\phi$$

then

$$\psi_{2px} = C_{2px} R_{2px} Y_{2px}$$

Similarly we call

$$R_{3px} = r\left(4 - \tfrac{1}{3} r\right) e^{-r/6}$$

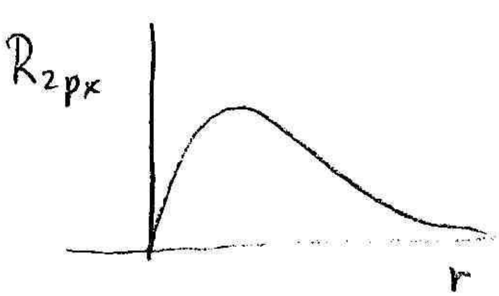
$$Y_{3px} = \sin\theta \cos\phi .$$

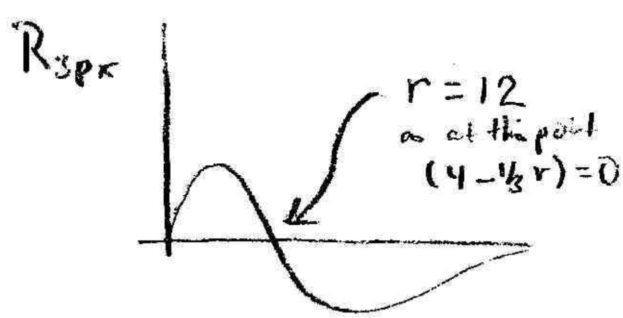
&

$$\psi_{3px} = C_{3px} R_{3px} Y_{3px} .$$

But note $Y_{3px} = Y_{2px}$, so we just call this part Y_{px}

(2e) We can now plot R_{2px} & Y_{px} separately.

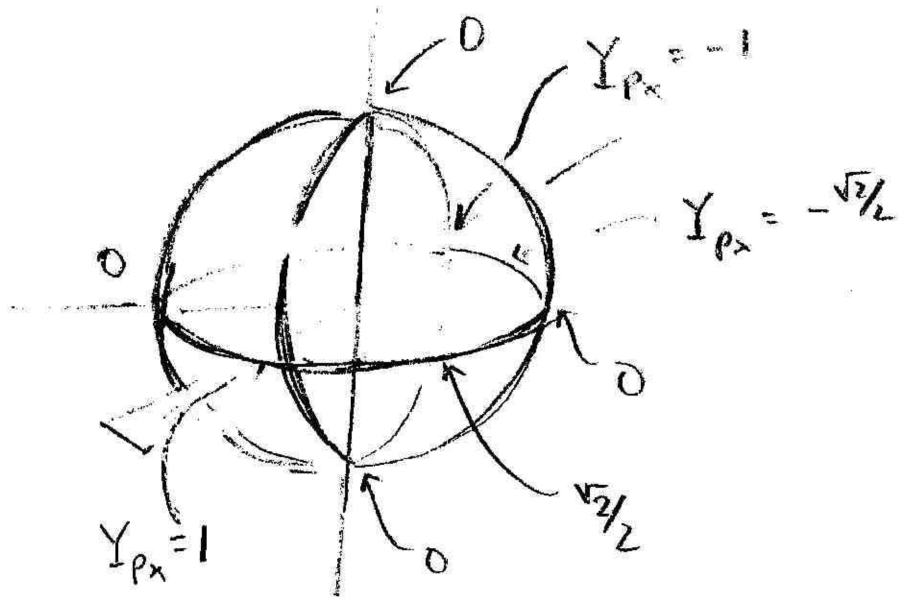




(2f) We now are left with plotting the

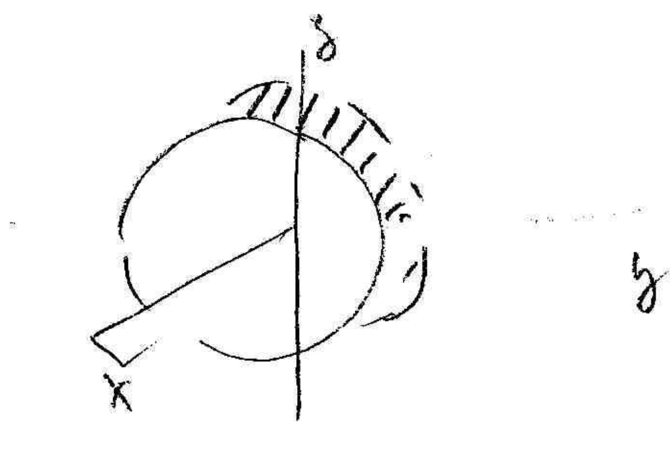
$$Y_{px} = \sin\theta\cos\phi \quad \text{function.}$$

(2g) One way commonly used to plot this function involves "unit-sphere plots". Let's determine the value of $\sin\theta\cos\phi$ along the unit sphere



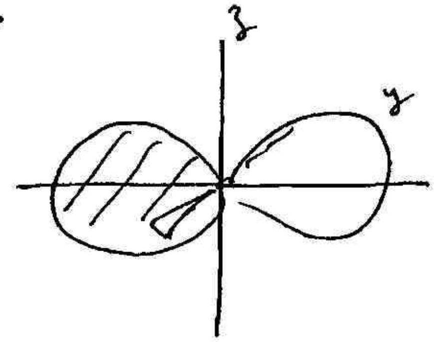
etc.

