Electrons in atoms

- Atomic units (a.u.) --> standard usage
  - electron mass m_e unit of mass
  - elementary charge e unit of charge
  - length and time such that numerical values of $\hbar$ and $4\pi\epsilon_0$ are unity
  - then atomic unit of length Bohr radius

$$\text{a.u. (length)} = a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} \approx 5.29177 \times 10^{-11} \text{ m}$$

  - and time $$\text{a.u. (time)} = \frac{a_0}{\alpha c} \approx 2.41888 \times 10^{-17} \text{ s}$$
  - where $$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$$ is the fine structure constant
  - energy unit = Hartree $$E_H = \frac{\hbar^2}{m_e a_0^2} \approx 27.2114 \text{ eV}$$

Hamiltonian in a.u.

- Most of atomic physics can be understood on the basis of

$$H_N = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2} - \sum_{i=1}^{N} \frac{Z}{|\boldsymbol{r}_i|} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + V_{mag}$$

- for most applications $V_{mag} \Rightarrow V_{so}^{eff} = \sum_i \zeta_i \, \boldsymbol{\ell}_i \cdot \boldsymbol{s}_i$

- Relativistic description required for heavier atoms
  - binding sizable fraction of electron rest mass
  - binding of lowest s state generates high-momentum components
- Sensible calculations up to Kr without V_{mag}
- Shell structure well established

Shell structure

- Simulate with

$$H_0^N = \sum_{i=1}^{N} H_0(i)$$

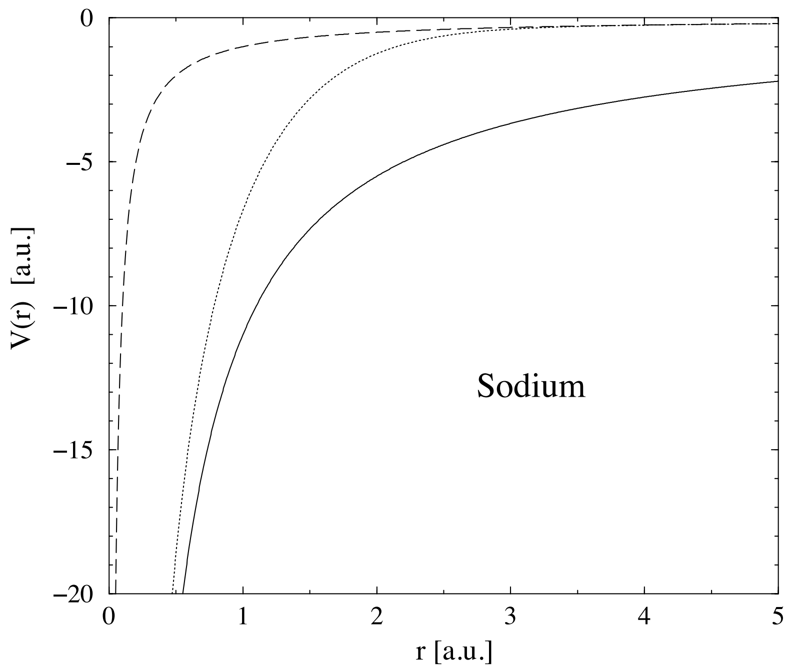
- with

$$H_0(i) = \frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{r_i} + U(\boldsymbol{r}_i)$$

- even without auxiliary potential $\Rightarrow$ shells
  - hydrogen-like: $(2\ell + 1) * (2s + 1)$ degeneracy
  - but $\varepsilon_n = -\dfrac{Z^2}{2n^2}$ does not give correct shell structure (2,10,28...
  - degeneracy must be lifted
  - how?

Effect of other electrons in neutral atoms

- Consider effect of electrons in closed shells for neutral Na
- large distances: nuclear charge screened to 1
- close to the nucleus: electron "sees" all 11 protons
- approximately:



- lifts H-like degeneracy: $\varepsilon_{2s} < \varepsilon_{2p}$

$$\varepsilon_{3s} < \varepsilon_{3p} < \varepsilon_{3d}$$

- "Far away" orbits: still hydrogen-like!

