5.5 Summary : the spectrum of the hydrogen atom.

The spectrum of $H = -\Delta - \frac{1}{\|x\|}$ in $L^2(\mathbb{R}^3)$ consists of continuous spectrum, $\sigma_c(H) = [0, \infty)$, and point spectrum, $\sigma_p(H) = \{-\frac{1}{4n^2},\ n = 1, 2, \dots\}$. The eigenvectors are

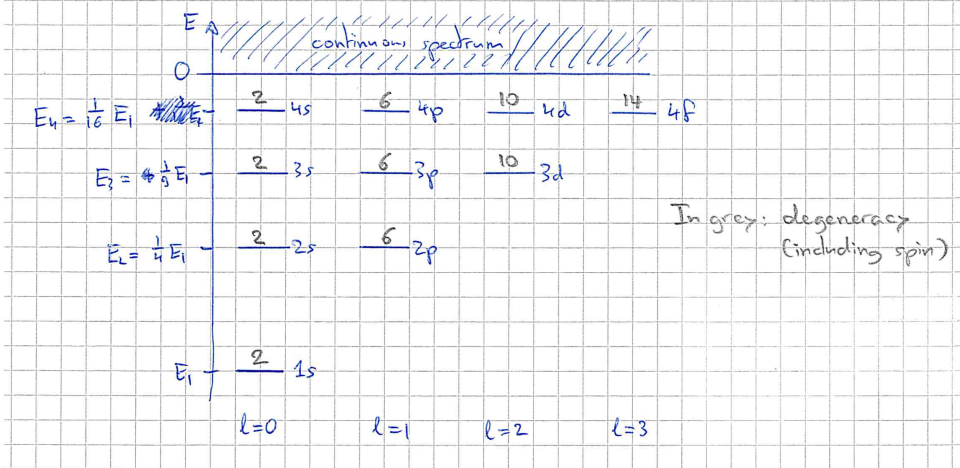
$$f_{n,\ell,m}(r, \theta, \varphi) = R_{n,\ell}(r)\, Y_\ell^m(\theta, \varphi)$$

where $n = 1, 2, 3, \dots$; $\ell = 0, \dots, n-1$; $m = -\ell, -\ell+1, \dots, \ell$.
The functions $R_{n,\ell}$ are of the form

$$R_{n,\ell}(r) = \frac{1}{n}\left(\frac{r}{n}\right)^\ell e^{-\frac{r}{2n}}\, F_{n,\ell}\left(\frac{r}{n}\right)$$

where $F_{n\ell}$ is a polynomial. The fcts Y_ℓ^m are the spherical harmonics.

The spectrum is usually represented as follows :



In a hydrogen atom at rest, the lone electron occupies the eigenstate with the lowest eigenvalue. If we neglect the interactions between electrons, the situation for bigger atoms is similar, all electrons occupy the states with lowest energy. But we must take into account

- the Pauli exclusion principle : two electrons cannot be in the same state, because they are fermions ;
- the spin of the electron : this is an internal degree of freedom, and the consequence is that each eigenvector has degeneracy 2.

Then the electronic structure is obtained by populating the "bands" with lower energy, with 2 electrons in 1s, 8 electrons in 2s and 2p, etc... One could expect that the presence of electron interactions makes this description too naive, but it stays relevant in the "central potential approximation". The effect of interactions is to modify the energy of the bands, so 2s becomes smaller than 2p, etc... Since this approximation is at the centre of our understanding of the periodic table of elements, it is worth discussing it.

The full Hamiltonian for the Z electrons around a nucleus with atomic number Z is

$$H = \sum_{j=1}^{Z} \left(\vec{P}_j^{\,2} - \frac{Z}{\|x_j\|} \right) + \sum_{1 \le i < j \le Z} \frac{1}{\|x_i - x_j\|}$$

$\vec{P}_j^{\,2}$: kinetic energy of jth electron

$$\approx \sum_{j=1}^{Z} \left(\vec{P}_j^{\,2} + V(\|x_j\|) \right).$$

This is justified by the fact that electrons should be spread in a spherically uniform way, and by Newton's theorem (the charges can be considered as all located at the centre, at least those that closer to the origin). This suggests that the effective potential $V(r)$ should behave as

$$V(r) \approx \begin{cases} -\frac{Z}{r} & \text{if } r \text{ is small} \\ -\frac{1}{r} & \text{if } r \text{ is large} \end{cases}$$

The eigenvalue equation for the hydrogen atom still applies, but the radial equation becomes

$$\left(-\Delta_r + \frac{\ell(\ell+1)}{r^2} + V(r) \right) R(r) = E(r).$$

The effective potential has the same qualitative behaviour as before, $V(r) \sim -\frac{1}{r}$ both around 0 and at ∞. We still get solutions indexed by n, ℓ, m with $n = 1, 2, \ldots$; $\ell = 0, \ldots, n-1$; $m = -\ell, \ldots, \ell$. But energy levels (i.e. eigenvalues) depend on both n and ℓ, not only on n.

The order of succession of the levels is essentially independent of Z and is

$$1s,\ 2s,\ 2p,\ 3s,\ 3p,\ [4s, 3d],\ 4p,\ [5s, 4d],\ 5p, \ldots$$

where $[\,,\,]$ means that the levels have almost identical energy.

From these considerations follow the basic principles of Chemistry! This accounts for the amazing regularity of the periodic table of elements (discovered principally by Mendeleev, 1869) and this explains chemical bonds and the formation of molecules, at least qualitatively.