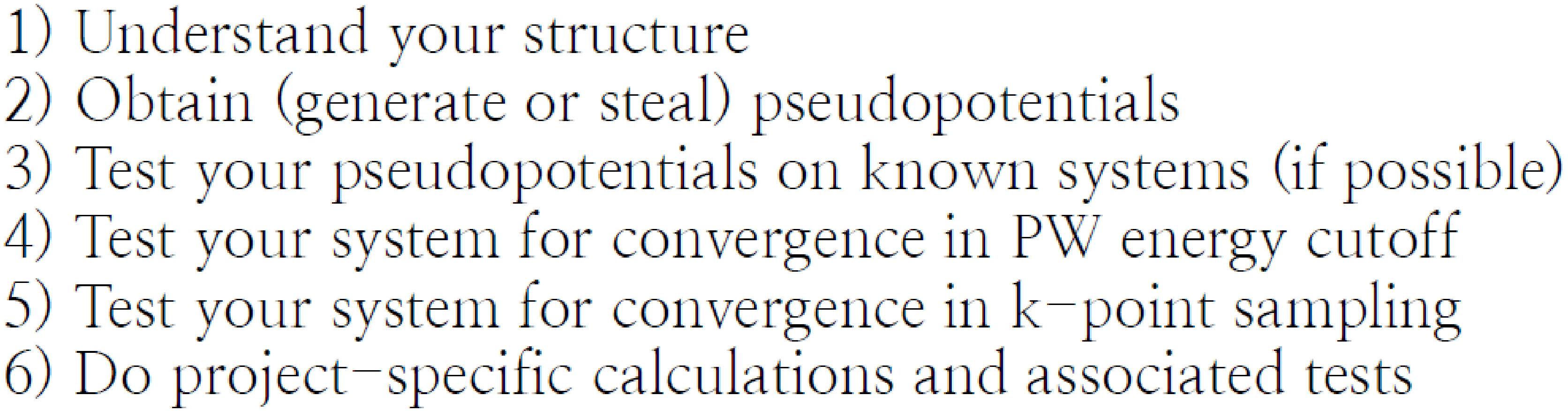
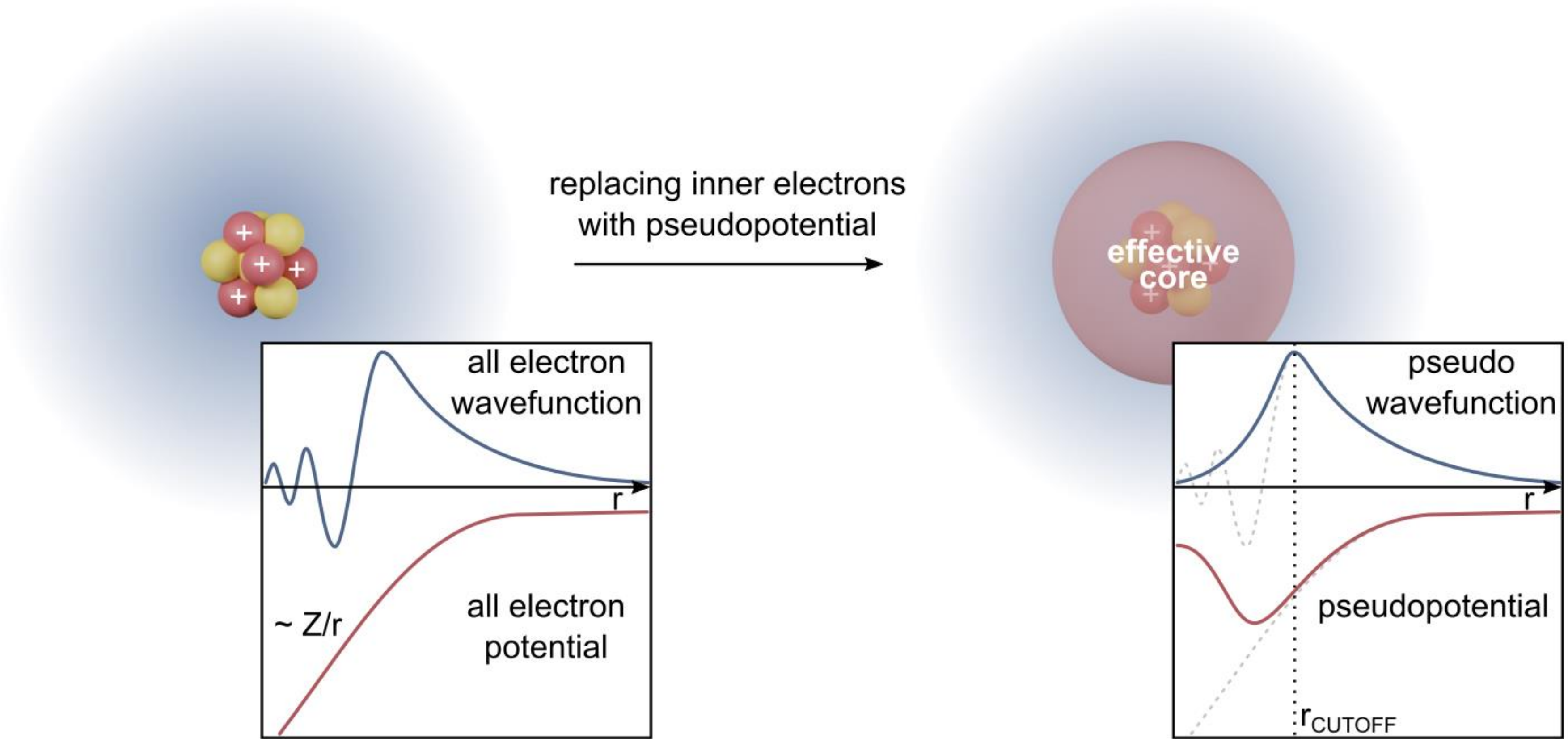
WHY DFT? Besides E(k) and DoS?

Equilibrium crystal structures
Elastic constants
Charge densities
Vibrational properties
Qualitative prediction of band topology

How to Do DFT with Quantum Espresso?



1) Understand your structure
2) Obtain (generate or steal) pseudopotentials
3) Test your pseudopotentials on known systems (if possible)
4) Test your system for convergence in PW energy cutoff
5) Test your system for convergence in k−point sampling
6) Do project−specific calculations and associated tests


replacing inner electrons
with pseudopotential
effective
core
all electron
wavefunction
r
~ Z/r
all electron
potential
pseudo
wavefunction
r
pseudopotential
r_{CUTOFF}

What will almost always get wrong?

