DENSITY-FUNCTIONAL THEORY (DFT)

It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

-PAM Dirac, 1929

FROM LAST TIME:

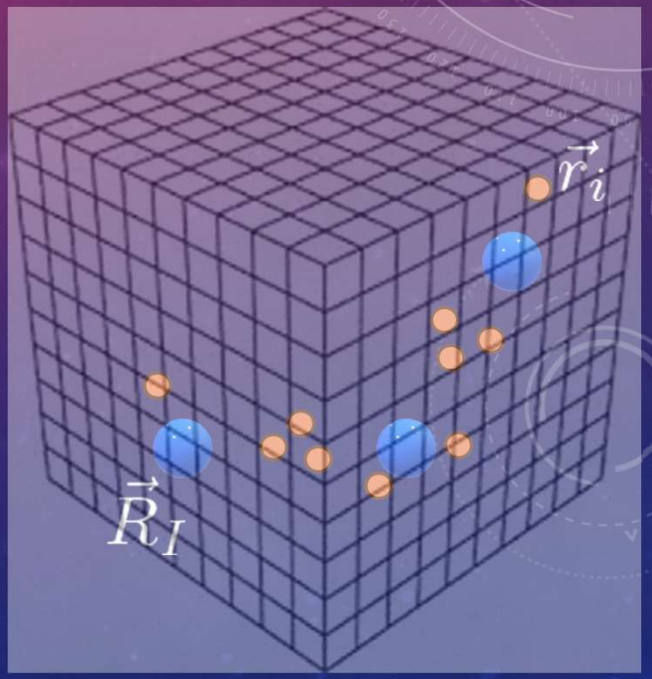
Now, must solve …

$$\hat{H}(\vec{R}_1, \vec{R}_2, \dots)\Psi_n(\vec{r}_1, \vec{r}_2, \dots) = E_n(\vec{R}_1, \vec{R}_2, \dots)\Psi_n(\vec{r}_1, \vec{r}_2, \dots)$$

Even for a **coarse** 10 x 10 x 10 grid …

- each particle has 1000 choices
- resulting in $1000^{10} = 10^{30}$ arrangements
- requiring 10^{30} c-numbers x 16 B/c-num
  $= 1.6 \times 10^{31}$ B $\approx 10^{10}$ ZB $\approx 10^{9}$ x [internet]

Saved 9 orders of magnitude (🤓!),
need more… (😐)

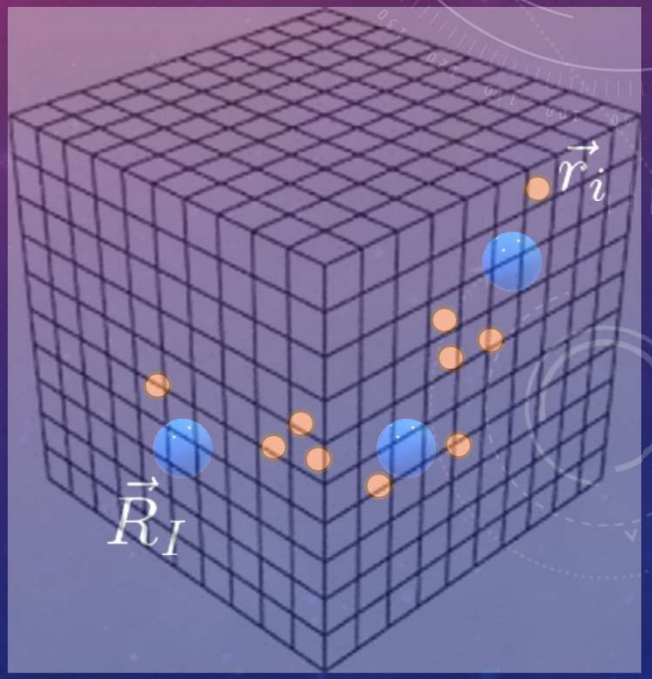


IDEA: FOCUS ON ELECTRONIC GROUND STATES

Focus on `ground state' (GS), n=0 …

$$\hat{H}(\vec{R}_1, \vec{R}_2, \dots)\Psi_0(\vec{r}_1, \vec{r}_2, \dots) = E_0(\vec{R}_1, \vec{R}_2, \dots)\Psi_0(\vec{r}_1, \vec{r}_2, \dots)$$

- Fast e^- dynamics allows settling into Ψ_0 (can put excited states back later)
- Space of electronic GS's is radically reduced
- GS's contain wealth of information …