(2h) If we plot the value of this function in the direction of the point on the unit sphere we find:

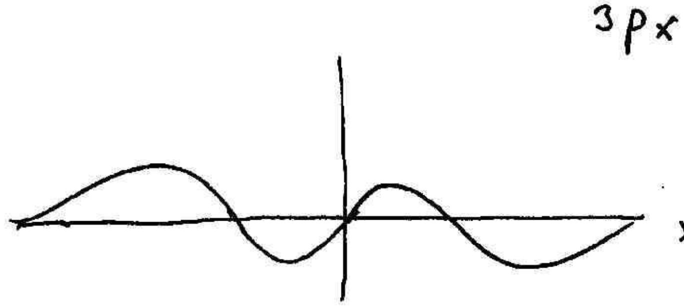


the classic picture of a p_x orbital.

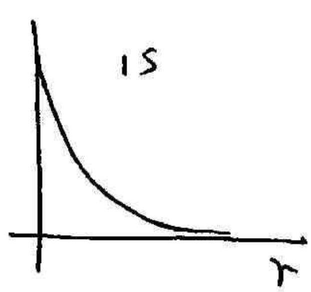
③ Putting together our pictures of 3px, we learn that the angular portion of the orbital looks like this

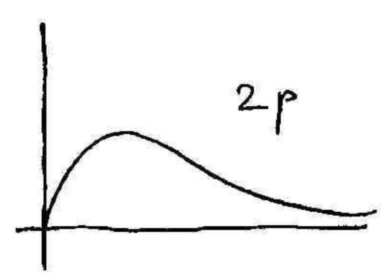


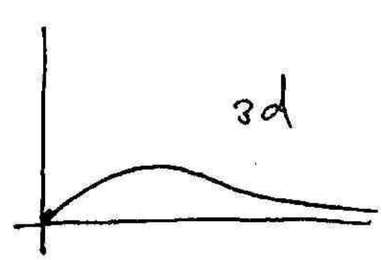
but if we took a crossection of values along the x axis we would find



④ Rules for radial functions. The 1s, 2p, 3d & 4f rad. functions all have <u>no</u> nodes (a node is when a function = 0) except at r = 0 (excepts) & r = ∞.







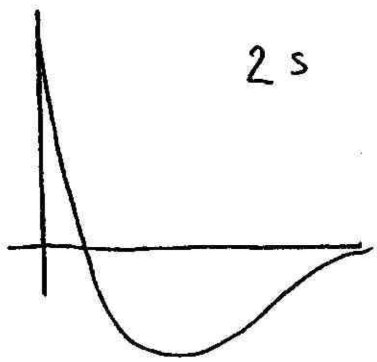
etc...

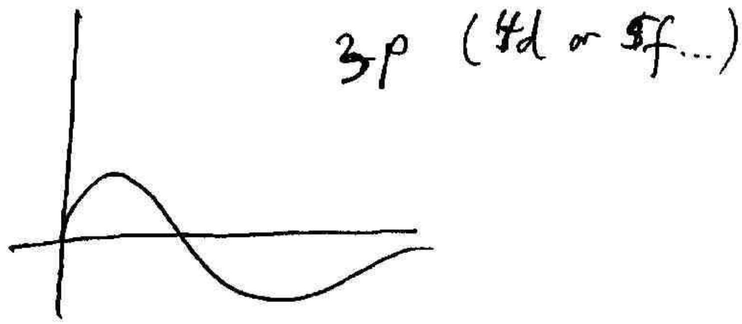
⑤ Radial function $2p_x = 2p_y = 2p_z$

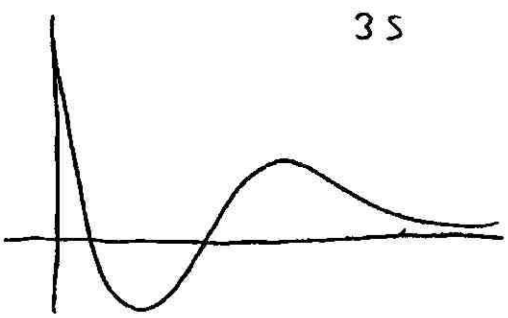
" $3d_{x^2-y^2} = 3d_{z^2}$ etc...