Example: Na

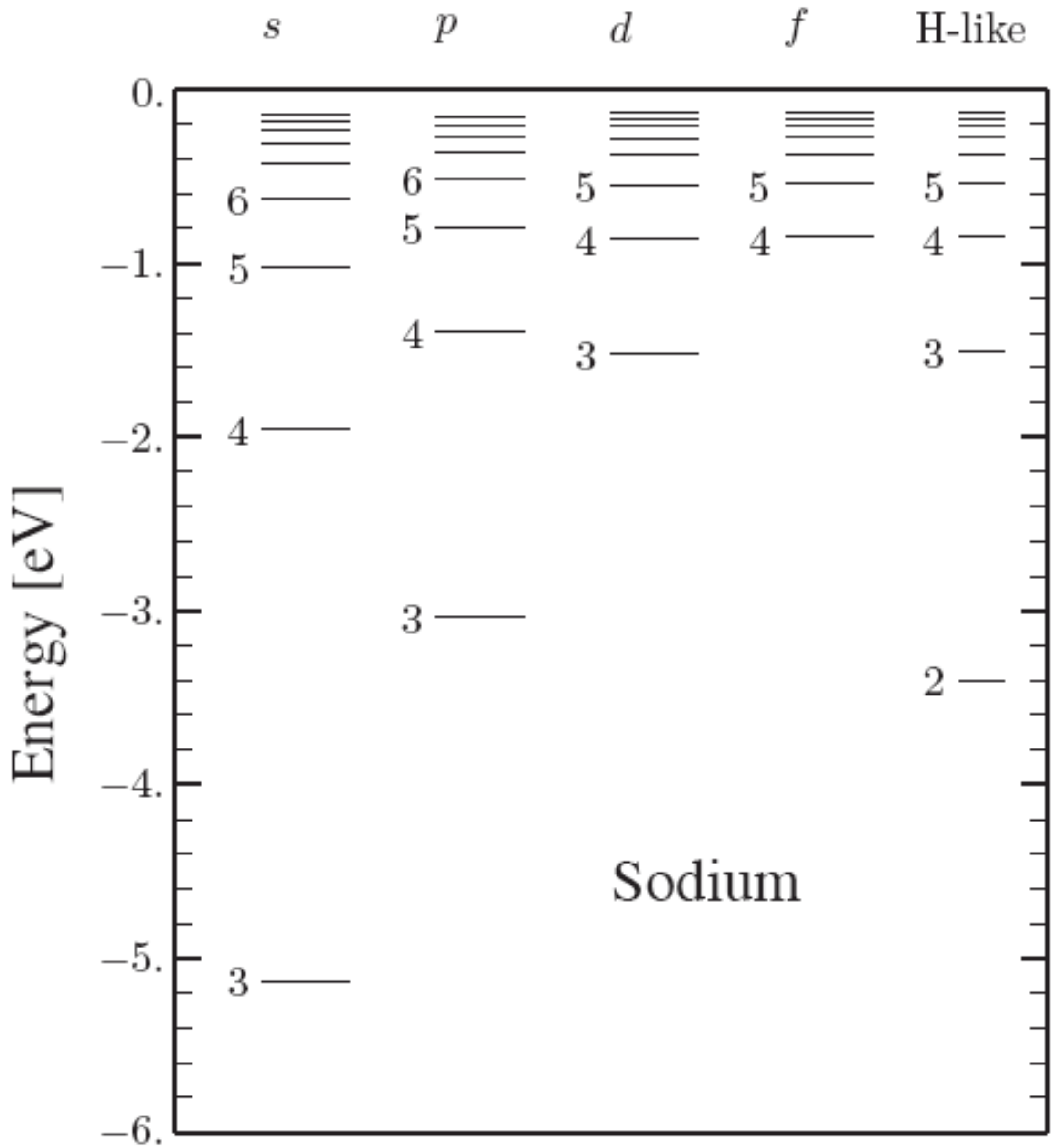
- Fill the lowest shells
- Use schematic potential

$$H_0 \left| n\ell m_\ell m_s \right\rangle = \varepsilon_{n\ell} \left| n\ell m_\ell m_s \right\rangle$$

- Ground state: fill lowest orbits according to Pauli

$$\left| 300 m_s, 211\tfrac{1}{2}, 211 -\tfrac{1}{2}, \ldots, 100\tfrac{1}{2}, 100 -\tfrac{1}{2} \right\rangle \equiv \left| \Phi_0(\mathrm{Na}) \right\rangle$$

- Excited states?