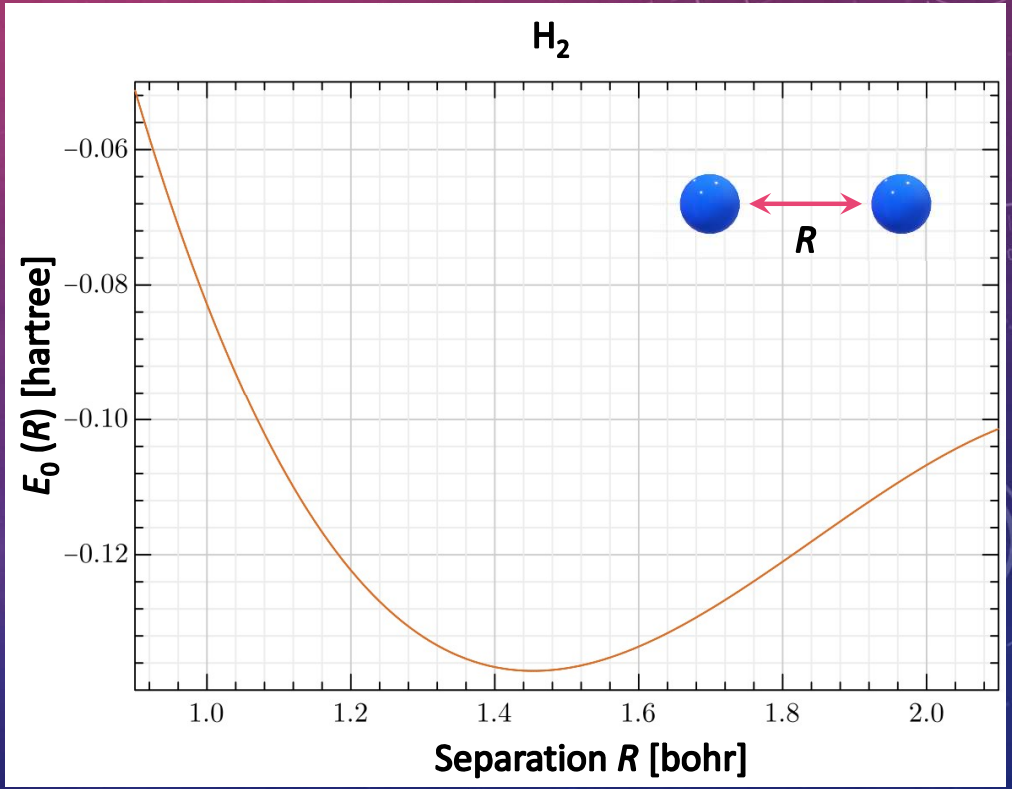


FOCUS ON ELECTRONIC GROUND STATES

$$\hat{H}(\vec{R}_1, \vec{R}_2, \dots)\Psi_0(\vec{r}_1, \vec{r}_2, \dots) = E_0(\vec{R}_1, \vec{R}_2, \dots)\Psi_0(\vec{r}_1, \vec{r}_2, \dots)$$

From $E_0(\vec{R}_1, \vec{R}_2, \dots)$, we can obtain …

- Chemical energies $E = \min E_0(\vec{R}_1, \dots)$
- Structures $\vec{R}_1^{(0)}, \dots = \arg\min E_0(\vec{R}_1, \dots)$
  - bond lengths, angles
  - lattice constants, structurs
- Spring constants $k_{IJ} = \partial^2_{\vec{R}_I, \vec{R}_J} E_0(\vec{R}_1^{(0)}, \dots)$
  - vibrational frequencies, modes
  - phonons, elastic moduli
- Atomic forces $\vec{F}_I = -\nabla_{\vec{R}_I} E_0(\vec{R}_1, \dots)$
  - atomic trajectories $\vec{F}_I = M_I \frac{d^2}{dt^2} \vec{R}_I$
  - diffusion, deposition, melting



FINDING GROUND STATES:

VARIATIONAL PRINCIPLE

$$E_0(\vec{R}_1, \vec{R}_2, \dots) = \min_{\Psi(\vec{r}_1, \vec{r}_2, \dots)} \left\langle \Psi \middle| \hat{H}(\vec{R}_1, \vec{R}_2, \dots) \middle| \Psi \right\rangle$$

$$E_0 = \min_{\Psi} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle$$

where, from Born-Oppenheimer (frozen nuclei):

$$\begin{aligned} \hat{H} &= \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN} \\ &= \hat{T}_e + V_{NN} + \hat{V}_{ee} + \hat{V}_{eN} \end{aligned}$$

VARIATIONAL PRINCIPLE

$$E_0 = \min_{\Psi}\left(\langle \Psi | \hat{T}_e + V_{NN} + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle \right)$$

Because $\langle \Psi | \hat{A} + C | \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle + \langle \Psi | C | \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle + C$ …

VARIATIONAL PRINCIPLE

$$E_0 = \min_{\Psi}\left(V_{NN} + \langle \Psi | \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle \right)$$

Because $\min_x \left(C + f(x)\right) = C + \min_x f(x)$ ...

