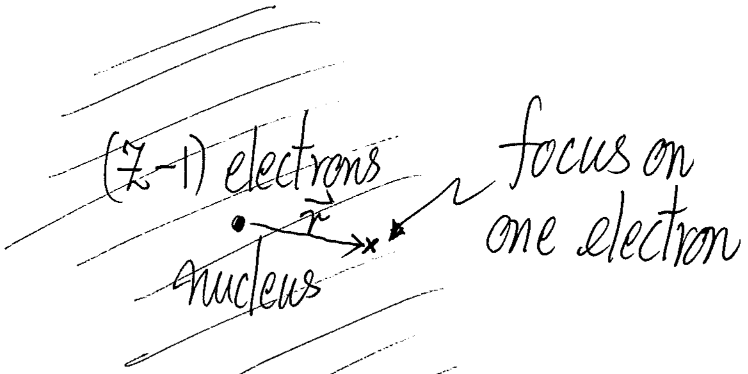
D. Independent-Particle Approximation (IPA): Basic Ideas

- Focus on one electron (there are $(Z-1)$ other electrons)
- That electron sees $(+Ze)$ nucleus plus averaged effect of $(Z-1)$ other electrons (as discussed in Sec. A, B, C)



$\boxed{\text{What is } V(\vec{r})\text{?}}$

pretends to have a single-electron problem (this is $V^{\text{eff}}(\vec{r})$)

- Approximately, $V(\vec{r}) = \underbrace{V(r)}_{\text{spherically symmetric}^{+}}$

so that nice features are retained...

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

and $\varepsilon_{n\ell}$

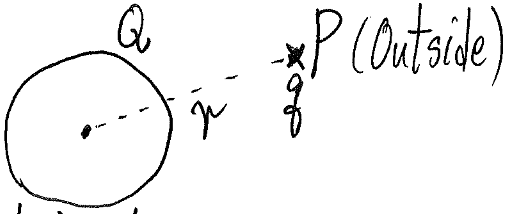
and $\hat{L}^2\, Y_{\ell m_\ell} = \ell(\ell+1)\hbar^2\, Y_{\ell m_\ell}$

$\hat{L}_z\, Y_{\ell m_\ell} = m_\ell\hbar\, Y_{\ell m_\ell}$

[+] Also called "Central-field approximation"

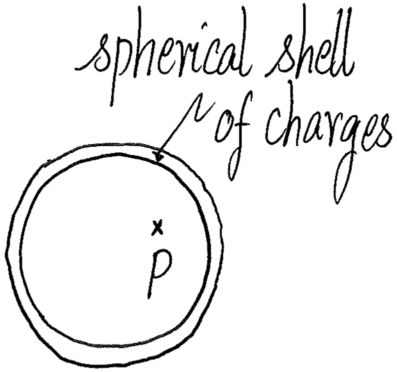
- Roughly, how does $V(r)$ look like?

(a)



Total charge Q [nucleus + other electrons] distributed spherically

(b)



EM theory: test charge q at P feels NO Net force from charges in the shell

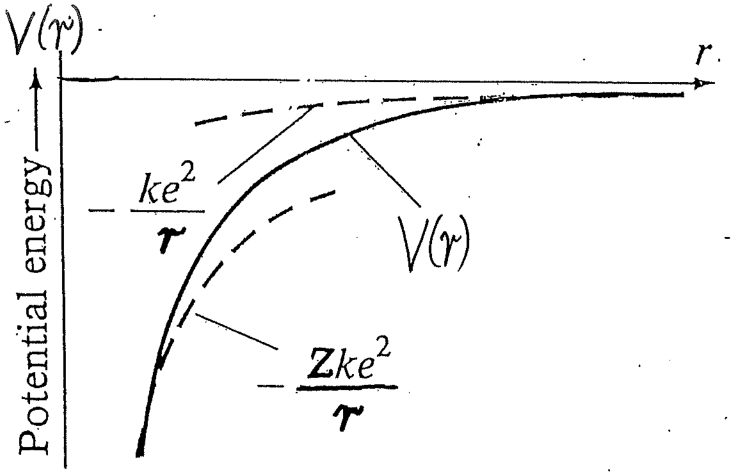
Force on test charge q at $\vec{r}$

$$= \frac{qQ}{4\pi\varepsilon_0 r^2} \leftarrow \text{[Net charge in sphere]}$$

$\therefore$ r far away from nucleus, see net charge $+Ze-(Z-1)e=+e$ [screening]

$\therefore$ r close to nucleus, electron sees the $+Ze$ nucleus (other $(Z-1)$ electrons are the outer shells)

$$V(r) \approx \begin{cases} -\dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{r} & (r \text{ outside other electrons}) \\ -\dfrac{1}{4\pi\varepsilon_0}\dfrac{Ze^2}{r} & (\text{as } r\to 0\text{, OR } r \text{ "inside" other electrons} \end{cases}$$



