

Introduction

In quantum chemistry, theoretical models are essential for understanding electronic structures and predicting molecular behaviors. The Hückel and Pariser-Parr-Pople (PPP) models are particularly notable in this field.

The Hückel model, introduced by Erich Hückel in 1931 [1], offers a simplified method for estimating molecular orbital energies by focusing on π -electrons in conjugated systems. This model has significantly influenced the initial understanding of molecular orbitals.

The PPP model, developed in the early 1950s [1], extends this concept by incorporating electron-electron interactions, providing a more comprehensive understanding of molecular electronic structures [2]. This enhancement allows for a deeper exploration of molecules, especially those with extensive conjugated systems.

Our study analyzes these model Hamiltonians using advanced software tools and modern quantum chemistry methods. We utilize the PyBEST software package to explore the electronic structure and properties of large conjugated systems [3, 4]. We focus on pCCD-based methods for modeling prototypical organic molecules, demonstrating the effectiveness of these approaches in contemporary quantum chemistry [5, 6].

This poster presents our methodologies and findings, emphasizing today's relevance and application of the Hückel and PPP models.

Computational Strategy

The Hückel Model Hamiltonian:

$$\hat{H}_{\text{Hückel}} = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i - \sum_{\langle i,j \rangle} t (\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i)$$

- ϵ_i : On-site energy for the π -electron at site i .
- $\hat{c}_i^\dagger, \hat{c}_i$: Creation and annihilation operators for an electron at site i .
- t : Hopping integral between neighboring sites i and j .

The PPP Model Hamiltonian:

$$\hat{H}_{\text{PPP}} = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i - \sum_{\langle i,j \rangle} t (\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i) + \frac{1}{2} \sum_{i \neq j} V_{ij} (\hat{n}_i - 1)(\hat{n}_j - 1)$$

- Includes terms from the Hückel model.
- $\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$: Number operator for site i .
- V_{ij} : Electron-electron interaction potential between electrons at sites i and j .

Relation Between Hückel and PPP Models:

- PPP model expands on Hückel by adding electron-electron interactions.
- Hückel model approximates π -electron systems; PPP offers greater accuracy.
- PPP accounts for electron repulsion, enhancing realism in electronic structure.
- The PPP model is ideal for studying the electronic properties of complex organic molecules.

Computational Tools:

- PyBEST Software Package:** PyBEST [3, 4] for advanced electronic structure calculations, includes HF and pCCD-based methods for accurate electronic structure modeling.
- pCCD-Based Methods:** pair Coupled-Cluster Doubles (pCCD) efficiently capture electron correlations, ideal for strongly correlated systems like conjugated molecules [5, 6].

The Hückel Model: Hartree-Fock (HF) and pair Coupled Cluster Doubles (pCCD) Orbital Energies for Benzene