VARIATIONAL PRINCIPLE

$$E_0 = V_{NN} + \min_{\Psi}\left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle \right)$$

Because $\langle \Psi | \hat{A} + \hat{B} | \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle + \langle \Psi | \hat{B} | \Psi \rangle$ …

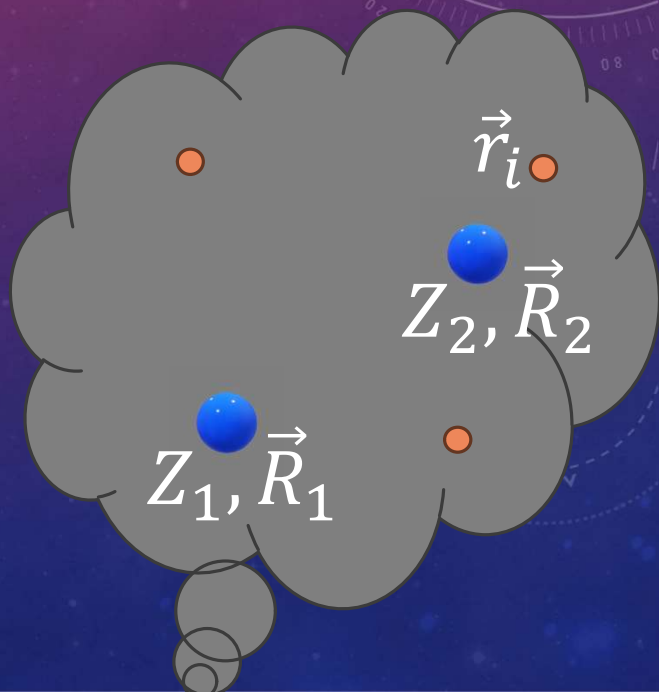
VARIATIONAL PRINCIPLE

$$E_0 = V_{NN} + \min_{\Psi}\left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \underbrace{\langle \Psi | \hat{V}_{eN} | \Psi \rangle}_{\text{Key term that differentiates materials}} \right)$$

MANY-BODY ELECTRON DENSITY

$$\langle \Psi | \hat{V}_{eN} | \Psi \rangle = \left\langle \sum_i \sum_I \frac{(-1)(+Z_I)}{|\vec{r}_i - \vec{R}_I|} \right\rangle_\Psi = \left\langle \sum_i V_{\text{nuc}}(\vec{r}_i) \right\rangle_\Psi$$

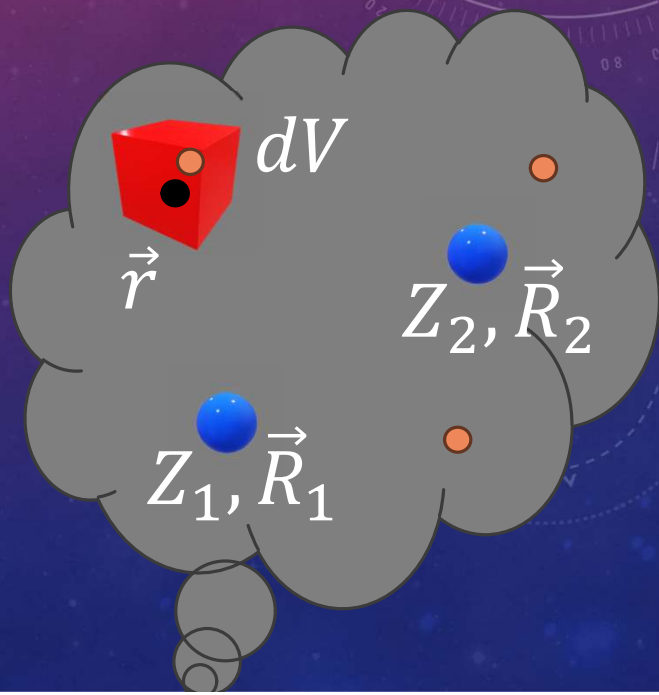
$$V_{\text{nuc}}(\vec{r}) \equiv \sum_I \frac{-Z_I}{|\vec{r} - \vec{R}_I|}$$



MANY-BODY ELECTRON DENSITY

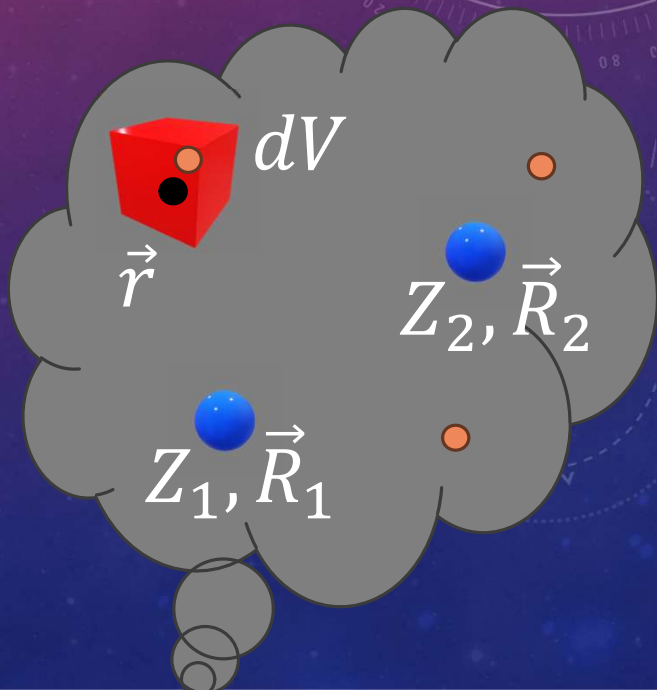
$$\langle \Psi | \hat{V}_{eN} | \Psi \rangle = \left\langle \sum_i V_{\text{nuc}}(\vec{r}_i) \right\rangle_\Psi$$

