The background features a dark blue gradient with a starry space pattern. Overlaid on this are several technical diagrams in a lighter blue color. These include circular gauges with numerical scales (e.g., 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260), circular arrows indicating clockwise or counter-clockwise rotation, and dashed lines representing paths or orbits.

PRACTICAL APPROACHES AND APPROXIMATIONS

Laws are like sausages; it is better not to see them being made.

-Otto von Bismarck

Making quality sausage requires watching the process.

-Tomás Arias, 2023

THIS LECTURE

- Practical approximations for $E_{xc}[n(\vec{r})]$
- Computational representation of $\psi_i(\vec{r})$
- Numerical minimization
- Plane wave cutoff E_{cut}
- Pseudopotentials (help reduce E_{cut})



Exact theory!!!

FULL, EXACT THEORY (ONE SLIDE! 😊)

$$E_0 = V_{NN} + \min_{\{\psi_i(\vec{r})\}} \left(\sum_i f_i \int \left(-\frac{1}{2} \right) \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r}) dV + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{nuc}(\vec{r}) n(\vec{r}) dV \right)$$

where,

$$V_{NN} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad V_{nuc}(\vec{r}) = - \sum_I \frac{Z_I}{|\vec{r} - \vec{R}_I|} \quad n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2$$

$$E_H[n(\vec{r})] = \frac{1}{2} \int dV \int dV' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

What about $E_{xc}[n(\vec{r})]$? ...

EXCHANGE-CORRELATION FUNCTIONALS

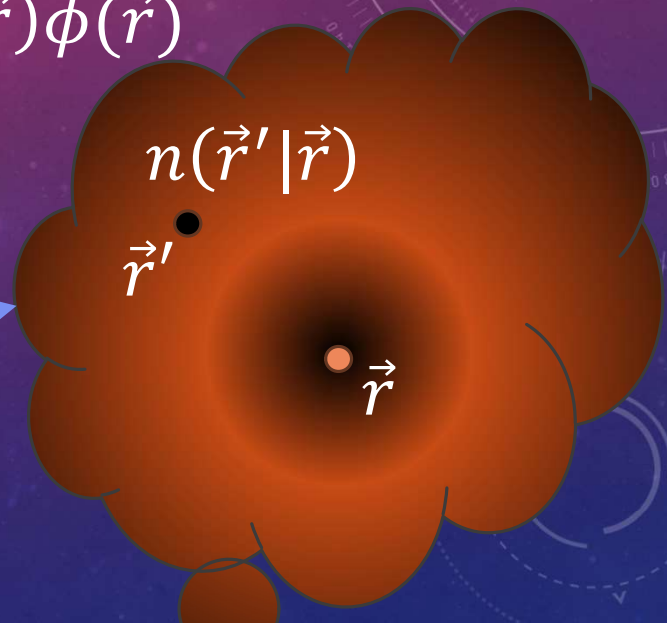
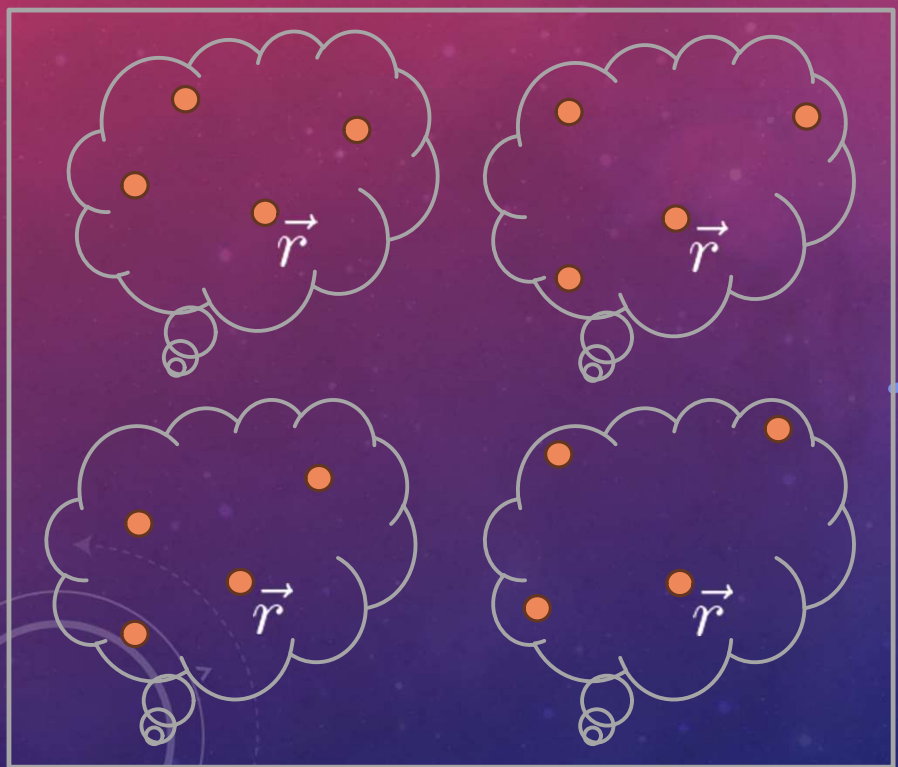
$$\begin{aligned} E_H[n(\vec{r})] &= \frac{1}{2} \int dV \int dV' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} = \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} \\ &= \frac{1}{2} \int dV n(\vec{r}) \phi(\vec{r}) \end{aligned}$$