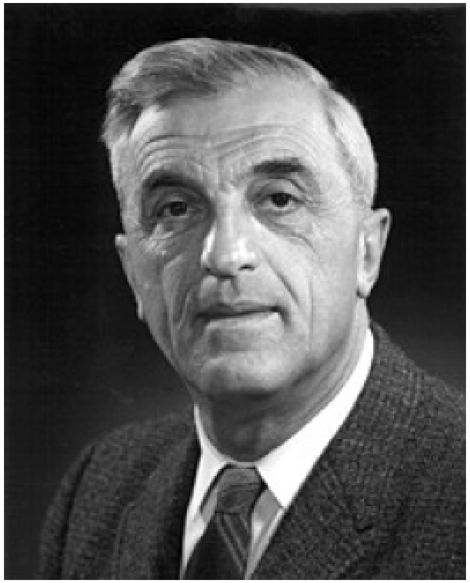
Excited state properties:

- Band gaps [can do GW instead]
- Optical properties (electron–hole interactions) [can do BSE]

Other missing bits and trouble areas:

- Overbinding in LDA, underbinding in GGA
- Strongly correlated systems (narrow d– and f– bands)
- Lack of van der Waals interactions [can be added through the use of various schemes in addition to DFT]
- Presence of self–interaction error (electron interacts with its own charge density) [reduced by using hybrid functionals with some fraction of exact–exchange, but expensive]

- Wavefunctions
- Collective motions of the atoms



Bloch

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{\mathbf{k}}(\mathbf{r})$$

equivalently:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = u_{\mathbf{k}}(\mathbf{r})$$

Allowed form of the Bloch vectors:

$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\mathbf{b}_i$$

where m_i are integers

We say the solutions are “Plane Waves”
→ requires periodic boundary conditions

Bloch form of solution:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

can be satisfied by expansion of the form:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{G}=0}^{\infty} c_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

AB INTIO SOFTWARE

Plane Wave Software (for periodic system)

Quantum Espresso
VASP

Requires PERIODIC boundary conditions to work (not great for molecules

→Solution for molecules make the unit cell so large (typically 1.5 nm is enough) that the atoms in the cell can't possibly interact (how to do th https://www.youtube.com/watch?v=Z8TEpaW7RNc)

Atomic based (site-based)

Gaussian
QChem

The 1st calculation iteration is complected when all states are filled below a cutoff energy

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}=0}^{\infty} c_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) \qquad \phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Coefficients decay with increasing wavevector magnitude, and thus can be truncated without loss of accuracy:

$$\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 < E_{\mathrm{cut}}$$

Plane wave energy cutoff, typically expressed in Ry (e.g., QE) or eV (e.g. VASP)

- Many-body wavefunction (keep it simple: only 3 electrons)

$$\psi(\mathbf{r}) \to \Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

- Probability of finding electron $\#1$ at the point $\mathbf{r}$

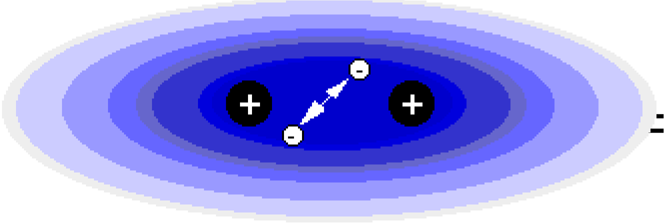
$$\mathrm{prob}(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 \, d\mathbf{r}_2 d\mathbf{r}_3$$

- Electron density at the point $\mathbf{r}$

$$n(\mathbf{r}) = \mathrm{prob}(\mathbf{r}_1 = \mathbf{r}) + \mathrm{prob}(\mathbf{r}_2 = \mathbf{r}) + \mathrm{prob}(\mathbf{r}_3 = \mathbf{r})$$

- Electrons are indistinguishable

$$n(\mathbf{r}) = 3 \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 \, d\mathbf{r}_2 d\mathbf{r}_3$$



$$= \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

Kohn and Sham said the (Helmholtz) Energy of the system is:

$$\begin{aligned} F_{HK}[\rho] = F_{KS}[\rho] &= T_s[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}' + E_{xc}[\rho] \\ &= T_s[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho] \end{aligned}$$

1) Kinetic energy of the system of non-interacting electrons at the same density.

2) Coulomb is the electrostatic term (Hartree)

3) Exchange-correlation is everything else $V_{XC}[\mathbf{r}] = \left(\frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}\right)$

How would you compute the total charge density of a crystal of N electrons?

$$n(\mathbf{r}) = \int \Psi^*(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)\,\mathrm{d}^3r_2\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N +$$

$$+\int \Psi^*(\mathbf{r}_1,\mathbf{r},\cdots,\mathbf{r}_N)\Psi(\mathbf{r}_1,\mathbf{r},\cdots,\mathbf{r}_N)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N + \cdots$$

$$+\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r})\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r})\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_{N-1} =$$

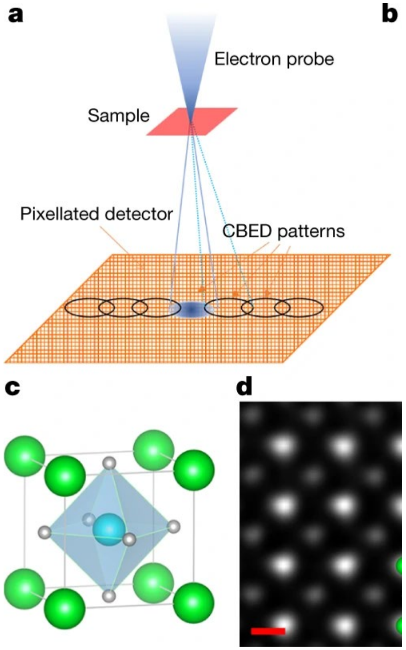
$$= \int \left(\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}-\mathbf{r}_2)+\cdots+\delta(\mathbf{r}-\mathbf{r}_N)\right)$$

$$\Psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N =$$

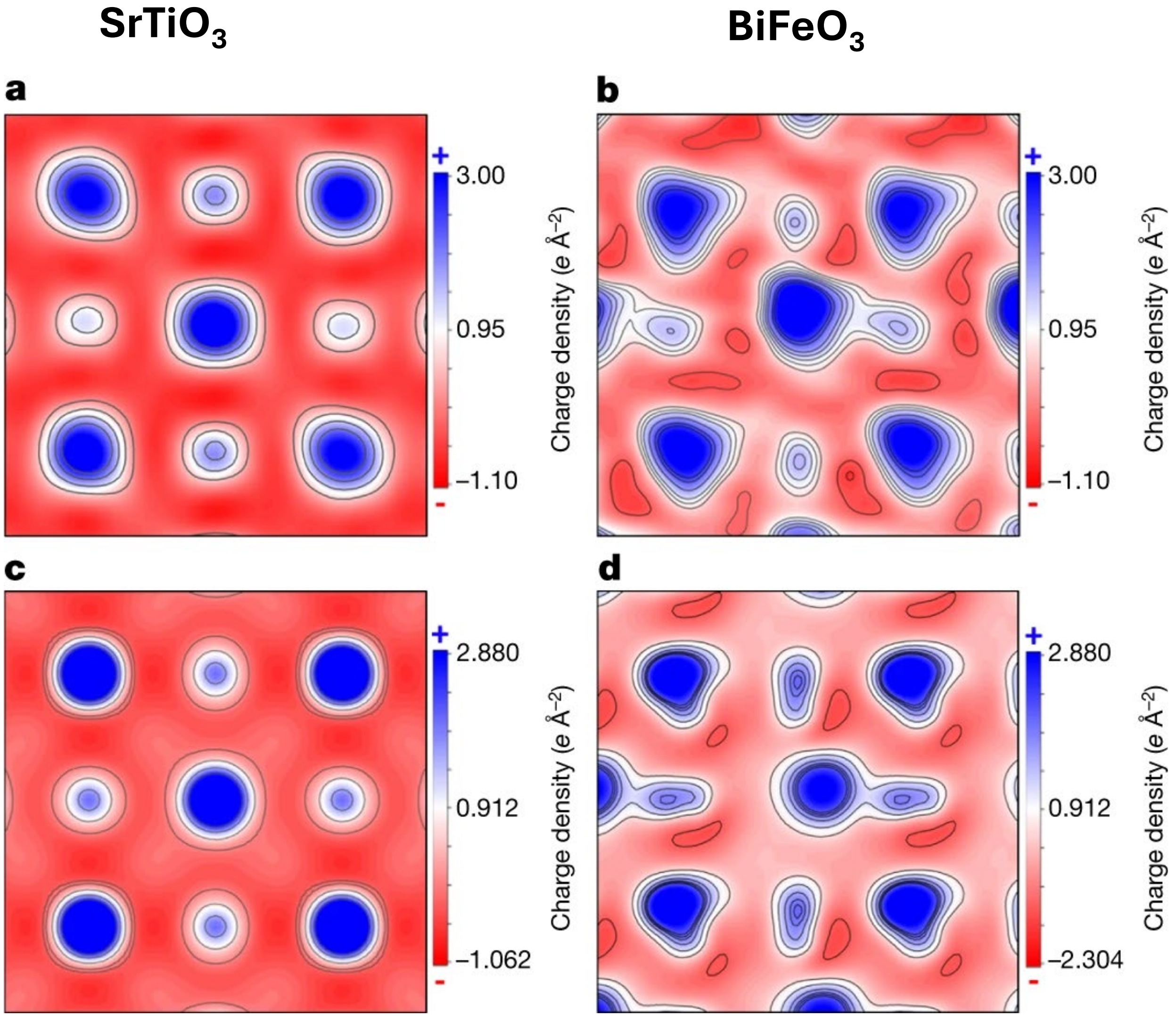
$$= \sum_{i=1}^{N}\int \langle\Psi|\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N\rangle\,\delta(\mathbf{r}-\mathbf{r}_i)\,\langle\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N|\Psi\rangle\;\mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N =$$