Closed-shell atoms

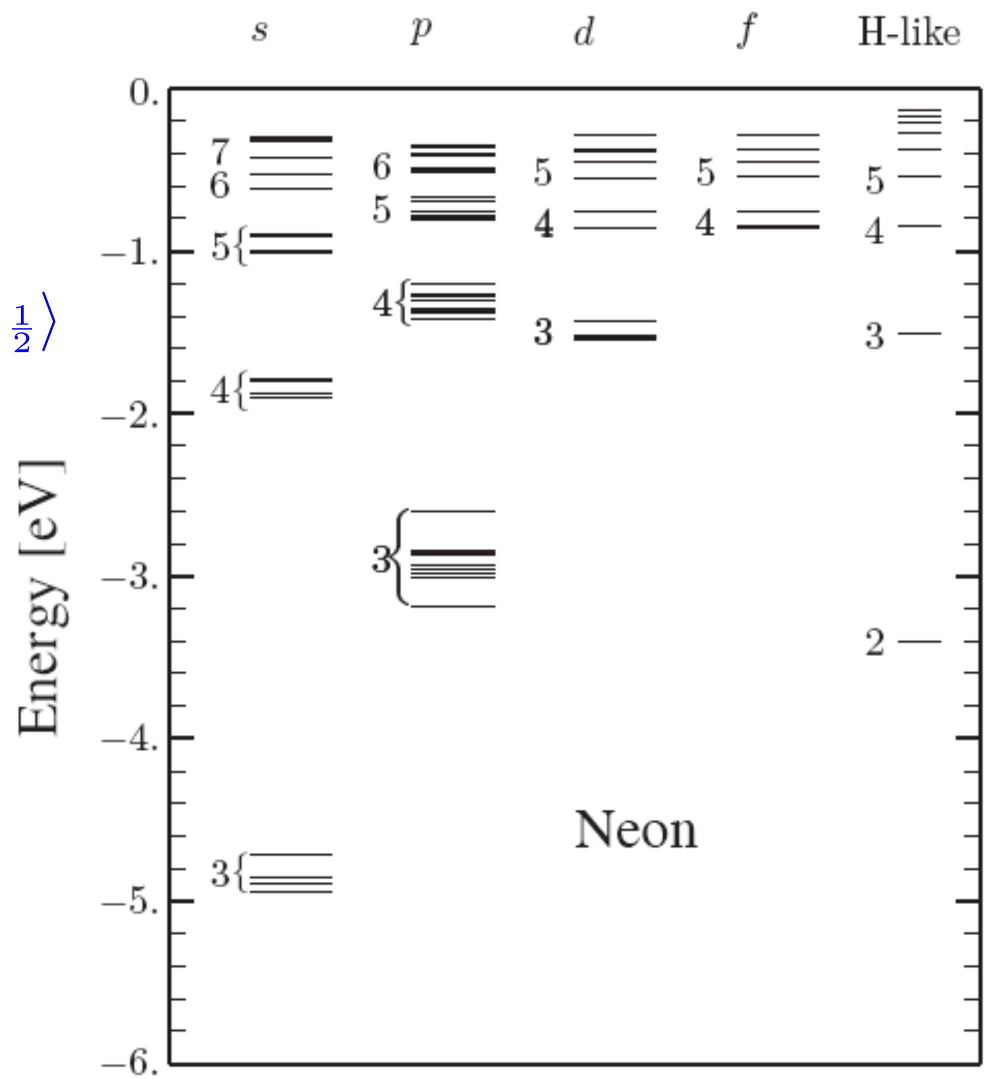
- Neon
- Ground state

$$|\Phi_0(\mathrm{Ne})\rangle = |211\tfrac{1}{2}, 211-\tfrac{1}{2}, ..., 100\tfrac{1}{2}, 100-\tfrac{1}{2}\rangle$$