$E_H[n(\vec{r})]$ has e^- 's at \vec{r} 'seeing' potential from simple average $n(\vec{r}')$...

EXCHANGE-CORRELATION FUNCTIONALS

$$\begin{aligned} E_H[n(\vec{r})] &= \frac{1}{2} \int dV \int dV' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} = \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} \\ &= \frac{1}{2} \int dV n(\vec{r})\phi(\vec{r}) \end{aligned}$$



But, e^- 's at r 'see' instead $n(\vec{r}'|\vec{r})$
 \Rightarrow missing correlations!

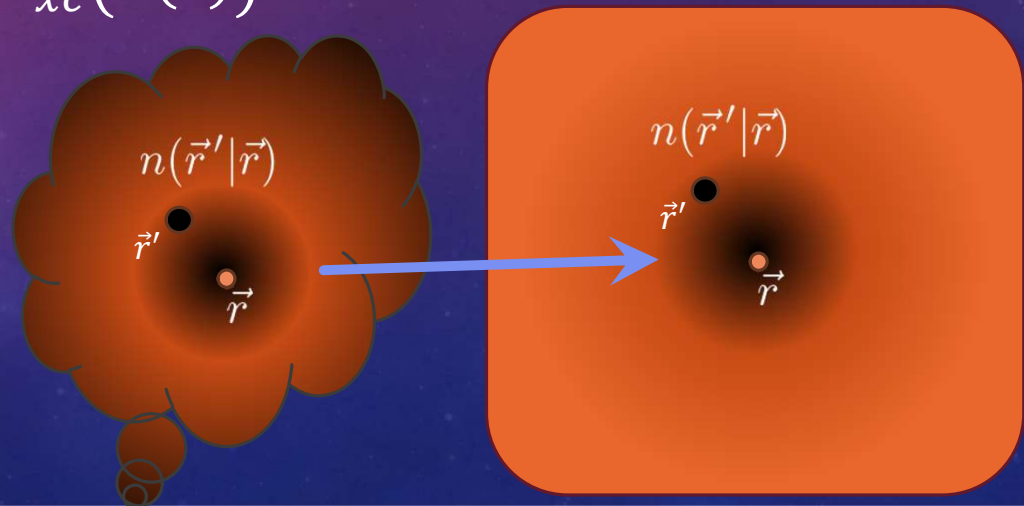
APPROXIMATE EXCHANGE-CORRELATION FUNCTIONALS

$$\begin{aligned}
 V_{ee}[n(\vec{r})] &= \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}') + h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} \\
 &= E_H[n(\vec{r})] + \int dV n(\vec{r}) \frac{1}{2} \int dV' \frac{h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = E_H[n(\vec{r})] + E_{xc}[n(\vec{r})]
 \end{aligned}$$

