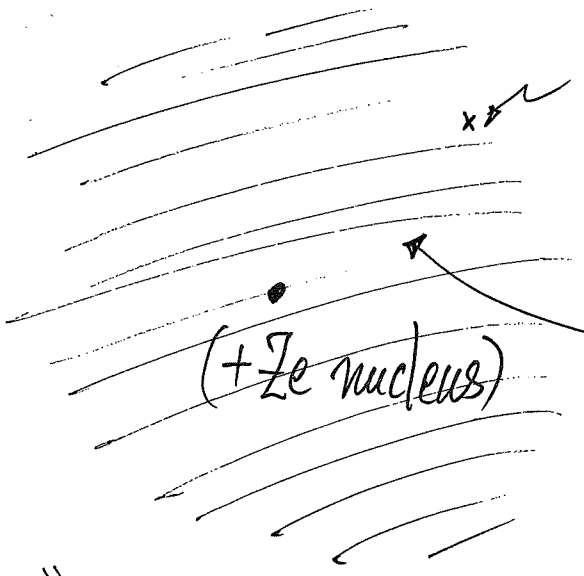
E. Independent-Particle Approximation (IPA): Basic ideas

- Save the nice features of single-electron problems

"Make approximations to turn problem into effective single-electron problem"



Other $(Z-1)$ electrons treated as providing an averaged $V_{\text{other electrons}}(\vec{r})$ on the electron in focus

"atomic orbitals"

$$\left[\underbrace{\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + V_{\text{other electrons}}(\vec{r})}\right]\phi(\vec{r}) = \mathcal{E}\phi(\vec{r}) \qquad (25)$$

$$\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + V_{\text{eff}}(\vec{r})\right]\phi(\vec{r}) = \mathcal{E}\phi(\vec{r}) \qquad (26)$$

$\Rightarrow$ hopefully (wanted it to be!) spherically symmetric $V(r)$

- Strictly speaking, even the approximated $V_{eff}(\vec{r})$ is not $V_{eff}(r)$ only
- Further approximate $V_{eff}(\vec{r}) = \underbrace{V_{eff}(r)}_{\text{spherically symmetric}} = V(r)$ [for simplicity]

[also called "central-field approximation"]

so the single-electron states [atomic orbitals] retain the nice features

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi) \quad \underline{\text{AND}} \quad \mathcal{E}_{n\ell}$$

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

Aside:

$$\hat{H} = \sum_{i=1}^{Z}\left(\frac{-\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i}\right) + \sum_{(ij)\,\text{pairs}} \frac{e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{r}_j|} \qquad \text{(actual problem)}$$

$$\hat{H} = \sum_{i=1}^{Z}\left(\frac{-\hbar^2}{2m}\nabla_i^2 + V_{\text{eff}}(r_i)\right) + \left[\sum_{i=1}^{Z}\left(\frac{-Ze^2}{4\pi\varepsilon_0 r_i} - V_{\text{eff}}(r_i)\right) + \sum_{(ij)\,\text{pairs}} \frac{e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{r}_j|}\right]$$

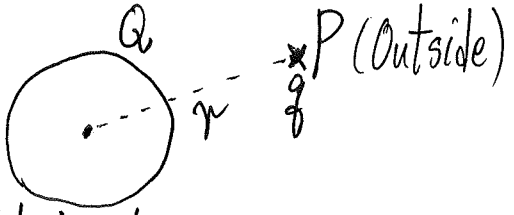
(actual problem)

$$= \sum_{i=1}^{Z}\left(\frac{-\hbar^2}{2m}\nabla_i^2 + V_{\text{eff}}(r_i)\right) + V_{\text{residual electrostatic interaction}} \qquad \text{(actual problem)}$$

Treat $\hat{H} \approx \sum_{i=1}^{Z}\left(\frac{-\hbar^2}{2m}\nabla_i^2 + V_{\text{eff}}(r_i)\right)$ and turn actual problem into single-electron QM problems, then Eq. (25) follows

* Roughly, how does V(r) look like?