$$= N\int \langle\Psi|\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N\rangle\,\delta(\mathbf{r}-\mathbf{r}_1)\,\langle\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N|\Psi\rangle\;\mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N =$$

ELECTRON DENSITY MAPS, ρ(r)

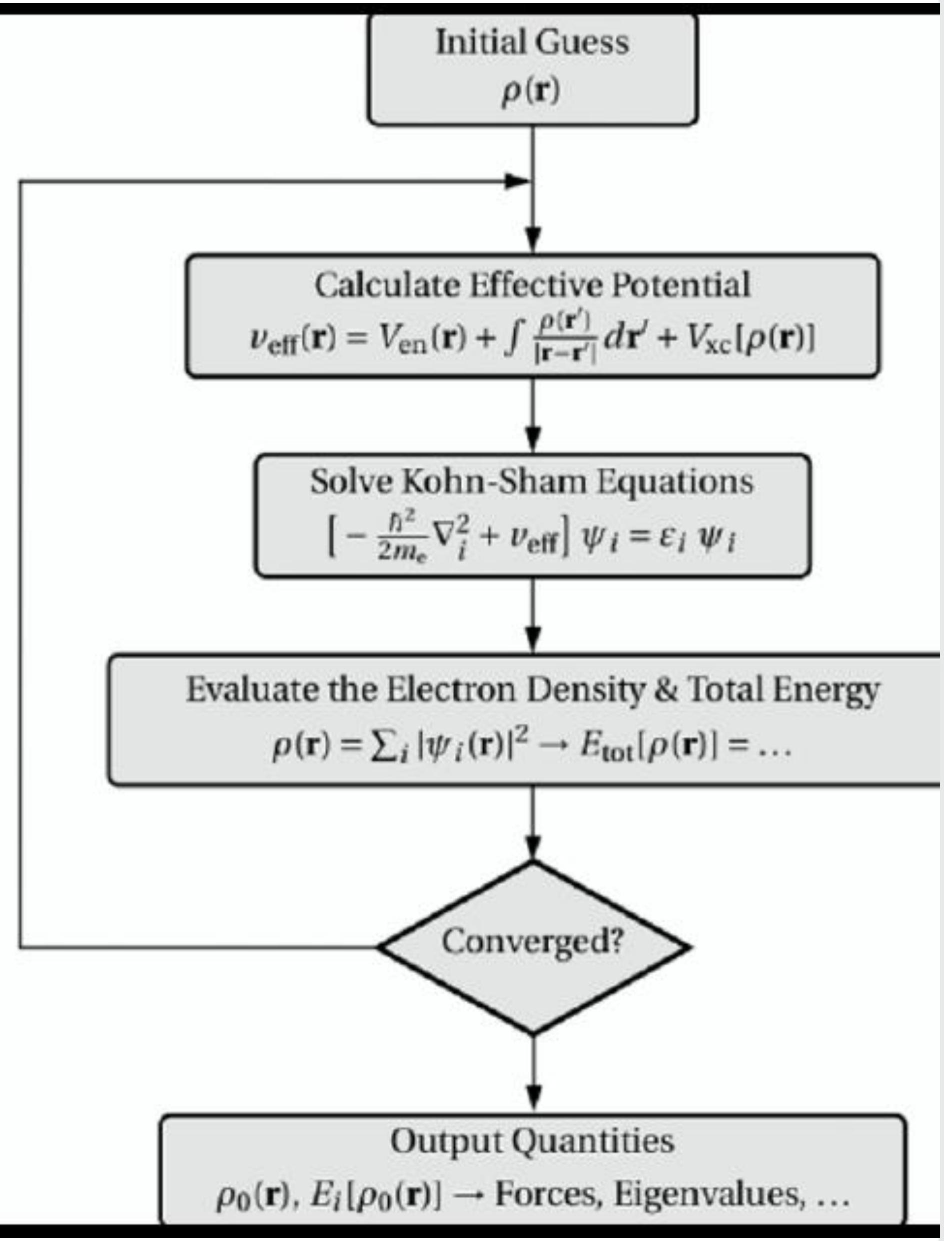


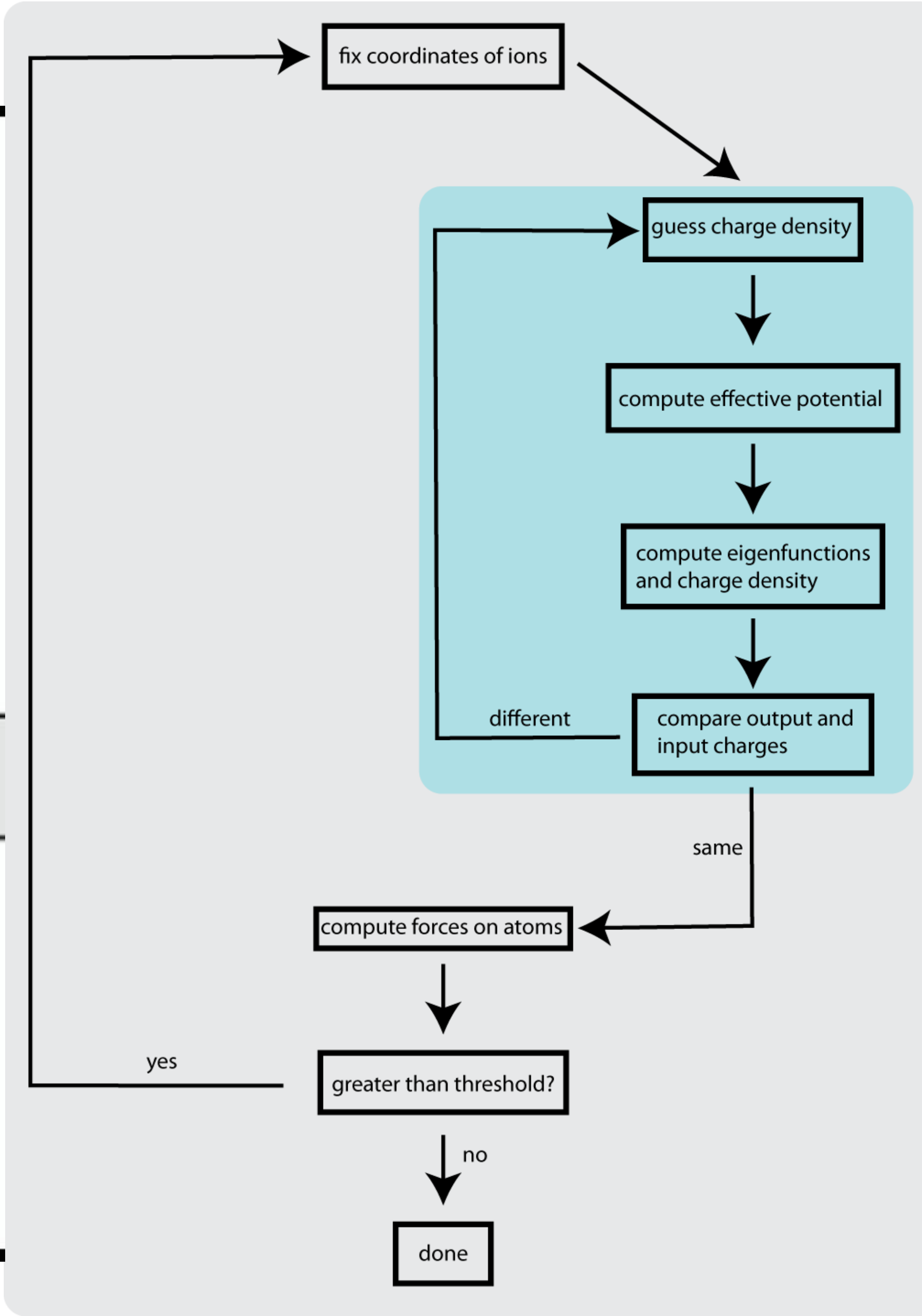
EXPERIMENT



THEORY (DFT)

Real-space charge-density imaging with sub-ångström resolution by four-dimensional electron microscopy. *Nature* **575**, 480–484 (2019). https://doi.org/10.1038/s41586-019-1649-6


Initial Guess
$\rho(\mathbf{r})$
Calculate Effective Potential
$v_{\text{eff}}(\mathbf{r}) = V_{\text{en}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}[\rho(\mathbf{r})]$
Solve Kohn-Sham Equations
$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + v_{\text{eff}} \right] \psi_i = \varepsilon_i \psi_i$
Evaluate the Electron Density & Total Energy
$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \rightarrow E_{\text{tot}}[\rho(\mathbf{r})] = \ldots$
Converged?
Output Quantities
$\rho_0(\mathbf{r}),\ E_i[\rho_0(\mathbf{r})] \rightarrow$ Forces, Eigenvalues, …


fix coordinates of ions
guess charge density
compute effective potential
compute eigenfunctions and charge density
different
compare output and input charges
same
compute forces on atoms
yes
greater than threshold?
no
done

$$
\begin{aligned}
F_{HK}[\rho] = F_{KS}[\rho] &= T_s[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}' + E_{xc}[\rho] \\
&= T_s[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho]
\end{aligned}
$$

Take the functional derivative wrt ρ, and evaluating at LCAO orbitals gives the Kohn-Sham equations

$$
\left[-\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})
$$