- Divide space into small boxes at locations $\vec{r}$
- Average number of terms in each `box'
  $= n_\Psi(\vec{r})\, dV$ …
- $\langle \sum_i V_{\text{nuc}}(\vec{r}_i) \rangle = \int V_{nuc}(\vec{r})\, n_\Psi(\vec{r}) dV$



MANY-BODY ELECTRON DENSITY

$$\langle \Psi | \hat{V}_{eN} | \Psi \rangle = \int V_{\text{nuc}}(\vec{r})\, n_{\Psi}(\vec{r})\, dV$$



MANY-BODY ELECTRON DENSITY

$$E_0 = V_{NN} + \min_{\Psi}\left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{eN} | \Psi \rangle \right)$$

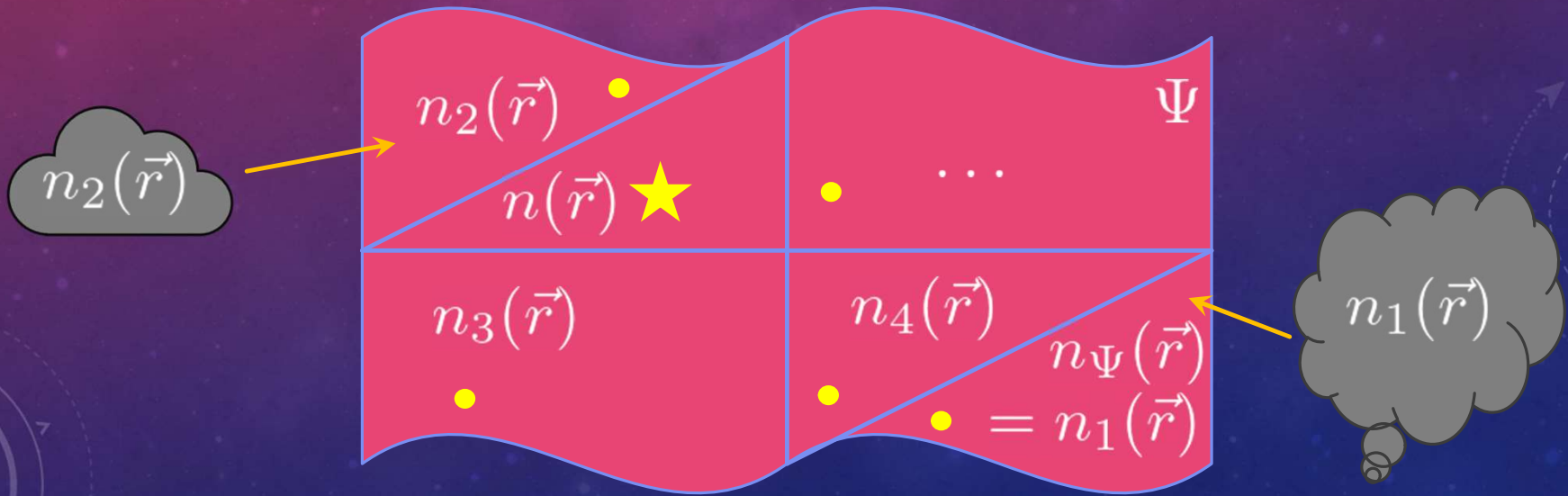
$$= V_{NN} + \underbrace{\min_{\Psi}\left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \int V_{\mathrm{nuc}}(\vec{r})\, n_{\Psi}(\vec{r})\, dV \right)}$$

$$\equiv V_{NN} + E_0'$$

CONSTRAINED OPTIMIZATION

$$E_0{}' = \min_{\Psi} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \int V_{\text{nuc}}(\vec{r})\, n_\Psi(\vec{r})\, dV \right)$$

