AB INITIO THEORY

Fulfillment of a 2,500 year quest:

At one time through love all things come together into one, at another time through strife's hatred, they are borne each of them apart.

-Empedocles

***Ab initio* theory**

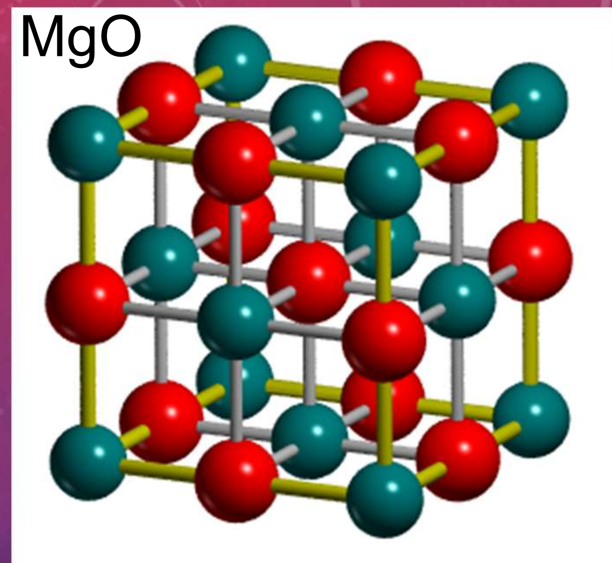
Empedocles (450 BC)

- Basic constituents
  - Earth, Air, Fire, Water
- Basic interactions
  - Love, Strife
- Method of Inquiry
  - Philosophical dielectic

Modern Science

- Basic constituents
  - Electrons, Nuclei
- Basic interactions
  - Electric Force
- Method of Inquiry
  - Schrödinger Equation

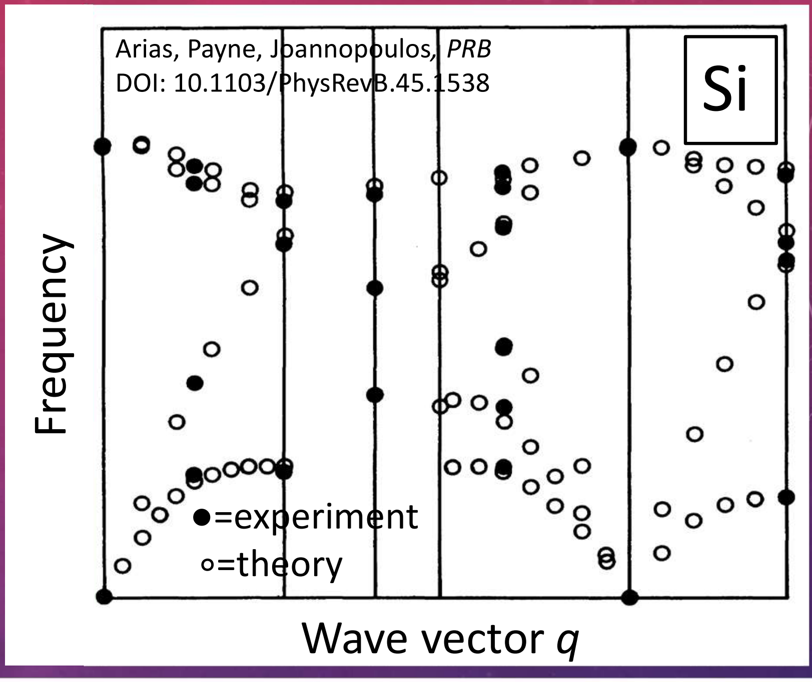
LATTICE CONSTANT, ENERGY, BULK MODULUS

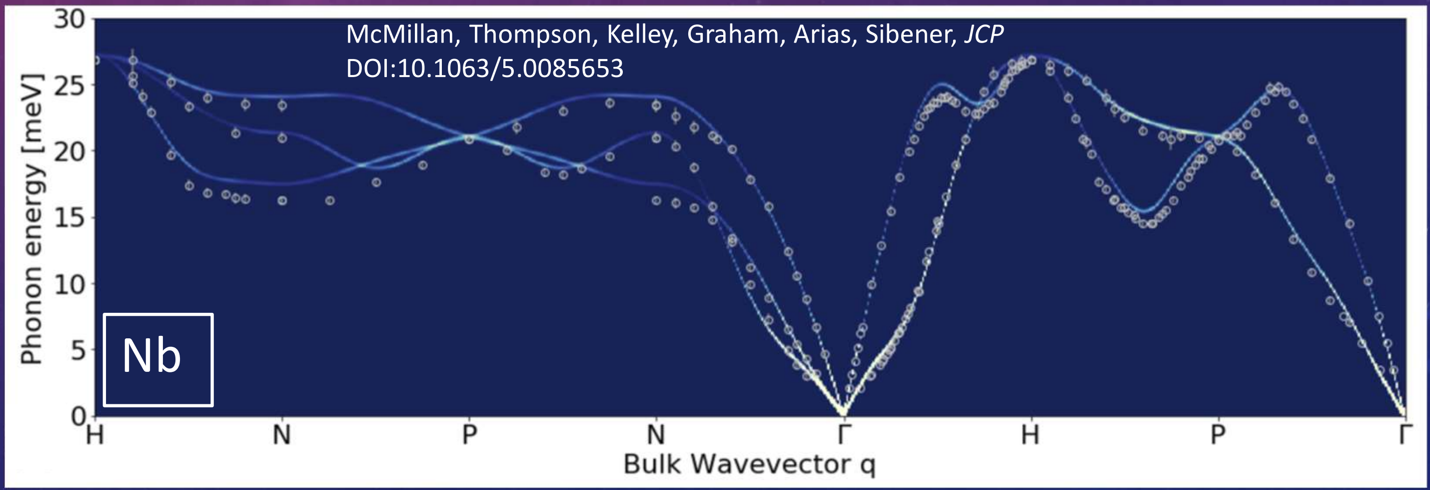


	a (Å)	E_0 (eV per MgO)	$B = \frac{C_{11}+2C_{12}}{3}$ (Mbar)
Expt	4.21	10.33	1.55-1.62
LDA	4.161 (1.1%)	11.80 (+14%)	1.71 (+7.9%)
GGA	4.221 (+0.3%)	10.4 (+0.7%)	1.64 (+3.4%)