The IPA potential energy $V(r)$ of an atomic electron in the field of the nucleus plus the average distribution of the $Z-1$ other electrons. As $r \to \infty$, V approaches $-ke^2/r$; as $r \to 0$, V approaches $-Zke^2/r$.

$$\boxed{V(r) \text{ is } \underline{\text{NOT}} \text{ of } \underline{\text{Coulombic Form}}}$$

<u>e.g.</u>

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Z_{eff}(r)\, e^2}{r}$$

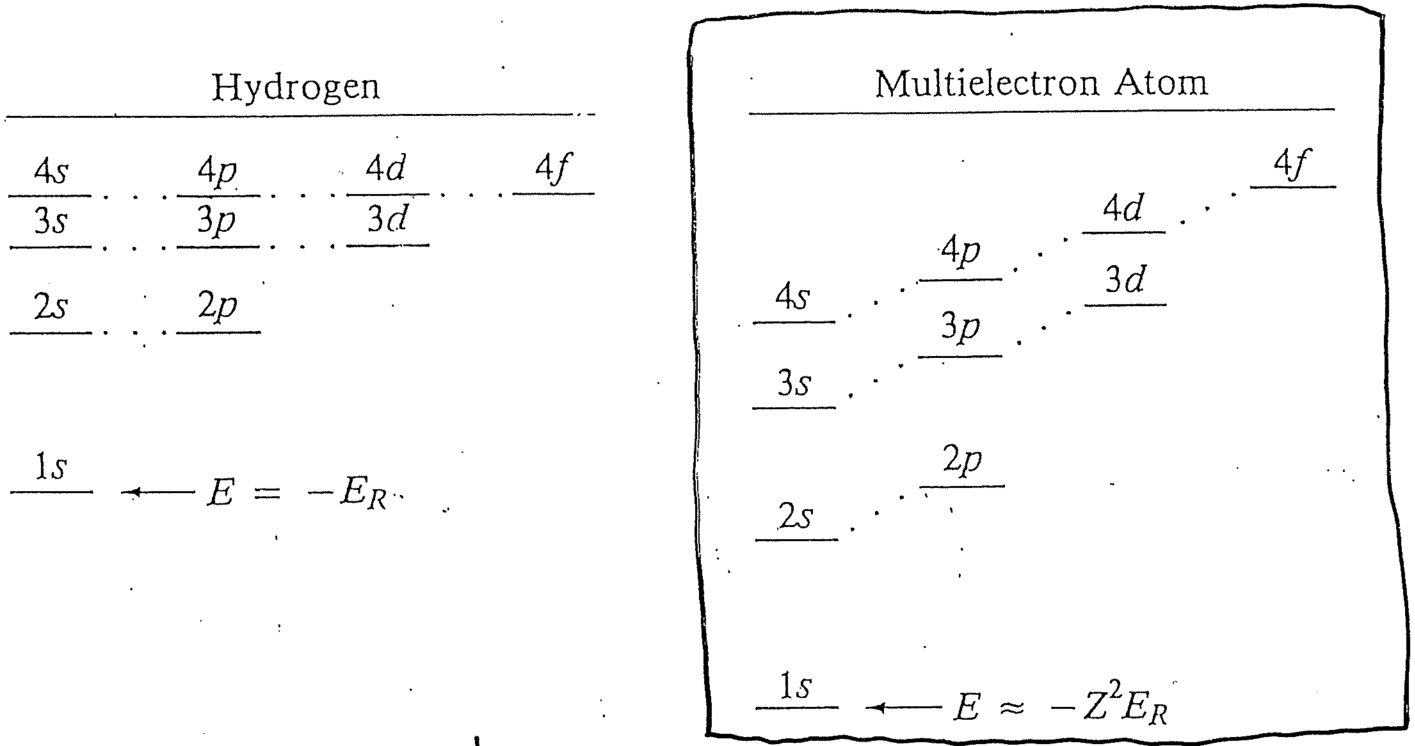
with $Z_{eff}(r)$ = r-dependent "effective charge"

$$\approx \begin{cases} 1 & \text{far away from nucleus} \\ Z & \text{close to nucleus} \end{cases}$$

- Spherically symmetric
- NOT strictly Coulombic
- $V(r)$ goes into single-electron TISE