$$F_{HK}[\rho] = F_{KS}[\rho] = T_s[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}' + E_{xc}[\rho]$$

$$= T_s[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho]$$

Take the functional derivative wrt ρ, and evaluating at LCAO orbitals gives the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

where the Kohn-Sham potential is given as:

$$V_{ks}[\rho](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r})$$

$$V_{Hartree}[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'$$

$$V_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

WHY?

In the Kohn-Sham equation the atoms are not interacting (i.e Schrodinger Equation), **Instead ρ keeps track of all interactions!**

V_{XC}: LDA Local Density Approximation

Approximate as that of a homogeneous electron gas where each nuclei replaced by a uniform positively charge background electron density ρ_{gs}

$$V_{xc}(\mathbf{r};n) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \epsilon_{xc}(\mathbf{r};n) + \int n(\mathbf{r}')\frac{\delta \epsilon_{xc}(\mathbf{r}';n)}{\delta n(\mathbf{r})}\mathrm{d}^3r'$$

LDA potential:

$$V_{xc}(\mathbf{r};n) = \epsilon_{xc}^{LD}(n) + n\frac{\mathrm{d}\epsilon_{xc}^{LD}(n)}{\mathrm{d}n} = \frac{\mathrm{d}}{\mathrm{d}n}\left(n\epsilon_{xc}^{LD}(n)\right) = V_{xc}^{LD}(n)$$

the electron gas exchange term

$$V_{xc}^{LD} = V_x^{LD} + V_c^{LD}$$

$$\epsilon_x^{LD}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{\frac{1}{3}} \longrightarrow V_x^{LD} = -\frac{1}{\pi}(3\pi^2 n)^{\frac{1}{3}} = \frac{4}{3}\epsilon_x^{LD}$$

$$V_c^{LD} = \frac{A}{2}\left\{\ln\left(\frac{y^2}{Y(y)}\right) + \frac{2b}{Q}\arctan\left(\frac{Q}{2y+b}\right) + \right.$$

$$\left. -\frac{by_0}{Y(y_0)}\left[\ln\left(\frac{(y-y_0)^2}{Y(y)}\right) + \frac{2(b+2y_0)}{Q}\arctan\left(\frac{Q}{2y+b}\right)\right]\right\} +$$

