

ppp and Methods Report

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1 Methods in Quantum Chemistry

1.1 Coupled Cluster (CC)

- The Coupled Cluster (CC) method is a powerful technique in quantum chemistry that models molecules by incorporating electron interactions, leading to more accurate predictions of their properties.
- CC methods improve the wave function by including effects from excited states, offering a more comprehensive view of the system, especially when electron interactions are significant.
- While CC can be computationally expensive for large systems, it provides highly accurate results for many chemical problems.
- The CC method is most effective for systems where a **single electronic configuration accurately describes the system**. It is best suited for simple closed-shell systems.
- Example: Molecules such as H_2 and N_2 are ideal for CC methods because they have strong bonds and can be described with a single main electron configuration.

1.2 Pair Coupled Cluster (pCC)

- The pair coupled cluster (pCC) method is an extension of the CC approach that focuses on electron-pair excitations, making it particularly useful for modeling closed-shell systems with an even number of electrons, where electron interactions are strong.
- pCC is less computationally expensive than full CC methods while still offering a good balance of accuracy and efficiency. It is particularly effective for handling multi-reference problems, which traditional single-reference methods struggle with.
- Example: Molecules like C_2 and O_2 are suitable for pCC, as they exhibit significant electron correlation effects that can be captured through pair excitations.

1.3 Pair Coupled Cluster with Doubles (pCCD)

- The pCCD method is an extension of pCC that handles open-shell systems with unpaired electrons, while still being applicable to closed-shell systems.
- Example: Diradical species like benzyne isomers (e.g., ortho-, meta-, and para-benzyne) are ideal examples for pCCD. These systems exhibit multi-reference characteristics that pCCD can model effectively by considering various configurations involving unpaired electrons.
- In closed-shell systems, all electrons are paired in orbitals. However, in open-shell systems, such as diradicals, there are unpaired electrons that need to be treated differently. Traditional CC methods work with systems that have a single reference state, meaning the electron configurations can be described with one main wave function. pCCD extends this concept to handle unpaired electrons by allowing for the superposition of multiple states, which is essential for accurate descriptions of open-shell systems.
- **Why does pCCD pair electrons in different orbitals?**
pCCD pairs electrons in different orbitals to better capture the correlation between electrons in systems with unpaired electrons, like diradicals or excited states. By considering different configurations, pCCD can more accurately describe the electronic structure of these systems.
- **Better Representation of Electron Correlation:** In systems with unpaired electrons, electron interactions are more complex. By allowing pairing in different orbitals, pCCD captures these interactions more accurately, which is critical for systems with strong electron-electron repulsion.
- **Improved Accuracy for Open-Shell Systems:** Traditional methods, such as Hartree-Fock or full CC, often struggle with open-shell systems. pCCD overcomes this by considering various configurations, leading to a more realistic description of the system's behavior.
- **Efficiently Handling Multiple Unpaired Electrons:** pCCD can handle up to 4 unpaired electrons, which traditional methods cannot do efficiently. It models the electronic structure of such systems by considering all possible configurations of unpaired electrons, leading to more accurate predictions of properties like bond strengths or excited states.
- **Capturing Excited States:** Since pCCD allows for various electron configurations, it is particularly suited for modeling excited states, where electrons occupy higher energy orbitals. This flexibility enables more accurate modeling of excited-state properties, which is crucial in many chemical and material science applications.

1.4 pCCD in PyBEST

- The pCCD method in PyBEST is an extension of the pCC method. It can handle closed-shell systems but is currently not available for open-shell systems.
- In PyBEST, pCCD is implemented using spin-restricted orbitals and can optimize configurations for closed-shell molecules.
- The method is computationally efficient and offers results similar to traditional coupled-cluster methods, but at a lower computational cost.

1.5 Orbital Optimization in pCCD (OOpCCD)

- Orbital optimization improves the accuracy of quantum wave functions by adjusting electron orbitals to minimize errors in the wave function and better account for electron interactions. This is particularly useful for systems with stretched bonds, such as excited states in diradicals or stretched H_2 molecules.
- Example: Real systems using orbital optimization (OOpCCD) include molecules with bond stretching or electron correlation issues, such as excited states in diradicals or stretched H_2 molecules.

1.6 EOM-pCCD

- The EOM-pCCD method calculates excited states using the pCCD reference wavefunction within the Equation-of-Motion formalism, focusing on electron-pair or singly and electron-pair excitations. The results include excitation energies, CI vectors, and singles amplitudes, stored in an IOData container and saved to a checkpoint file.