- Assume 'hole' is the same as in a uniform electron gas at the local density $n(\vec{r})$
- Then, correction for each e^- at r depends only on $n(\vec{r})$

$$E_{xc}[n(\vec{r})] \approx E_{xc}^{LDA}[n(\vec{r})] \equiv \int dV n(\vec{r}) \epsilon_{xc}(n(\vec{r}))$$

- Fit $\epsilon_{xc}(n)$ to asymptotic behavior and numerical data for uniform e^- gas



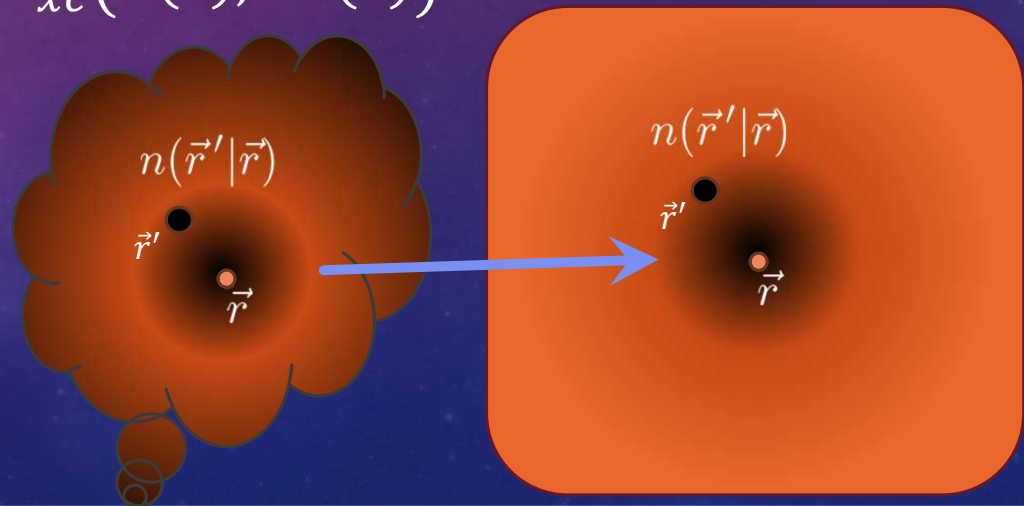
APPROXIMATE EXCHANGE-CORRELATION FUNCTIONALS

$$\begin{aligned}
 V_{ee}[n(\vec{r})] &= \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = \frac{1}{2} \int dV n(\vec{r}) \int dV' \frac{n(\vec{r}') + h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} \\
 &= E_H[n(\vec{r})] + \int dV n(\vec{r}) \frac{1}{2} \int dV' \frac{h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = E_H[n(\vec{r})] + E_{xc}[n(\vec{r})]
 \end{aligned}$$

- Assume 'hole' is the same as in electron gas with same $n(\vec{r})$ and $\nabla n(\vec{r})$
- Then, correction for each e^- at r depends only on $n(\vec{r})$ and $\nabla n(\vec{r})$

$$E_{xc}[n(\vec{r})] \approx E_{xc}^{GGA}[n(\vec{r})] \equiv \int dV n(\vec{r}) \epsilon_{xc}(n(\vec{r}), \nabla n(\vec{r}))$$

- Fit $\epsilon_{xc}(n, \nabla n)$ to asymptotic/numerical data for uniform e^- gas



FULL THEORY (ONE SLIDE! 😊)

😊
Few % error
only!

