

Extended Hückel Calculations on Solids Using the Avogadro Molecular Editor and Visualizer

By Patrick Avery

Overview

1. Motivation
2. Extended Hückel Theory Overview
3. Avogadro with YAeHMOP

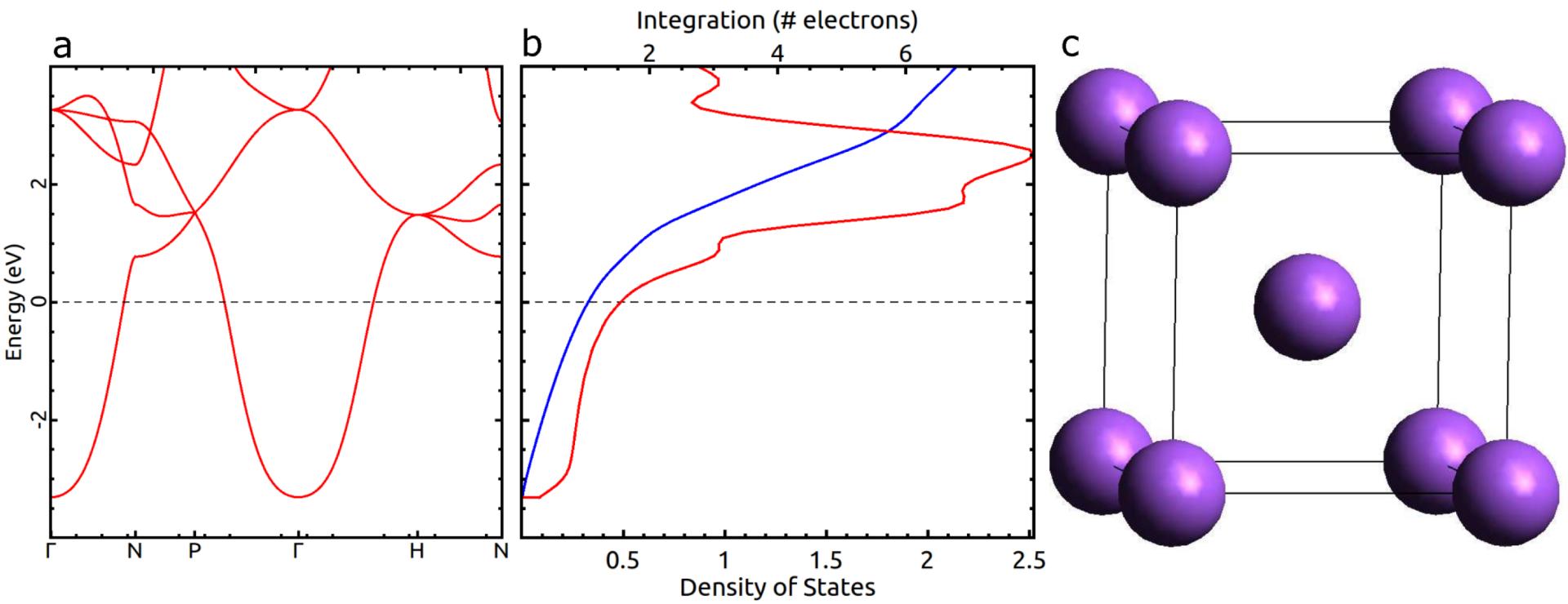


Motivation



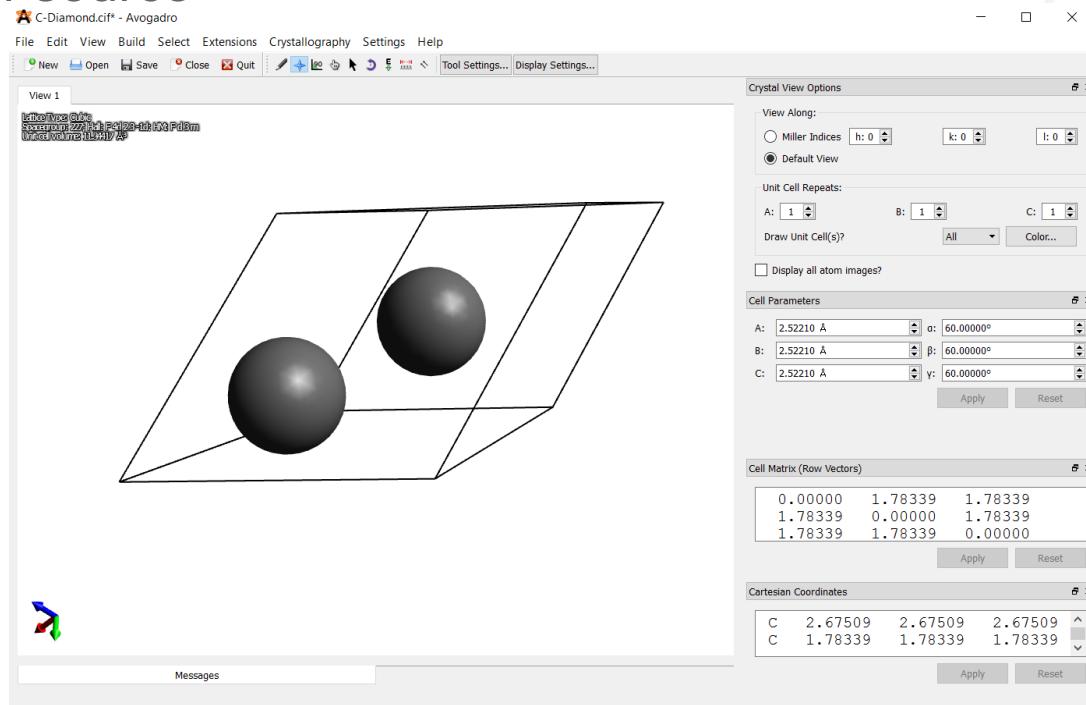
Why Extended Hückel Calculations in Avogadro?