1.7 Understanding Stretched Bonds and Certain Materials

- **Stretched Bonds:** In molecules like N_2 or H_2 , as the bond between two atoms stretches, the distance between them increases. This changes how the electrons interact, making electron correlation more significant. For example, in the nitrogen dimer (N_2), as the N-N bond nears breaking (around 2.00 Å), conventional CC methods struggle to capture the necessary correlation effects, leading to overestimation of orbital-pair correlations and total energies.
- **Certain Materials:** Materials with strong electron correlation, such as transition metal complexes or high-temperature superconductors, require advanced computational methods like pCCD to model their electronic structure accurately. These materials often exhibit complex phenomena

such as magnetism or superconductivity, necessitating precise treatment of electron interactions.

2 1D Hubbard Model

$$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_i U n_{i\uparrow} n_{i\downarrow} \quad (1)$$

Explanation of the Hubbard Hamiltonian:

- ϵ_i : On-site energy at site i , representing the energy associated with an electron occupying site i .
- t_{ij} : Hopping parameter between sites i and j , describing the kinetic energy of electrons hopping between neighboring sites.
- c_i^\dagger and c_i : Creation and annihilation operators for an electron at site i .
- $n_{i\uparrow}$ and $n_{i\downarrow}$: Number operators for spin-up and spin-down electrons at site i , respectively.
- U : On-site interaction strength, accounting for the repulsion between electrons with opposite spins located on the same site.
- Correlation Strength (U/t): The ratio U/t indicates the strength of electron correlation in the system. When U/t is low (weak correlation limit), electron interactions are weak, and pCCD methods provide reliable results. However, as U/t increases, the system enters a strong correlation regime, where pCCD methods may overestimate electron interactions.
- **Weak Correlation Limit:** In this regime, pCCD methods can accurately model the system's behavior, as electron interactions are weak and manageable.
- **Strong Correlation Regime:** As U/t increases, electron interactions become more localized, and the pCCD method may struggle to provide accurate predictions, leading to overcorrelation.

2.1 pCCD-LCC

- The Linearized Coupled Cluster (LCC) method improves the description of electron interactions in the system. Applied with a pCCD reference function, LCC helps include dynamical electron correlation and improves the accuracy of electronic structure predictions.
- The Linearized Coupled Cluster (LCC) method is a technique in quantum chemistry used to better describe how electrons interact in a system. It is based on coupled cluster (CC) theory, which is one of the most accurate methods for calculating electronic structures. The LCC method is applied

using a pCCD reference function, which helps include dynamical electron correlation—important for improving the accuracy of electronic structure predictions. This means that the LCC method is used in combination with pCCD (pair coupled-cluster doubles) as the starting point (reference function) for calculations.

- **pCCD reference function:** The initial wavefunction used in LCC calculations is based on the pCCD method, which focuses on electron pairs.
- **Dynamical correlation:** This refers to the short-range interactions between electrons that are not fully captured by pCCD alone. LCC helps correct and improve this aspect by adding more flexibility to the wavefunction.
- **Improving accuracy:** By including dynamical correlation, the LCC method provides more precise predictions of electronic structures, making the model closer to real physical behavior.
- **Where is LCC Most Useful?**
- **Weakly correlated systems**, where electron interactions are not dominant.
- **Molecules near their equilibrium geometries**, where their structures are stable.
- **One-dimensional systems**, such as the 1D Hubbard model, where electron behavior is highly dependent on correlation effects.
- **Where is LCC Most Useful?**
 - **Weakly correlated systems**, where electron interactions are not dominant.
 - **Molecules near their equilibrium geometries**, where their structures are stable.

2.2 Advantages of LCC-pCCD for the Hubbard Model

- The LCC-pCCD method, which incorporates linearized coupled cluster corrections on top of the pCCD reference function, shows improved performance. The LCC corrections help to refine the predictions of orbital-pair correlations, especially in weak-correlation limits and near equilibrium geometries. This means that while pCCD alone may struggle with strong correlations, the LCC corrections enhance its accuracy and reliability in these scenarios. LCC corrections can provide accurate and reliable orbital-pair correlation spectra, which are crucial for understanding the electronic structure of systems like the Hubbard model. This makes LCC-pCCD a more suitable approach for studying such strongly correlated electron systems.

