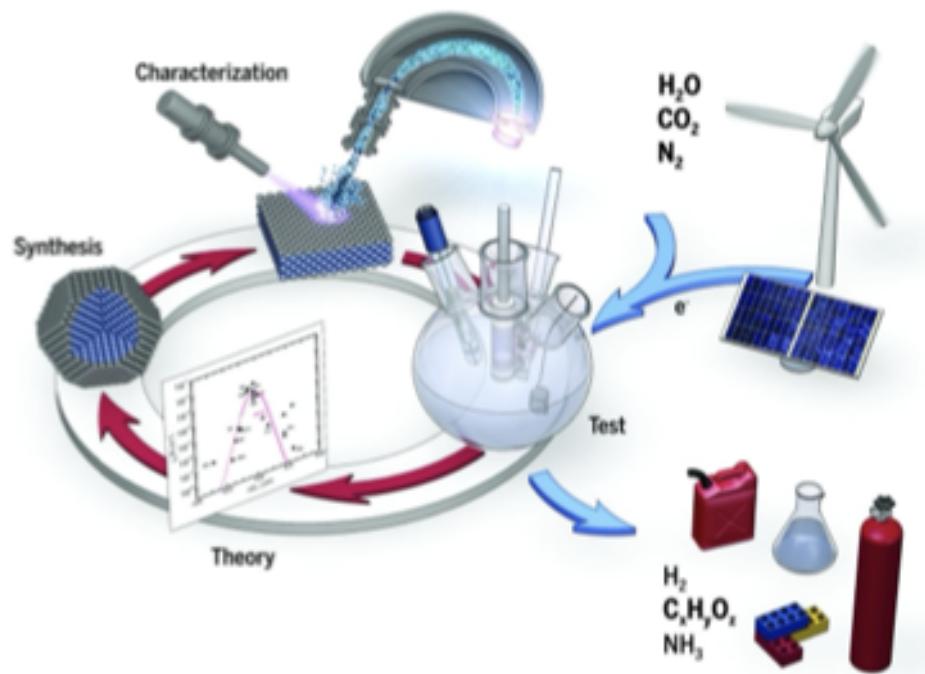




Hands-on 1. DFT bulk

Notice: Student presentation google sheet

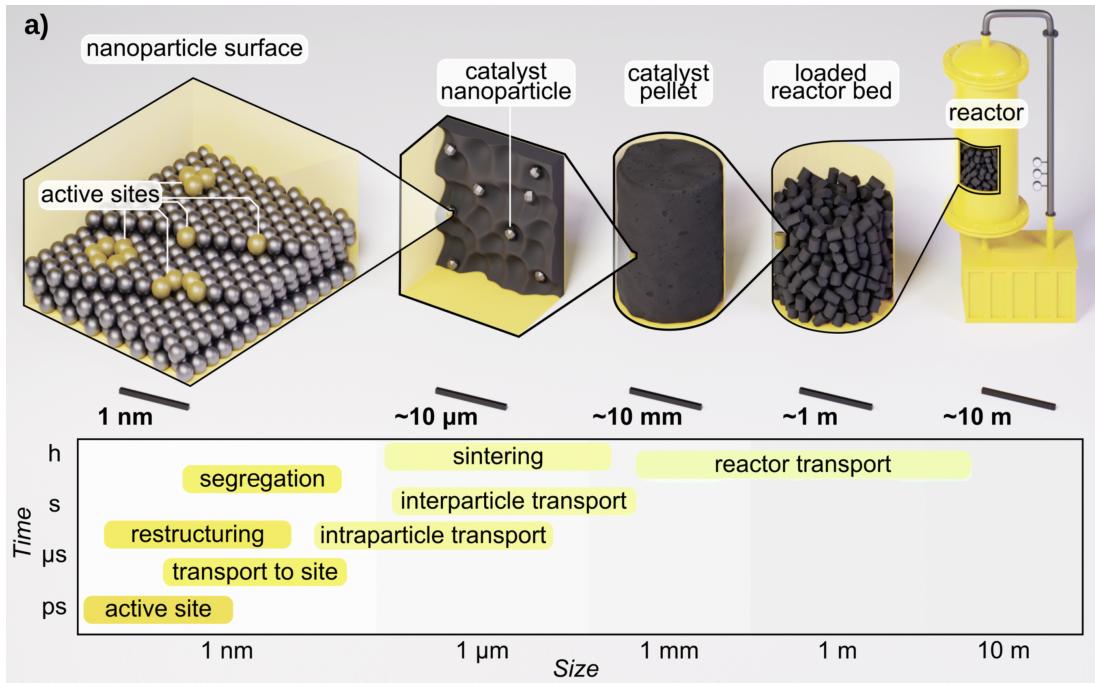
Need for dft simulations in catalyst research