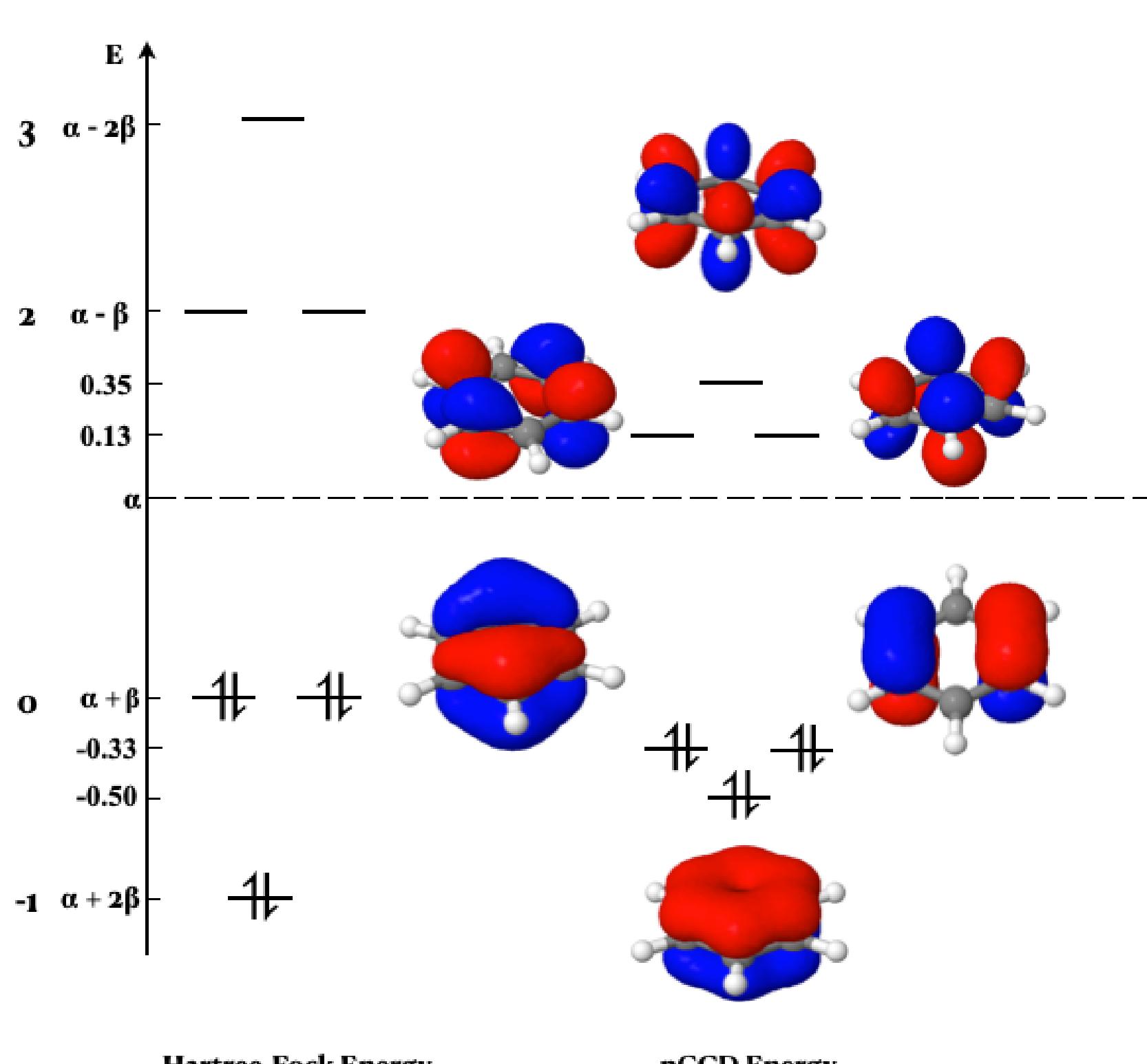


Figure 1: $\alpha = \epsilon_i$ and $\beta = t$ in the Hückel Hamiltonian

The PPP Model: HF and pCCD Orbital Energies for Benzene

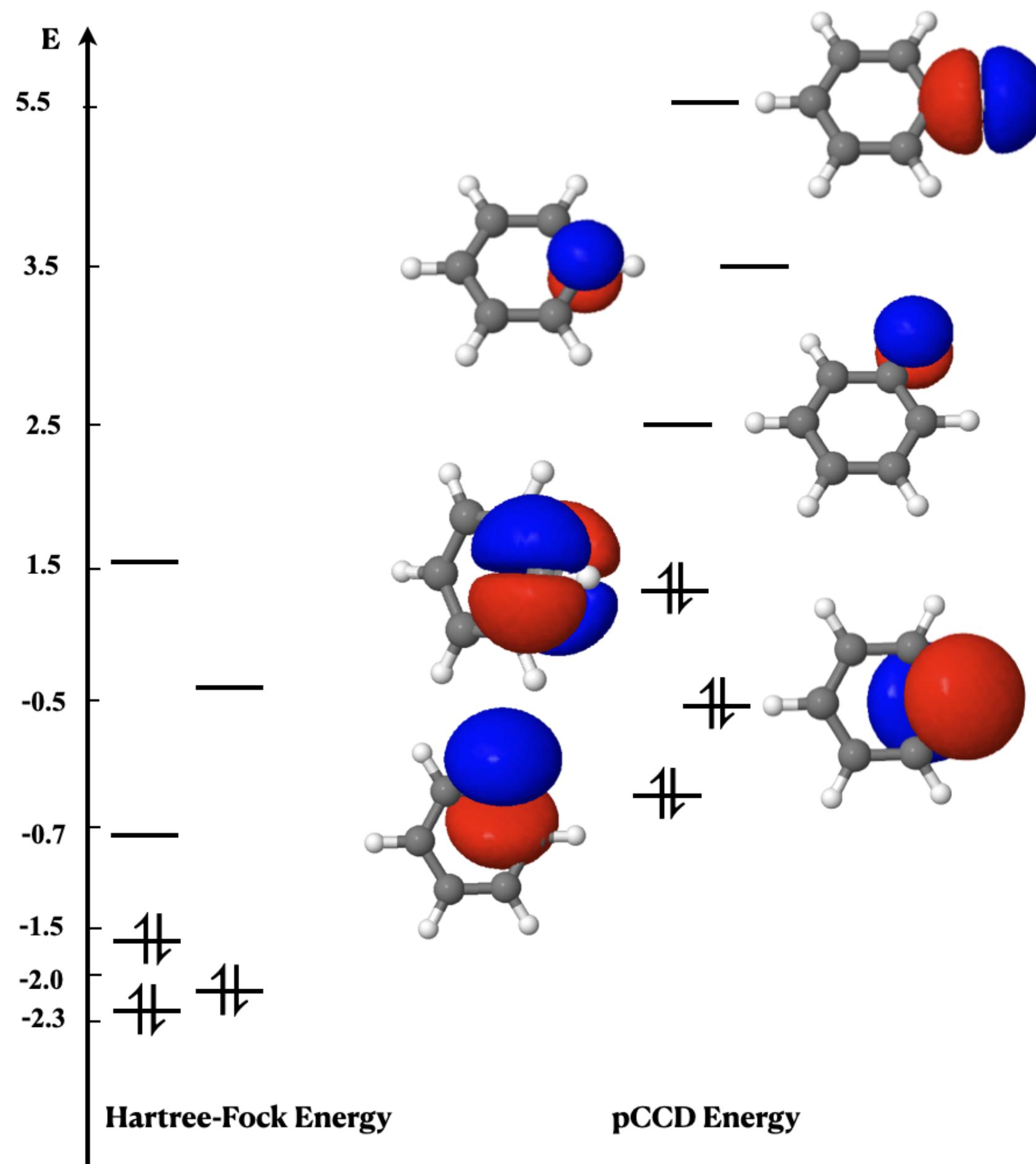


Figure 2: $\epsilon_i = 1$, $t = 1$ and $U=2$ in the PPP Hamiltonian

The PPP and Hubbard Models: HF and pCCD result for benzene

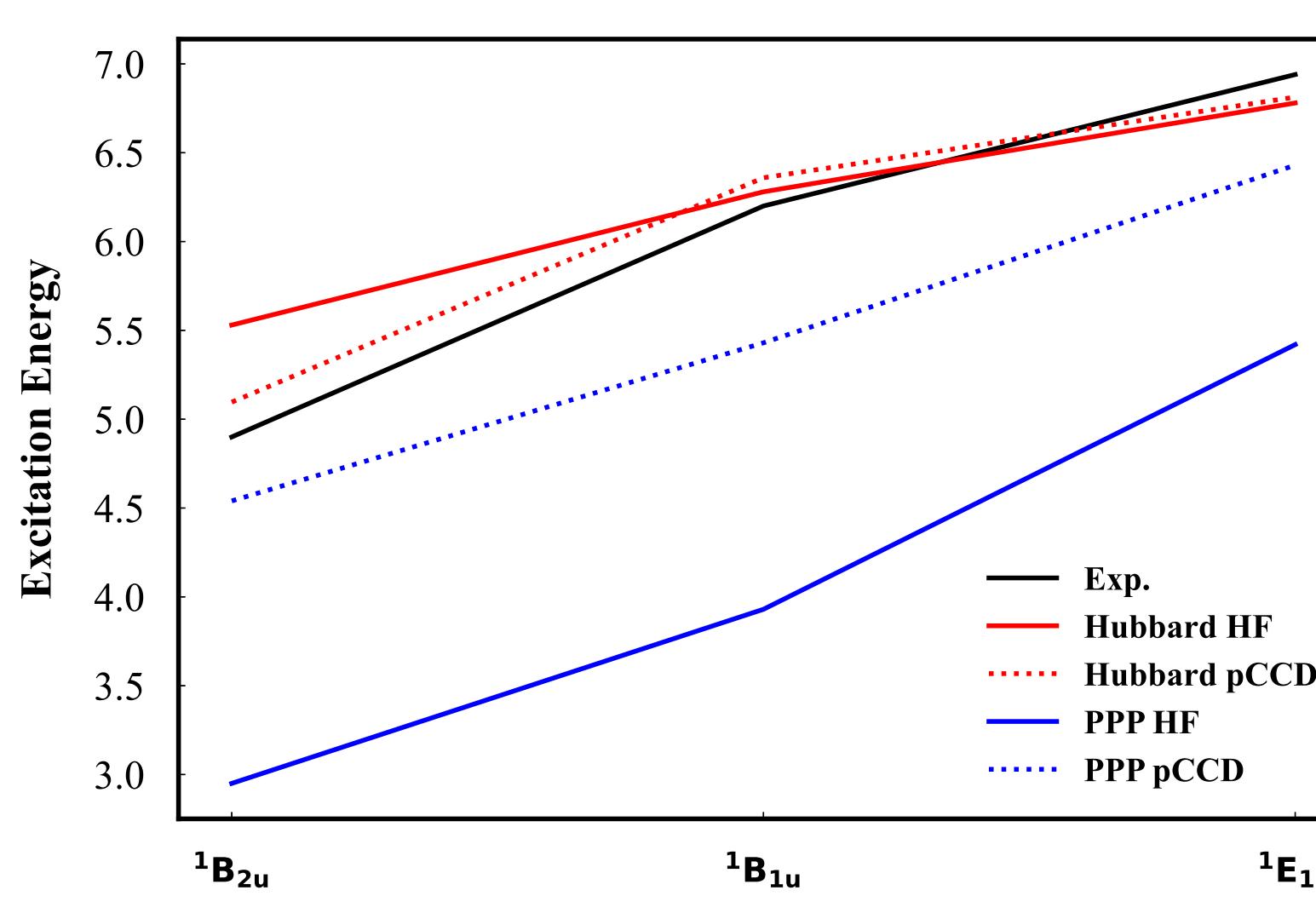


Figure 3: Comparison of excitation energies.

Excitation Energies: HF vs. pCCD

Comparison of Methods and Models

Hubbard Hamiltonian

HF: The HF method with the Hubbard model predicts excitation energies that are consistently above the experimental values but relatively close.

pCCD: The pCCD method with the Hubbard model aligns more closely with the experimental data compared to HF, especially for the highest symmetry level ($^1E_{1u}$).

PPP Hamiltonian

HF: The HF method with the PPP model significantly underestimates the excitation energies compared to experimental values.

pCCD: The pCCD method with the PPP model provides a better approximation than HF under the same Hamiltonian but still underestimates the excitation energies.