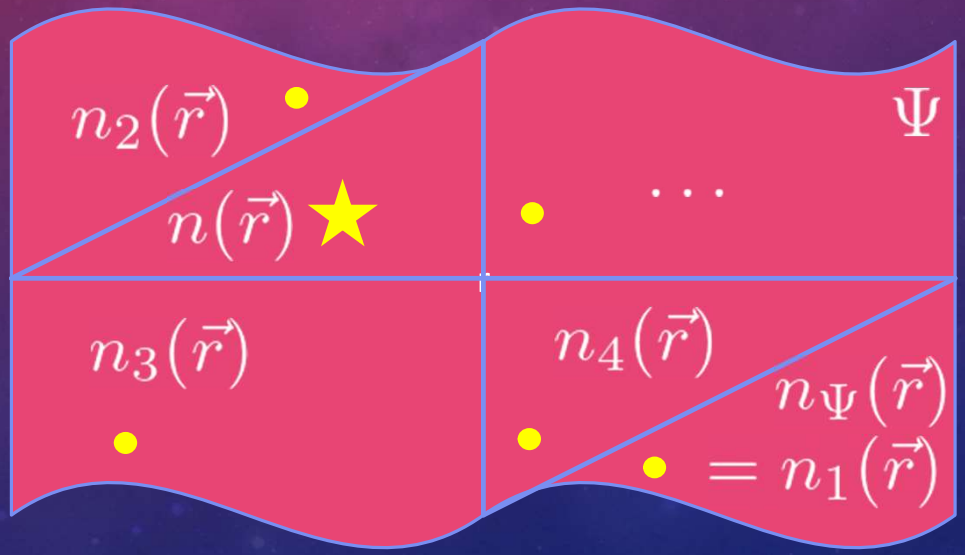
$$E_0{}' = \min_{n(\vec{r})} \left\{ \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \int V_{\text{nuc}}(\vec{r})\, n_\Psi(\vec{r})\, dV \right) \right\}$$



CONSTRAINED OPTIMIZATION

$$E_0{}' = \min_{n(\vec{r})} \left\{ \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \int V_{\text{nuc}}(\vec{r})\, n_\Psi(\vec{r})\, dV \right) \right\}$$

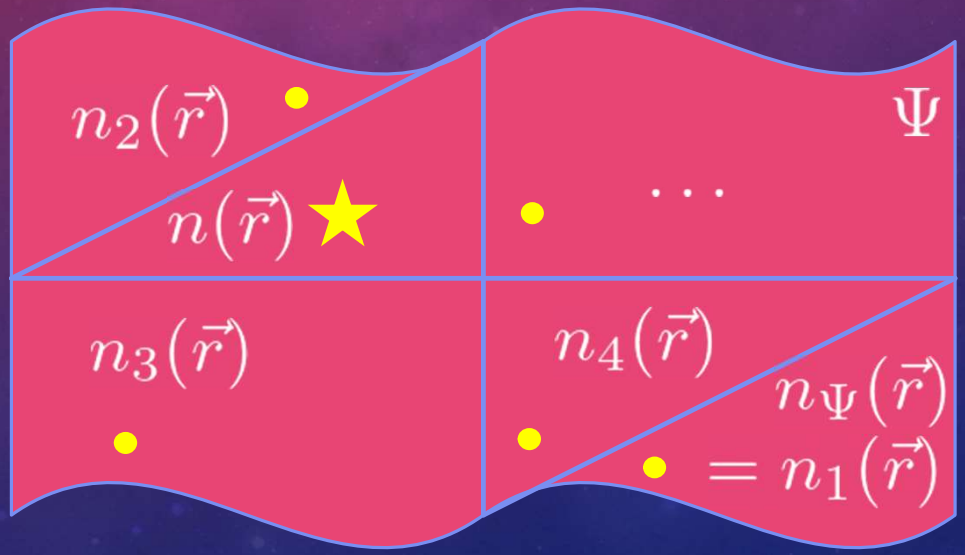
For the inner minimization, $n_\Psi(\vec{r}) = n(\vec{r})$ …



CONSTRAINED OPTIMIZATION

$$E_0{}' = \min_{n(\vec{r})} \left\{ \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right) \right\}$$

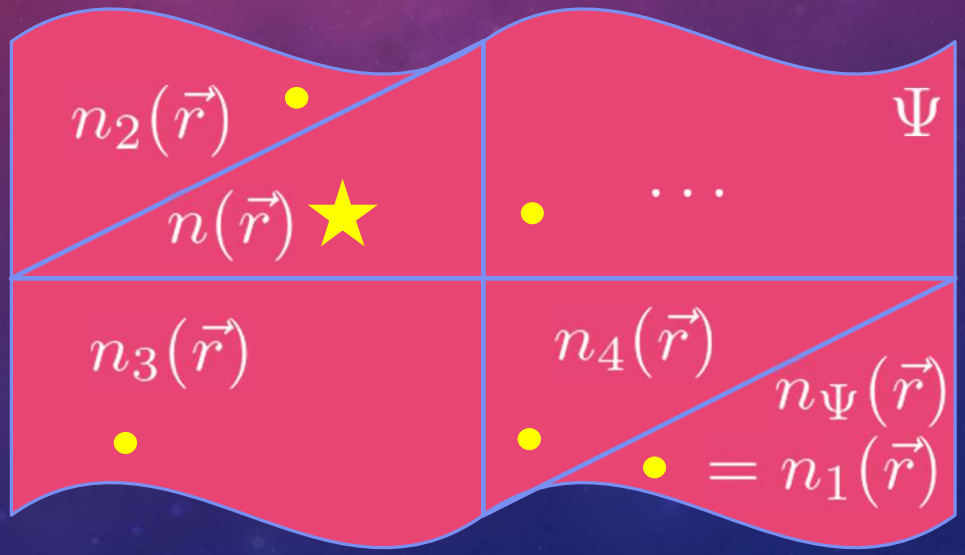
Because $\min_x \big(C + f(x)\big) = C + \min_x f(x)$ …



CONSTRAINED OPTIMIZATION

$$E_0{}' = \min_{n(\vec{r})} \left\{ \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle \right) + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

Now, define $F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle \right)$ ...

