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})

FULL, EXACT THEORY (ONE SLIDE! 🤓)

Exact theory!!!

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

where,

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

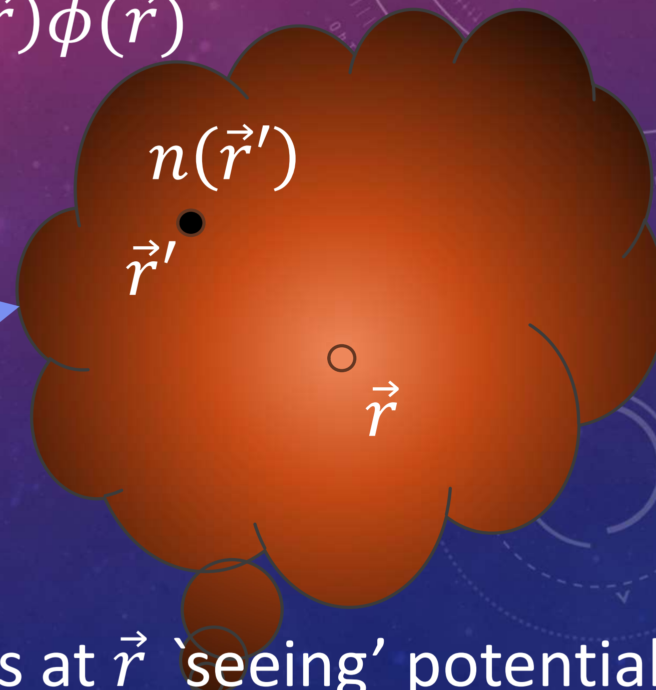
$$E_H[n(\vec{r})] = \frac{1}{2} \int dV \int dV' \, \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

What about $E_{xc}[n(\vec{r})]$? …

EXCHANGE-CORRELATION FUNCTIONALS

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

$$= \frac{1}{2}\int dV\, n(\vec{r})\phi(\vec{r})$$

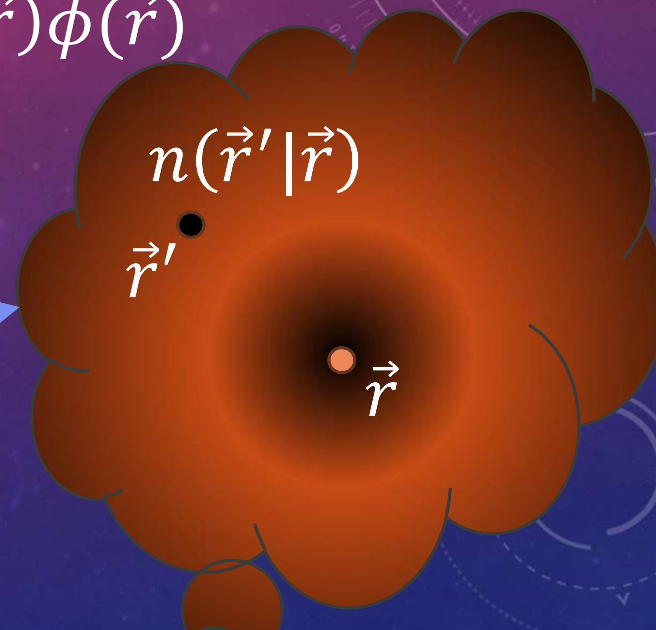


$E_H[n(\vec{r})]$ has e^-'s at $\vec{r}$ `seeing' potential from simple average $n(\vec{r}')$ …

EXCHANGE-CORRELATION FUNCTIONALS

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

$$= \frac{1}{2}\int dV\, n(\vec{r})\phi(\vec{r})$$



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

⇒ missing correlations!