2.3 Suitable Values for pCCD and LCC-pCCD

- **Weak Correlation Limit:** For $U/t < 2$, both pCCD and LCC-pCCD methods perform well, with LCC corrections providing qualitative improvements in orbital-pair correlation spectra. This range is considered suitable for accurate predictions of electron correlation effects.
- **Moderate Values:** As U/t approaches 4, the performance of pCCD-LCCSD begins to degrade, leading to unphysical results in orbital-pair correlation spectra. Thus, values around $U/t = 4$ are critical points where the reliability of these methods diminishes.
- **Strong Correlation Limit:** For $U/t \geq 4$, the pCCD method fails to provide reliable results due to overcorrelation, and the LCCSD corrections also break down. Therefore, this range is not suitable for accurate modeling using these methods.

References

- [1] Katharina Boguslawski, "Targeting excited states in all-trans polyenes with electron-pair states," J. Chem. Phys-234105 (2016).
- [2] Boguslawski, K.; "Open-shell extensions to closed-shell pCCD," Chem. Commun.57-12277 (2021).
- [3] Nowak, A.; Boguslawski, K.; Legeza, O.; "Orbital entanglement and correlation from pCCD-tailored Coupled Cluster wave functions," October 6, 2020.

3 PPP Model

$$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} V_{ij} (n_i - 1)(n_j - 1) \quad (2)$$

- V_{ij} represents the on-site and long-range Coulomb interactions.

Key Concepts

1. Electron Interactions:

- **Coulomb Repulsion (U):** This parameter quantifies the energy cost when two electrons occupy the same site or orbital. A higher U implies stronger repulsion, which tends to localize electrons—i.e., they're more likely to remain in their specific orbital rather than hopping to neighboring sites. This affects how easily the electrons can delocalize across the molecule.

- **Hopping Integral (t):** This represents the energy associated with an electron moving from one site to another. In tight-binding models like the PPP model, t is often defined as negative, indicating an energy gain when electrons delocalize. A larger absolute value of t (i.e., smaller t number-wise) indicates that delocalization is energetically favorable, promoting conductivity.

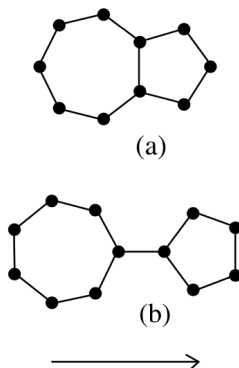


Fig. 1. Schematic view of the carbon network in azulene $C_{10}H_8$ (a) and pentaheptafulvalene $C_{12}H_{10}$ (b). The arrow indicates the direction of the positive x -axis (needed to correctly interpret the results for the dipole moments).

2. Model Predictions:

- **Hubbard Model:** Higher U/t ratios (greater than approximately 6) suggest that the electron-electron repulsion is dominant, leading to more localized electrons. In these systems, electrons do not hop freely, which can result in insulating behavior.
- **PPP Model:** Lower U/t ratios (and potentially negative U/t values) indicate that the kinetic energy associated with hopping is significant compared to the electron-electron repulsion. This balance promotes delocalization (hopping), consistent with behaviors seen in conductive organic materials.

Ranges for U and t in the PPP Model

The specific ranges for U and t can vary based on the molecule under study, but some typical values derived from literature for the PPP model are as follows:

- **Hopping Integral (t):**
 - For π -conjugated systems like polyacetylene or other organic molecules, typical values of t are around -2.5 eV to -3 eV.

- Depending on the bond lengths and molecule types, values can span roughly from -1.5 eV to -3 eV for systems with significant π overlap, with variations depending on the structural and electronic configurations.

- **Coulomb Repulsion (U):**

- Values for U in the PPP model typically range from about 5 eV to 15 eV for various organic molecules, with some reports suggesting values upwards of 20 eV in more localized systems.
- Again, the specific value can depend on the exact nature of the interactions within the molecule being studied.

References

- [1] San-Fabián, E.; Guijarro, A.; Vergés, J. A.; Chiappe, G.; Louis, E. PPP Hamiltonian for polar polycyclic aromatic hydrocarbons. *Eur. Phys. J. B* **2011**, *81*, 253–262.

4 Investigated Rules of Molecules in pCCD Calculations

all-trans polyenes

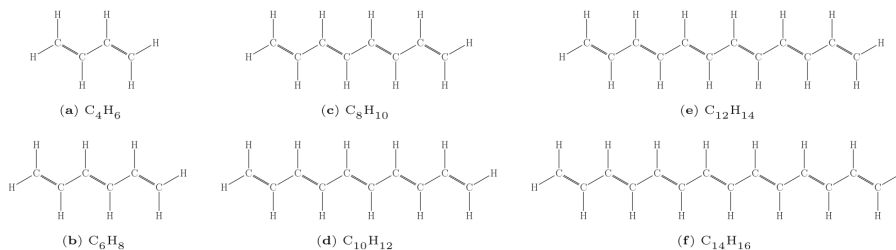


FIG. 1. Lewis structures of all investigated all-trans polyenes.