- Excited states

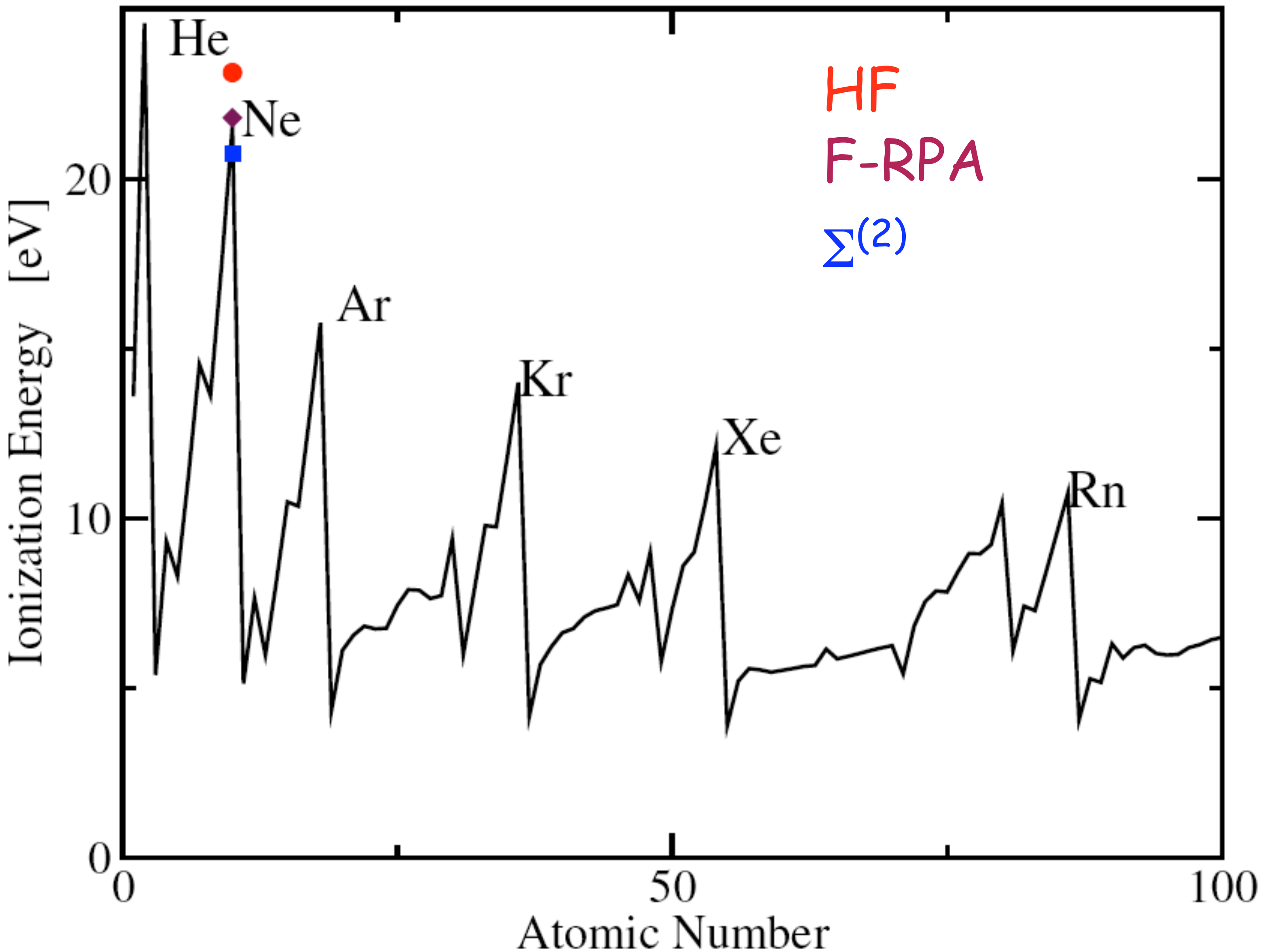
$$|n\ell\ (2p)^{-1}\rangle = a^\dagger_{n\ell} a_{2p}\, |\Phi_0(\mathrm{Ne})\rangle$$

- operators: see later
- Note the H-like states
- Splitting?