APPROXIMATE EXCHANGE-CORRELATION FUNCTIONALS

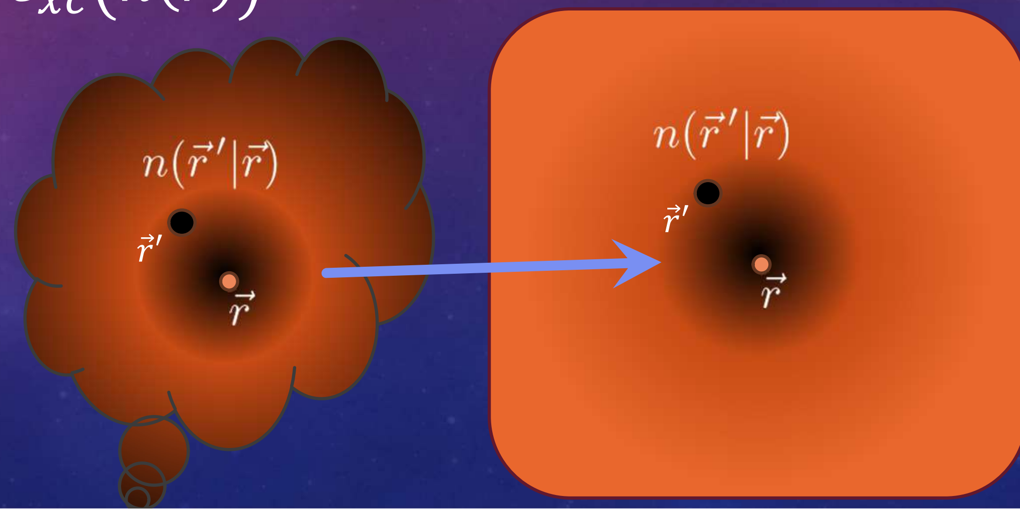
$$V_{ee}[n(\vec{r})] = \frac{1}{2}\int dV\, n(\vec{r}) \int dV' \frac{n(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = \frac{1}{2}\int dV\, n(\vec{r}) \int dV' \frac{n(\vec{r}')+h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|}$$

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

- 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 $n(\vec{r})$

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

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



APPROXIMATE EXCHANGE-CORRELATION FUNCTIONALS

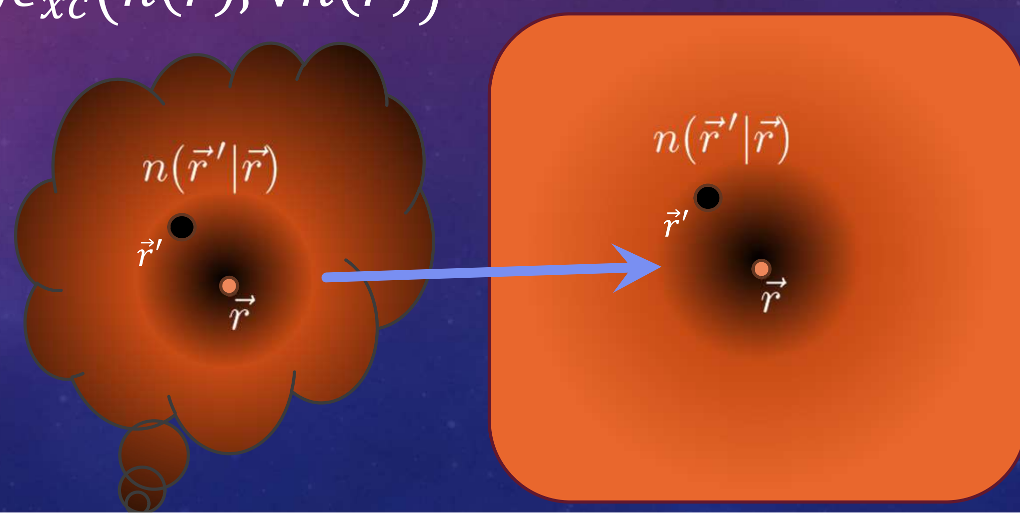
$$V_{ee}[n(\vec{r})] = \frac{1}{2}\int dV\, n(\vec{r}) \int dV' \frac{n(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|} = \frac{1}{2}\int dV\, n(\vec{r}) \int dV' \frac{n(\vec{r}')+h(\vec{r}'|\vec{r})}{|\vec{r}-\vec{r}'|}$$

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

- 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* $\nabla n(\vec{r})$

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

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



FULL THEORY (ONE SLIDE! 🤓)

🤓
Few % error only!

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

where,

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

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

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

FULL THEORY (ONE SLIDE! 🤓)

Few % error only!