$$-\frac{A}{6}\frac{c(y-y_0) - by_0y}{(y-y_0)Y(y)}$$

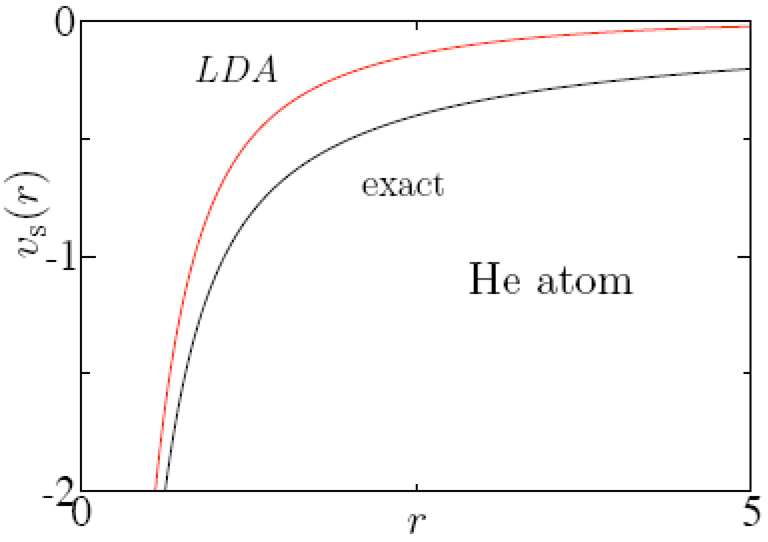
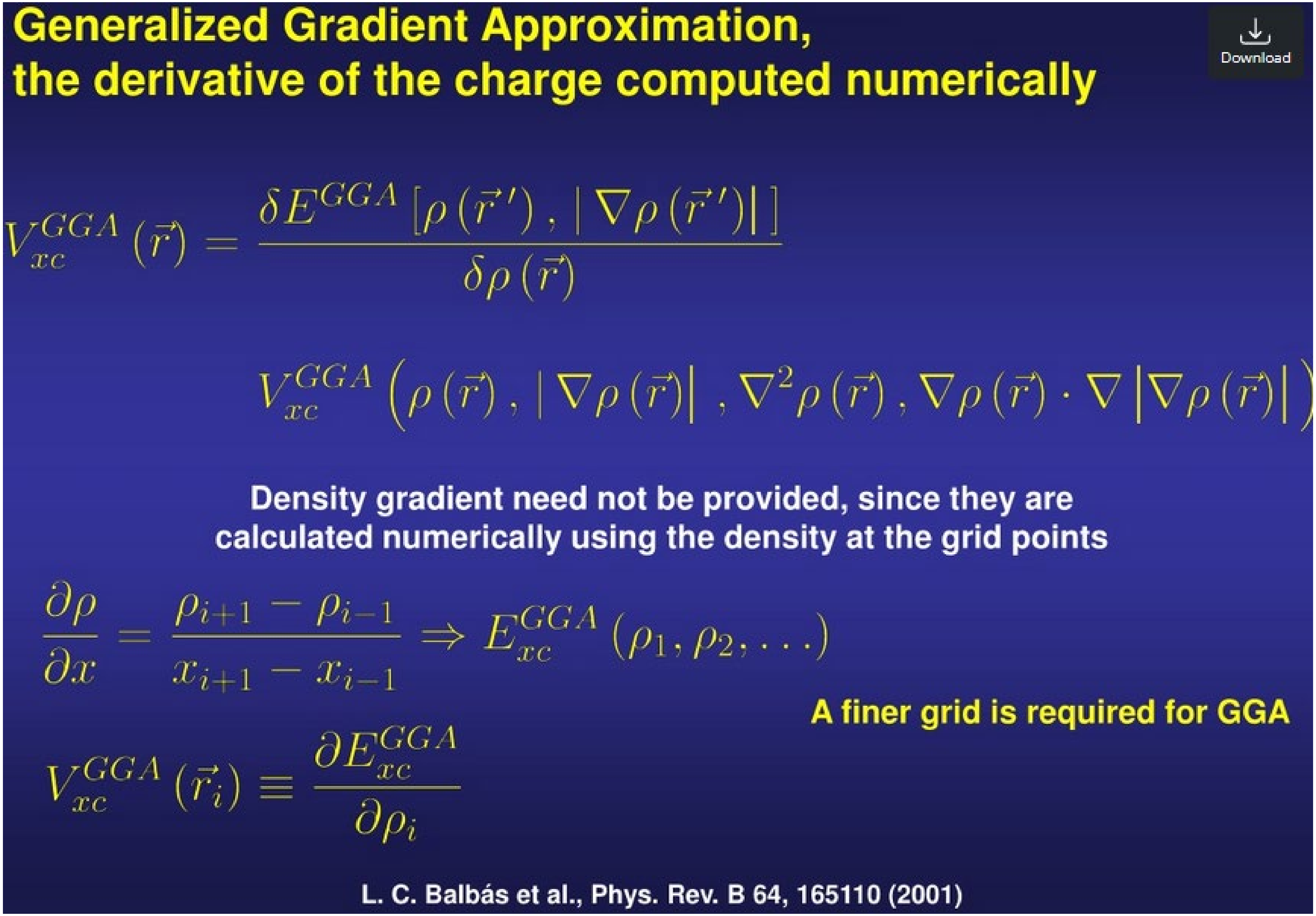


FIG. 7: Exact and LDA KS potentials for the He atom.

LDA potential for the He atom. It decays far too rapidly, and so its orbitals are far too shallow. The HOMO is at -0.5704 H, while the LUMO is not bound at all.

V_{XC}: GGA Generalized Gradient Approximation



Generalized Gradient Approximation, the derivative of the charge computed numerically

$$V_{xc}^{GGA}(\vec{r}) = \frac{\delta E^{GGA}[\rho(\vec{r}\,'), |\nabla\rho(\vec{r}\,')|]}{\delta\rho(\vec{r})}$$

$$V_{xc}^{GGA}\left(\rho(\vec{r}), |\nabla\rho(\vec{r})|, \nabla^2\rho(\vec{r}), \nabla\rho(\vec{r})\cdot\nabla\left|\nabla\rho(\vec{r})\right|\right)$$

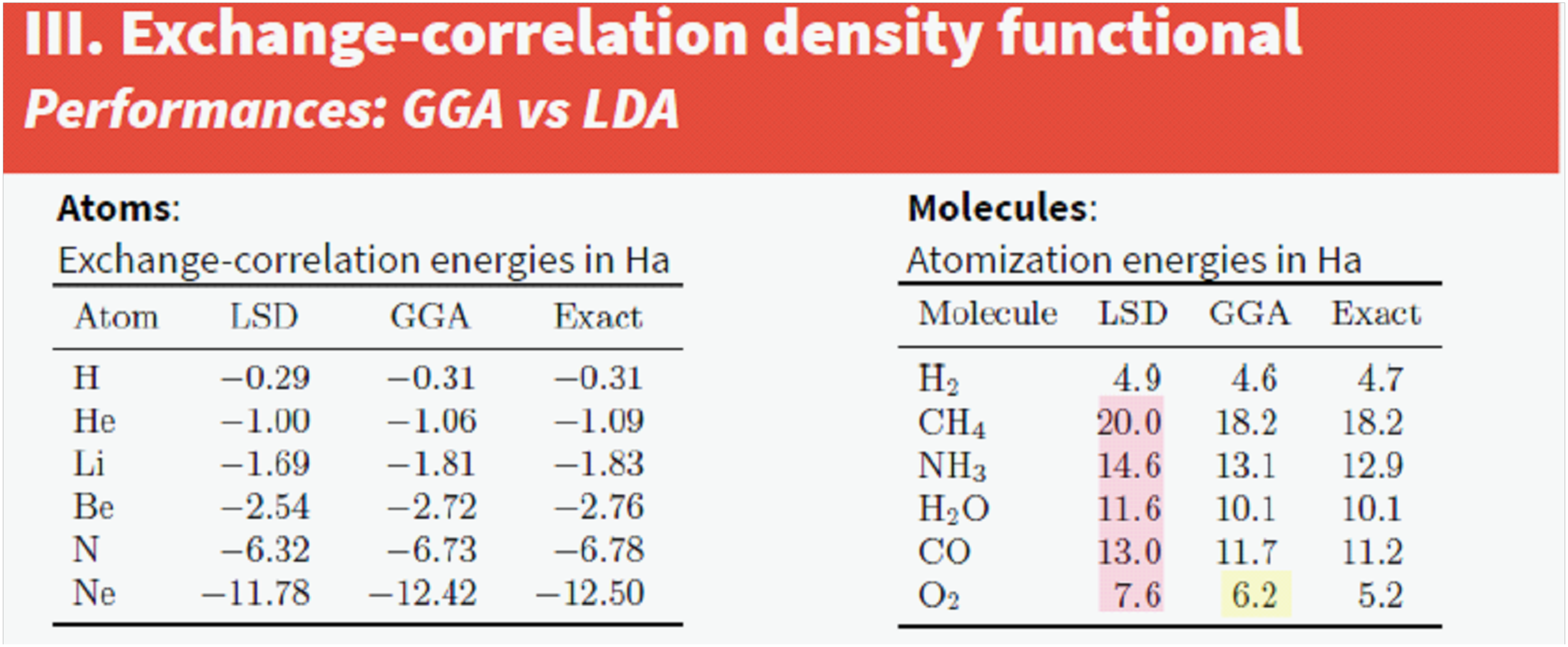
Density gradient need not be provided, since they are calculated numerically using the density at the grid points

$$\frac{\partial\rho}{\partial x} = \frac{\rho_{i+1} - \rho_{i-1}}{x_{i+1} - x_{i-1}} \Rightarrow E_{xc}^{GGA}(\rho_1, \rho_2, \ldots)$$