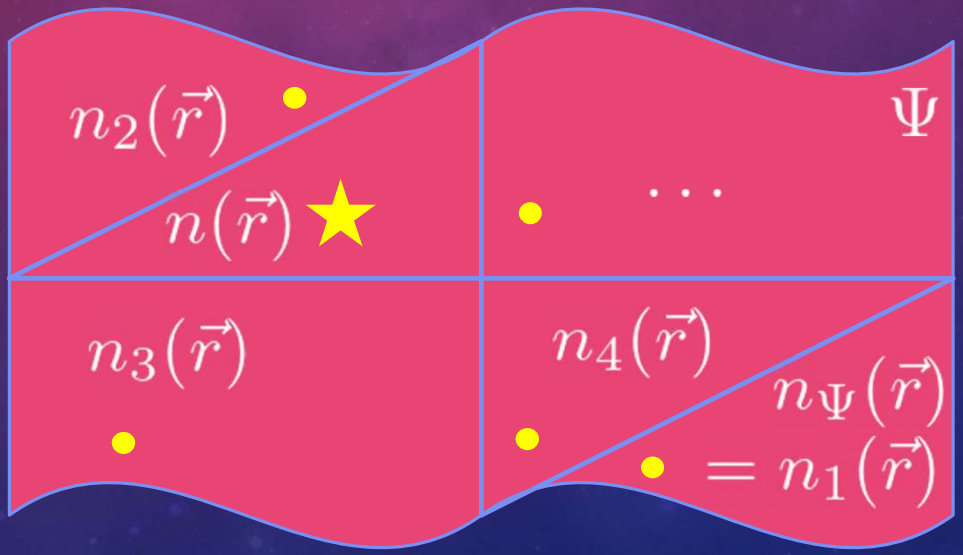


CONSTRAINED OPTIMIZATION

$$E_0{}' = \min_{n(\vec{r})} \left\{ F[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

Hohenberg-Kohn 1 (HK1) !

where $F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle \right)$ is *universal* !

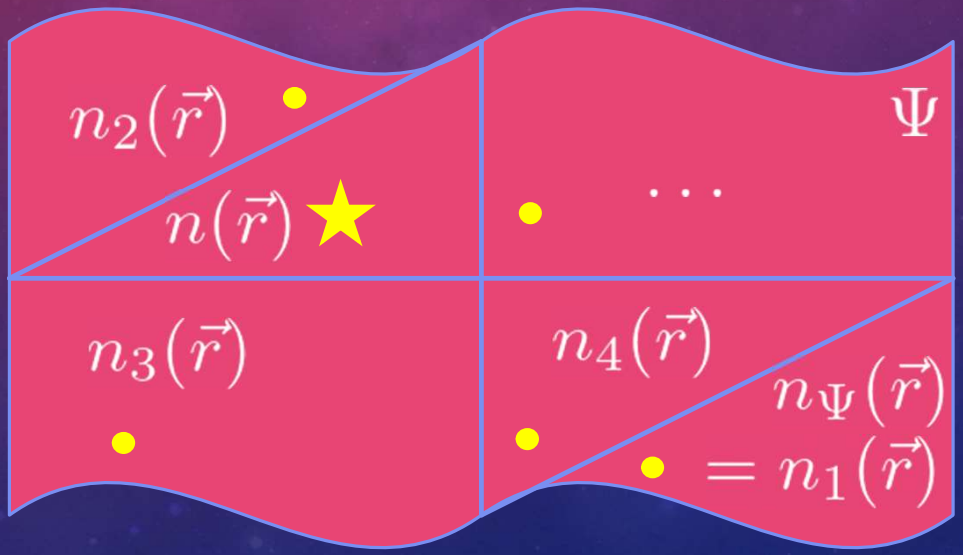


CONSTRAINED OPTIMIZATION

$$n(\vec{r}) = \arg\min_{n(\vec{r})} \left\{ F[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

Hohenberg-Kohn 2 (HK2) !

where $F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle \right)$ is *universal* !



UNIVERSAL FUNCTIONAL

$$F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r})=n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle\right)$$

- No mention of material, depends only on density and nature of e^-'s
- Gives value of least possible *internal* energy consistent with $n(r)$
- Used to efficiently find

$$E_0 = V_{NN} + \min_{n(\vec{r})} \left(F[n(\vec{r})] + \int V_{nuc}(\vec{r}) n(\vec{r}) dV\right)$$

$$n(\vec{r}) = \arg\min_{n(\vec{r})} \left(F[n(\vec{r})] + \int V_{nuc}(\vec{r}) n(\vec{r}) dV\right)$$

- What is the function?
  - See definition above (😐 !)
  - But, we have some very good practicable approximations!

