Physics 8164 - Many-Particle Quantum Theory - Prof. Umar

1 Radial probability densities for electrons in an atom

In our lecture notes (chapter 3, p. 10) we derived a simple expression for the ground state density of an N-electron atom if we neglect the electron-electron interaction. In this case the electron density of an atom is simply the sum of the probability densities (= absolute value squared of the wave functions) for all occupied single particle states.

The spatial part of the electronic wave functions has the structure

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta,\phi)$$

In Niels Bohr's semi-classical atomic model, the radii r_n of the spherical electronic orbits increase with the square of the principal quantum number n, i.e.

$$r_n = n^2 \left(\frac{a_0}{Z}\right), \quad (n = 1, 2, 3, ...)$$

where $a_0 = 0.55$ Å is the Bohr radius of the hydrogen atom, and Z denotes the atomic number (= number of protons in the nucleus). In quantum mechanics, the radial probability densities

$$r^2 [R_{n,\ell}(r)]^2$$

are most closely related to these classical radii. The factor r^2 in the last expression arises from the volume element in spherical coordinates.

Below we plot the 1-D radial probability densities for the lowest quantum states with principle quantum numbers n = 1, 2, 3.





Figure 1: For n = 1, the probability density peaks at 1 Bohr radius / Z.





Figure 2: For n = 2, the probability densities peak at 3-5 Bohr radii /Z (for the two angular momentum substates).



Figure 3: For n = 3, the probability densities peak at 8-13 Bohr radii / Z (for the three angular momentum substates).

From these plots we infer that the probability densities for n = 1, 2, 3 peak at different radial positions which roughly agree with the semi-classical Bohr radii r_n given above. This suggests that the total density of an N-electron atom (which can be measured) might reveal the shell structure of the occupied orbitals! This is indeed the case. We will look at atomic electron densities later in Chapter 7 within the context of atomic Hartree-Fock calculations which take the electron-electron interaction into account "on average" (via the one-body mean field potential).

2 Position probability densities in 3-D ('atomic orbitals')

We calculate now the position probability densities in 3-D space. In cylindrical coordinates (z, r, ϕ) we have

$$\rho_{n,\ell,m_\ell}(z,r,\phi) = [\psi^*\psi]_{n,\ell,m_\ell}(z,r,\phi) +$$

The probability densities are axially symmetric around the z-axis. In the contour plots below we show the quantities

$$\rho_{n,\ell,m_\ell}(z,r,\phi=0) \; .$$



Figure 4: Probability density $\psi^* \psi$ for the state $|n = 1, \ell = 0, m_\ell = 0 > .$



Figure 5: Probability densities $\psi^*\psi$ for the state $|n = 2, \ell = 1 >$. Left side: for the magnetic substate $|m_\ell = 0 >$. Right side: for the magnetic substates $|m_\ell = \pm 1 >$.



Figure 6: Probability density $\psi^*\psi$ for the state $|n=4,\ell=2,m_\ell=0>$.