(a)



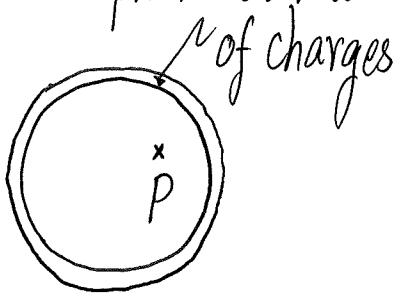
Total charge Q [nucleus + other electrons] distributed spherically

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

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

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

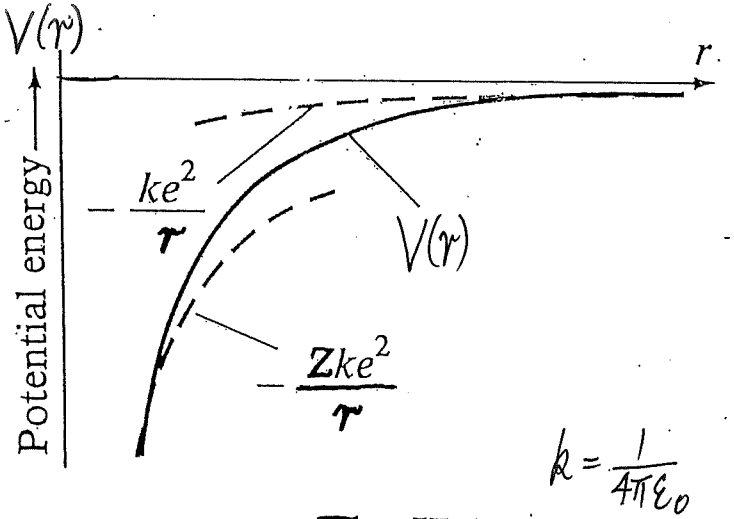
(b)



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

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

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



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 $-Zke^2/r$.

$V(r)$ is NOT of Coulombic Form

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

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

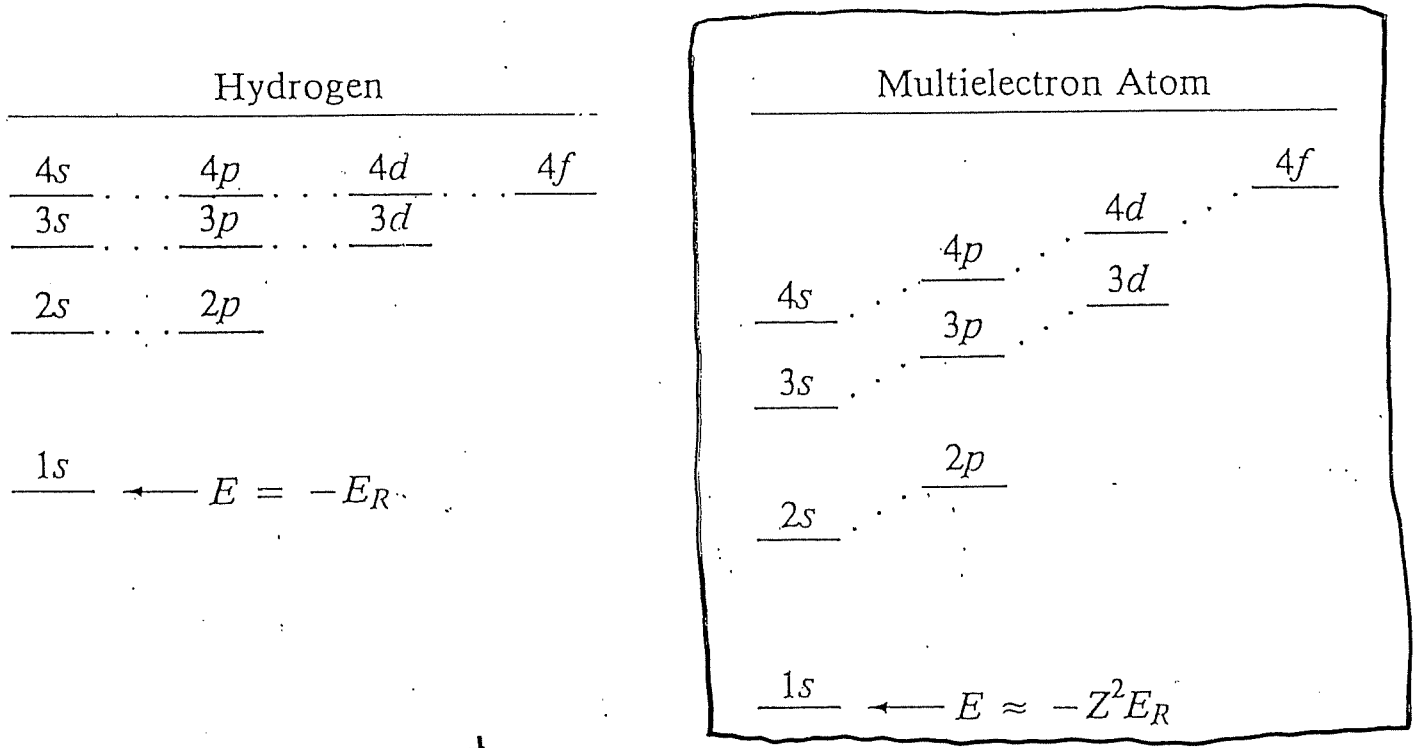
$$\approx \begin{cases} 1 & \text{far away from nucleus} \\ Z & \text{close to nucleus} \end{cases}$$