⑥ The 2s, 3p, 4d, 5f have 1 node
3s, 4p, 5d, 6f " 2 "s
4s, 5p, 6d, " 3 "s

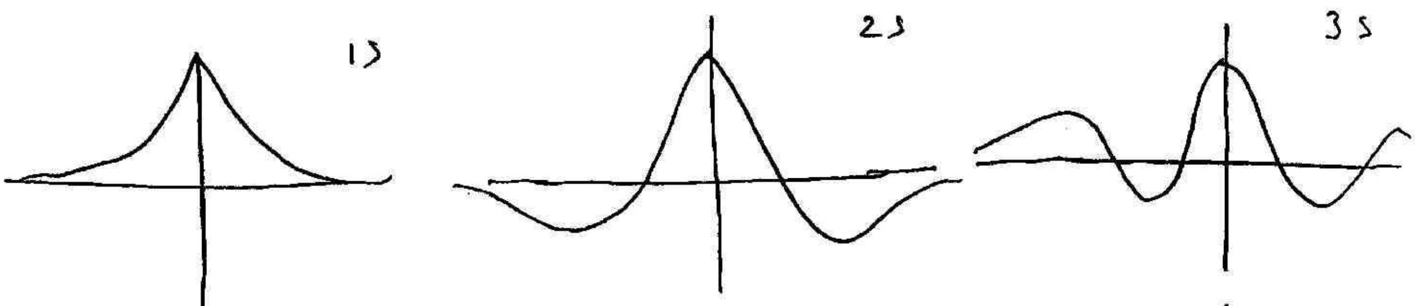
etc...







⑦ Crossection of ns orbitals along x-direction



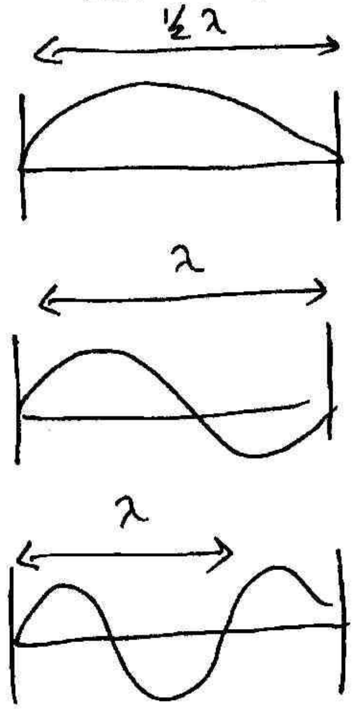
lowest energy

2nd lowest s orbital

3rd lowest energy s orbital

- demonstration -

⑧ The more nodes the higher the energy.



easy (lowest energy)

harder (higher energy)

hardest (highest energy)

rule $E \propto \frac{1}{\lambda^2}$ wavelength

for particles w/ mass

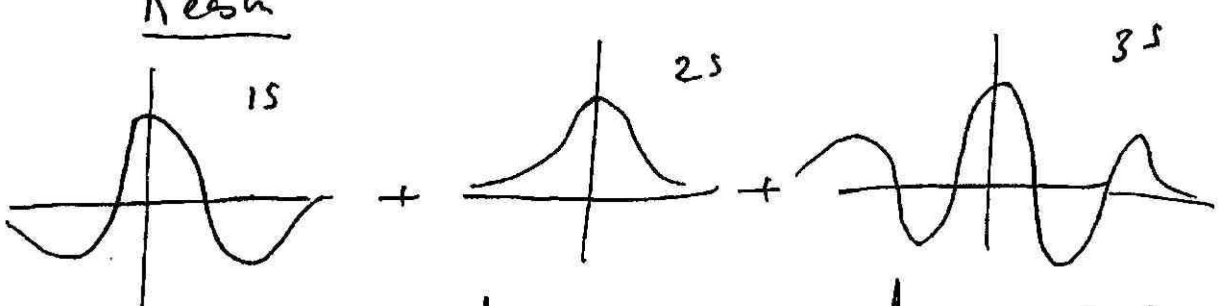
⑨ - Violin -

(i) low vs. high frequency

(ii) pizzicato vs. normal vs. vibrato

⑩ Pizzicato sounds like several notes put together.

Reason



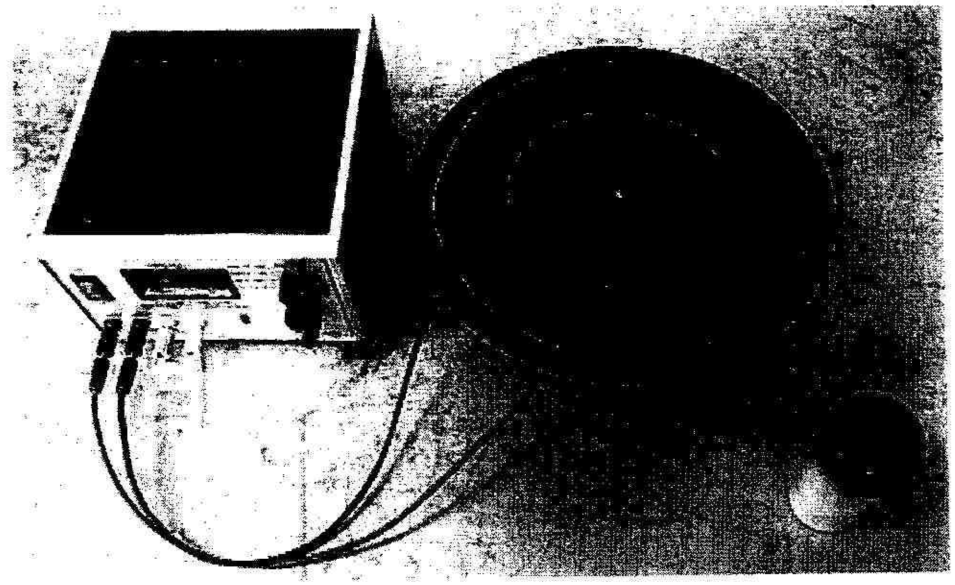
Our ears / brains resolve sounds into their component frequencies!