KOHN-SHAM THEOREM

$$F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r})=n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle\right)$$

$$\approx F_{NI}[n(\vec{r})] + E_H[n(\vec{r})]$$

- $F_{NI}[n(\vec{r})] \equiv F[n(\vec{r})]$ for a system of *non-interacting* electrons:

$$F_{NI}[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r})=n(\vec{r})} \left(\langle \Psi | \hat{T}_e | \Psi \rangle\right)$$

- $E_H[n(\vec{r})] \equiv$ Coulomb energy of average electron-density cloud:

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

- *Both* are *universal*, and known!

Now, make this **exact** …

KOHN-SHAM THEOREM

$$F[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r})=n(\vec{r})} \left(\langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle\right)$$

$$\equiv F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})]$$

- Including $E_{xc}[n(\vec{r})]$ makes $F[n(\vec{r})]$ **exact!** 🤓
- $E_{xc}[n(\vec{r})]$ depends only on $n(\vec{r})$ and is *universal* !
- What *is* the function?
  - $E_{xc}[n(\vec{r})] \equiv F[n(\vec{r})] - F_{NI}[n(\vec{r})] - E_H[n(\vec{r})]$ (😐!)
- But, with most important components subtracted, easier to approximate (🤓)

Now, let's use this **exact** result …

KOHN-SHAM THEOREM

$$E_0{}' = \min_{n(\vec{r})} \left\{ F[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

$$= \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

where

$$F_{NI}[n(\vec{r})] \equiv \min_{\Psi:\, n_\Psi(\vec{r}) = n(\vec{r})} \left(\langle \Psi | \hat{T}_e | \Psi \rangle \right)$$

$$\equiv \min_{\{\psi_i(\vec{r})\}:\, \sum_i f_i |\psi_i(\vec{r})|^2 = n(\vec{r})} \left(\sum_i f_i \int -\frac{1}{2} \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r})\, dV \right)$$

$\psi_i(\vec{r})$ ≡ NI wave functions, f_i ≡ occupancies

So …

KOHN-SHAM THEOREM

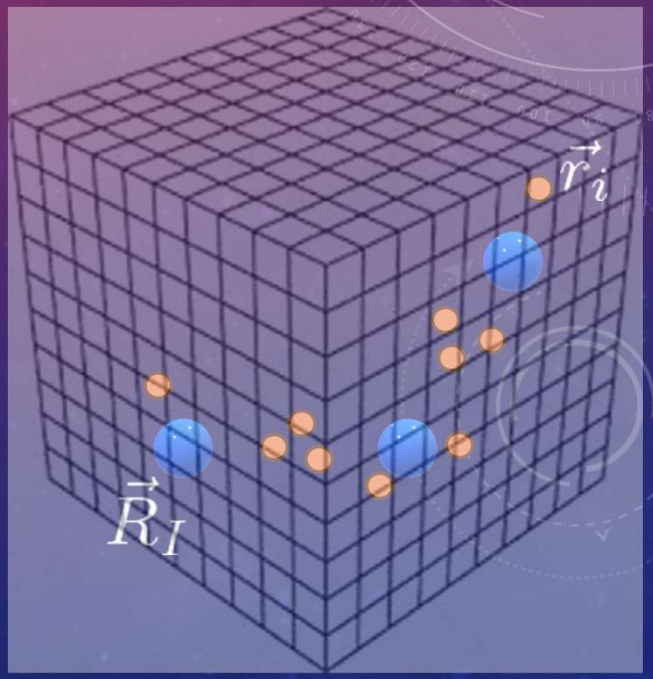
For 10 e^-'s on a **coarse** 10 x 10 x 10 = 1000 point grid …

$\Psi(\vec{r}_1, \vec{r}_2, \dots)$ represents

- $1000^{10} = 10^{30}$ arrangements
- requiring 10^{30} c-numbers x 16 B/c-num
  $= 1.6 \times 10^{31}$ B $\approx 10^{10}$ ZB $\approx 10^{9}$ x [internet]

$\{\psi_i(\vec{r})\}$ represents

- 10 wave functions i
  $\times$ 1000 points $\vec{r}$
  $\times$ 16 B/c-num
  = 160,000 B = 0.16 MB ($<10^{-4}$ laptop)