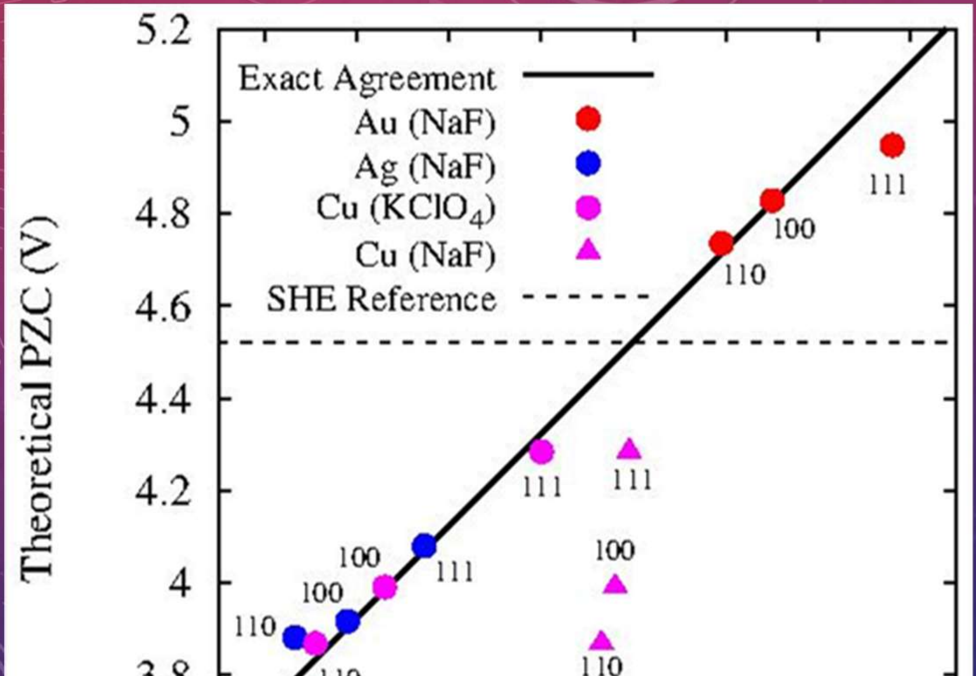
Daykov, Engeness, Arias, *PRL*
DOI: 10.1103/PhysRevLett.90.216402

CRYSTAL VIBRATIONS (PHONONS)



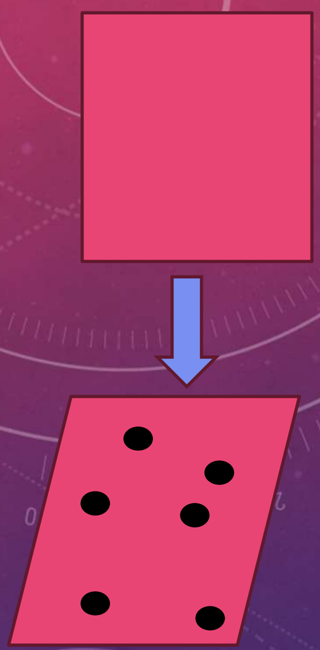


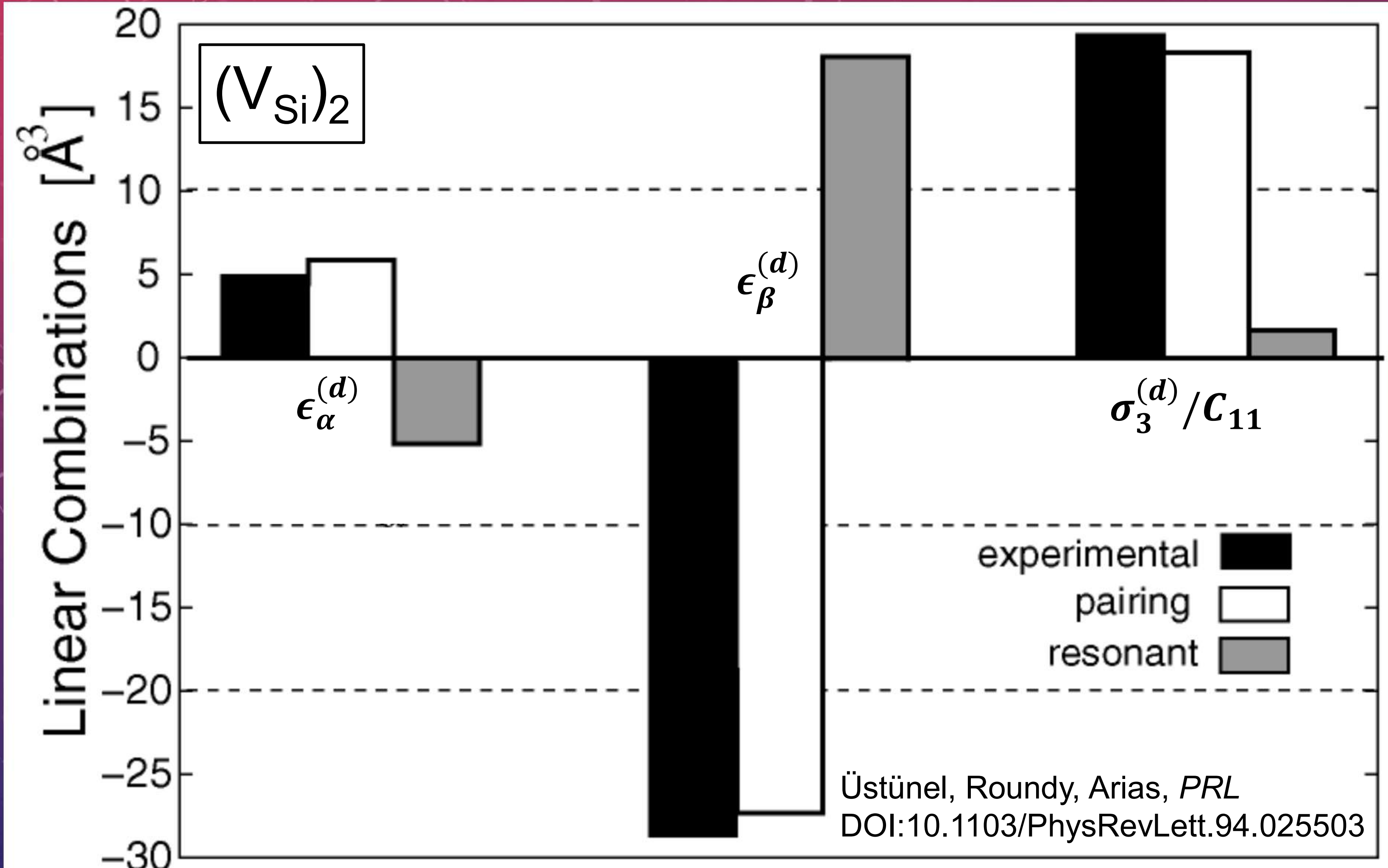
EQUILIBRIA BETWEEN QUANTUM MECHANICAL AND CLASSICAL FLUID SYSTEMS: POTENTIALS OF ZERO CHARGE