Seh *et al.* Science, **355**, 6321 (2017).

A synergy between theory and experiment has become apparent during the last decade in the heterogeneous catalysis field.

| Scale of material simulations

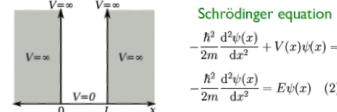


<https://pubs.rsc.org/en/content/articlelanding/2023/dd/d3dd00163f>

1. Density functional theory calculations

By Solving S.E., Energy of the system can be obtained. But it's challenging to solve.

Simplest Particle in a box problem



$$\text{Schrödinger equation}$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (1)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (2)$$

boundary conditions

$$\psi(0) = \psi(L) = 0 \quad (4)$$

$$\psi(x) = A \sin(kx) \quad (5)$$

$$\psi(L) = A \sin(kL) = 0 \quad (6)$$

Possible to Solve

general solution

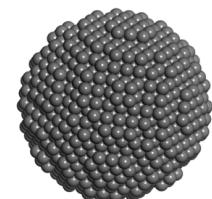
$$\psi(x) = A \sin(kx) + B \cos(kx)$$

$$E = \frac{k^2 \hbar^2}{2m} \quad (3)$$

solution

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (9)$$

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2m L^2} = \frac{n^2 \hbar^2}{8m L^2} \quad (10)$$



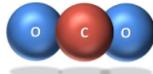
$$\hat{\mathcal{H}} \Psi(\vec{r}_1, \dots, \vec{r}_N) = E \Psi(\vec{r}_1, \dots, \vec{r}_N)$$