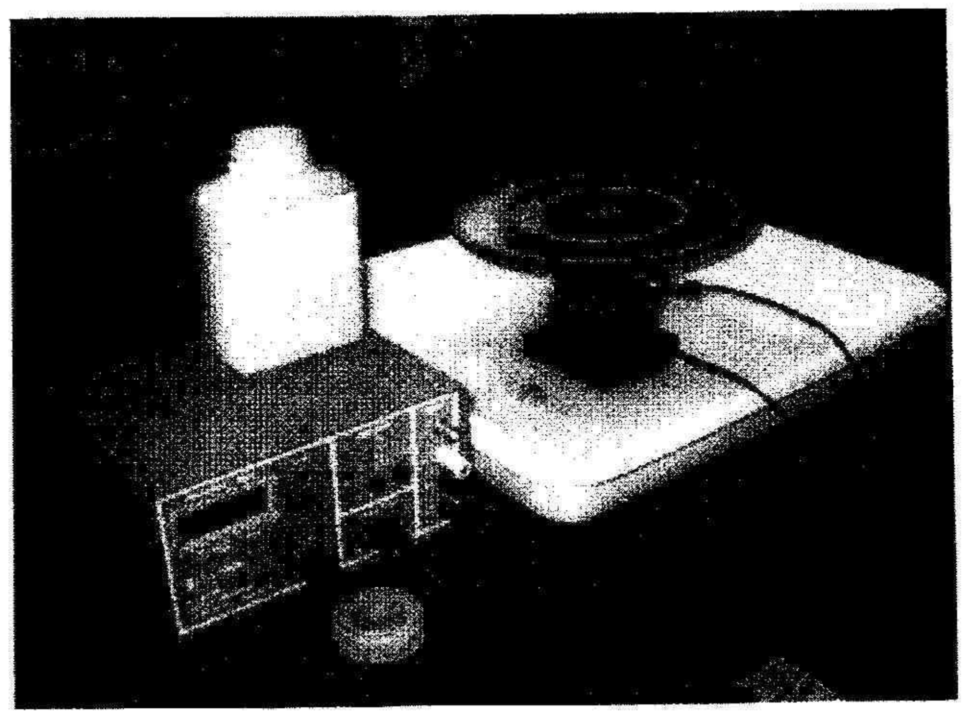

sand arranges along
nodal circles
level
djembe
loudspeaker
(sine wave)


M9 (1335 Hz)


M4 (844 Hz)

Two pictures of
Chladni plates.