Letchworth-Weaver and Arias, *PRB*
DOI: 10.1103/PhysRevB.86.075140

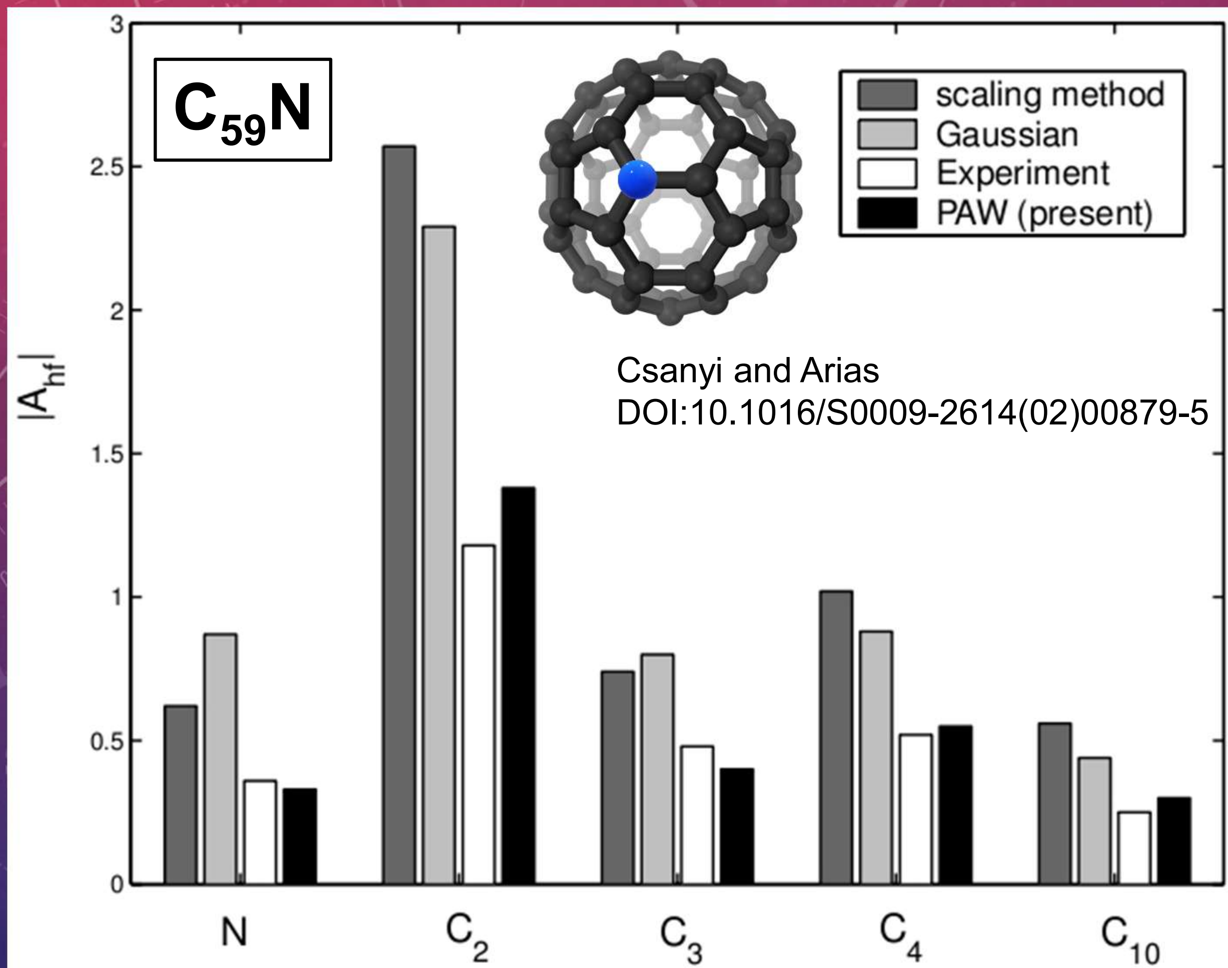
CHEMICAL STRAIN AND STRESS



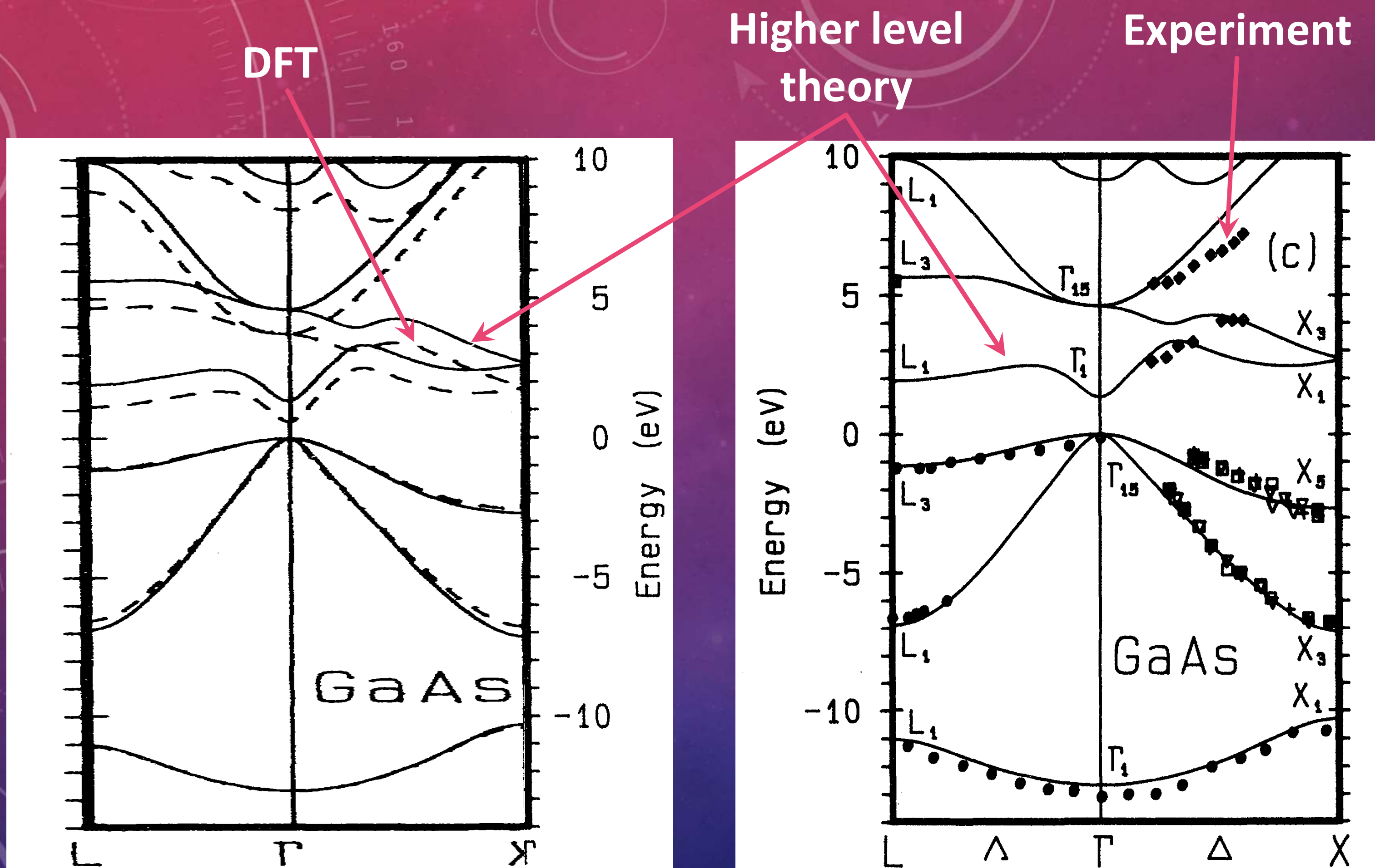


Üstünel, Roundy, Arias, *PRL*
DOI:10.1103/PhysRevLett.94.025503

HYPERFINE COUPLINGS (NUCLEAR-SPIN WITH ELECTRON SPIN)