$$E_0 = V_{NN} + \min_{\{\psi_i(\vec{r})\}} \left(\sum_i f_i \int \left(-\frac{1}{2} \right) \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r}) dV + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{nuc}(\vec{r}) n(\vec{r}) dV \right)$$

where,

$$V_{NN} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad V_{nuc}(\vec{r}) = - \sum_I \frac{Z_I}{|\vec{r} - \vec{R}_I|} \quad n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2$$

$$E_H[n(\vec{r})] = \frac{1}{2} \int dV \int dV' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad E_{xc}^{GGA}[n(\vec{r})] = \int dV n(\vec{r}) \epsilon_{xc}(n(\vec{r}), \nabla n(\vec{r}))$$

V_{NN} and V_{nuc} computable from \vec{R}_I . To represent continuous $\psi_i(\vec{r})$...

FULL THEORY (ONE SLIDE! 😊)

😊
Few % error
only!

$$E_0 = V_{NN} + \min_{\{\psi_i(\vec{r})\}} \left(\sum_i f_i \int \left(-\frac{1}{2} \right) \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r}) dV + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{nuc}(\vec{r}) n(\vec{r}) dV \right)$$

where,

$$V_{NN} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad V_{nuc}(\vec{r}) = - \sum_I \frac{Z_I}{|\vec{r} - \vec{R}_I|} \quad n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2$$

$$E_H[n(\vec{r})] = \frac{1}{2} \int dV \int dV' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad E_{xc}^{GGA}[n(\vec{r})] = \int dV n(\vec{r}) \epsilon_{xc}(n(\vec{r}), \nabla n(\vec{r}))$$

Expand $\psi_i(\vec{r}) = \sum_{\vec{G}} C_{i,\vec{G}} e^{i\vec{G} \cdot \vec{r}}$ and re-express $E_0 = \min_{C_{i,\vec{G}}} E_0(C_{i,\vec{G}})$, then minimize ...

THIS LECTURE

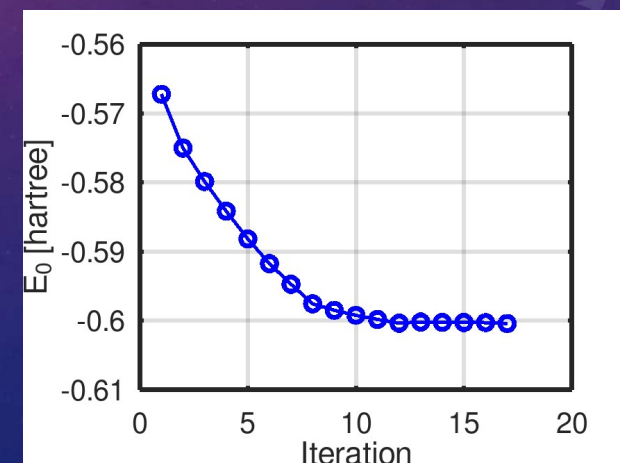
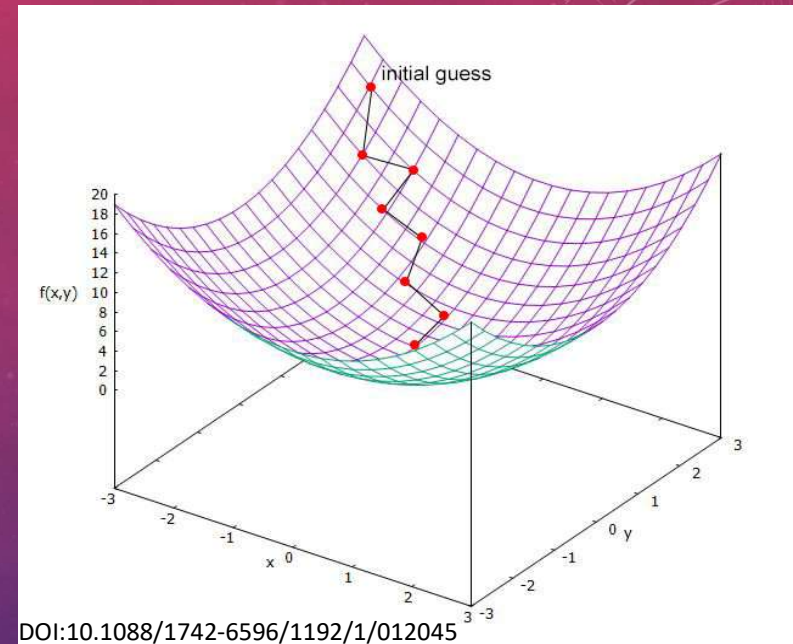
- Practical approximations for $E_{xc}[n(\vec{r})]$
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MINIMIZATION AND ITERATIVE CONVERGENCE