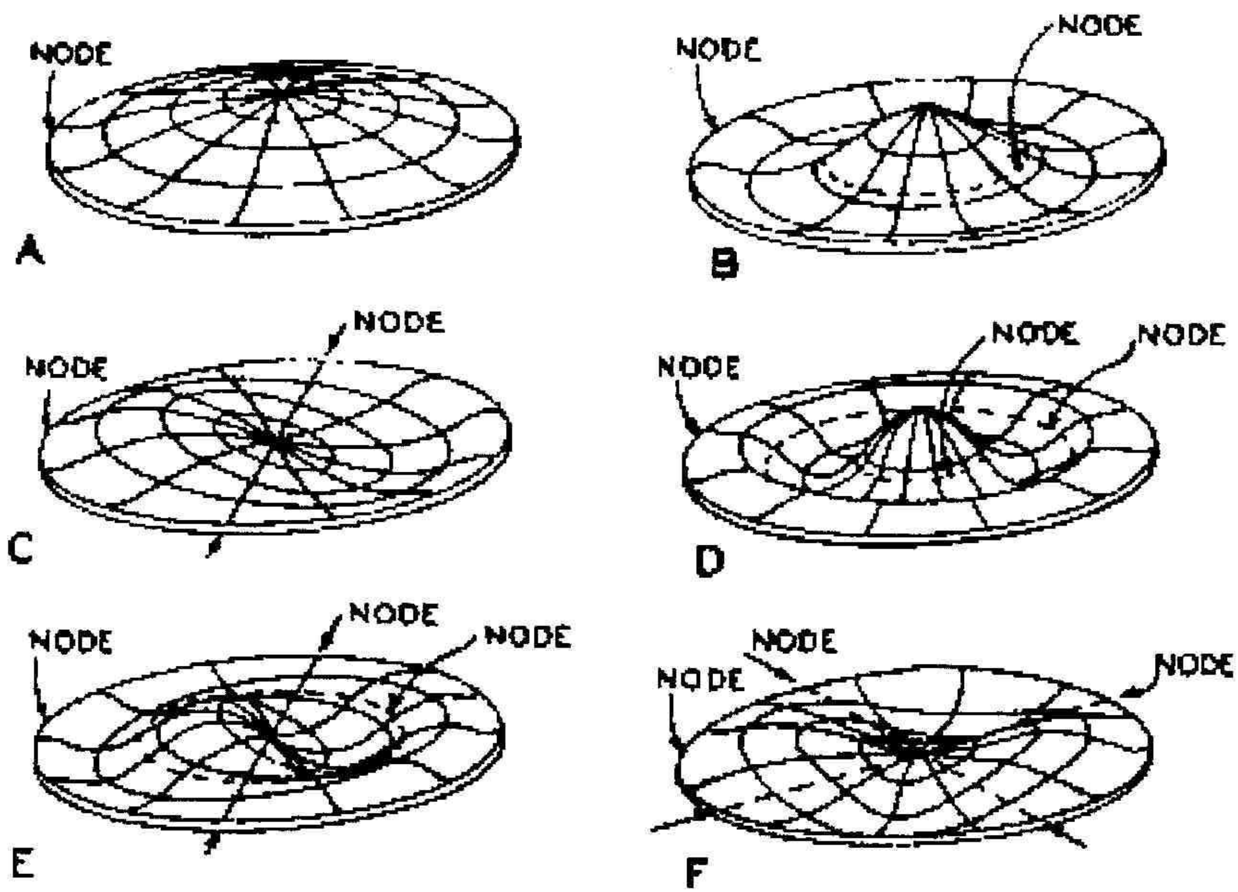
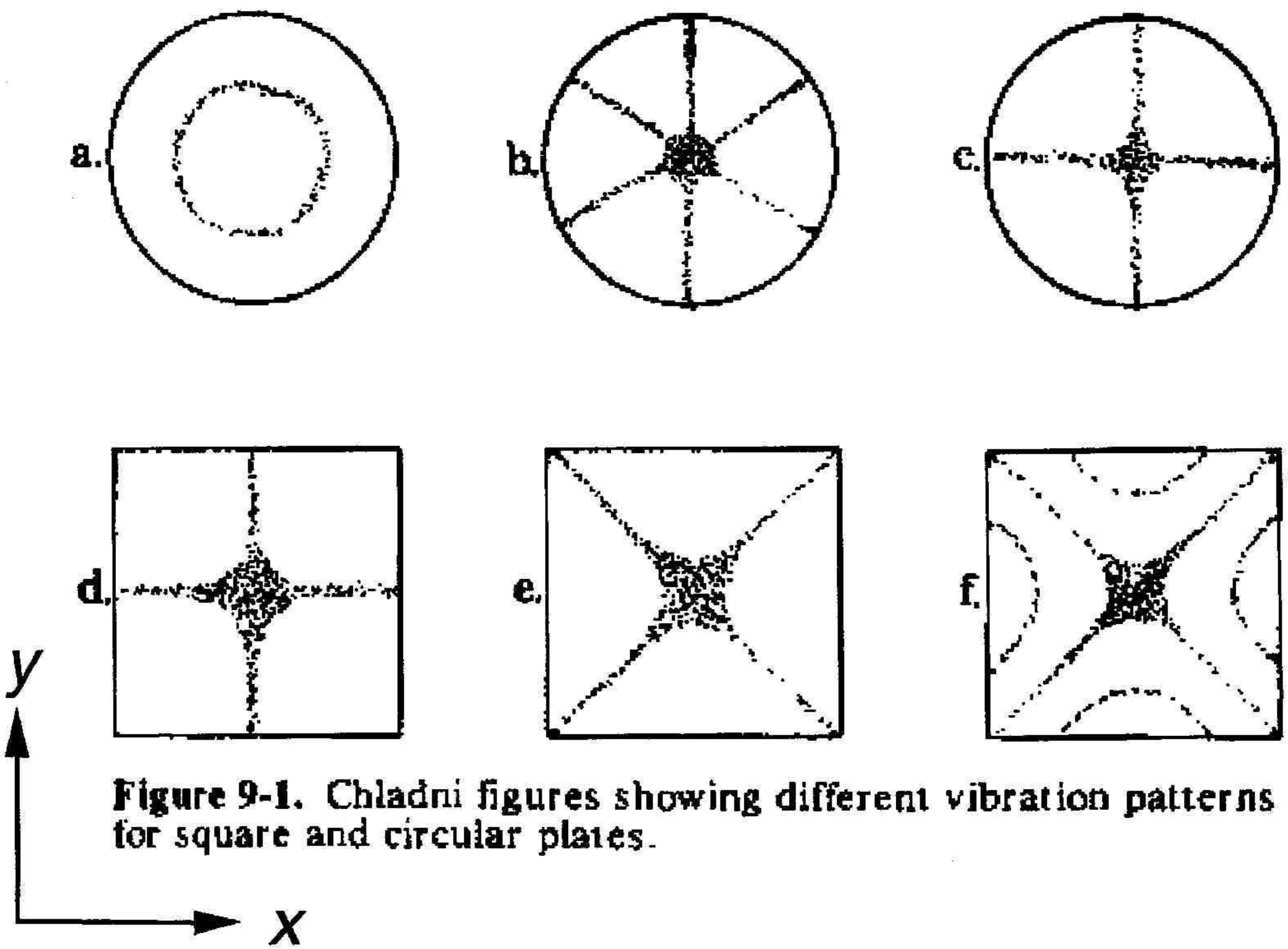


