Density-Functional Theory Pedagogy with Jupyter Notebooks

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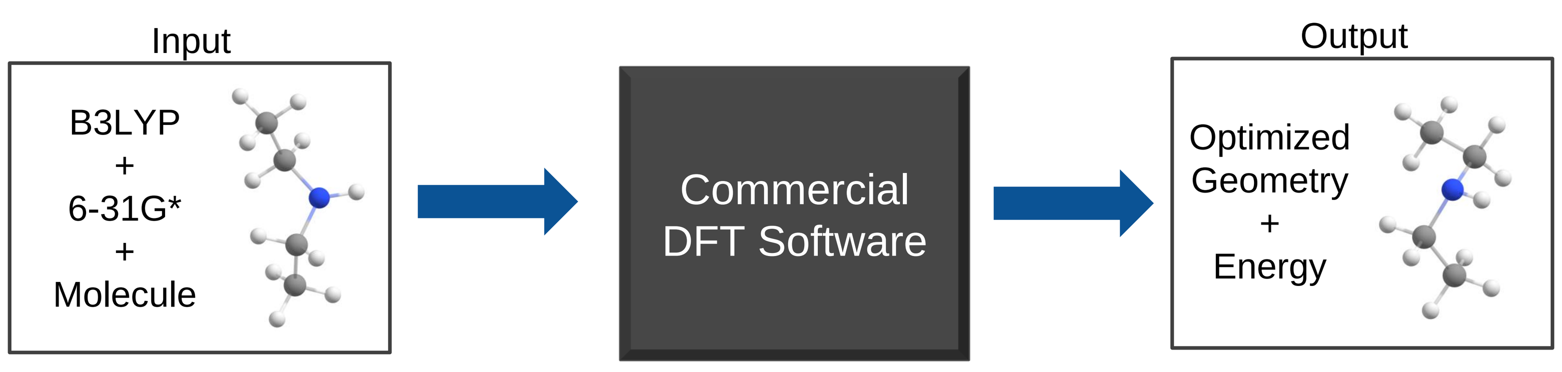
GitHub Repo

Motivation

- Density-Functional Theory (DFT) is largely is a black-box[1] method to users of commercial electronic structure packages.
- Typically, a molecule, functional, and basis set are provided as input and an optimized geometry and energy are provided as output.