many-body Schrödinger equation



Impossible to Solve

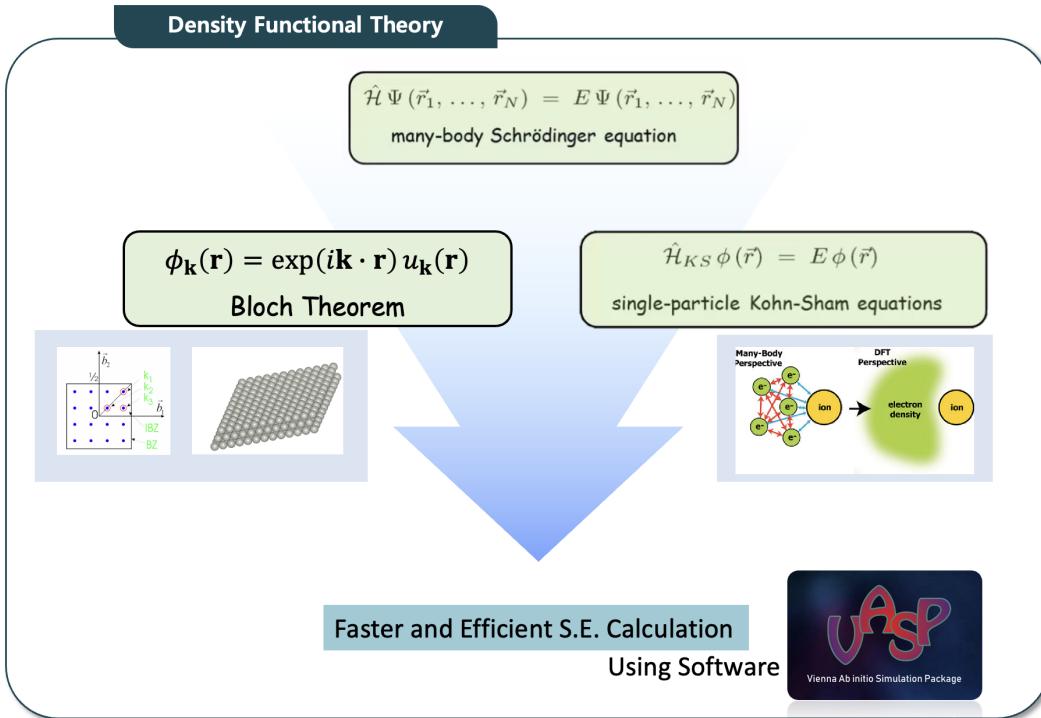
CO₂ molecule



$$(8 + 6 + 8) \times 3 = 66$$

Difficult but Solvable

Density
Functional
Theory



2. Plane-wave cutoff

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}),$$

$u_{\mathbf{k}}$'s periodicity

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}],$$

$$\therefore \phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}].$$

solution at even a single point in k space involves a summation over an infinite number of possible values of \mathbf{G} .

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2.$$

$$E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2.$$

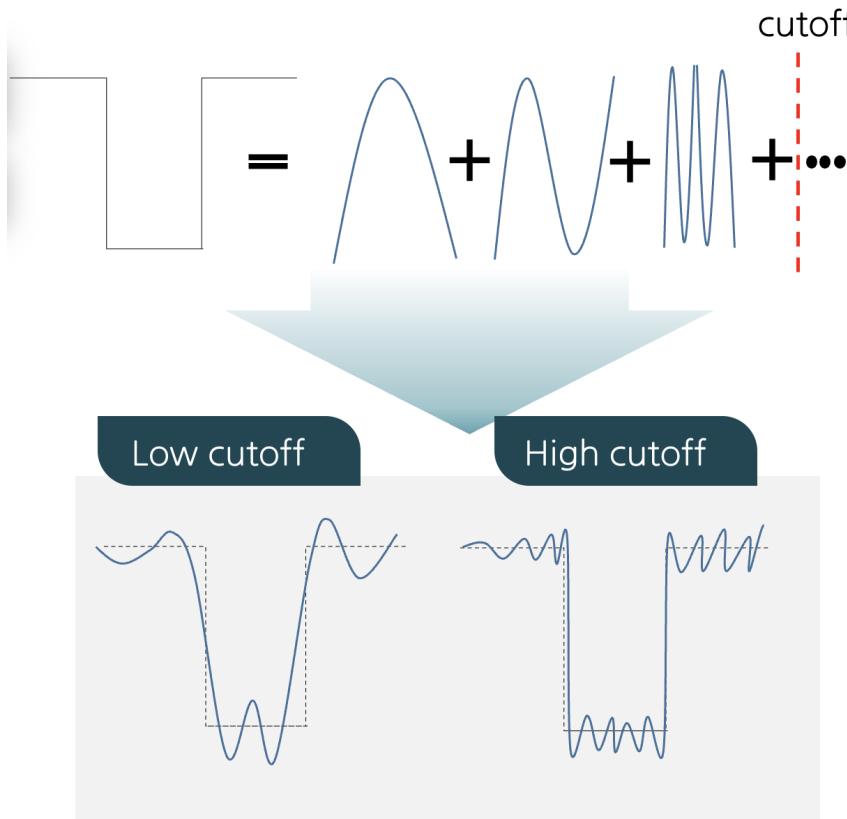
High-frequency term in the expansion:

- Hard to handle numerically (high-cost)
- Minor contribution to the summation (like the n higher order term in Taylor series)

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}].$$

The key point to remember here is whenever DFT calculations for **multiple systems** are compared to calculate energy **differences**, the **same energy cutoff** should be used in all calculations.

so that the errors of energy differences can be reduced by canceling two comparable systematic errors of each calculation.