To minimize $E_0(C_{i,\vec{G}})$...

Steepest Descent:

- Make initial guess for $C_{i,\vec{G}}$
 - $C_{i,\vec{G}} \leftarrow C_{i,\vec{G}} - \varepsilon \nabla E_0(C_{i,\vec{G}})$
 - ❖ Stop when results stop changing
-
- Always verify iterative convergence (😞)



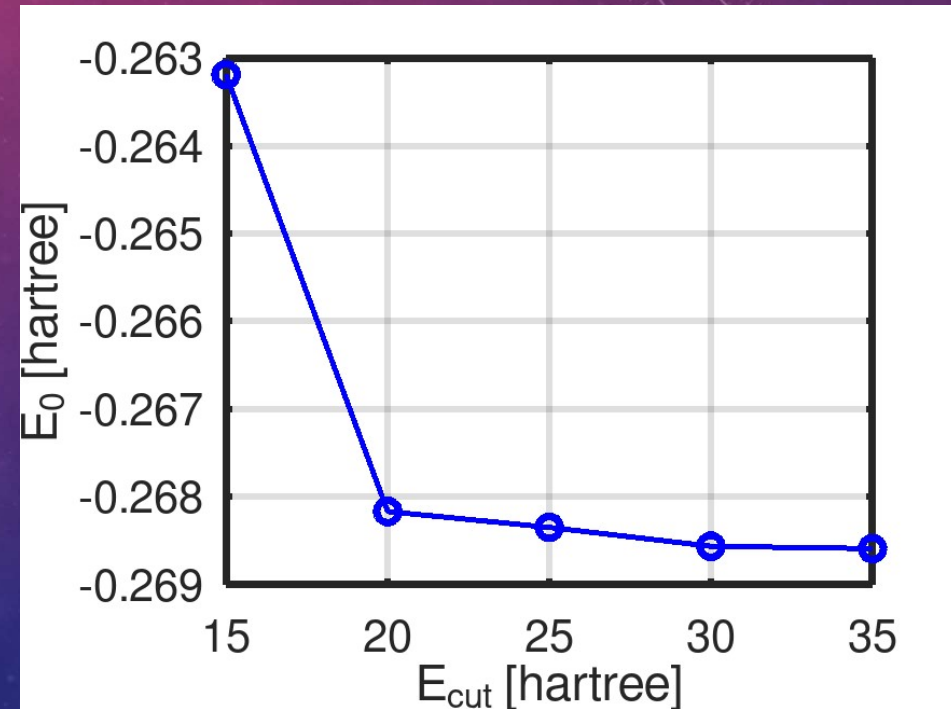
THIS LECTURE

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BASIS-SET EXPANSION AND PLANE-WAVE CONVERGENCE

For *finite* calculation, let $\psi_i(\vec{r}) = \sum_{\vec{G}} C_{i,\vec{G}} e^{i\vec{G}\cdot\vec{r}}$ for all $|\vec{G}| < G_c$