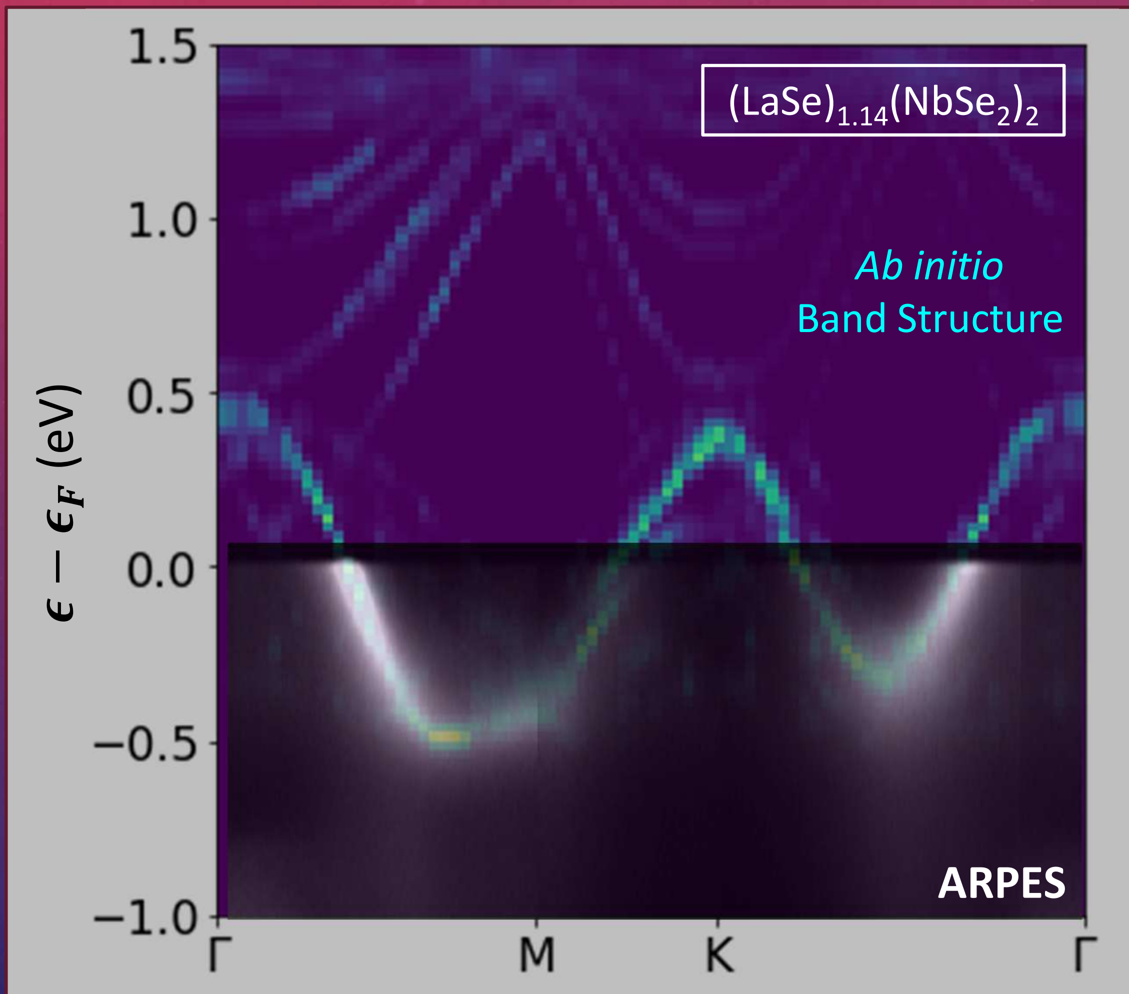


ELECTRONIC BAND STRUCTURE



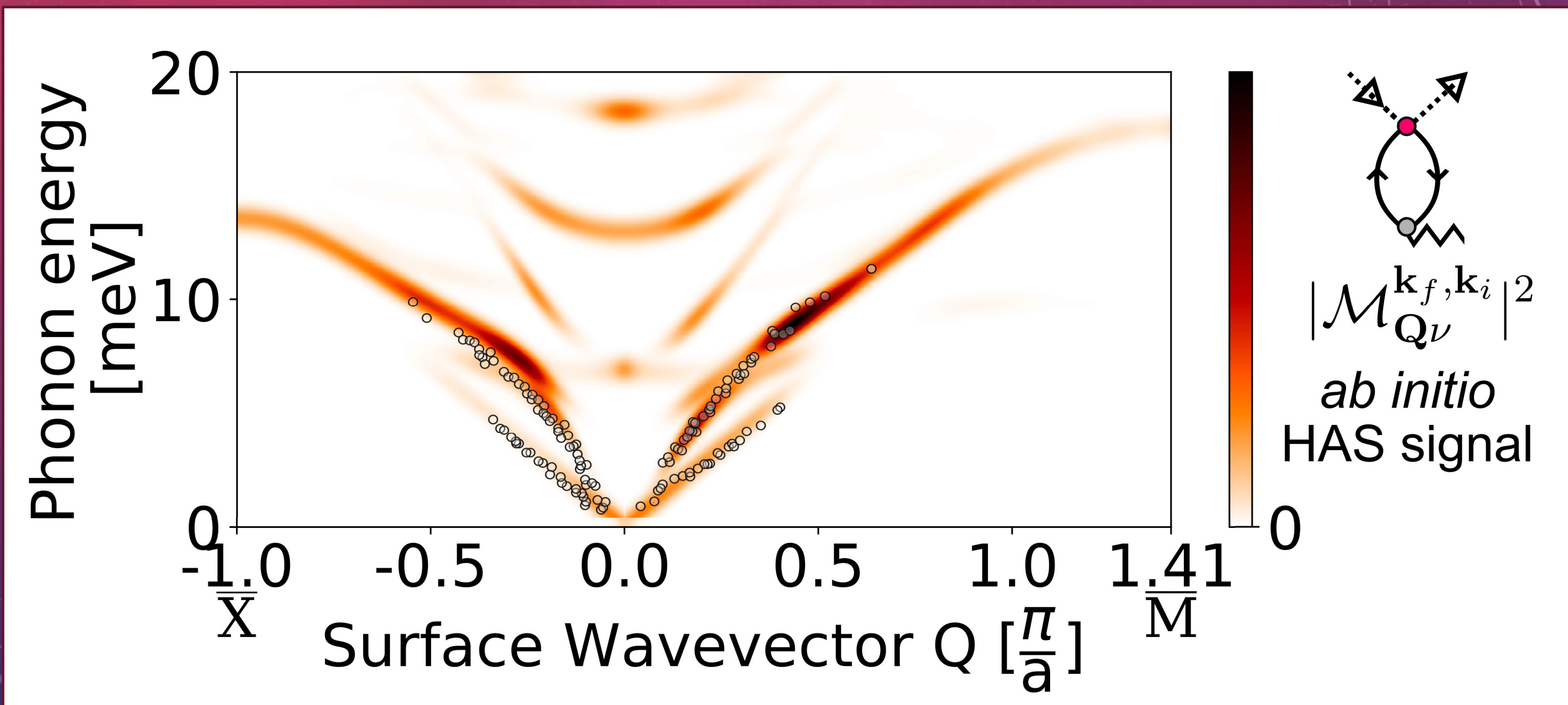
DOI: 10.1103/PhysRevB.48.17791

ANGULAR RESOLVED PHOTOEMISSION (ARPES)