- 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: $E_{n\ell}$ (<u>not</u> E_n as in hydrogen)
- Given ℓ, $m_\ell = \ell, \cdots, -\ell \Rightarrow (2\ell+1)$ values of m_ℓ
- Electron has spin quantum number $s = 1/2$; $m_s = +1/2, -1/2$
- $E_{n\ell}$ has degeneracy $\underset{\text{spin}}{2} \cdot \underbrace{(2\ell+1)}_{\text{from } m_\ell}$ e.g. $3d$ ($n=3$, $\ell=2$) $2\cdot(2\ell+1) = 10$ states
- Including spin, states are labelled by $(n, \ell, m_\ell, (s), m_s)$ (s = ½ always)
- <u>Each atom has its own set of $E_{n\ell}$ energy levels</u> ($\because V(r)$ is different)

  [each atom has its effective $V(r)$]

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**: $1s$ $(n=1, \ell=0)$ degeneracy $= 2$ (due to spin m_s)

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

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

- **$n=2$** $(\ell=0, \ell=1$ OR $2s, 2p)$

  $\mathcal{E}_{2s} \neq \mathcal{E}_{2p}$ ($\because$ $V(r)$ not Coulombic)

  Which one is lower? $\mathcal{E}_{2s} < \mathcal{E}_{2p}$

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

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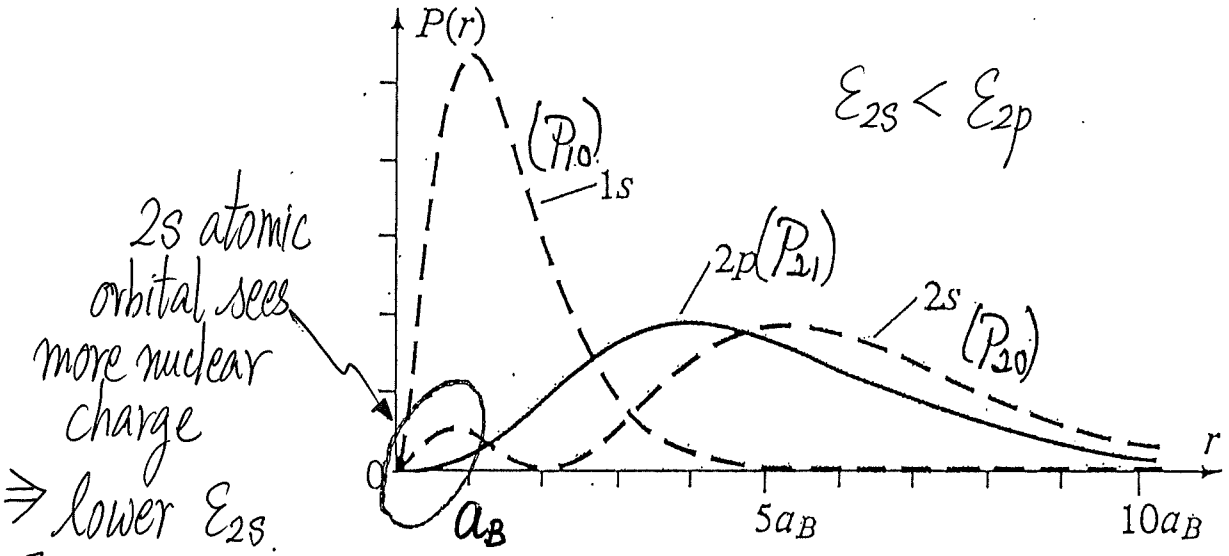
† Although each atom is a new QM problem, it is useful to bear in mind properties of hydrogen wavefunctions as a tool.

- 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 ⇒ lower $\mathcal{E}_{2s}$ ⇒ More negative

The radial probability density for the $2p$ states (solid curve). The most probable radius is $r = 4a_B$. For comparison the dashed curves show the $1s$ and $2s$ 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. $\mathcal{E}_{4s} < \underbrace{\mathcal{E}_{3d}}$ transition metals

Q: 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? (see Appendix B)
- How to fill in the electrons?
  How to handle electrons' spins in multi-electron atoms?