- Characterize G_c using $E_{\text{cut}} \equiv \frac{1}{2} G_c^2$
- For each new material, always verify convergence w.r.t. E_{cut} (☹)

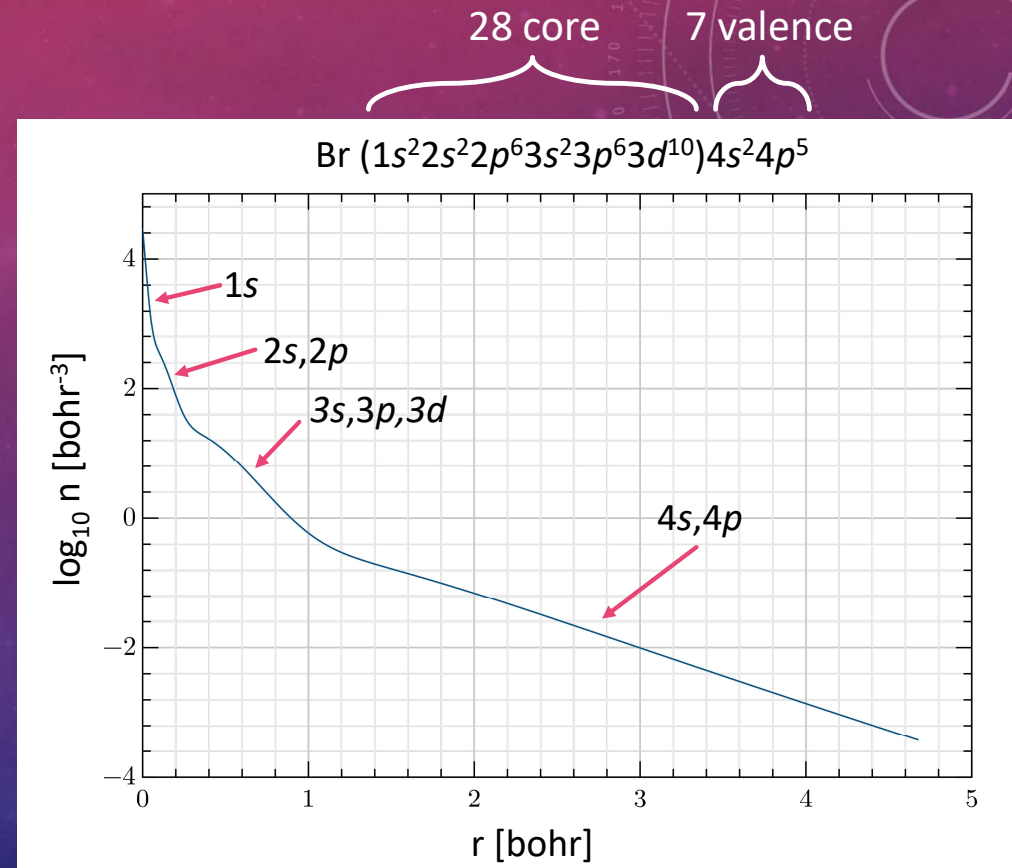


THIS LECTURE

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PSEUDOPOTENTIALS & VERIFICATION

- Atomic orbitals $\psi(\vec{r}) \sim e^{-Z_{\text{scr}} r/n}$
- Core e^- 's tightly bound
 - need high resolution & E_{cut}
 - many of them
 - chemically inert
- 💡 Replace nucleus + core electrons with effective, pseudopotential with same scattering properties for valence electrons!
- For each new element, always verify by computing known physical quantities (😞)



The background is a gradient from dark purple at the top to dark blue at the bottom. It features numerous out-of-focus circular bokeh lights in shades of purple and blue. On the left side, there are several semi-transparent technical diagrams, including a large circular scale with numerical markings from 140 to 260, and various smaller circular and rectangular shapes with arrows and dashed lines, suggesting a scientific or engineering context.

THANK YOU!

TAA2@CORNELL.EDU