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

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

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 …

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MINIMIZATION AND ITERATIVE <u>*CONVERGENCE*</u>

To minimize $E_0(C_{i,\vec{G}})$ …

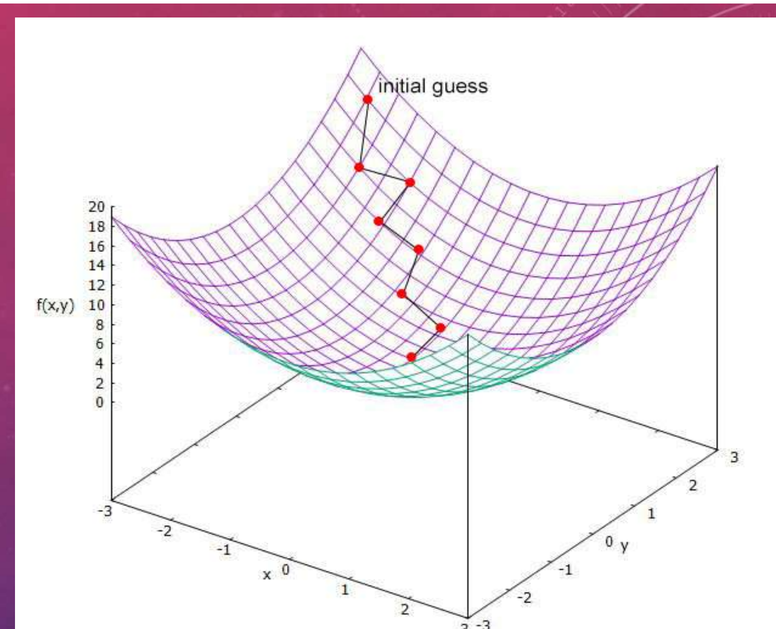
Steepest Descent:

- Make initial guess for $C_{i,\vec{G}}$

$\circlearrowright\ C_{i,\vec{G}} \leftarrow C_{i,\vec{G}} - \varepsilon\, \nabla E_0(C_{i,\vec{G}})$

- Stop when results stop changing

- *<u>Always</u>* verify iterative convergence (😠)



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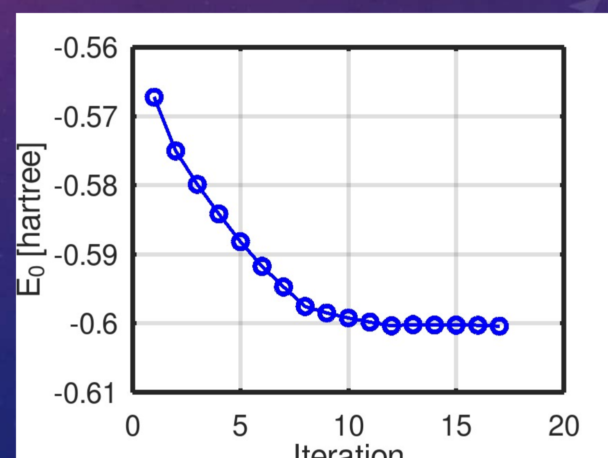

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- Practical approximations for $E_{xc}[n(\vec{r})]$
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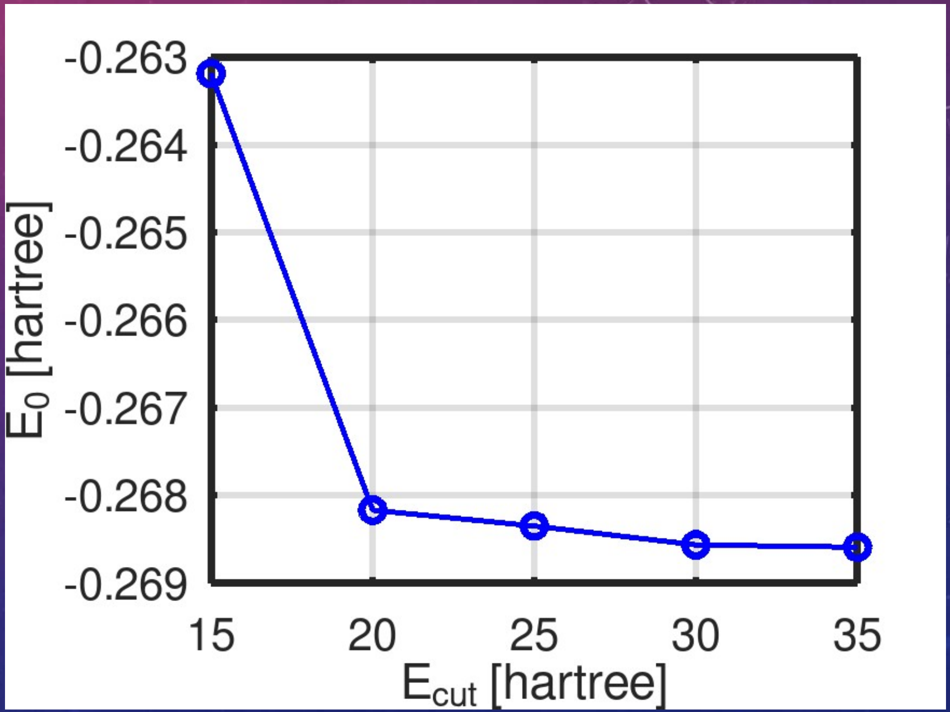
BASIS-SET EXPANSION AND PLANE-WAVE *CONVERGENCE*