- An education tool: Very few options exist for students to perform band structure/DOS calculations without a terminal or super computing cluster
- Sometimes quick, qualitative calculations are very helpful for research



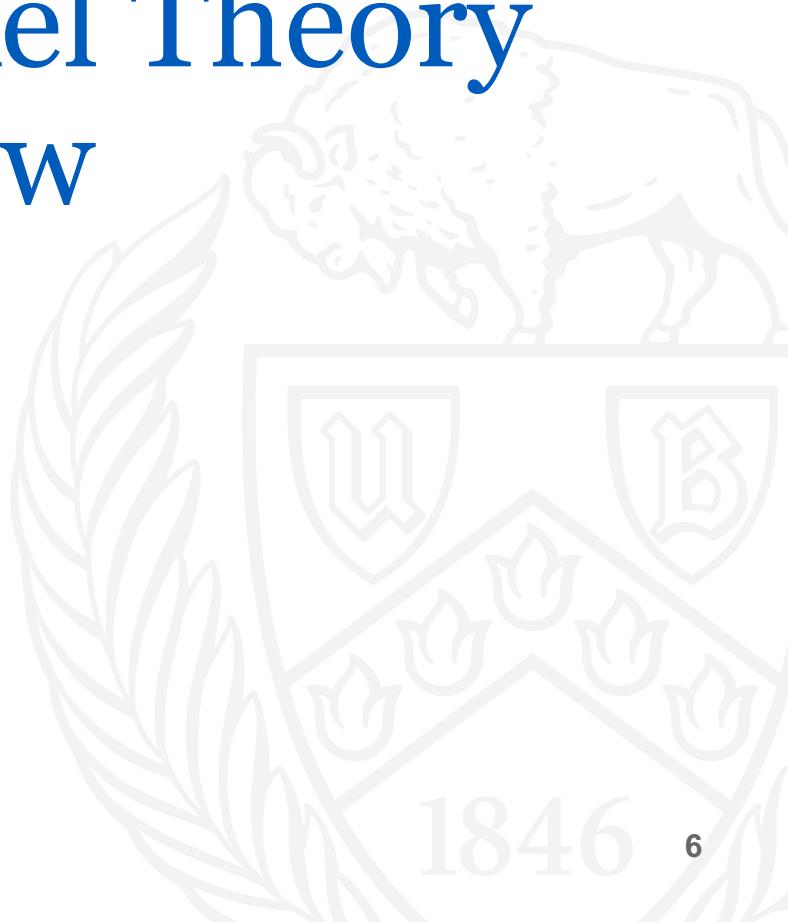
Why YAeHMOP in Avogadro?

- **Avogadro** provides an easy-to-use interface for editing molecules/crystals
- **YAeHMOP** (Yet Another extended Hückel Molecular Orbital Package) is very fast for qualitative calculations
- Both are open-source



<http://avogadro.cc>
<https://github.com/greglandrum/yaehmop>

Extended Hückel Theory Overview

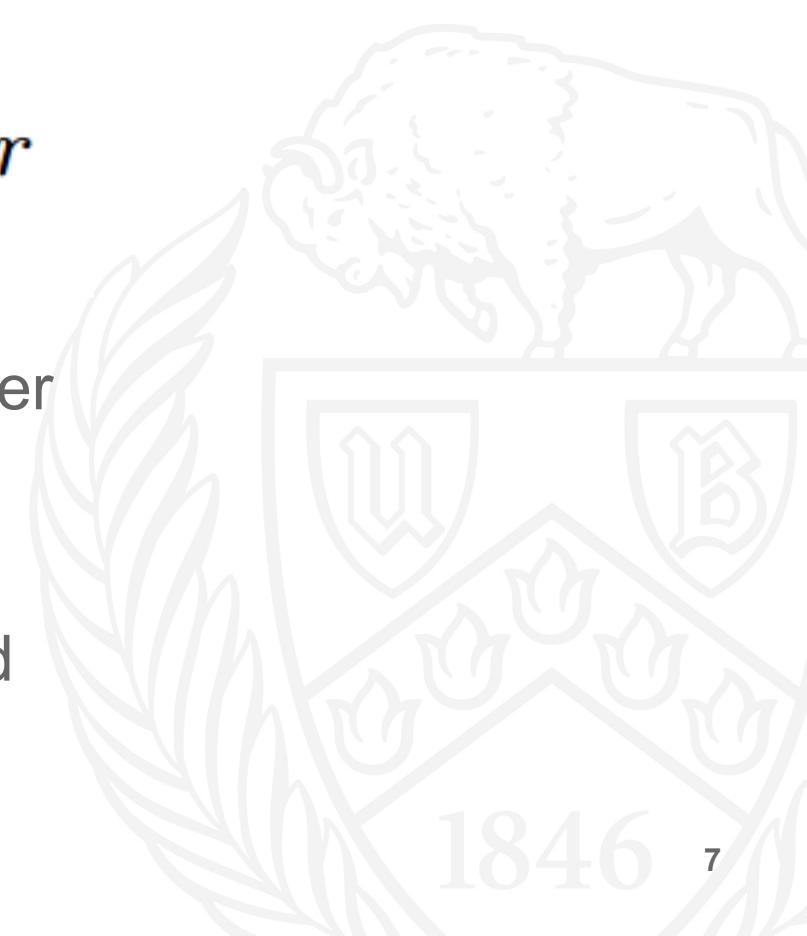


Characteristics of EHT

- Single STO for each AO

$$R_n(r, \zeta) = r^{n-1} e^{-\zeta r}$$

- ζ is given as an empirical parameter
- LCAO to construct MOs
- H_{ii} supplied as ionization potential
- Overlap matrix explicitly calculated