A finer grid is required for GGA

$$V_{xc}^{GGA}(\vec{r}_i) \equiv \frac{\partial E_{xc}^{GGA}}{\partial\rho_i}$$

L. C. Balbás et al., Phys. Rev. B 64, 165110 (2001)



III. Exchange-correlation density functional

Performances: GGA vs LDA

Atoms:

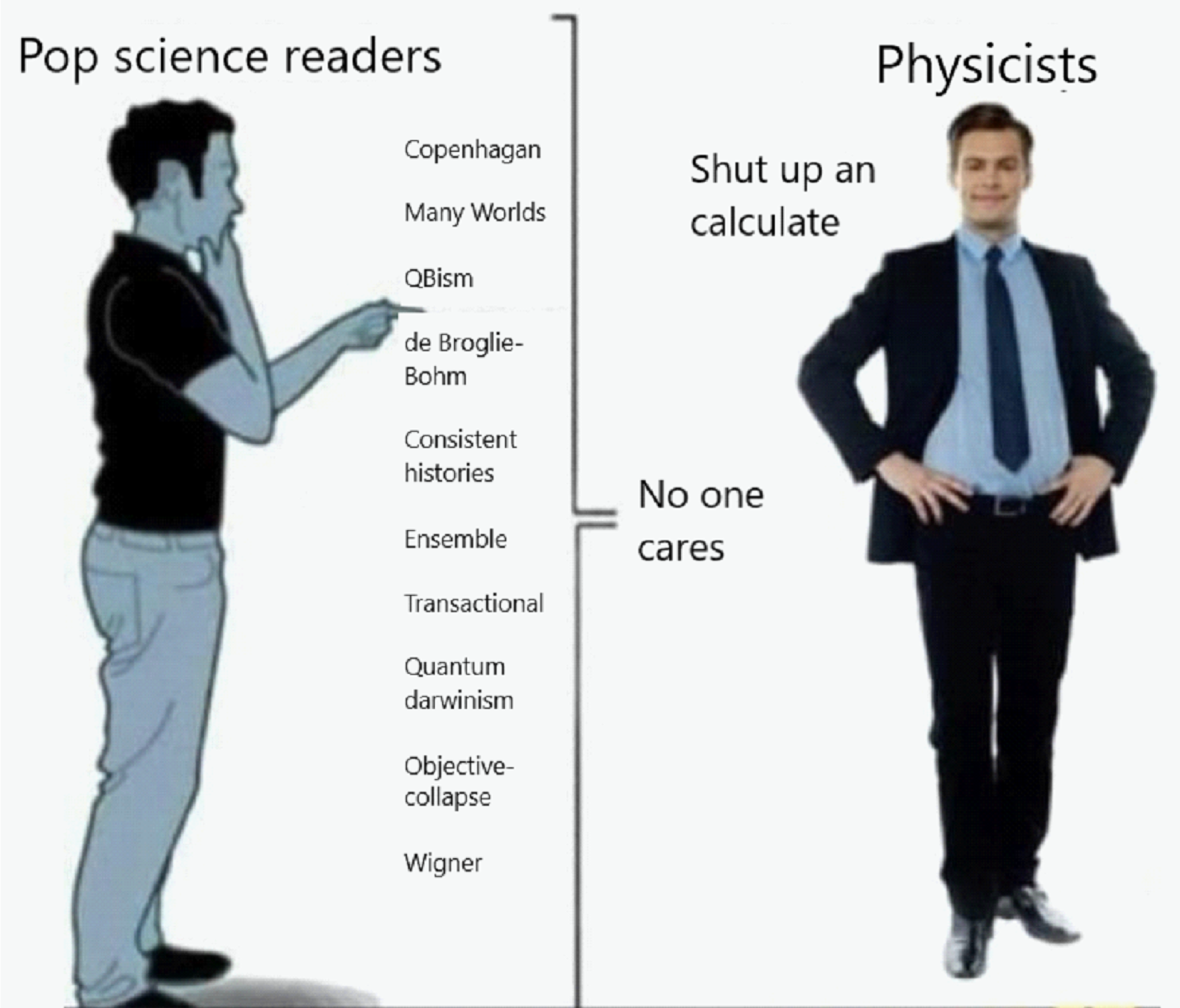
Exchange-correlation energies in Ha

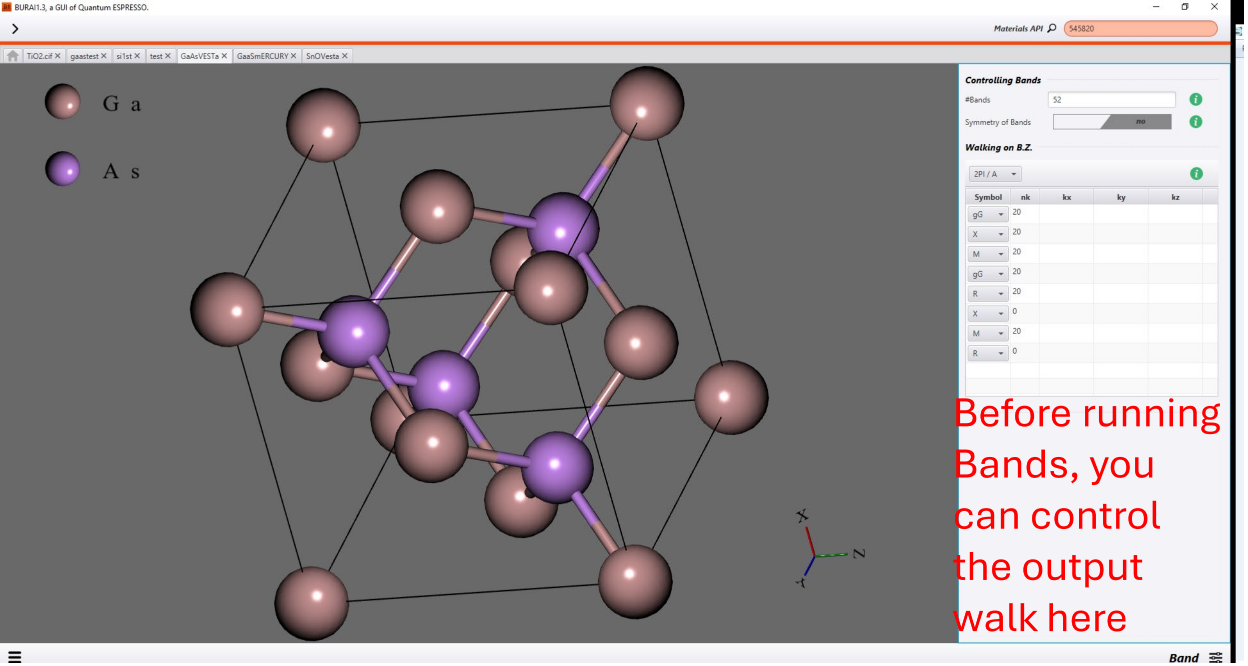
Atom	LSD	GGA	Exact
H	−0.29	−0.31	−0.31
He	−1.00	−1.06	−1.09
Li	−1.69	−1.81	−1.83
Be	−2.54	−2.72	−2.76
N	−6.32	−6.73	−6.78
Ne	−11.78	−12.42	−12.50