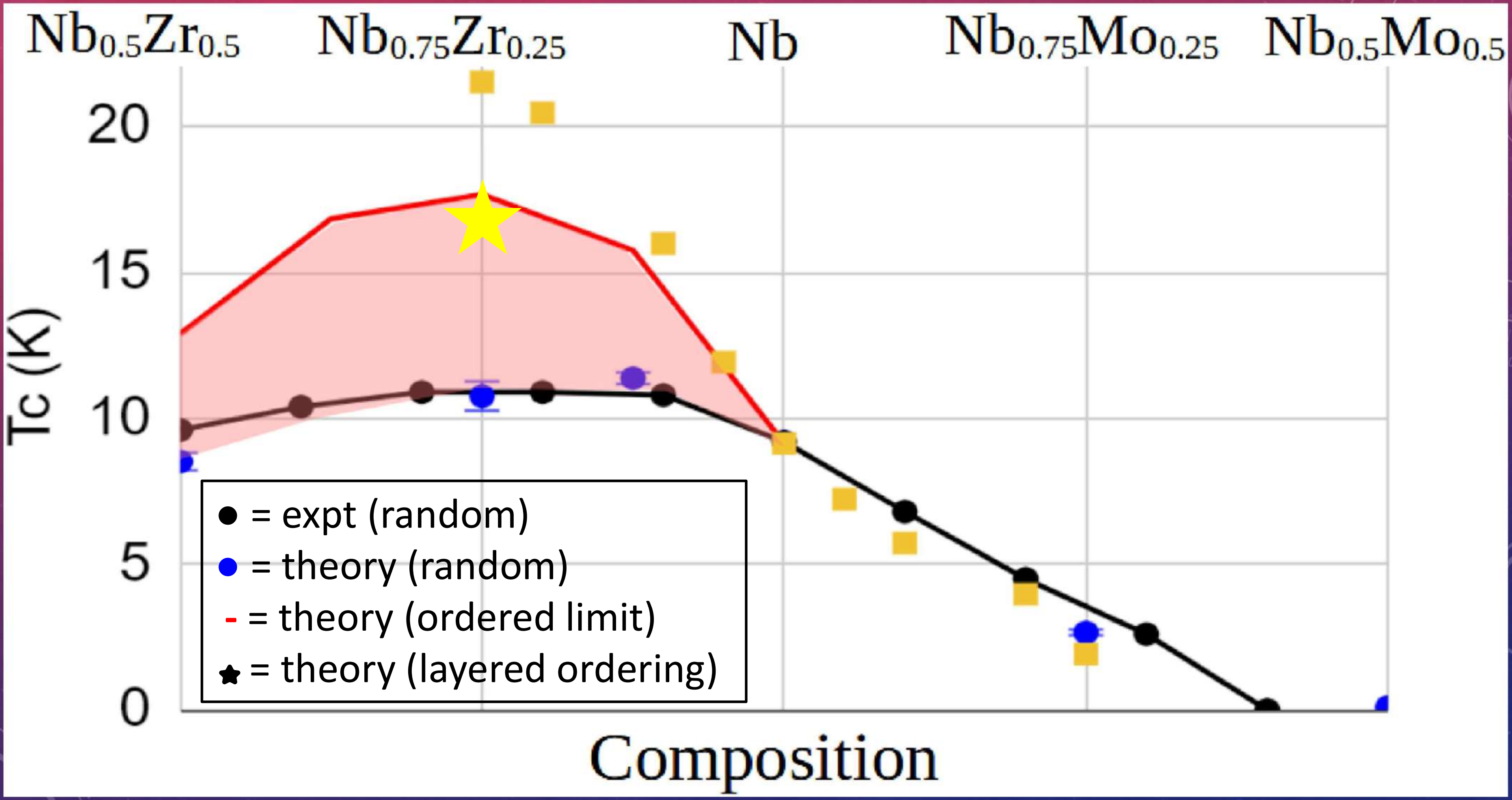
Niedzielski and Arias,
in preparation

INELASTIC HELIUM ATOM SCATTERING (HAS)



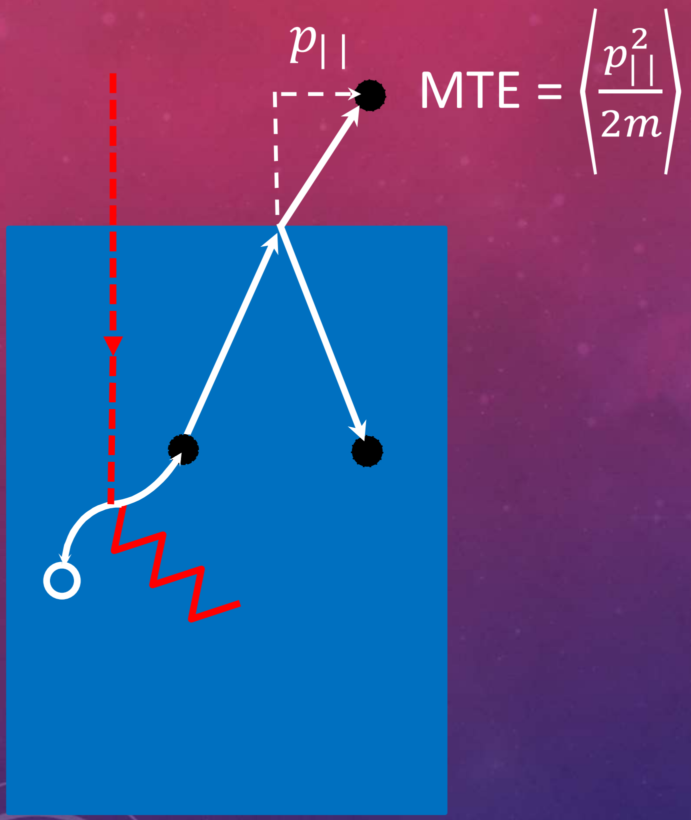