Wolfsberg-Helmholtz Relation

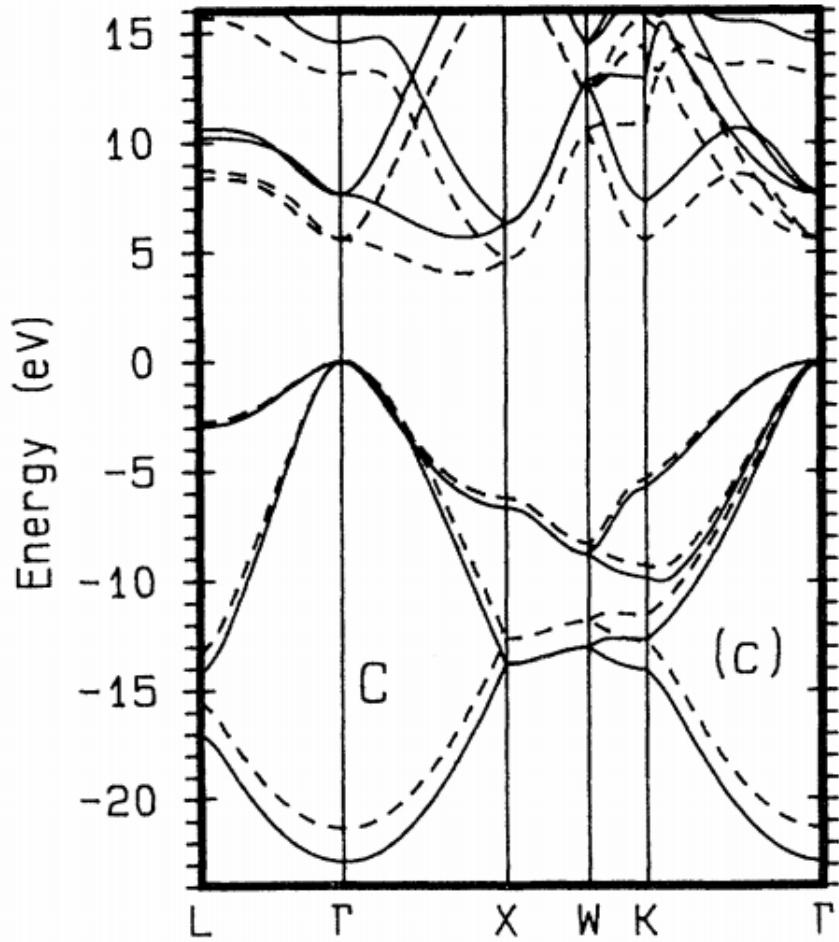
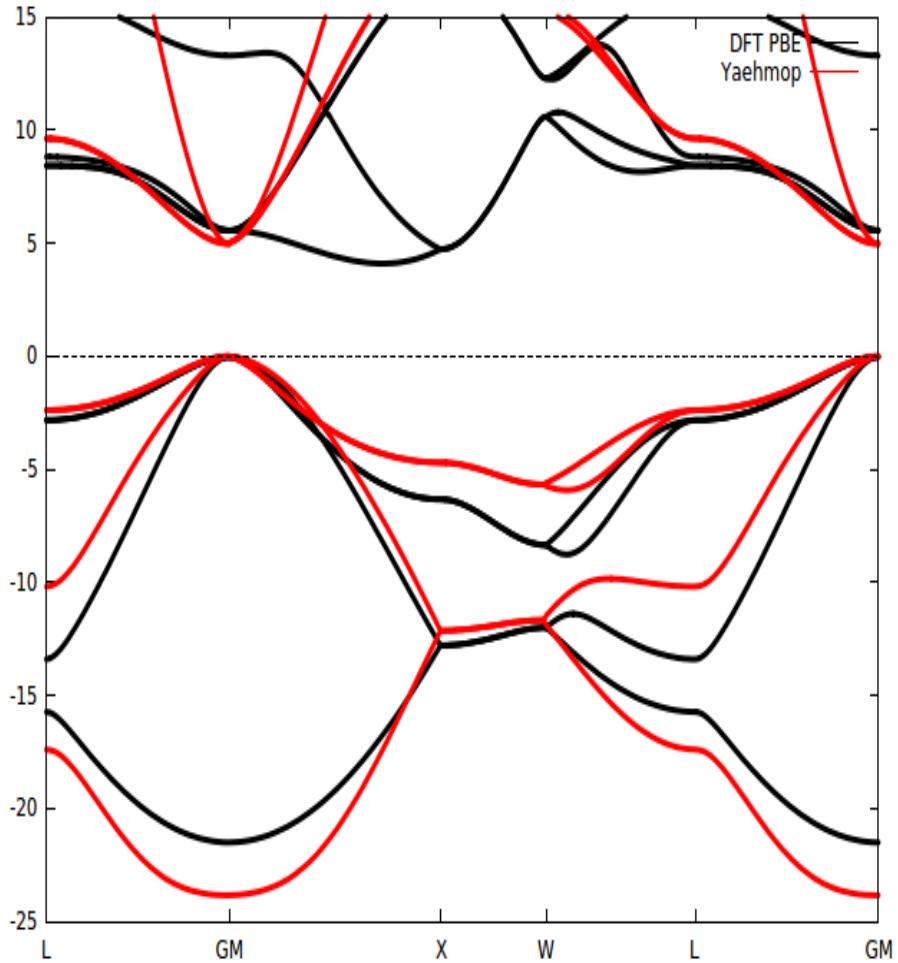
$$H_{ij} = \frac{K}{2}(H_{ii} + H_{jj})S_{ij}$$

H_{ii} values supplied as parameters (related to VSIP)
 K was originally chosen to be 1.75