Molecules:

Atomization energies in Ha

Molecule	LSD	GGA	Exact
H_2	4.9	4.6	4.7
CH_4	20.0	18.2	18.2
NH_3	14.6	13.1	12.9
H_2O	11.6	10.1	10.1
CO	13.0	11.7	11.2
O_2	7.6	6.2	5.2


Pop science readers
Copenhagen
Many Worlds
QBism
de Broglie-Bohm
Consistent histories
Ensemble
Transactional
Quantum darwinism
Objective-collapse
Wigner
No one cares
Physicists
Shut up an calculate



Controlling Bands

#Bands: 52

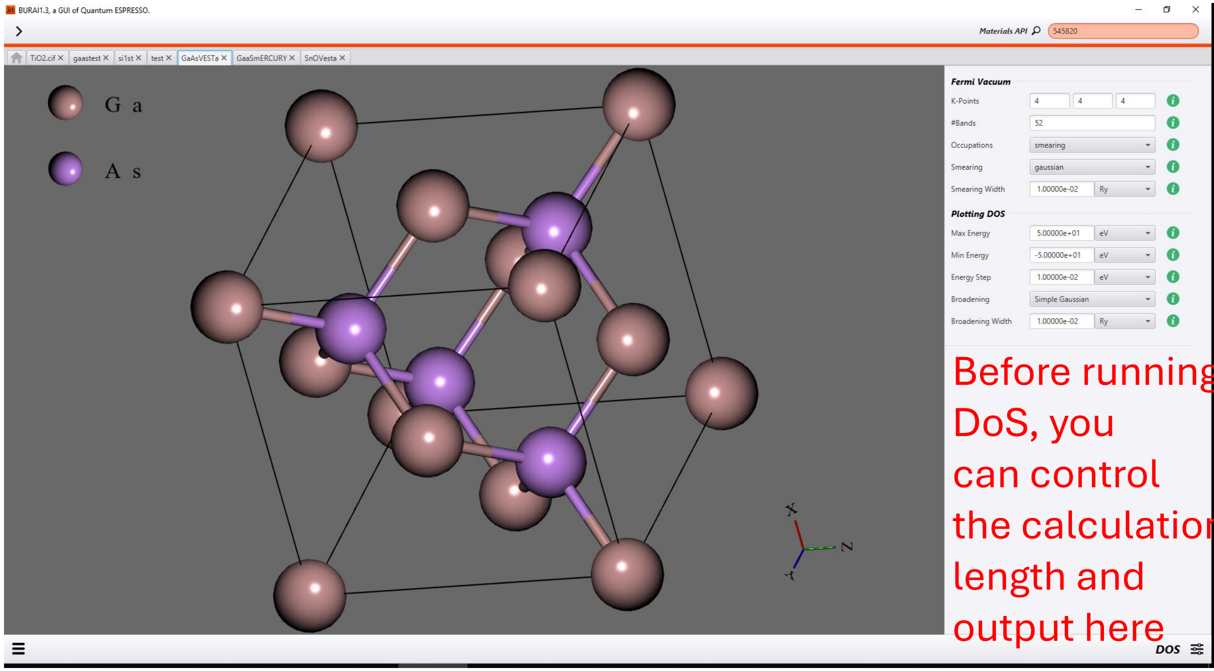
Symmetry of Bands: no

Walking on B.Z.

2PI / A

Symbol	nk	kx	ky	kz
gG	20			
X	20			
M	20			
gG	20			
R	20			
X	0			
M	20			
R	0			

Before running Bands, you can control the output walk here



Fermi Vacuum

K-Points: 4 4 4

#Bands: 52

Occupations: smearing

Smearing: gaussian

Smearing Width: 1.00000e-02 Ry

Plotting DOS

Max Energy: 5.00000e+01 eV

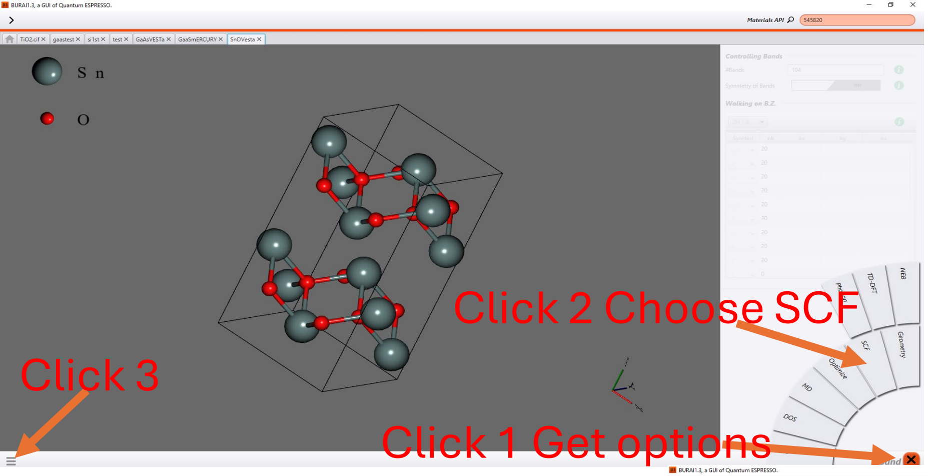
Min Energy: -5.00000e+01 eV

Energy Step: 1.00000e-02 eV

Broadening: Simple Gaussian

Broadening Width: 1.00000e-02 Ry

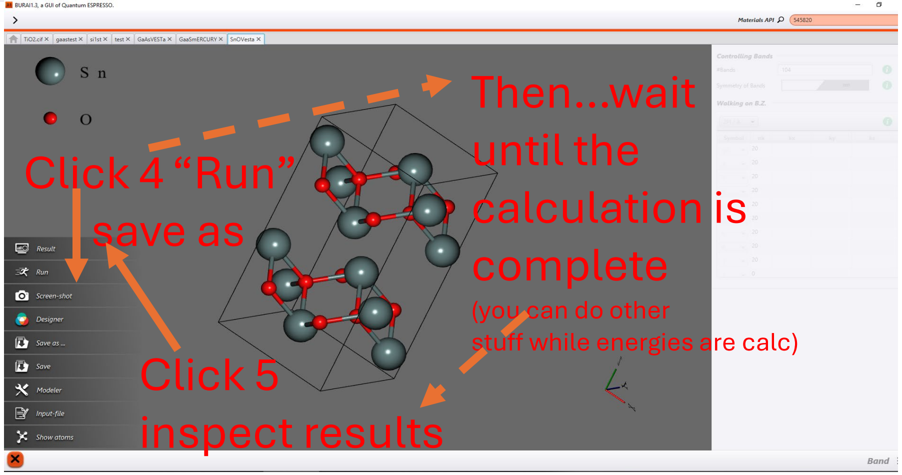
Before running DoS, you can control the calculatio length and output here