Kelley, Sundararaman, Arias, DOI: 10.48550/arXiv.2306.01892

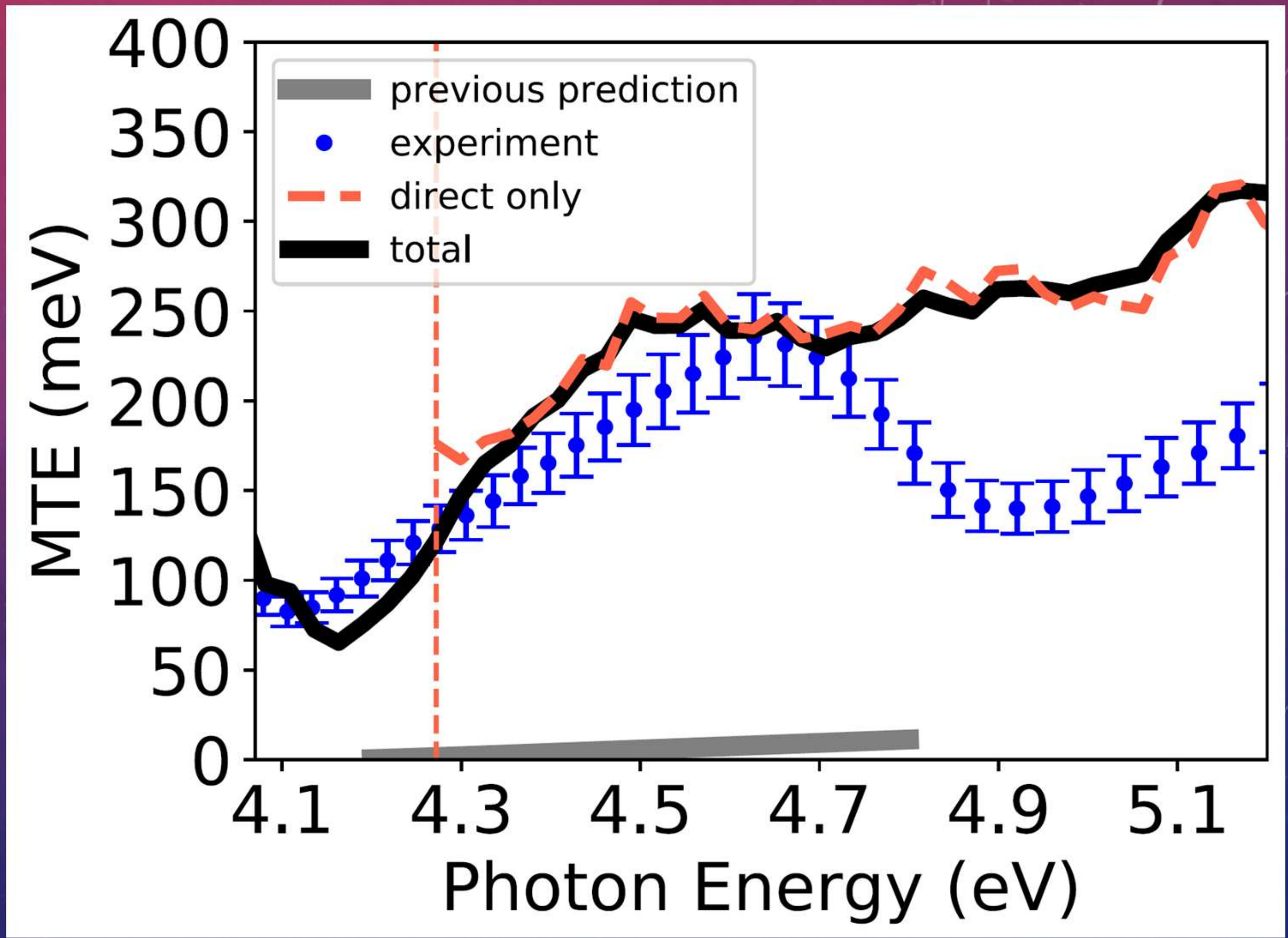
SUPERCONDUCTIVITY IN RANDOM AND ORDERED ALLOYS