Figure 9-5. Modes of vibration of a clamped circular plate. Courtesy of *Harry F. Olsen*, **Musical Engineering**, McGraw-Hill Book Co., Inc., 1952.

Exercise 2: Identify corresponding name for an atomic orbital (ie., 1s, $2p_x$, $3d_{x^2-y^2}$. etc...).



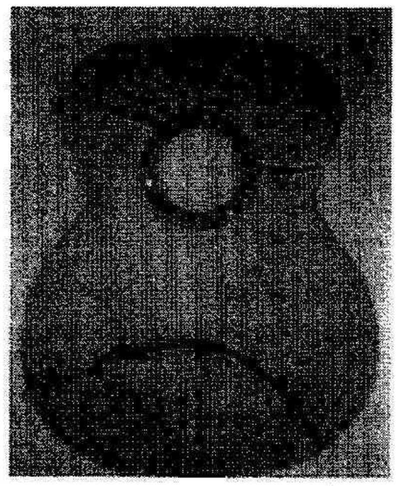
for this problem guess which atomic orbital contributed most heavily to its form

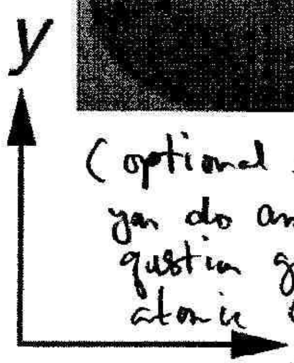
Figure 9-1. Chladni figures showing different vibration patterns for square and circular plates.

Exercise 2 continued

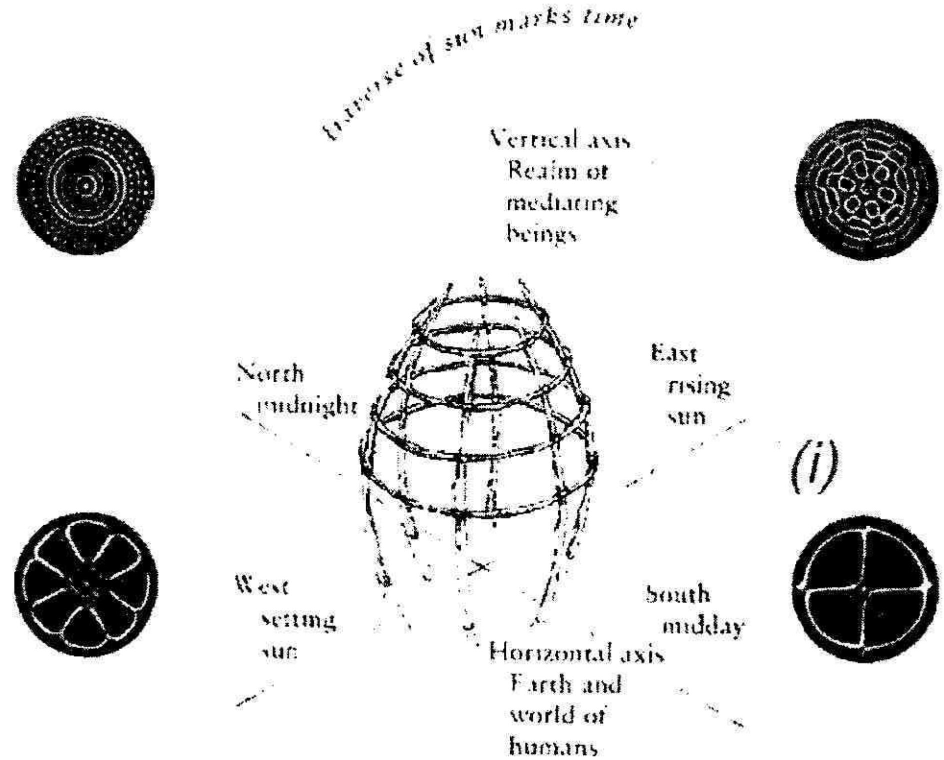
(g)

(h)





(optional: if you do answer this question guess what atomic orbitals made this orbital)



(i)

Problem Set #1.

① & ② are excercises given in the preceding page.