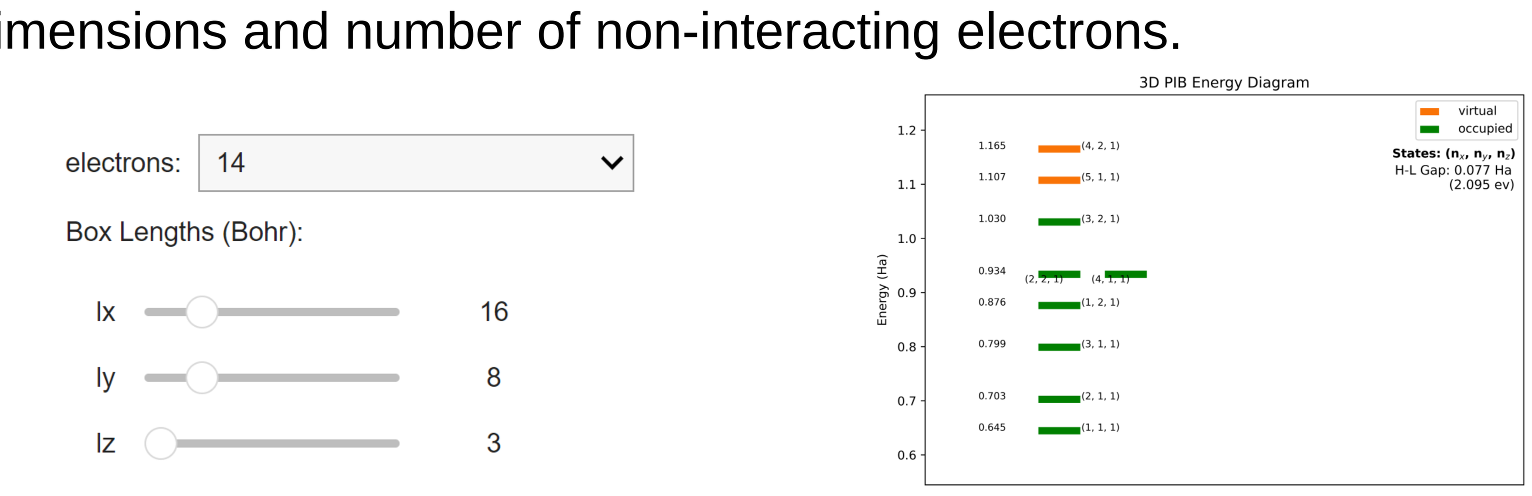


- To help remedy this knowledge gap, we have developed three Jupyter Notebooks that explain the fundamentals of DFT through a model system and compare the results to real chemical systems in the form of polycyclic aromatic hydrocarbons (PAHs).

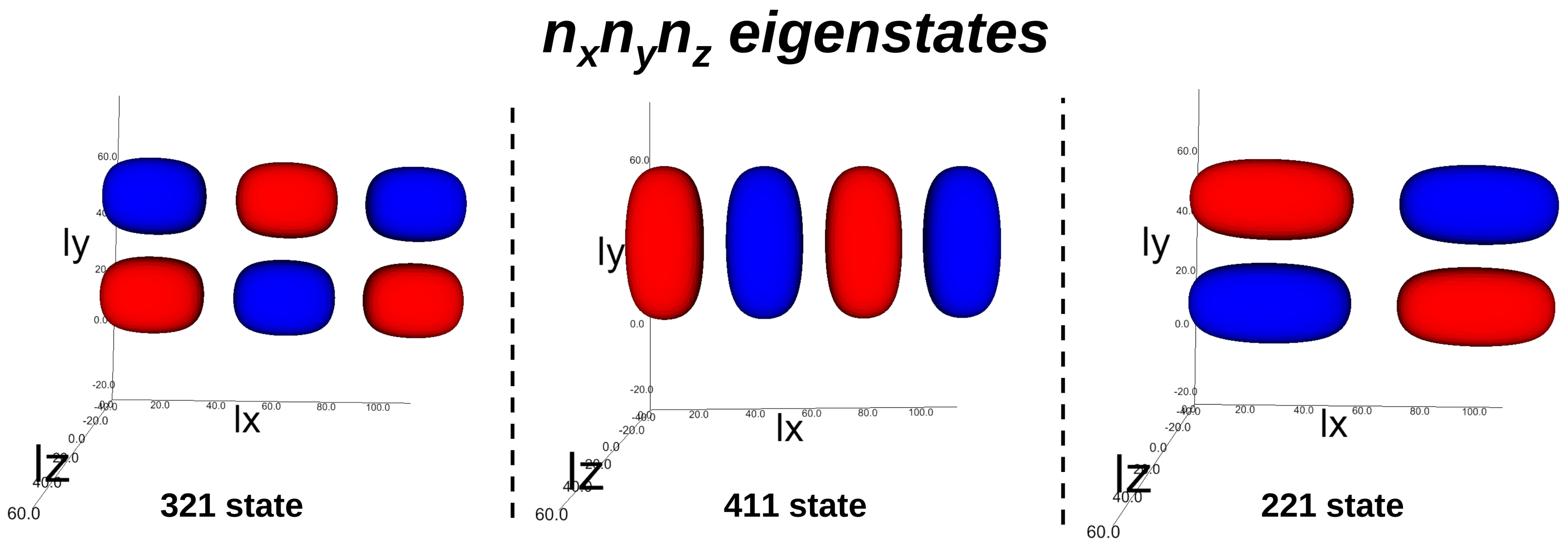
Particle in a Box (PIB) Model

Eigenenergies

- 3D PIB textbook[2] solutions can be realized from user-defined box dimensions and number of non-interacting electrons.