Sitaraman, … , Arias, …, DOI: 10.48550/arXiv.2208.10678

DISTRIBUTION OF PHOTOEMITTED ELECTRONS





Nangoi, … , Arias, …, PRB (201)
DOI: 10.1103/PhysRevB.104.115132

MANY-BODY THEORY

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

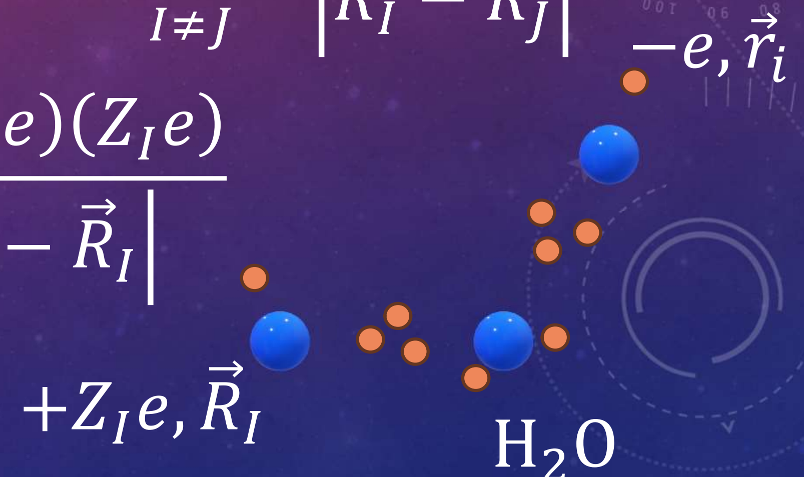
-PAM Dirac, 1929

QUANTUM MECHANICS OF MATERIAL SYSTEMS

$$\hat{H} = \hat{T} + \hat{V} = \hat{T}_e + \hat{T}_N + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN}$$

$$= \sum_i \left(-\frac{\hbar^2}{2m_e}\nabla_i^2\right) + \sum_I \left(-\frac{\hbar^2}{2M_I}\nabla_I^2\right) + \frac{1}{2}\sum_{I\neq J}\frac{k_c(Z_I e)(Z_J e)}{\left|\vec{R}_I - \vec{R}_J\right|}$$

$$+\frac{1}{2}\sum_{i\neq j}\frac{k_c(-e)(-e)}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{Ii}\frac{k_c(-e)(Z_I e)}{\left|\vec{r}_i - \vec{R}_I\right|}$$



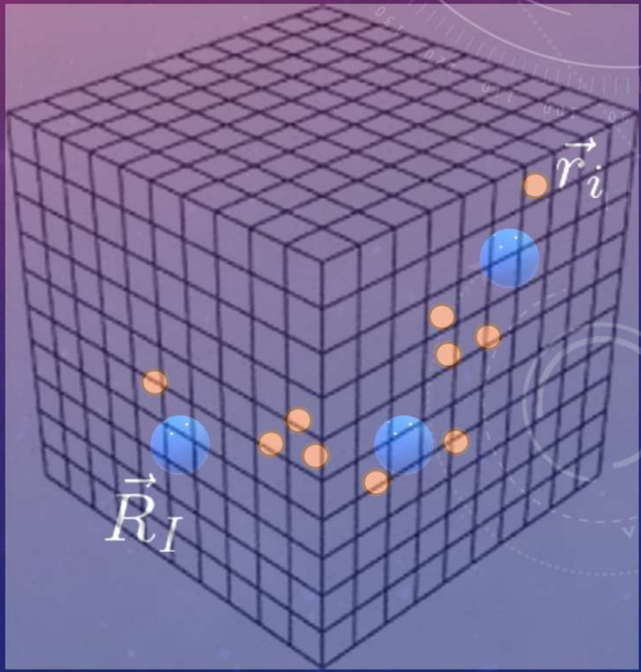
QUANTUM MECHANICS OF MATERIAL SYSTEMS

Must solve …

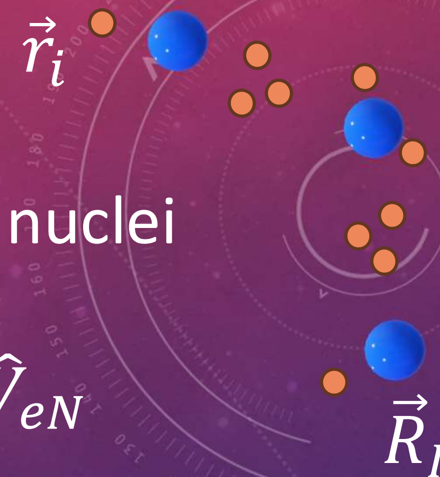
$$\hat{H}\,\Psi_n(\vec{R}_1, \vec{R}_2, \dots; \vec{r}_1, \vec{r}_2, \dots) = E_n\,\Psi_n(\vec{R}_1, \vec{R}_2, \dots; \vec{r}_1, \vec{r}_2, \dots)$$