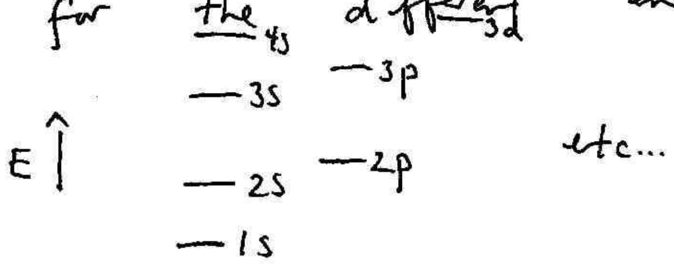
③ Draw pictures (radial & angular) for the (a) $4d_{z^2}$ (recall z^2 is short-hand for $2z^2-x^2-y^2$ (b) $3d_{xz}$ (c) $5f_{x(y^2-z^2)}$ orbitals.

④ Draw a picture for z^2 (an angular picture) where $z^2 = z^2$ not $2z^2-x^2-y^2$. How does it differ from the $2z^2-x^2-y^2$ picture?

⑤ Using the methods outlined in class draw the places where the $4d_{x^2-y^2}$ "orbital" would have sand accumulate in a Chladni type picture.

⑥ Draw the orbitals (angular picture only) (a) $1+2x$ (b) 1 (c) $x+y$. Using the s, p & d notation find names for these orbitals. For example $d_{xz+yz} - p_z + s$ would be a name for an orbital in the s, p & d notation. Find two different names in the case of $x+y$.

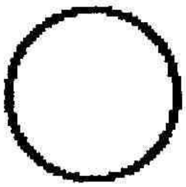
⑦ For the atomic orbitals we could draw a picture for the different energies of the orbitals

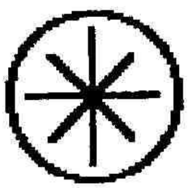


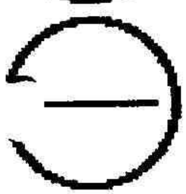
7 continued. For a drum the following modal pattern & energy (note energy $\propto$ frequency) were found. Please – draw an E diagram for drum modes.

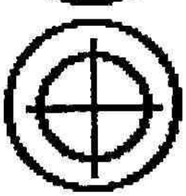
Diagram (Mode designation) Relative Frequency

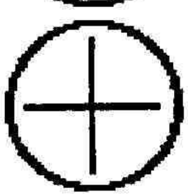
Frequency $\propto$ E

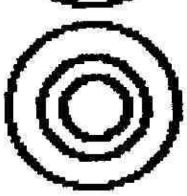

(0,1) 1.000 1S

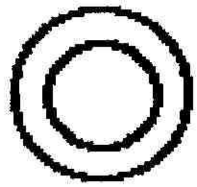

(4,1) 3.156

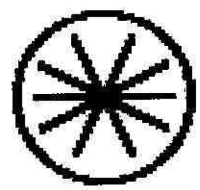

(1,1) 1.594 2p

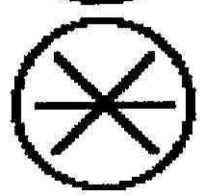

(2,2) 3.501

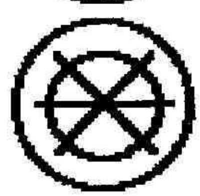

(2,1) 2.136 3d

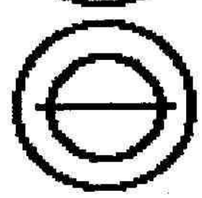

(0,3) 3.600

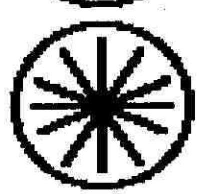

(0,2) 2.296 2S


(5,1) 3.652


(3,1) 2.653


(3,2) 4.060


(1,2) 2.918 3P


(6,1) 4.154

Lecture IV continued.

① We have been told a certain number of "facts" in this course

① e^- lie in orbitals

② orbitals have n, l, m_l & m_s quantum numbers. The orbitals have names such $4d_{xz}$ & $3p_x$.

③ The energies of the orbitals follow the Aufbau principle

② In the last class(es) we discovered that these same facts (or should I call them pseudo-facts) parallel the facts underlying sound & music.

① sound lies in sound waves.

② Sound waves have names such as $4d_{xz}$ & $3p_x$. (∴ sound wave have n, l & m_l "quantum" numbers)

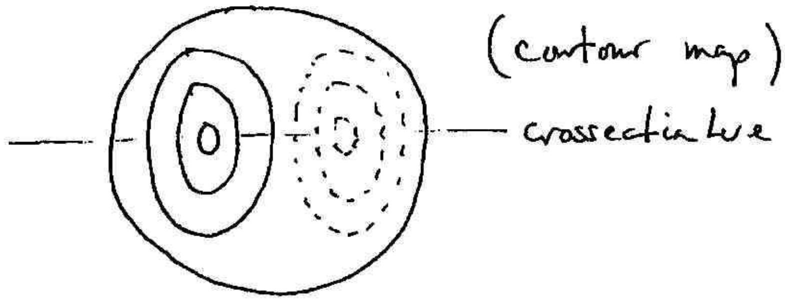
③ Each of these fundamental sound waves has a specific energy [see problem set 1, problem 7] and we can set up a sound wave "Aufbau principle".