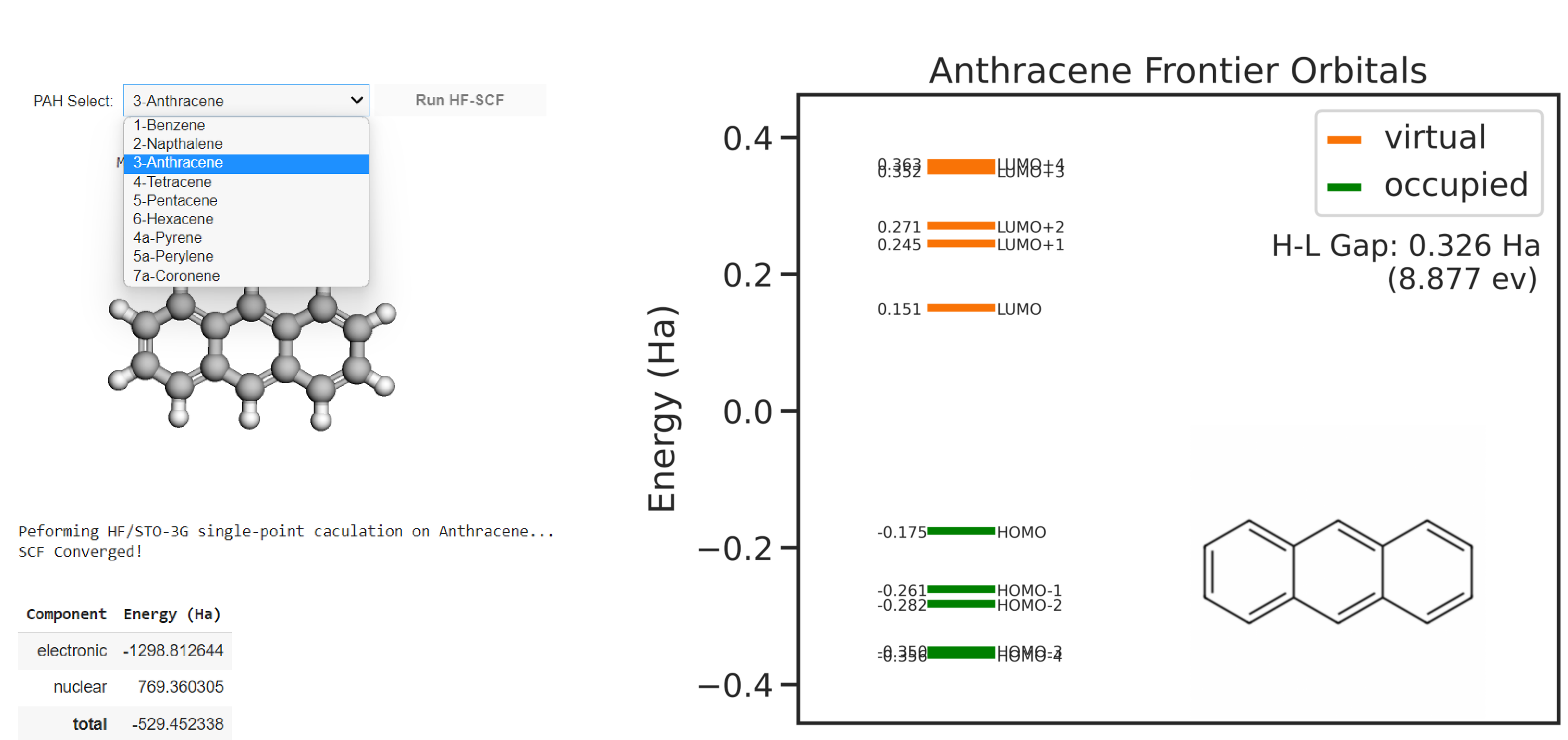
$n_x n_y n_z$ eigenstates



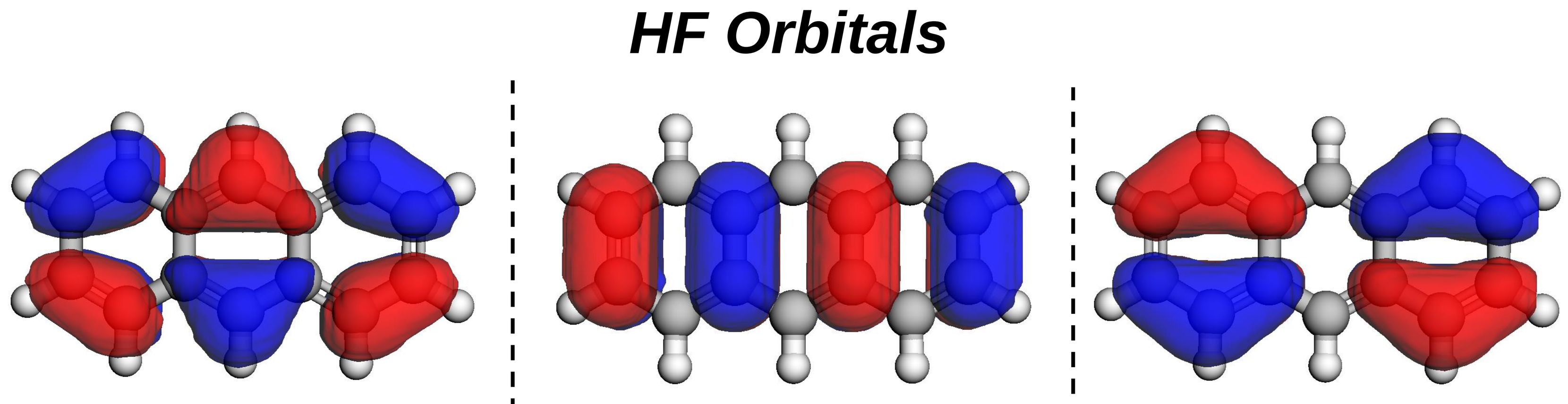
PAH Molecules

HF Orbital Energies

- HF/STO-3G calculations with PySCF[3] can be performed on PAH molecules selected from a dropdown menu. These results can be juxtaposed with the above 3D PIB calculation using comparably sized boxes.