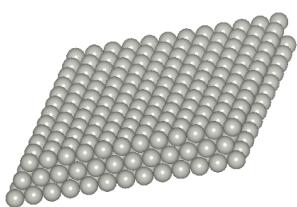
3. Monkhorst-Pack k-points

For periodic sys., the solution to the Schrodinger eq'n must satisfy Bloch's theorem, which states that the solution can be expressed as a sum of terms of the following form,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r})$$

Bloch Theorem

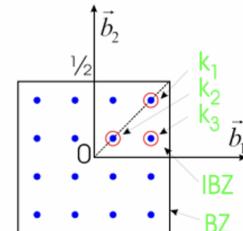
In periodic sys., there is **exactly one value of \mathbf{k} for each cell** constituting large supercell volume. For many properties such as total energies, the property should be averaged over \mathbf{k} 's corresponding to each cell to get "per unit cell" property, for general property, f ,



$$\bar{f} = \frac{1}{N} \sum_{\mathbf{k}} f(\mathbf{k})$$

$$\bar{f} = \frac{1}{\Omega_{BZ}} \int_{BZ} d\mathbf{k} f(\mathbf{k}) = \frac{\Omega_{cell}}{(2\pi)^3} \int_{BZ} d\mathbf{k} f(\mathbf{k})$$

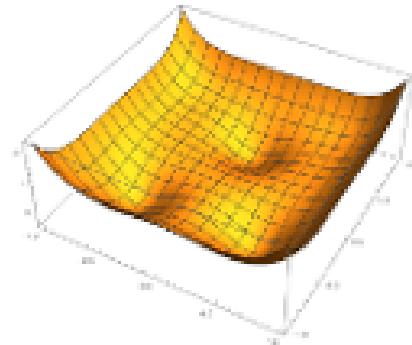
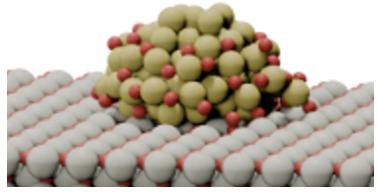
; in the limit of continuous \mathbf{k} .



How well multi-dimensional integrals are evaluated is crucial!

Martin, M. R. *Electronic structure: Basic Theory and Practical Methods*; Cambridge University Press: New York, 2004; p.88

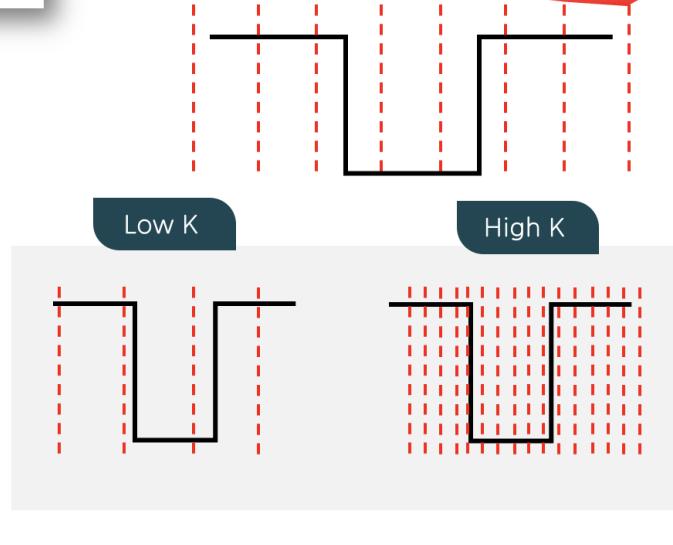
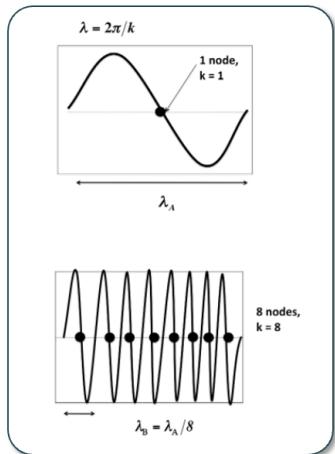
lets say there is a catalyst surface and its relevant potential energy surface