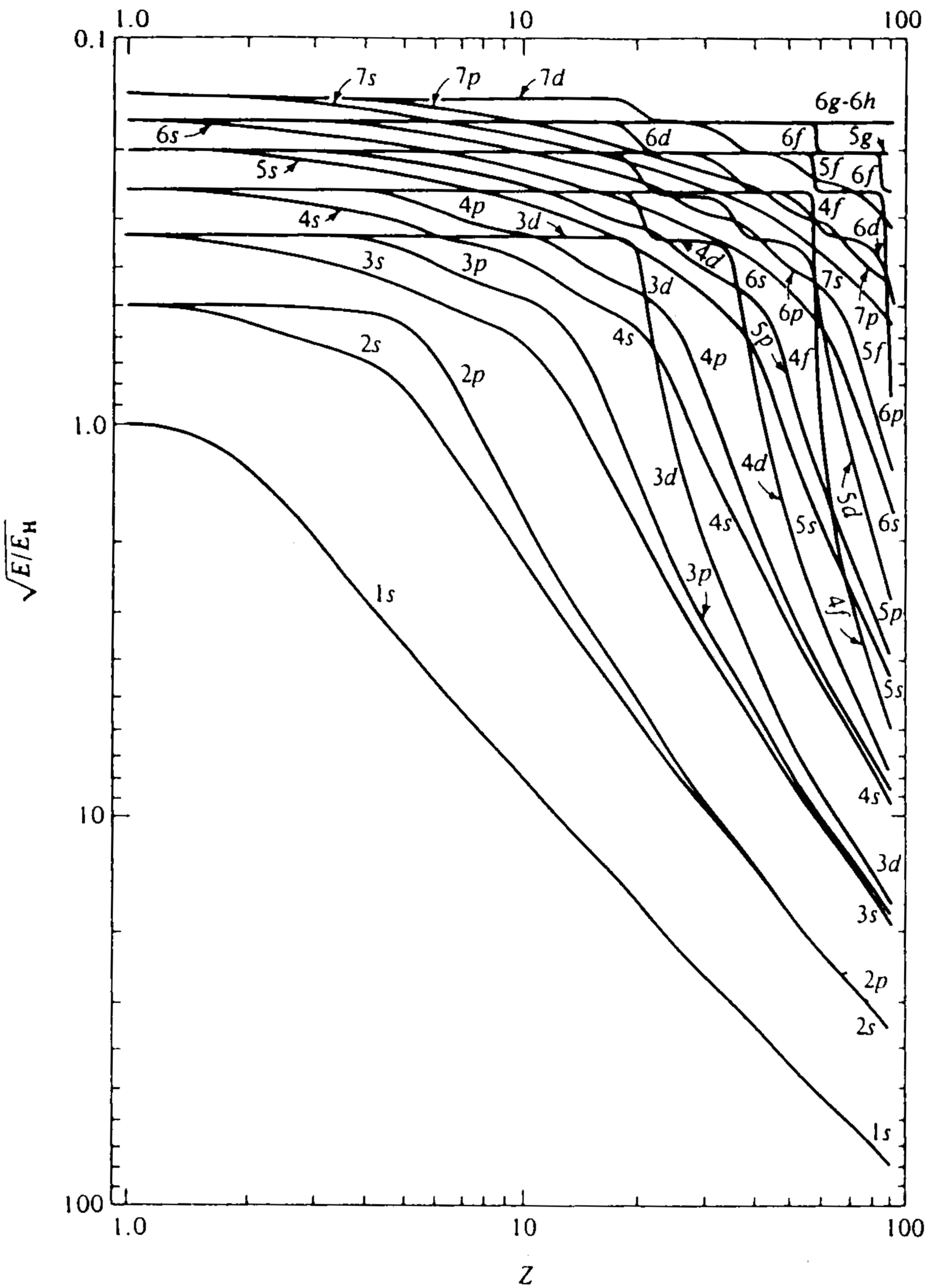


- Basic shell structure of atoms understood ⇒ IPM

Periodic table

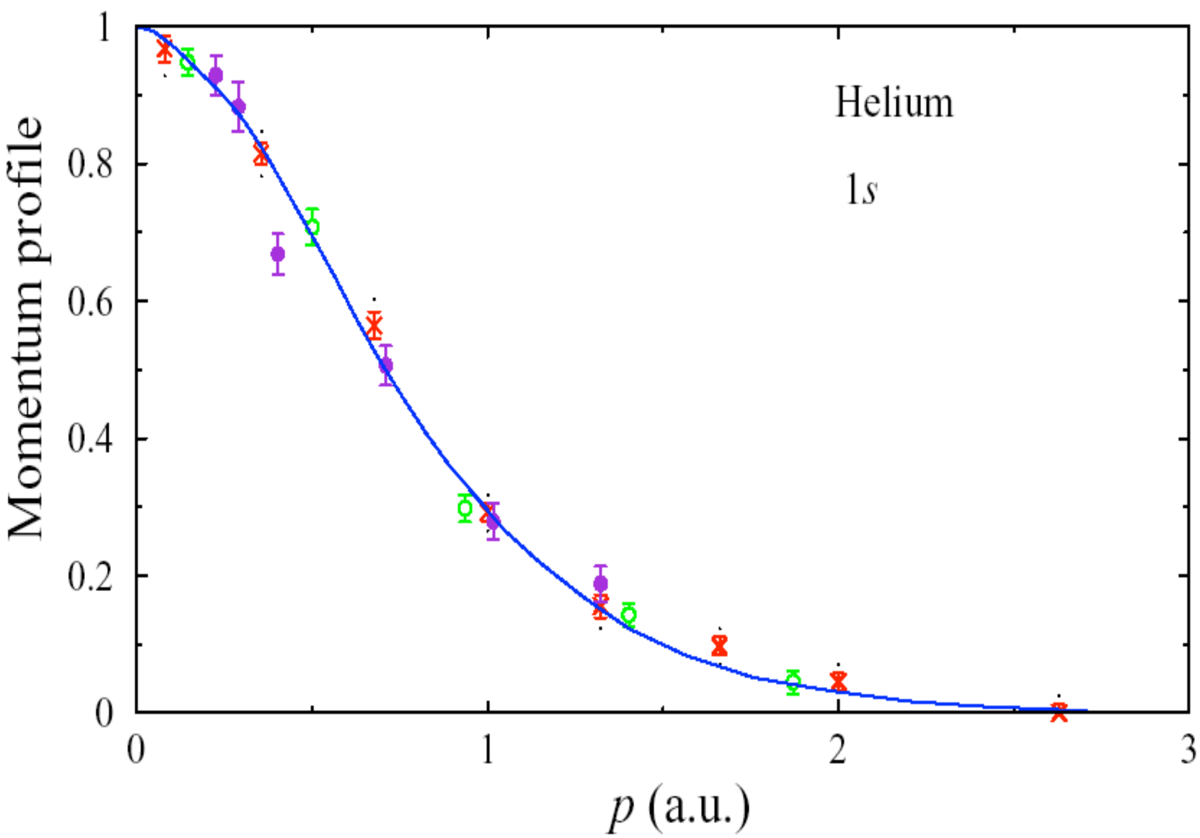


Level sequence (approximately)



Helium

- IPM description is very successful
- Closed-shell configuration $1s^2$
- Reaction more complicated than for Hydrogen
- DWIA (distorted wave impulse approximation)



$$S = \int d\boldsymbol{p} \left| \langle \Psi_n^{N-1} | \, a_{\boldsymbol{p}} \, | \Psi_0^N \rangle \right|^2$$

agreement with IPM!