③ In this lecture we will consider the analogy between sound & e^-. [See pp. 511-516 of Zumdahl] (In Zumdahl, the writing is about light, not sound. Light also goes by waves, but waves which travel at the speed of light.)

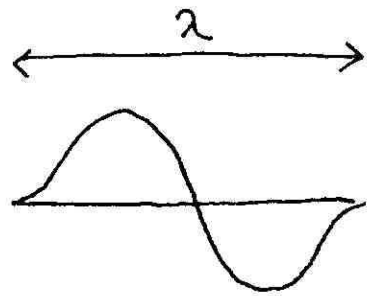
④ High sounds (high frequency & high energy) have <u>short</u> wavelengths, λ. The idea of wavelengths will be important both in chemistry & this course.

Consider (2 px)

drum mode :

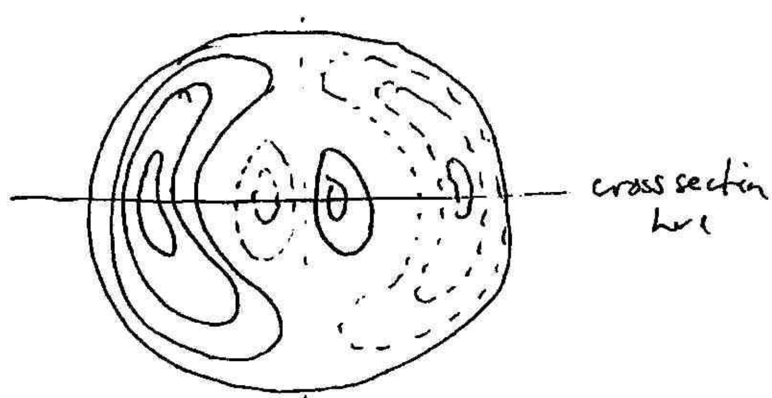


If we draw a cross-section

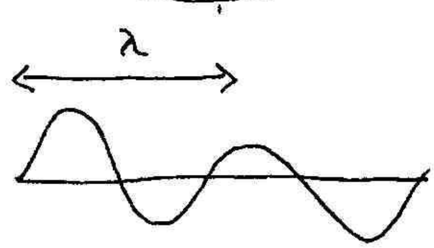


Compare to (3 px)

drum mode



with cross-section



$E(3p_x) > E(2p_x)$ $\lambda(3p_x) < \lambda(2p_x)$

E high $\Rightarrow$ λ short

⑤ In quantum mechanics

$$\lambda = \frac{h}{p} \quad \text{where } p = \text{momentum} = \text{mass} \cdot \text{velocity}$$

h = Planck's constant $\cong 6.6 \times 10^{-34}$ kg m^2/s

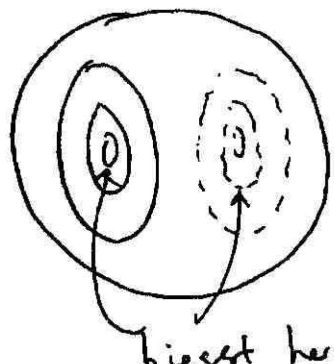
This is similar to the music case. As:

E high $\Rightarrow$ kinetic energy high $\Rightarrow$ momentum high $\Rightarrow \lambda$ short

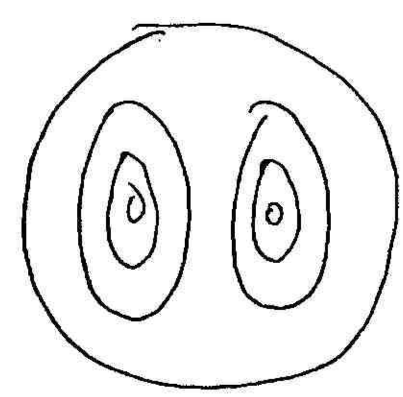
λ is the De Broglie wavelength.

⑥ If we were interested in finding out where the sound wave was most located:

As we would want to measure the heights of the drum to see where the values were biggest.

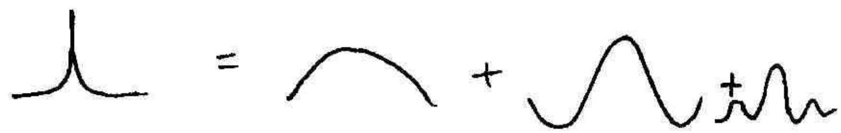


We want the absolute values of the height or the square



In just the same way for e^- we consider ψ^2 for electron location.

(7) All sounds can be made up of combination of the fundamental mode.

[Recall pizzacato 

+ ....]

All e^- "motion" (or activity) can be made up of a combination (we call it a linear combination) of the fundamental mods of the atomic orbitals.