- $\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\phi)$ "saved" single-electron states idea
- Energy of single-electron states: $\mathcal{E}_{n\ell}$ (not $\mathcal{E}_n$ as in hydrogen)
- Given ℓ, $m_\ell = \ell, \dots, -\ell \Rightarrow (2\ell+1)$ values of m_ℓ
- Electron has spin quantum number $s = 1/2$; $m_s = +1/2, -1/2$
- $\mathcal{E}_{n\ell}$ has degeneracy $\underset{\substack{\Uparrow \\ \text{spin}}}{2} \cdot \underbrace{(2\ell+1)}_{\text{from } m_\ell}$ e.g. $\overset{n=3}{3}\overset{\ell=2}{d}$ $2\cdot(2\ell+1) = \underline{10}$ states
- Including spin, states are labelled by $(n, \ell, m_\ell, \overset{\frac{1}{2}\text{ always}}{\overset{\parallel}{(s)}}, m_s)$
- Each atom has its own set of $\mathcal{E}_{n\ell}$ energy levels ($\because V(r)$ is different)

Schematic†



Schematic† energy-level diagrams for a hydrogen atom and for one of the electrons in a multielectron atom. In hydrogen, all states with the same n are degenerate. In multielectron atoms, states with lower l are more tightly bound because they penetrate closer to the nucleus. In many atoms this effect results in the 4s level being lower than the 3d, as shown here.

† Each atom is a separate QM problem. Thus, each atom has its own alignment of single-electron energy levels. Sorry! It is **not** one size fits all.

General Discussion on pattern of energy levels in IPA

- Lowest energy level : 1s $(n=1, l=0)$ degeneracy = 2 (due to spin m_s)

  1s wavefunction[+] – close to nucleus[+] $\Rightarrow Z_{eff} \approx Z$

  $$\varepsilon_{1s} \approx -Z^2 \cdot (13.6)\ \text{eV}$$ [Q: How are X-rays given out?]

- $n=2$ $(l=0, l=1$ OR $2s, 2p)$

  $\varepsilon_{2s} \neq \varepsilon_{2p}$ ($\because$ $V(r)$ not Coulombic)

  Which one is lower? $\varepsilon_{2s} < \varepsilon_{2p}$

  [2s wavefunction[+] has bump at small r, thus sees more nuclear charge $\Rightarrow$ more stable (lower energy))

[+] Although each atom is a new QM problem, it is useful to bear in mind properties of hydrogen wavefunctions as a tool.

- Qualitatively, use Hydrogen radial probability density to help us think

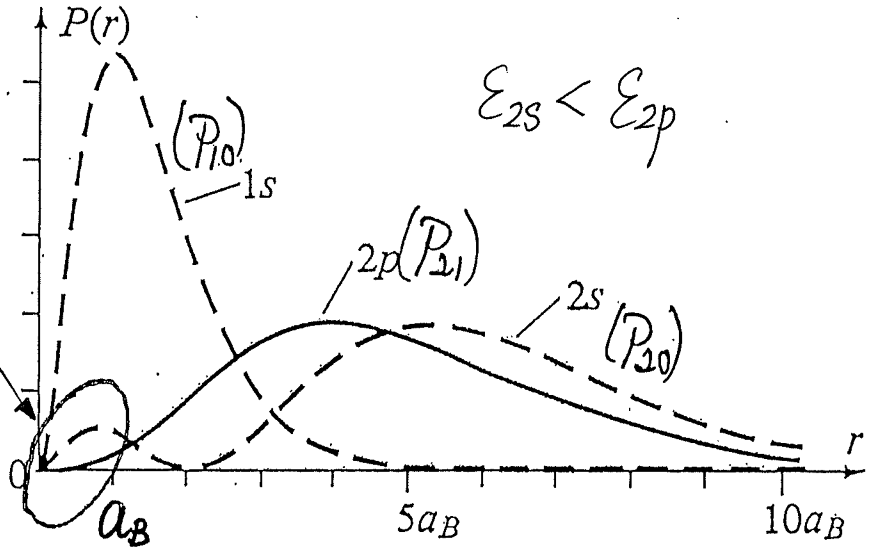
$\mathcal{E}_{2s} < \mathcal{E}_{2p}$

$P(r) \sim r^2 |R_{n\ell}(r)|^2$

2s atomic orbital sees more nuclear charge

$\Rightarrow$ lower $\mathcal{E}_{2s}$

More negative



The radial probability density for the 2*p* states (solid curve). The most probable radius is $r = 4a_B$. For comparison the dashed curves show the 1s and 2*s* distributions to the same scale.

- Similarly, $\mathcal{E}_{3s}^{[2]} < \mathcal{E}_{3p}^{[6]} < \mathcal{E}_{3d}^{[10]}$ [degeneracy]
- Possible crossing of levels for different n, e.g. $\mathcal{E}_{4s} < \underbrace{\mathcal{E}_{3d}}_{\text{transition metals}}$
- How to fill Z electrons into single-particle states?

This is the Big Picture

- Filling in electrons gives the "shell structure" and Periodic Table

Further Questions

- How possibly can effective single-particle problem(s) be formulated?
  What is the main idea?
- How to fill in the electrons?
  How to handle electrons' spins in multi-electron atoms?