HF Orbitals

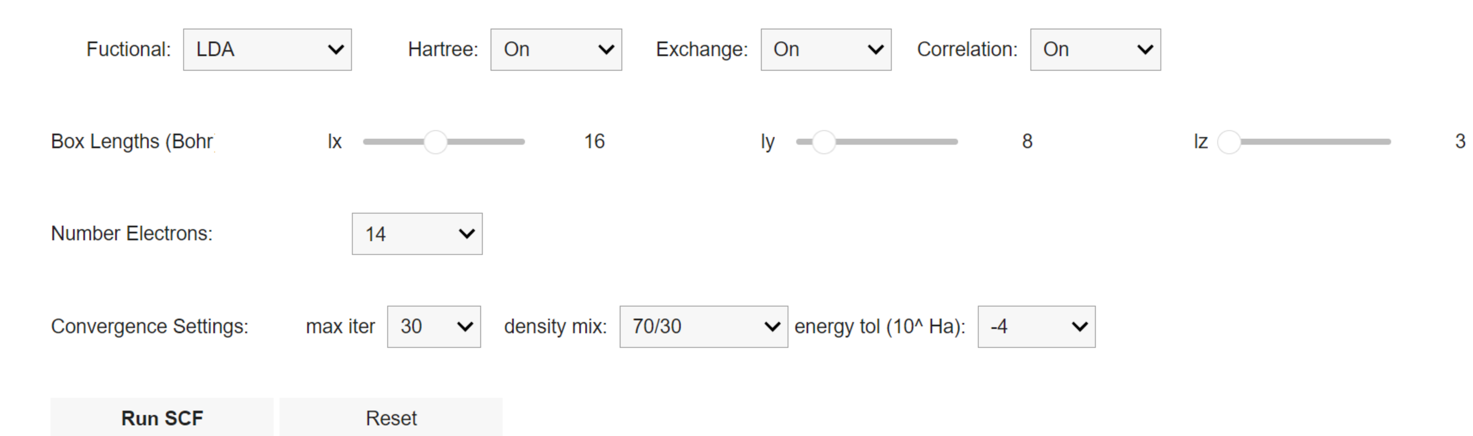


DFT-PIB Code

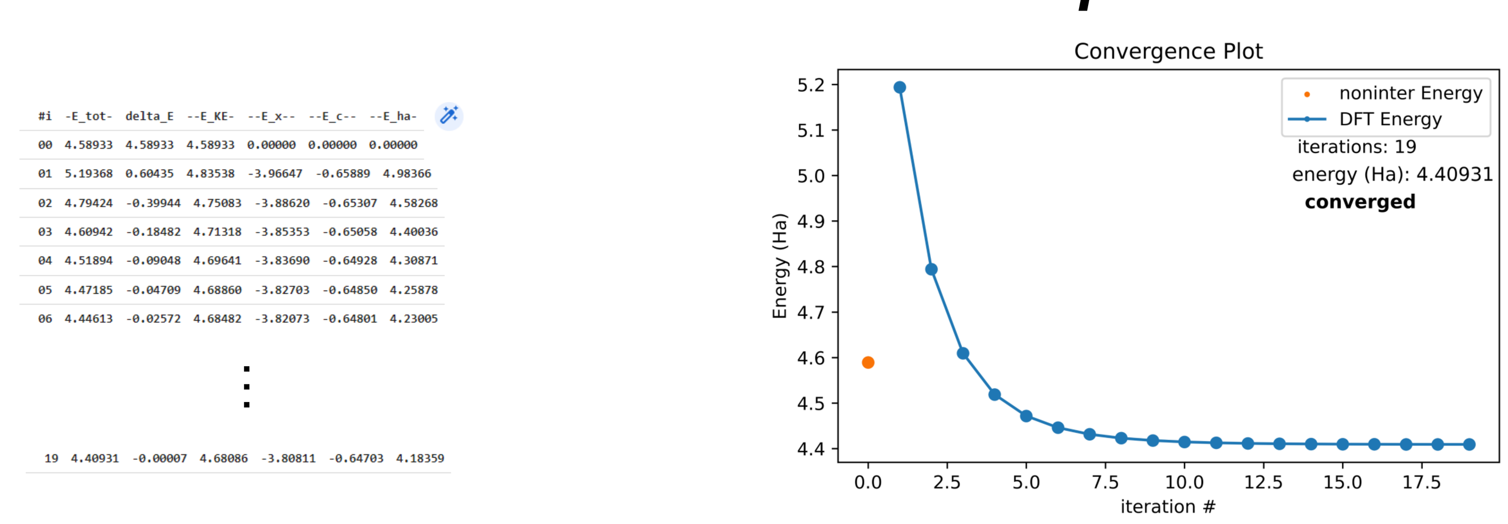
Construct Hamiltonian

- A single-particle Hamiltonian can be constructed for a system of electrons placed in a 3D box accounting for e⁻-e⁻ interaction through the KS-DFT potential[4], which can then be solved to self consistency.

$$\hat{h}_i = \hat{T}_{kin,i} + v_{Ha}(n(r)) + v_x^{LDA}(n(r)) + v_c^{LDA}(n(r))$$