$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}],$$

$$\text{Diagram showing the decomposition of a wave function into a sum of plane waves: } + + \dots$$



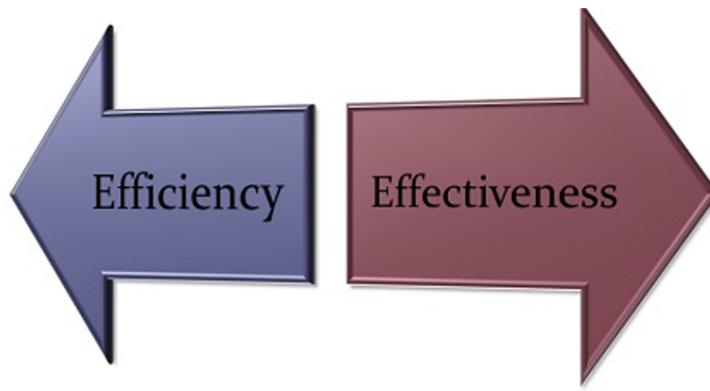


TABLE 3.3 Results from Computing the Total Energy of the Variant of fcc Cu with Broken Symmetry^a

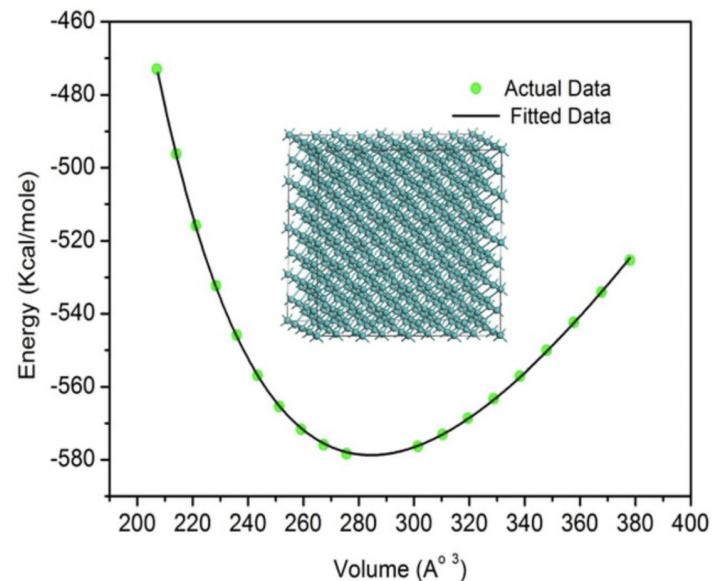
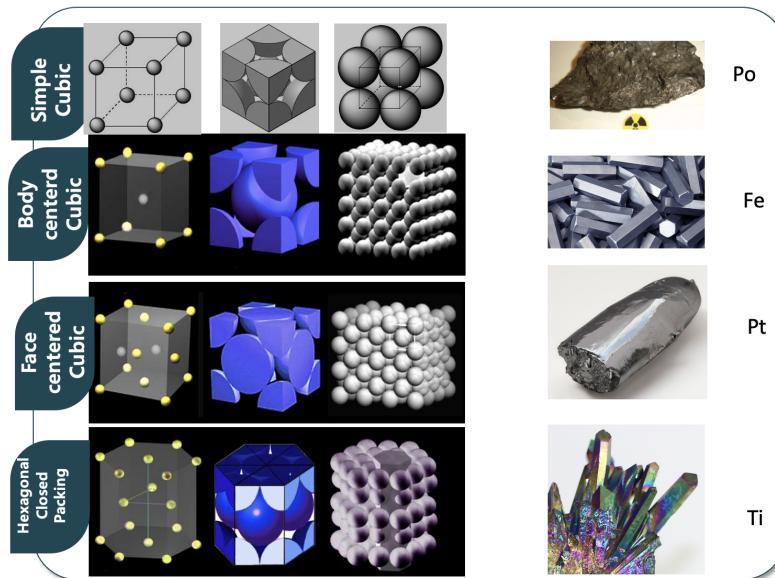
M	E/atom (eV)	$\Delta E/\text{atom}$ (eV)	No. of k Points in IBZ	τ_M/τ_1
1	-1.8148	-0.009	1	1.0
2	-3.0900	0.010	4	2.1
3	-3.6272	0.008	14	5.6
4	-3.6969	0.009	32	12.3
5	-3.7210	0.009	63	21.9
6	-3.7446	0.010	108	40.1
7	-3.7577	0.010	172	57.5
8	-3.7569	0.010	256	86.8