$\rightarrow 1$

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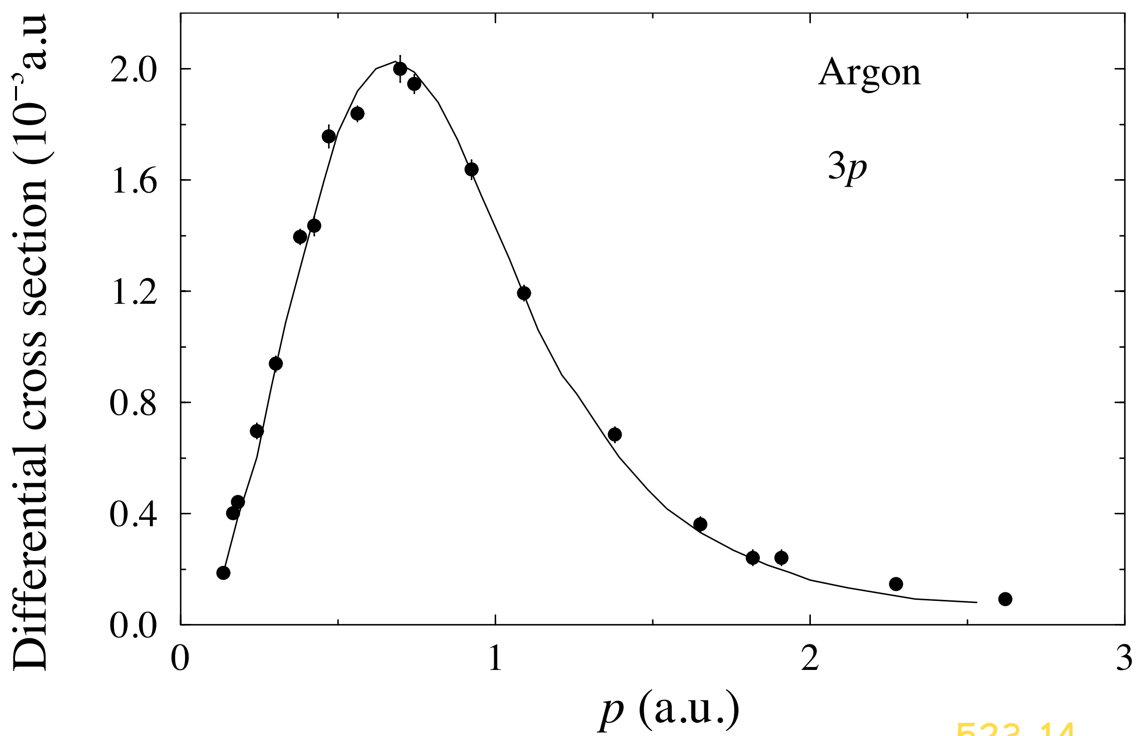
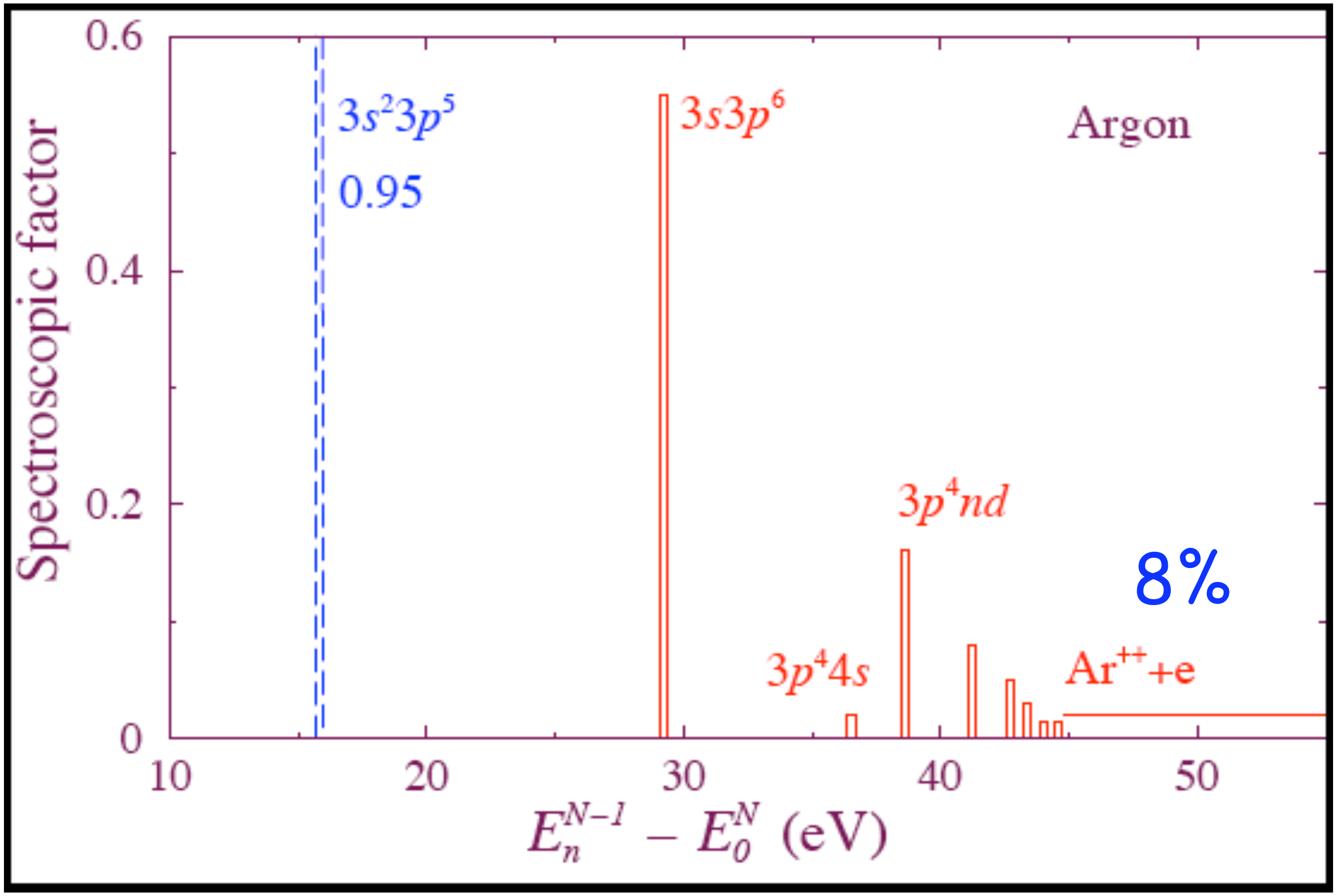
Other closed-shell atoms