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

Band Structures - Diamond

*Dashed – LDA
*Solid - GW

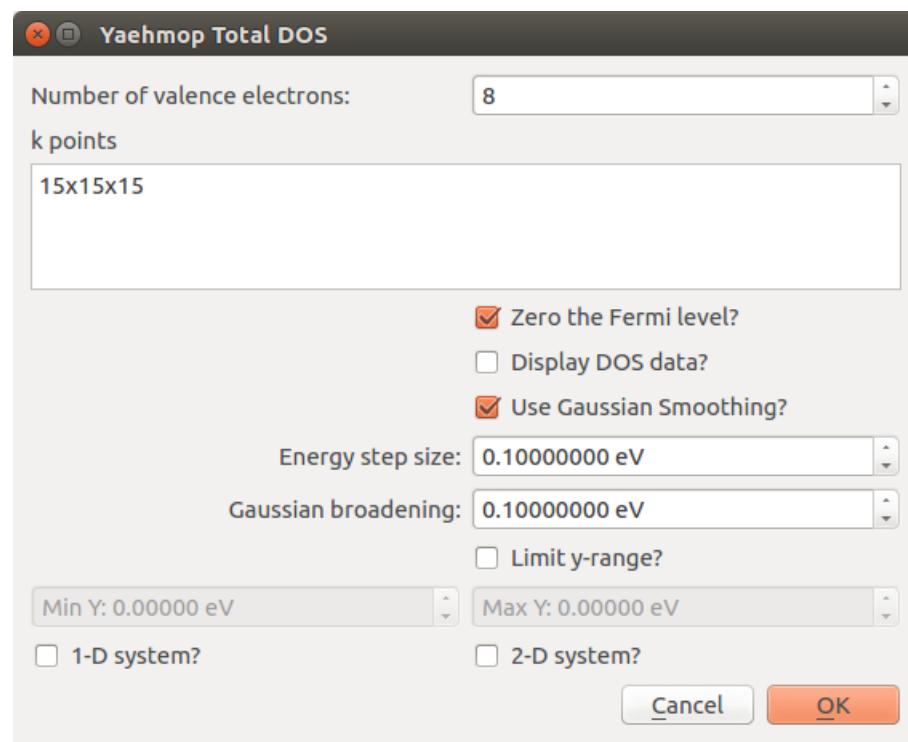
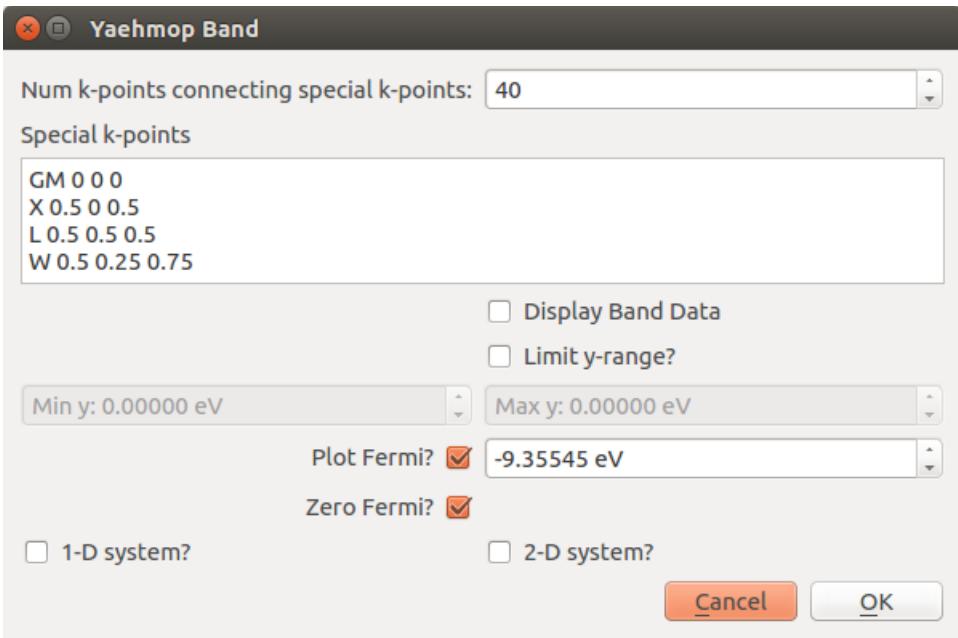


*M., Rohlfing, P. Kruger, and J. Pollmann, Phys. Rev. B 1993, 48(24), 17791-17805.