^aDescribed in the text with $M \times M \times M k$ points generated using the Monkhorst–Pack method.

Sholl, D. S.; Steckel, J. A. *Density Functional Theory: A Practical Introduction*; John Wiley & Sons, Inc.: New Jersey, 2009; Chapter 2.

https://gpaw.readthedocs.io/tutorials/exercises/structureoptimization/lattice_constants/lattice_constants.html

Equation of state



<https://pubs.aip.org/aip/jap/article/118/12/124305/141862/Mechanical-properties-of-stanene-under-uniaxial>

Thermodynamic equations of state (EOS) for crystalline solids describe material behaviors under changes in pressure, volume, entropy and temperature. Despite over a century of theoretical development and experimental testing of energy-volume (E-V) EOS for solids, there is still a lack of consensus with regard to which equation is optimal, as well as to what metrics are most appropriate for making this judgment.

Equation	$E(\nu^*)$	$K(\nu = 1)$	$K'(\nu = 1)$
Birch (Euler)	$E = E_o^{**} + BV_o \left((\nu^{-\frac{2}{3}} - 1)^2 + \frac{C}{2} (\nu^{-\frac{2}{3}} - 1)^3 \right)$	$\frac{8B}{9}$	$C + 4$
Birch (Lagrange)	$E = E_o + BV_o C - BV_o \nu^{\frac{2}{3}} \left((C - 2)(1 - \nu^{\frac{2}{3}})^2 + C(1 - \nu^{\frac{2}{3}}) + C \right)$	$\frac{16B}{9}$	$C - 2$
Mie-Gruneisen	$E = E_o + \frac{BV_o}{C} - \frac{BV_o}{C-1} \left(\nu^{-\frac{1}{3}} - \frac{1}{C} \nu^{-\frac{C}{3}} \right)$	$\frac{B}{9}$	$\frac{7+C}{3}$
Murnaghan	$E = E_o + \frac{BV_o}{(C+1)} \left(\frac{\nu^{-C}-1}{C} + \nu - 1 \right)$	B	$C + 1$
Pack-Evans-James	$E = E_o + \frac{BV_o}{C} \left(\frac{1}{C} (e^{3C(1-\nu^{\frac{1}{3}})} - 1) - 3(1 - \nu^{\frac{1}{3}}) \right)$	B	$C + 1$

Assignment

please pick one metal element in red box and perform the following tasks:

1. Draw the Equation of State (EOS) curve for the chosen metal.
2. Find the optimal lattice constant for the metal. (use kpoints $4\times4\times4$, PW(400))
3. Determine the converged plane wave cutoff and k-points for your simulations.(test out kpoints and PW(cutoff))

Please submit your results along with a brief explanation of your findings, limited to one page.(format: studentnumber_name.doc (.pdf or whatever), ex)12345_seokhyunchoung.doc)