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

- each particle has 1000 choices
- resulting in $1000^{3+10} = 10^{39}$ arrangements
- requiring 10^{39} c-numbers x 16 B/c-num
  $= 1.6 \times 10^{40}$ B $\approx 10^{19}$ ZB $\approx 10^{18}$ x [internet]



BORN-OPPENHEIMER APPROXIMATION



- $M_I > 1800\ m_e \Rightarrow e^-$'s move, respond much quicker than nuclei
- Treat nuclei as stationary (put back their motion later):

$$\hat{T}_N = 0,\ \hat{V}_{NN} = \text{constant} \ \Rightarrow \hat{H} = V_{NN} + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$$

$$V_{NN}(\vec{R}_1, \vec{R}_2, \dots) = \frac{1}{2}(k_c e^2) \sum_{I \neq J} \frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|} \qquad \hat{T}_e = -\frac{1}{2}\left(\frac{\hbar^2}{m_e}\right) \sum_i \nabla_i^2$$

$$\hat{V}_{eN}(\vec{R}_1, \vec{R}_2, \dots) = -(k_c e^2) \sum_{i,I} \frac{1}{\left|\vec{r}_i - \vec{R}_I\right|} \qquad \hat{V}_{ee} = \frac{1}{2}(k_c e^2) \sum_{i \neq j} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|}$$

ATOMIC UNITS

$$\hat{H}(\vec{R}_1, \vec{R}_2, \dots) = V_{NN} + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$$

$$V_{NN}(\vec{R}_1, \vec{R}_2, \dots) = \frac{1}{2}\cancel{(k_c e^2)} \sum_{I \neq J} \frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|} \qquad \hat{T}_e = -\frac{1}{2}\cancel{\left(\frac{\hbar^2}{m_e}\right)} \sum_i \nabla_i^2$$

$$\hat{V}_{eN}(\vec{R}_1, \vec{R}_2, \dots) = -\cancel{(k_c e^2)} \sum_{i,I} \frac{1}{\left|\vec{r}_i - \vec{R}_I\right|} \qquad \hat{V}_{ee} = \frac{1}{2}\cancel{(k_c e^2)} \sum_{i \neq j} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|}$$

Choose:

$$k_c e^2 = 1\ \mathrm{E\ L}, \quad \hbar^2/m_e = 1\ \mathrm{E\ L}^2$$

$$\Rightarrow 1\ \mathrm{E} = 1\ \mathrm{hartree} \approx 27.21\ \mathrm{eV}, 1\ \mathrm{L} = 1\ \mathrm{bohr} \approx 0.5291\ \mathrm{Å}$$

ATOMIC UNITS

$$\hat{H}(\vec{R}_1, \vec{R}_2, \dots) = V_{NN} + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$$

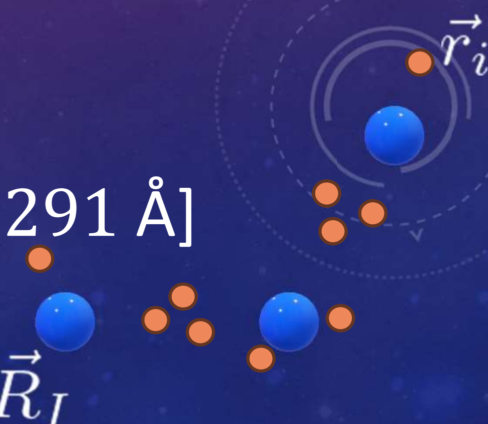
$$V_{NN}(\vec{R}_1, \vec{R}_2, \dots) = \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|}$$

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2$$

$$\hat{V}_{eN}(\vec{R}_1, \vec{R}_2, \dots) = -\sum_{i,I} \frac{1}{\left|\vec{r}_i - \vec{R}_I\right|}$$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{i \neq j} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|}$$

$[\Rightarrow 1\ \mathrm{E} = 1\ \mathrm{hartree} \approx 27.21\ \mathrm{eV}, 1\ \mathrm{L} = 1\ \mathrm{bohr} \approx 0.5291\ \text{Å}]$



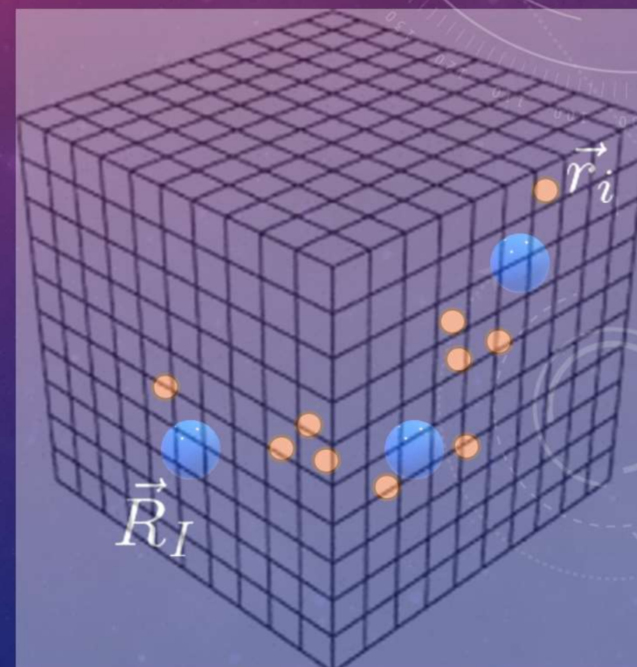
NEED FOR ADDITIONAL SIMPLIFICATIONS

Now, must solve …

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

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 ≈ 10^{10} ZB ≈ 10^{9} x [internet]



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

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

- bit.ly/43EPjXF

THANK YOU!

TAA2@CORNELL.EDU

SCAN