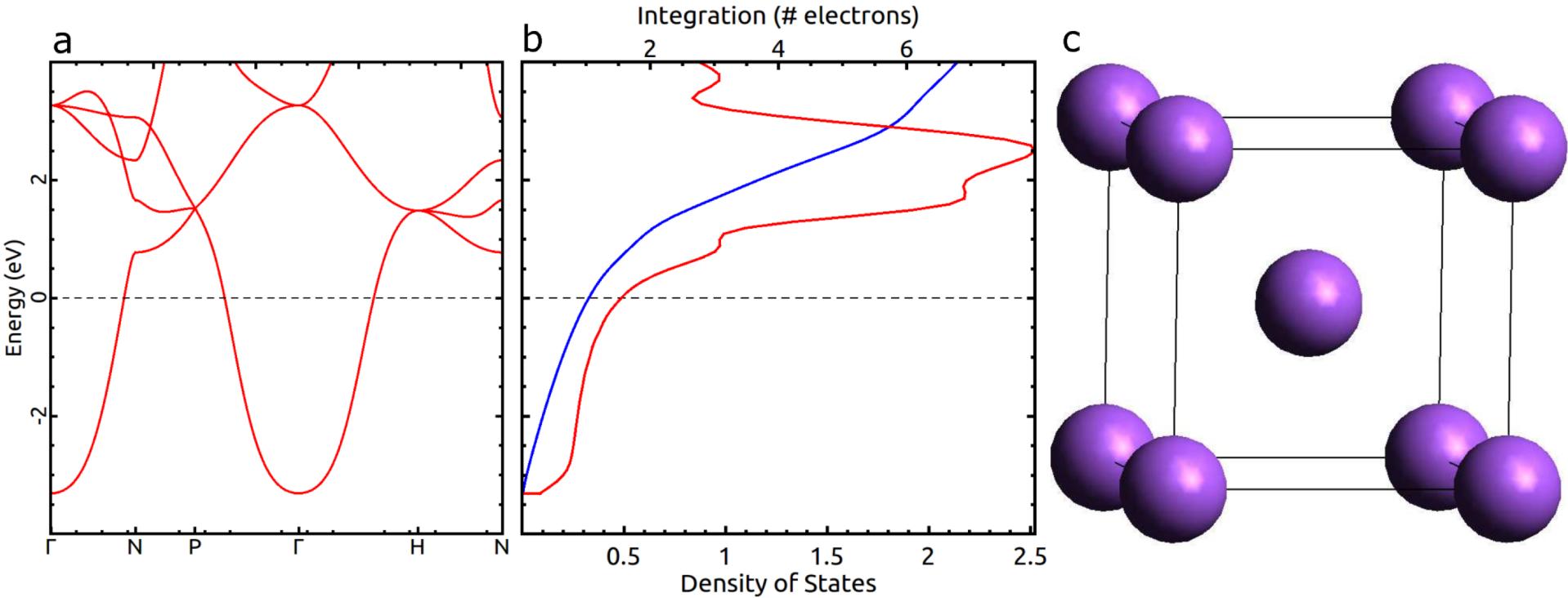
Avogadro with Yaehmop

With some examples...

