Lecture 5, Jan 19, 2023

Multi-Electron Systems

- For helium, we have the famed 2-body problem that cannot be solved due to the repulsion between the two electrons
- We can use an approximate solution: independent particle approximation: treat each electron as moving in a time-average potential defined by the other electron to define an effective potential
  - The electron will screen some of the positive charge but there will always be an effective charge of +1 or more
  - Assume a hydrogenic (central force) wavefunction ψ' for the two electrons, which gives us an average electron distribution, from which we can get an effective potential U'
    - i.e. assume a potential $U(r) = -Z_{eff}(r)\frac{ke^2}{r}$
    - The effects of other electrons are smeared out to be radially symmetric and expressed through the effective charge Z_{eff}
  - Solve for the first electron to define a new ψ', and repeat with the second electron
  - Repeat this until the calculated energy converges
- Variational theorem: the true wavefunction always gives the absolute minimum energy
  - This can be used to determine the effective charge Z_{eff} due to the screening
  - Make Z a parameter, use solution $\psi(\vec{r}_1, \vec{r}_2) = e^{-Z_{eff}(r_1+r_2)}$
  - Determine E in terms of Z_{eff}, and set $\frac{\mathrm{d}E}{\mathrm{d}Z_{eff}} = 0$ to find the effective charge that results in the minimum energy
- In a multi-electron atom, the energy levels are no longer degenerate and now it depends on the details of the solutions
- e.g. in the 2s orbital we have a little peak below the p orbitals (and the Bohr radius)
  - This makes it so that 2s and 2p are no longer degenerate
  - The 2s is more tightly held and so has a bigger effective charge
  - Energy depends on both n and l (but not m or m_s)

Pauli Exclusion Principle

- No two electrons in a quantum system can occupy the same state
- No two electrons can have the same quantum numbers, so n, l, m, m_s is a unique "quantum address"
- Hund's Rule: the mos stable electronic state within a degenerate set of orbitals is the state with maximum spin multiplicity (i.e. the one with the largest number of unpaired electron spins)