- Spectroscopic factor becomes less than 1
- Neon $2p$ removal: S = 0.92 with two fragments each 0.04
- IPM not the whole story: fragmentation of sp strength
- Summed strength: like IPM
- IPM wave functions still excellent
- Example: Argon $3p$ S = 0.95
- Rest in 3 small fragments



Argon spectroscopic factors

- s strength also in the continuum: $Ar^{++} + e$
- note vertical scale
- red bars: 3s fragments exhibit substantial fragmentation



Fragmentation in atoms

- ~All the strength remains below (above) the Fermi energy in closed-shell atoms
- Fragmentation can be interpreted in terms of mixing between

$$a_\alpha \left|\Phi_0^N\right\rangle$$

- and

$$a_\beta a_\gamma a_\delta^\dagger \left|\Phi_0^N\right\rangle$$

- with the same "global" quantum numbers
- Example: Argon ground state $\left|\Phi_0^N\right\rangle = \left|(3s)^2(3p)^6(2s)^2(2p)^6(1s)^2\right\rangle$
- Ar$^+$ ground state $\left|(3p)^{-1}\right\rangle = a_{3p}\left|\Phi_0^N\right\rangle = \left|(3s)^2(3p)^5(2s)^2(2p)^6(1s)^2\right\rangle$
- excited state $\left|(3s)^{-1}\right\rangle = a_{3s}\left|\Phi_0^N\right\rangle = \left|(3s)^1(3p)^6(2s)^2(2p)^6(1s)^2\right\rangle$
- also $\left|(3p)^{-2}4s\right\rangle = a_{3p}a_{3p}a_{4s}^\dagger\left|\Phi_0^N\right\rangle = \left|(4s)^1(3s)^2(3p)^4(2s)^2(2p)^6(1s)^2\right\rangle$
- and $\left|(3p)^{-2}nd\right\rangle = a_{3p}a_{3p}a_{nd}^\dagger\left|\Phi_0^N\right\rangle = \left|(nd)^1(3s)^2(3p)^4(2s)^2(2p)^6(1s)^2\right\rangle$