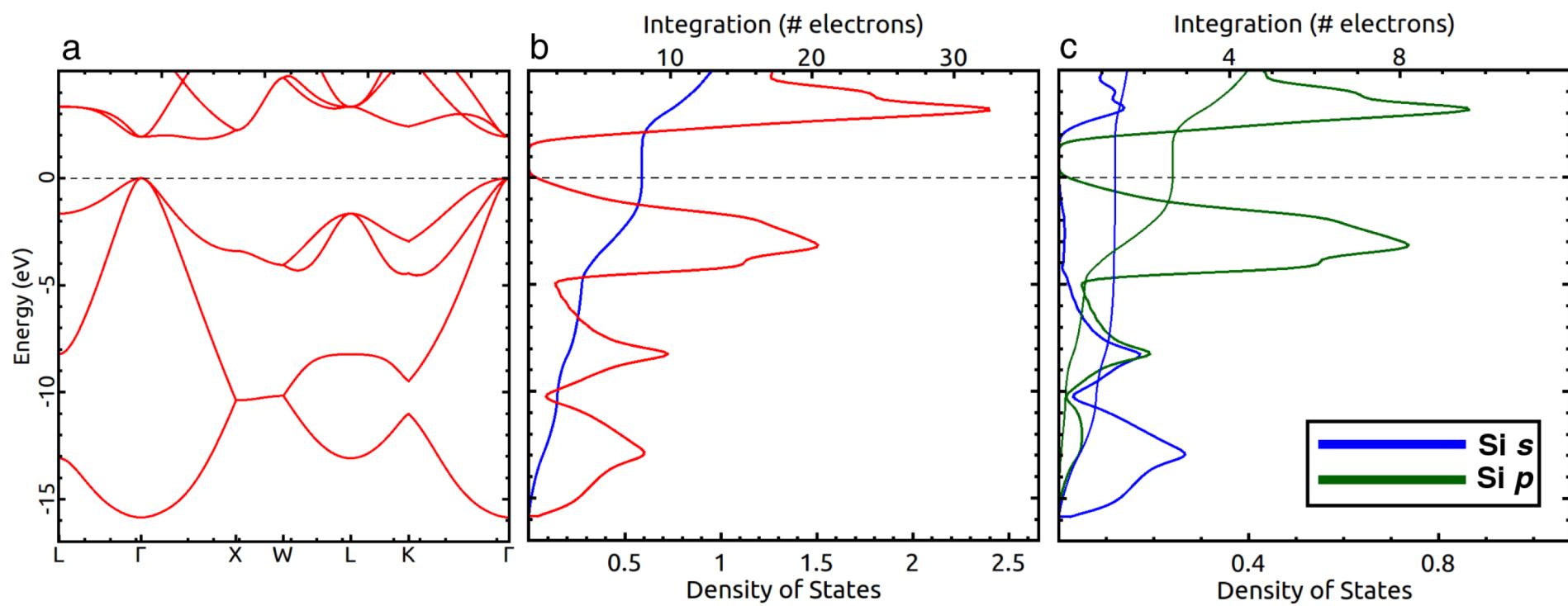
Dialogs



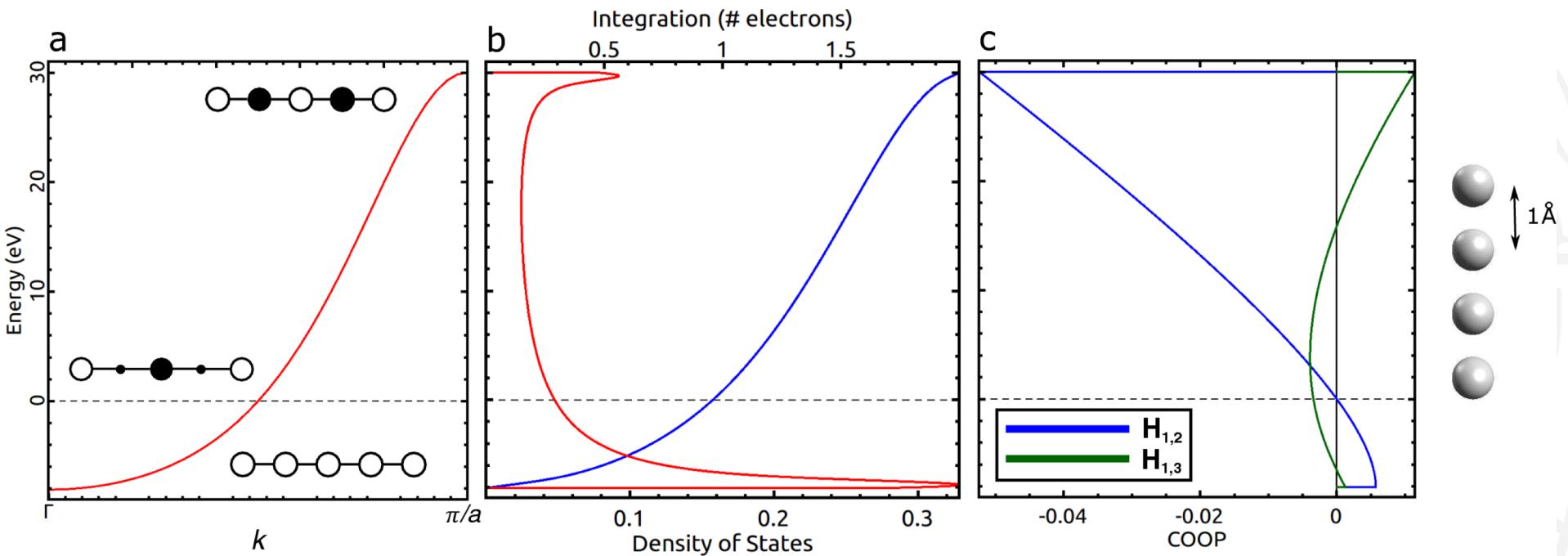
Sodium



Silicon



Theoretical Hydrogen Chain



Website

<https://avogadro-yaehmop.github.io/>

Avogadro with YAeHMOP

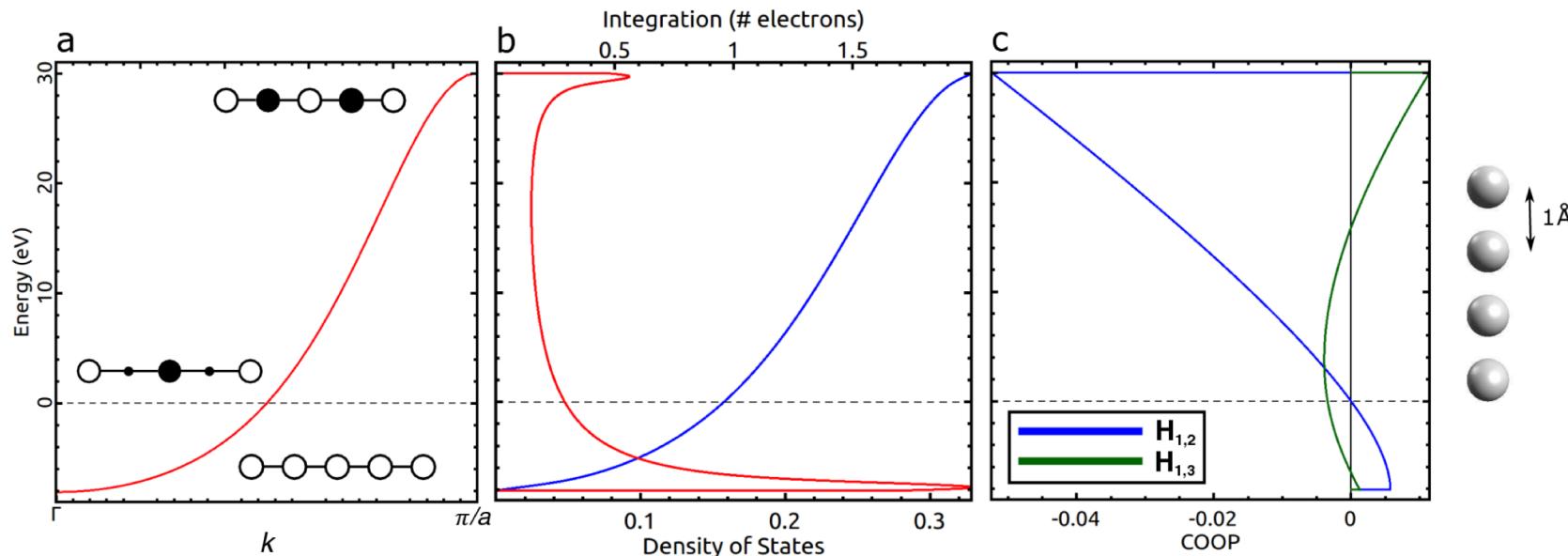
Windows

Mac OS X

Linux

Our recently published J. Chem. Ed. article can be found [here!](#)

YAeHMOP is an extended Hückel package that can be found [here](#).
It has been interfaced with the open-source molecular editor [Avogadro](#).



How Does it Work?