Click 2 Choose SCF

Click 3

Click 1 Get options

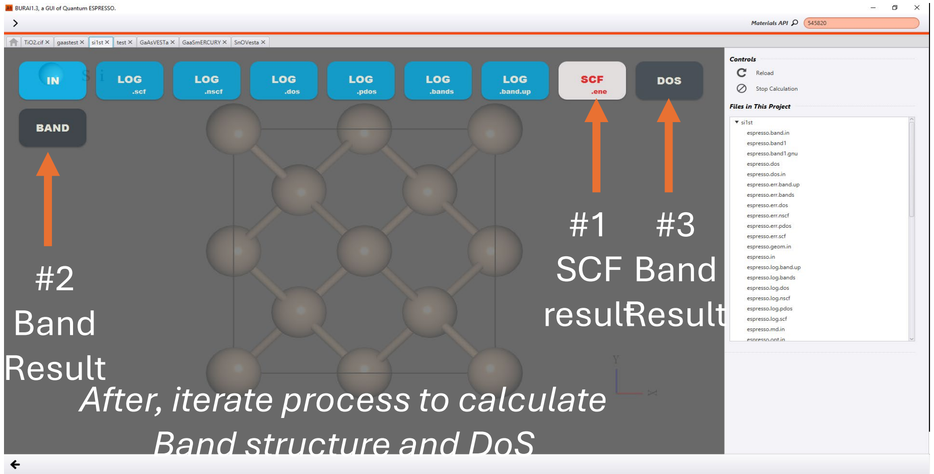


Click 4 "Run" save as

Click 5 inspect results

Then...wait until the calculation is complete

(you can do other stuff while energies are calc)

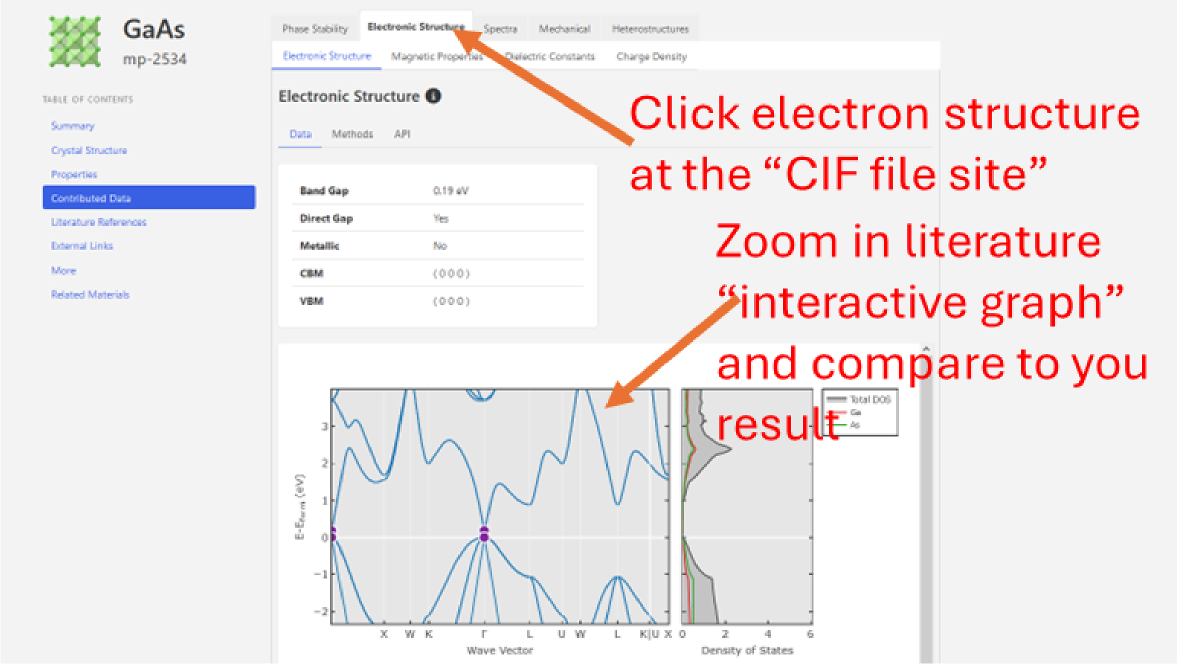


#1 SCF result

#3 Band Result

#2 Band Result

After, iterate process to calculate Band structure and DoS

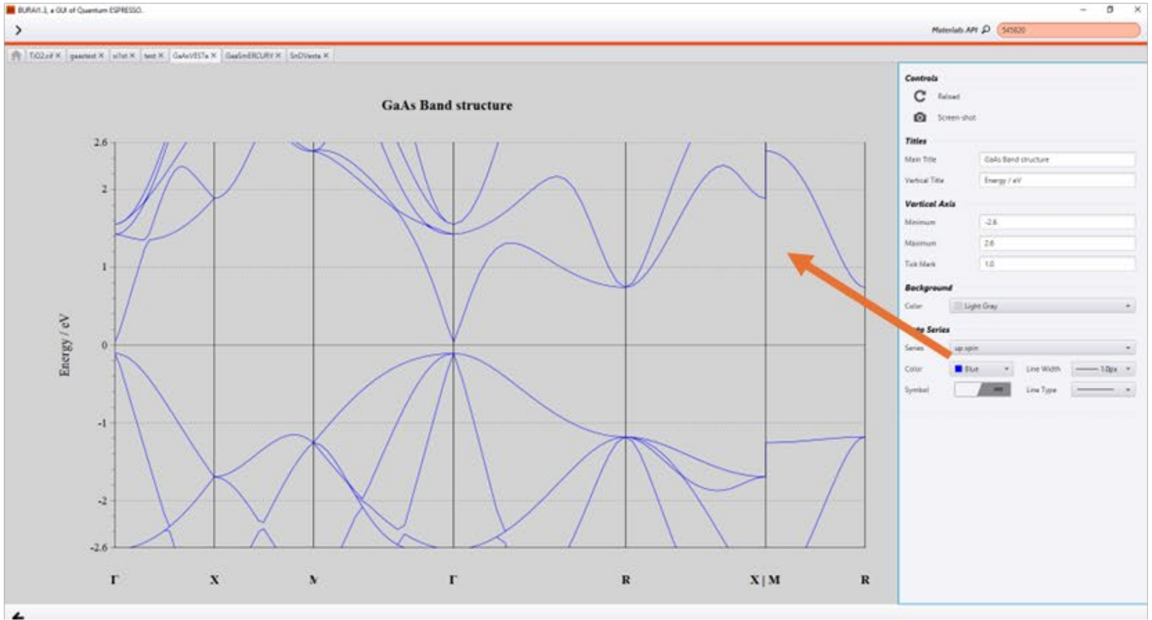


Band Gap	0.19 eV
Direct Gap	Yes
Metallic	No
CBM	(0 0 0)
VBM	(0 0 0)

Click electron structure at the “CIF file site”

Zoom in literature “interactive graph” and compare to you result

Does your result make sense with literature?



Materials API: 545820

Titles
Main Title: GaAs Band structure
Vertical Title: Energy / eV

Vertical Axis
Minimum: -2.6
Maximum: 2.6
Tick Mark: 1.0

Background
Color: Light Gray

Series
Series: up spin
Color: Blue
Line Width: 1.0px
Symbol
Line Type

Mostly good! But you took slight different path through k-space!
Change or address in your report!

Lastly, load the output file in Excel, adjust and re-plot in your favorite Sci-graphing program!