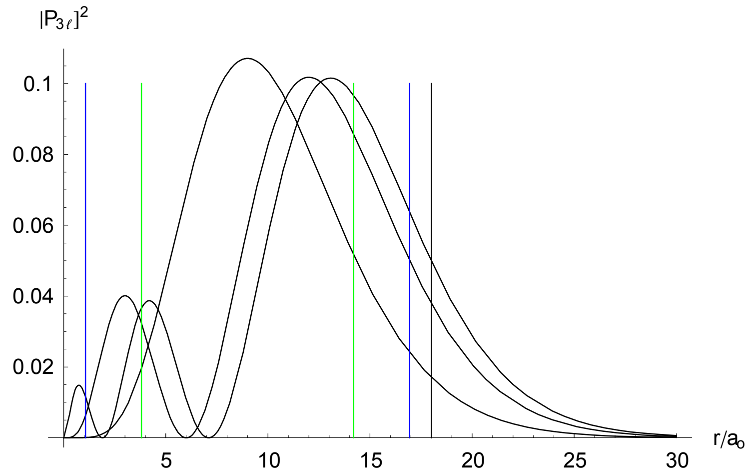
■ Penetration and shielding

We would like to understand the relative stability of many-electron subshells (fixed n but different ℓ) in terms of the distribution of electron density for the different subshells. Here are the electron densities for the $n = 3$ electrons in a hydrogen atom.



Hydrogen atom 3s (three peaks), 3p (two peaks) and 3d one peak) shell densities. Distance is in units of the Bohr radius, a_0. The vertical lines are the classical turning points (green for 3d, blue for 3p and black for 3s; the inner turning point for 3s is at $r = 0$), and so bracket the classically allowed region for each shell density.

The vertical lines mark the allowed region of each subshell. Since the allowed region for the 3d is bracketed by that for the 3p, which in turn is bracketed by that for the 3s, we expect the average distance of the 3d electron to be *closest* to the nucleus, followed by the average distance of the 3p electron, and the 3s electron to *farthest* from the nucleus. The actual average distances, computed as

$$\langle r_{3\ell} \rangle = \int_0^\infty \, | \, P_{3\ell}(r) \, |^2 \, dr \, ,$$

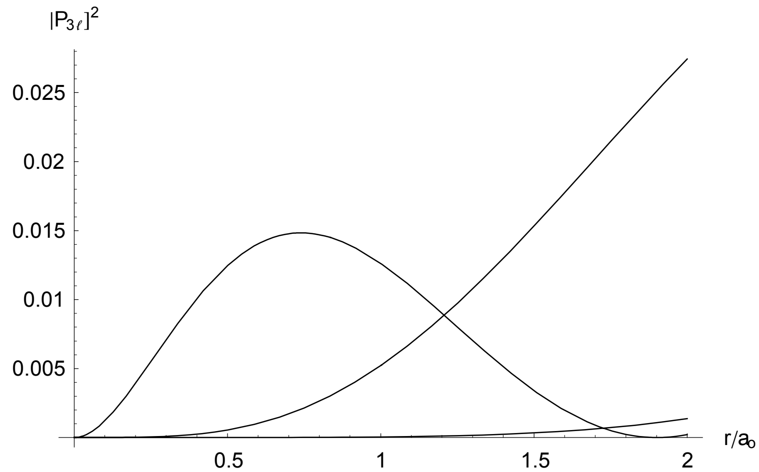
are

3s	13.5
3p	12.5
3d	10.5

Average distance, in $a_0 = 0.527$ Å, from the nucleus of hydrogen $n = 3$ electrons.

This ordering of average distances may seem surprising, since we know in many-electron atoms, the 3s subshell is more stable than the 3p subshell, which is more stable than the 3d subshell, and this in turn might lead us to believe that in many electron atoms the 3s electron would be *closes*t to the nucleus.

In fact, the origin of the greater stability of the 3s is due not to the average distance of the electron but instead to the *relative amount of the electron density close to the nucleus* in the different subshells. Here is a plot of the hydrogen 3s, 3p and 3d shell densities near the nucleus,



Hydrogen atom 3s (peak), 3p (quadratic rise from $r = 0$) and 3d (cubic rise from zero) shell densities near the nucleus. Distance is in units of the Bohr radius, a_0.

and here is the fraction of electron density in each subshell within 1 a_0 of the nucleus.

3s	0.0099
3p	0.0013
3d	6.5×10^{-6}

Fraction of hydrogen $n = 3$ electron density within 1 a_0 of the nucleus.

The results show that within 1 a_0 of the nucleus the 3p shell density is only 13% of the 3s shell density, and the 3d shell density is essentially zero.

This means that both 3 s and 3p electrons are present, a 3p electron will see less nuclear charge than a 3s electron, due to the shielding of the nucleus by the fraction of the 3s electron that is closer to the nucleus that the 3p electron. Similarly, a 3d electron will be shielded by both 3s and 3p electrons and so will see still less nuclear charge than a 3p electron. Since a 3d electron is shielded most, it will see the least nuclear charge and so be the least tightly bound. In this way we can understand why in many-electron atoms that within a shell, subshells fill in the order s, p, d, ….

Here is the fraction of electron density all of the subshells through $n = 4$ within 1 a_0 of the nucleus.

1s	0.32
2s	0.034
3s	0.0099
4s	0.0041
2p	0.0037
3p	0.0013
4p	0.00056
3d	6.5×10^{-6}
4d	3.9×10^{-6}
4f	3.4×10^{-9}

Fraction of hydrogen electron density within 1 a_0 of the nucleus for the $n = 1, 2, 3,$ and 4 subshells.

See if you use these fractional electron densities to understand the filling order 1s → 2s → 2p → 3s → 3p.