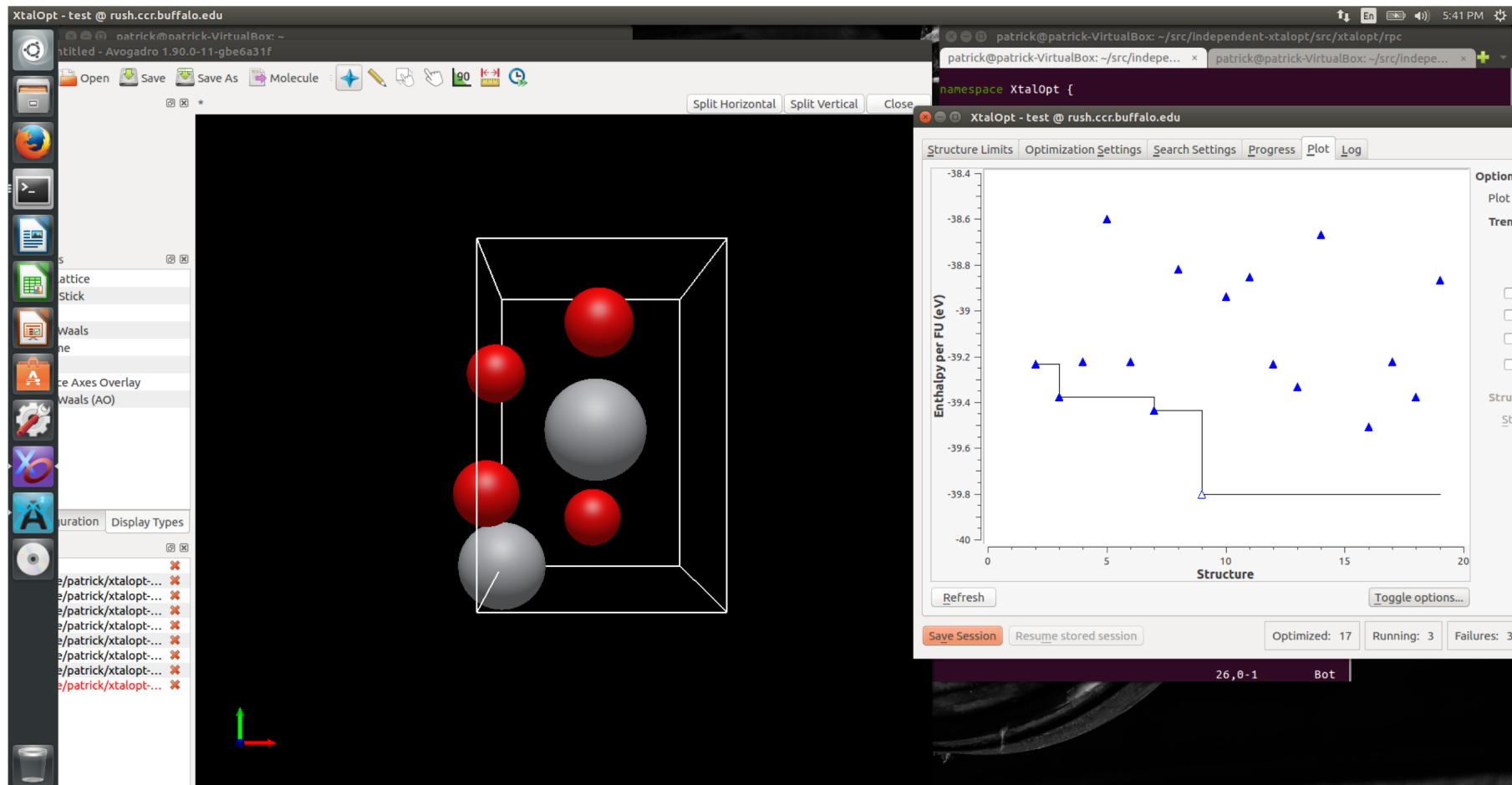
- YAeHMOP is a separate binary (not linked to Avogadro)
- It is called by Avogadro via QProcess
- Communication:
 - Avogadro provides YAeHMOP input via *stdin*
 - YAeHMOP provides Avogadro2 output via *stdout*
- Check out tutorials/Static-Binaries.md at
<https://github.com/OpenChemistry/avogadro-ugm2018>

Future Plans...

- Add YAeHMOP to Avogadro2 (in process now)
- Add molecular YAeHMOP features to Avogadro2
 - Molecular orbitals
 - Walsh diagrams
 - FMO (fragmented molecular orbitals)
- Maybe some geometry optimizations?



Side Note: Json RPC with Avogadro2



The End

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Bonus Slides



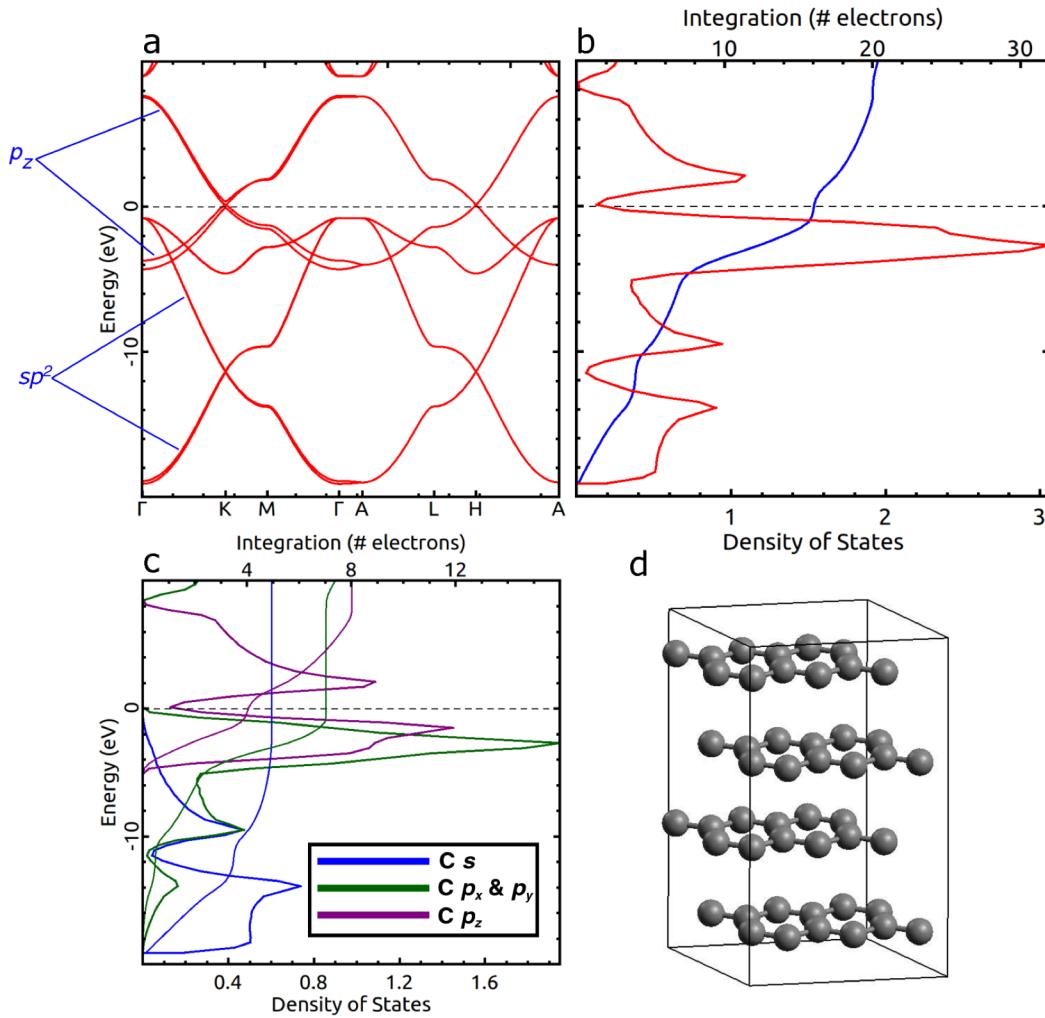
New K to minimize COM (Counter-intuitive Orbital Mixing)