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

- Practical approximations for $E_{xc}[n(\vec{r})]$
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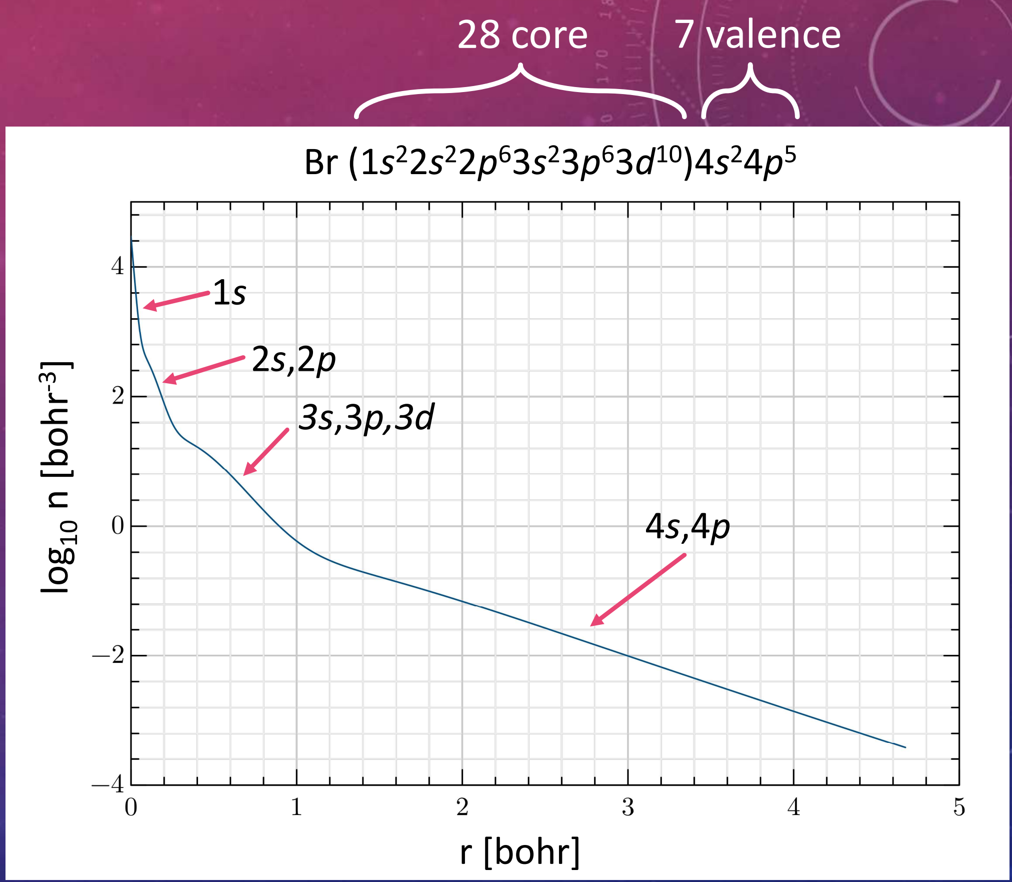
PSEUDOPOTENTIALS & *VERIFICATION*

- Atomic orbitals $\psi(\vec{r}) \sim e^{-Z_{\mathrm{scr}}\, r/n}$
- 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 (😠)



THANK YOU!

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