KOHN-SHAM THEOREM

$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

$$= \min_{n(\vec{r})} \left\{ \min_{\{\psi_i(\vec{r})\}:\, \sum_i f_i |\psi_i(\vec{r})|^2 = n(\vec{r})} \left(\sum_i f_i \int -\frac{1}{2} \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r})\, dV \right) \right.$$

$$\left. + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

KOHN-SHAM THEOREM

$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

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

Because $\min_x \left(C + f(x) \right) = C + \min_x f(x)$ …

KOHN-SHAM THEOREM

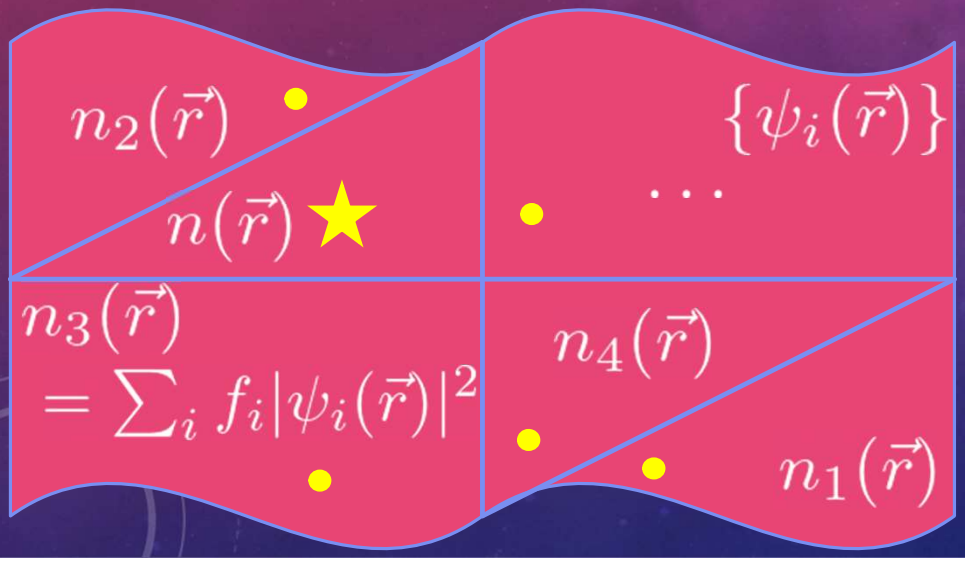
$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

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

KOHN-SHAM THEOREM

$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

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

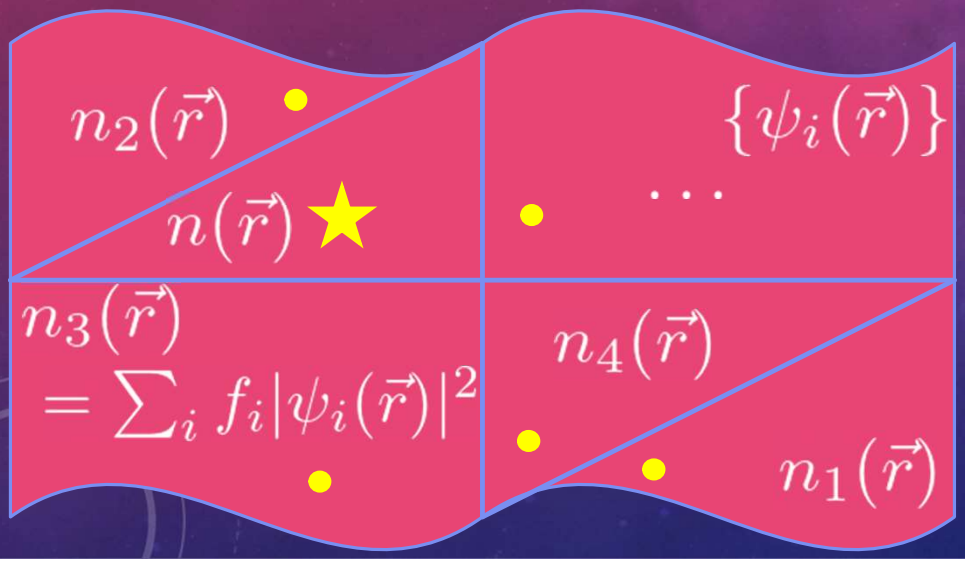


Reversing the logic from before …

KOHN-SHAM THEOREM

$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

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



KOHN-SHAM THEOREM

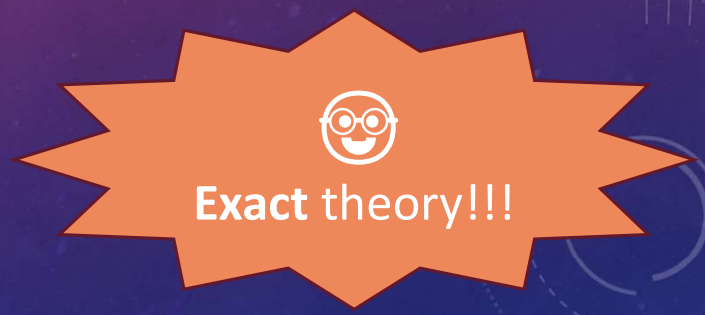
$$E_0' = \min_{n(\vec{r})} \left\{ F_{NI}[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + \int V_{\text{nuc}}(\vec{r})\, n(\vec{r})\, dV \right\}$$

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

Where,

$$n(\vec{r}) \equiv \sum_i f_i |\psi_i(\vec{r})|^2$$

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



What about $E_{xc}[n(r)]$? …

For more information see…

"Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients," by M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992).

- DOI: 10.1103/RevModPhys.64.1045

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THANK YOU!

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