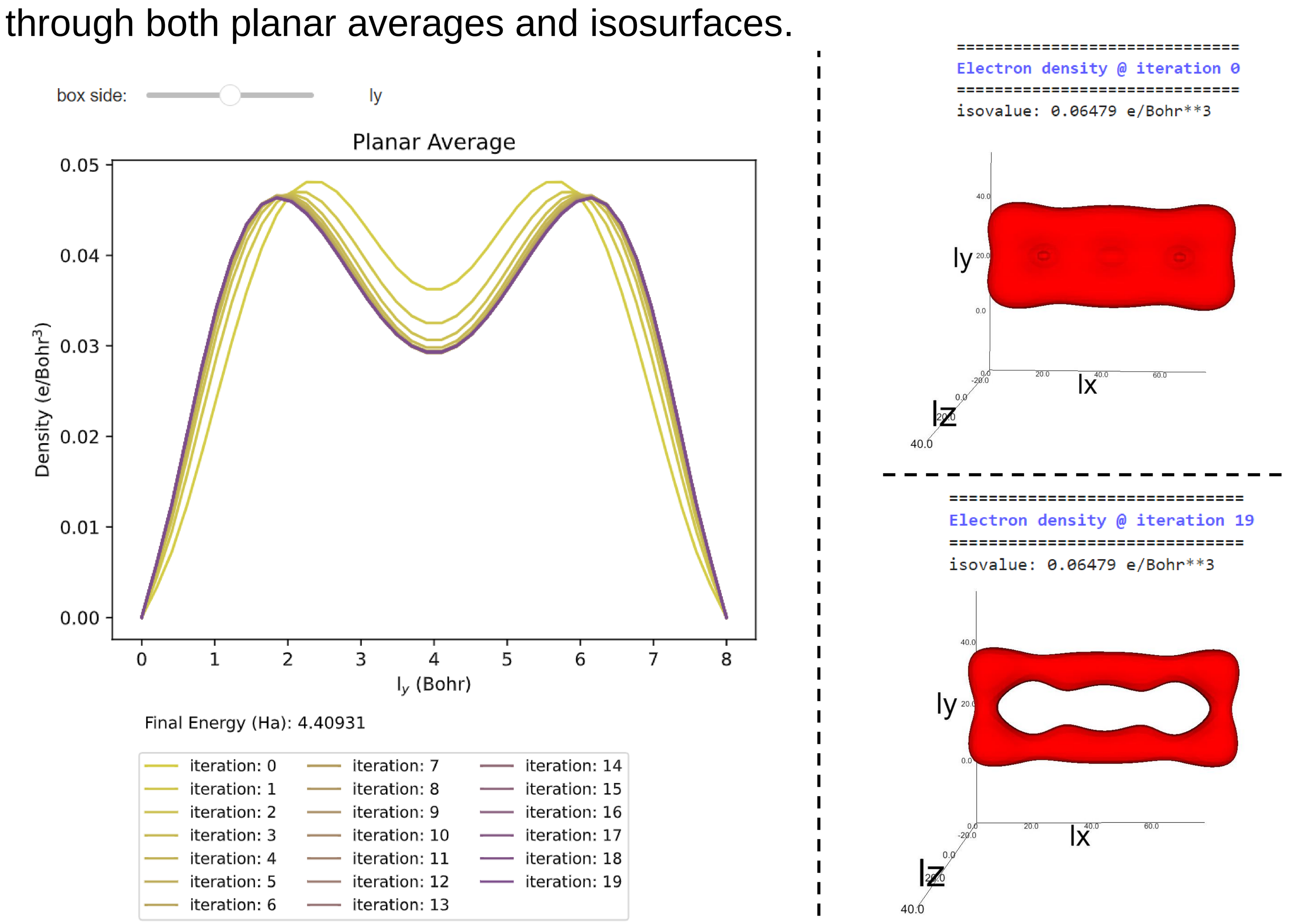


Self-Consistent Field Loop



Density Analysis Tools

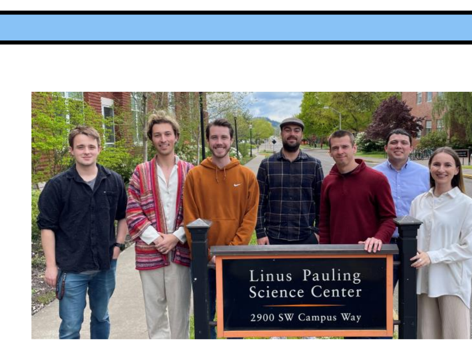
- The change in density upon self-consistent field optimization can be analyzed through both planar averages and isosurfaces.



Conclusion

- Developed with a problem worksheet for a graduate-level quantum chemistry course in the Fall 2022 Term at Oregon State University.
- Pre- and post-activity survey results show that DFT can be taught in an engaging and rigorous manner with Jupyter Notebooks.
- Approach uses the browser-based Google Colab service (fully reproducible across different machines), accessible through simple GitHub links.
- https://github.com/tjz21/DFT_PIB_Code

\+ jupyter +



Acknowledgements

Zuehlsdorff Group

OSU Chemistry Department

CH 651 class

References

[1] Johnson, L. E.; Engel, T. Integrating Computational Chemistry into the Physical Chemistry Curriculum. *J. Chem. Educ.* **2011**, *88*, 569–573. DOI: 10.1021/ed900064n.
[2] Silbey, R. J.; Alberty, R. A.; Bawendi, M. G. Physical Chemistry, 4th ed.; John Wiley & Sons, Inc: Hoboken, NJ, 2005.
[3] Sun, Q.; Zhang, X.; Banerjee, S.; Bao, P.; Barbry, M.; Blunt, N. S.; Bogdanov, N. A.; Booth, G. H.; Chen, J.; Cui, Z.-H.; et al. Recent Developments in the PySCF Program Package. *J. Chem. Phys.* **2020**, *153*, 024109. DOI: 10.1063/5.0006074.
[4] Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138. DOI: 10.1103/PhysRev.140.A1133.

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