Comparison of Hubbard and PPP Models

Hubbard HF: This method gives excitation energies closer to the experimental results than the PPP HF method.

PPP HF: This method underestimates the excitation energies more significantly.

Hubbard pCCD: This method is the closest to the experimental results across all symmetries, providing the best overall match.

PPP pCCD: While closer than the PPP HF method, it still underestimates compared to the experimental data but performs better than PPP HF.

Comparison of HF vs. pCCD

Closest to Experimental Results: The Hubbard pCCD method is the closest to the experimental results across all the symmetries considered.

HF vs. pCCD: The pCCD method generally provides closer approximations to the experimental data than the HF method for both Hamiltonians.

Example Python Code

```
#!/usr/bin/env python3
import numpy as np

from pybest import context
from pybest.gbasis import get_gbasis
from pybest.linalg import DenselinalgFactory
from pybest.modelhamiltonians.physmodham import PPP
from pybest.occ_model import AufbauUccModel
from pybest.wrappers import RHF
from pybest.geminals import RpCCD
from pybest.ee_eom import REOMpCCDS

#####
## Up scup molecule, define basis set #####
#####

# get the XYZ file from PyBEST's test data directory
coord = context.get_fn("test/c6h6.xyz")
obasis = get_gbasis("cc-pvdz", coord)

#####
## Define Occupation model, expansion coefficients and overlap #####
#####

lc = DenselinalgFactory(obasis.obasis)
occ_model = AufbauUccModel(lc, obasis)
orb_a = lc.create_orbital(obasis.obasis)

#####
## Construct PPP/Hückel Hamiltonian #####
#####

modelham = PPP(lf, pbc=True)
olp = modelham.compute_overlap()

#####
## One and two-body interaction terms defined for the on-site basis #####
#####

# t-param, t = -1, epsilon = 1 and U-param, U = 2
hopping = modelham.compute_one_body()
xyfile=coord, eparam=-1, tparam=-1, uparam=-2)
v_param = modelham.compute_two_body(xyfile=coord, uparam=-2)

#####
## Do a Hartree-Fock calculation #####
#####

hf = RHF(lf, occ_model)
hf_output = hf(hopping, v_param, olp, orb_a)
hf_output.to_file("c6h6_hf.molden")

#####
## Do Oo-pCCD optimization #####
## with frozen is orbitals of the oxygen atom #####
#####

opcccd = RpCCD(lf, occ_model)
opcccd_output = opcccd(
    hopping,
    v_param,
    hf_output,
)
opcccd_output.to_file("c6h6_pccd.molden")

#####
## Do REOMpCCDS calculation #####
## with frozen is orbitals of the oxygen atom #####
#####

eom = REOMpCCDS(lf, occ_model)
eom_output = eom(hopping, v_param, opcccd_output, nroot=10, davidson=False)
# #####
# ##
```

Summary and Outlook

Integration of Models: We explored the Hückel and PPP models for understanding electronic structures in conjugated systems.

Advanced Computations: Utilizing PyBEST, we combined these models with Hartree-Fock (HF) and pair Coupled-Cluster Doubles (pCCD) methods.

Key Findings:

Hückel Model: Provided simplified insights into molecular orbitals.

PPP Model: Offered more accurate representations by considering electron-electron interactions.

Hubbard and PPP Hamiltonians: pCCD methods closely matched experimental excitation energies, outperforming HF approaches.

Future Directions:

Extended Applications: Apply pCCD-based methods to larger, more complex conjugated systems.

Method Enhancements: Improve computational efficiency and accuracy for real-world organic molecules.

Software Development: Continue advancing PyBEST for broader use in computational chemistry and physics.

References

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The PyBEST code is available on Zenodo at <https://zenodo.org/record/10069179>
and on PyPI at <https://pypi.org/project/pybest/>