$$K = k' + \left\{ \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \right\}^2 + \left\{ \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \right\}^4 (1 - k')$$

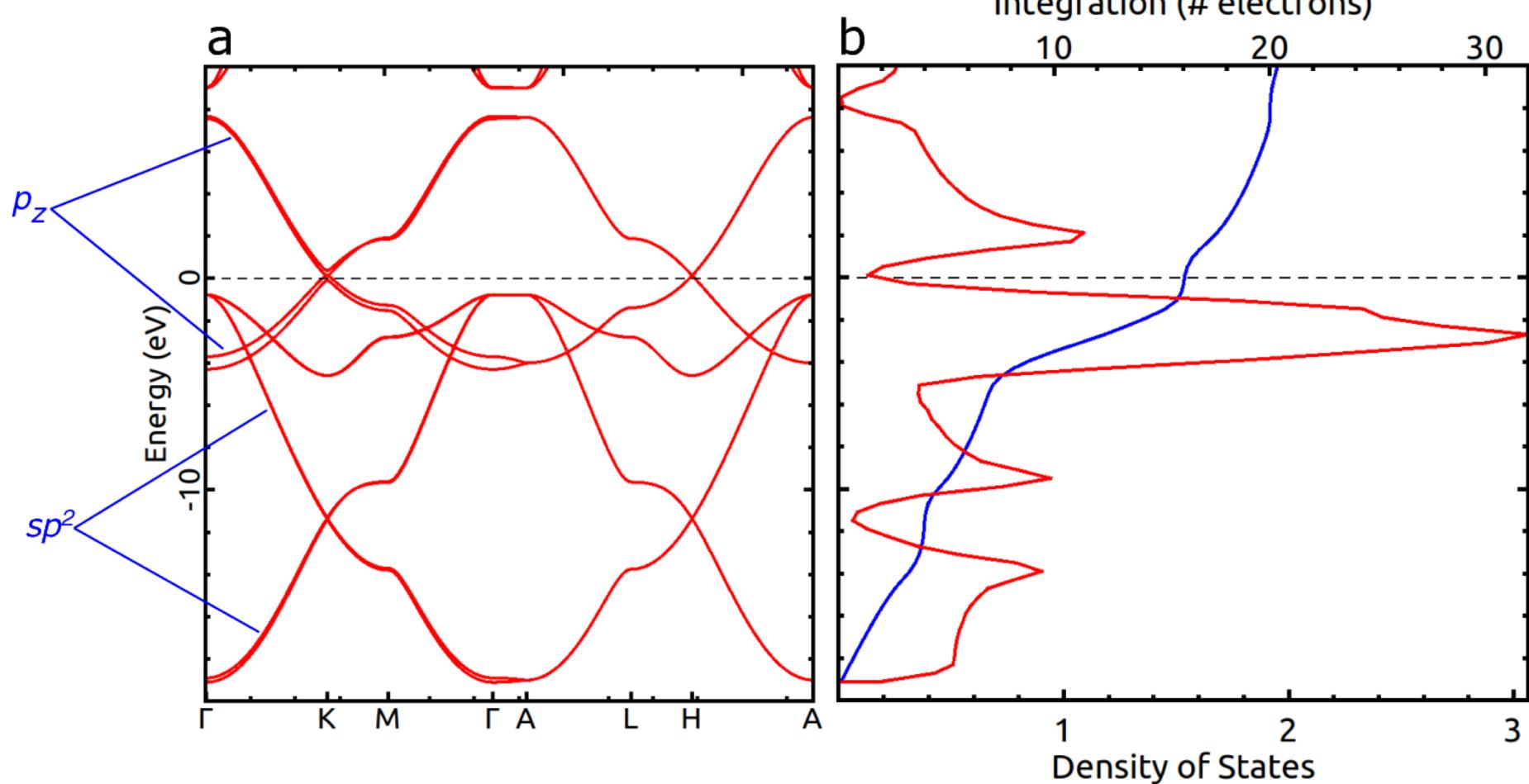
$$k' = 1.75$$

J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc. 1978, 100, 3686.

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