5 Hartree-Fock Results with Screened Parameters ($t=2.4$, $u=-8.0$, $k=2$, `hubbard=True`)

- we have HF results for two molecules C_4H_6 and C_8H_{10} . for other molecules "NoSCFConvergence". pCCD fail in both cases.


```
#!/usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinAlgFactory
from pybest.modelhamiltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import ACIS, ACISD
from pybest.wrappers import RHF
from pybest.geminats import RPOCD, RPOCCD
from pybest.cc import RPOCCOLCCD, RPOCCOLCCSD
from pybest.ee_eom import REOMpCOLCCD, REOMpCOLCCSD
from pybest.ee_eom import REOMpCCDS
from pybest.cc import RPOCCD, RPOCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fn("test/c4h6.xyz")

# Number of sites represented as a 'LinAlgFactory' object (indicating the number of supported atoms).
lf = DenseLinAlgFactory(4)

# Define the occupation model where 'nelt' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, nelt=6) # 6 C-H bond
orb_a = lf.create_orbital()
# h: hopping, u: u-moments, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huckel_output = modelham(
    parameters={
        "on_site": 0.0,
        "hopping": 12.4 * electronvolt,
        "u": -0.8 * electronvolt,
        "k": 2.0,
        "hubbard": True,
    }
)

Total number of atoms: 10
Entering the PPP Model Hamiltonian

Structure information for: c4h6

Symbols of supported atoms: ['C', 'C', 'C', 'C']

=====
Performing a core Hamiltonian guess.

Starting restricted closed-shell CDIS-SCF
=====

```

Iter	Error	CN	Last nv Method	Energy	Change
0	7.72948e-02	1			
0	4.99887e-02	2			
1	2.36893e-02	3			
1		1.831e+07	-0.23130	3 C	
2	3.09623e-02	4			
2		2.338e+08	3.24782	4 C	
3	1.38073e-02	5			
3		1.989e+09	1.65180	6 C	
4	8.94030e-03	6			
4		1.620e+15	0.61296	6 C	
5	1.32170e-04	6			
5		2.822e+16	0.86876	6 C	
6	9.33725e-06	6			
6		1.127e+18	0.97086	6 C	
7	5.89680e-07	6			
7		6.450e+24	1.06253	6 C	
8	3.52560e-10				(converged)

```

Contributions to the energy:
=====

```

term	Value
kin	-0.261356788160
hartree	-2.97642208370
h_hf	1.467786161069
external	0.000000000000
total	-1.739056929840

```

Print orbital information:
=====

```

orb_index	Energy[e_h]	Energy[eV]
1	-0.6392268	-16.869
2	-0.5961199	-16.221
HOMO	-0.3973414	-10.812
LUMO	-0.1585861	-4.698
LUMO-HOMO gap	0.2467553	6.715

```

=====

```

orb_index	Energy_hf [E_h]	Energy_hf [eV]	Energy_tb [E_h]	Energy_tb [eV]
1	-0.6392268	-16.869	-0.6362026	-11.803
2	-0.5961199	-16.221	-0.3480842	-9.483
HOMO	-0.3973414	-10.812	-0.2994608	-6.517
LUMO	-0.1585861	-4.698	-0.1512866	-4.117
LUMO-HOMO gap	0.2467553	6.715	0.0881964	2.408

```

=====
Please, cite the following references:

```

```

#!/usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.modelhamiltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import KCIS, KCISD
from pybest.wrappers import RHF
from pybest.geminals import RqCCD, RbqCCD
from pybest.cc import RqCCOLCCD, RbqCCOLCCD
from pybest.ee_eom import REQMqCCOLCCD, REQMqCCOLCCSD
from pybest.ee_eom import REQMqCCDSD
from pybest.cc import RfpCCD, RfpCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fn("test/Cb10.xyz")

# Number of sites represented as a 'LinalgFactory' object (indicating the number of supported atoms).
lf = DenseLinalgFactory(8)

# Define the occupation model where 'nel' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, nel=10) # 10 C-H bond
orb_a = lf.create_orbital()
# If hopping: u = repulsion, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huck_output = modelham(
    parameters={
        "on_site": 0.0,
        "hopping": 12.4 * electronvolt,
        "u": -5.0 * electronvolt,
        "k": 12.0,
        "hubbard": True,
    }
)

61 5.91546e-07 0
61 1.219e+05 -0.21410 0 C
62 5.27869e-07 0
62 4.384e+04 0.97839 0 C
63 7.95483e-07 0
63 6.427e+03 -0.61126 0 C
64 5.98328e-07 0
64 4.559e+03 -1.68174 0 C
65 4.83166e-07 0
65 1.883e+05 6.81876 0 C
66 9.69632e-08 0
66 2.767e+04 1.83863 0 C
67 1.35736e-07 0
67 2.724e+03 -0.95804 0 C
68 8.69693e-08 0
68 9.486e+04 5.33489 0 C
69 6.37329e-08 0
69 2.521e+05 3.89499 0 C
70 5.54543e-08 0
70 1.486e+05 0.21922 0 C
71 8.82827e-08 0
71 2.315e+04 -1.18811 0 C
72 4.24929e-08 0
72 1.222e+03 0.46827 0 C
73 5.31496e-08 0
73 4.387e+04 -5.43650 0 C
74 1.75582e-08 0
74 9.864e+04 -0.58917 0 C
75 1.86456e-08 0
75 1.322e+04 1.24864 0 C
76 9.78589e-09 (converged)

Contributions to the energy:
-----
term      Value
kin      -0.68721957155
hartree  -4.13268646700
1_hf      2.86639234603
external  0.00000000000
total     -2.754824191768

Print orbital information:
-----
orb_index  Energy[E_h]  Energy[eV]
1          -0.6368814  -17.328
2          -0.5389322  -16.447
3          -0.4943228  -13.451
4          -0.4425488  -12.842
HOMO      -0.3855588  -9.315
LUMO      -0.2466712  -6.712
7          -0.1478758  -4.082
8          -0.1368359  -3.782

LUMO-HOMO gap  0.8588876  1.682

-----
orb_index  Energy_hf [E_h]  Energy_hf [eV]  Energy_tb [E_h]  Energy_tb [eV]
1          -0.6368814  -17.328  -0.4597933  -12.511
2          -0.5389322  -16.447  -0.4591224  -11.677
3          -0.4943228  -13.451  -0.3821938  -10.480
4          -0.4425488  -12.842  -0.3246256  -8.834
HOMO      -0.3855588  -9.315  -0.2633636  -7.166
LUMO      -0.2466712  -6.712  -0.2857962  -5.680
7          -0.1478758  -4.082  -0.1588668  -4.323
8          -0.1368359  -3.782  -0.1292359  -3.489

LUMO-HOMO gap  0.8588876  1.682  0.8575674  1.566

```

6 Hartree-Fock Results with Screened Parameters($t=2.4$, $u=-8.0$, $k=2$, $hubbard=False$)

```
#!/usr/bin/env python
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.model.hamiltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import RCIS, RCISD
from pybest.wrappers import RHF
from pybest.gentials import RpCCD, R00pCCD
from pybest.cc import RpCDLCCD, RpCDLCCSD
from pybest.ee_eom import REOMpCDLCCD, REOMpCDLCCSD
from pybest.ee_eom import REOMpCCDPS
from pybest.cc import RpCCD, RpCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fn("test/c4h6.xyz")

# Number of sites represented as a 'LinalgFactory' object (indicating the number of supported atoms).
lf = DenseLinalgFactory(4)

# Define the occupation model where 'nel' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, nel=6) # 6 C-H bond
orb_g = lf.create_orbital()
# 1.1 hopping, u1 == repulsion, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huckel_output = modelham(
    parameters={
        "on_site": 0.0,
        "hopping": 12.4 * electronvolt,
        "u": -8.0 * electronvolt,
        "k": 2.0,
        "hubbard": False,
    }
)

=====
Total number of atoms: 18
Entering the PPP Model Hamiltonian

Structure information for: c4h6

Symbols of supported atoms: ['C', 'C', 'C', 'C']
=====
Performing a core Hamiltonian guess.

=====
Starting restricted closed-shell CDHIS-SCF

Iter   Error      CN      Last nv Method      Energy      Change
-----
0      3.57177e-02    1
0      1.75853e-02    2
0      1.597e+06      1.96982  2 C
1      1.51082e-03    3
1      1.101e+00      3.75100  3 C
2      5.03101e-03    4
2      1.159e+08      0.17748  4 C
3      4.78239e-03    5
3      4.167e+13      -48.47786  5 C
4      1.08633e-03    6
4      5.947e+15      0.36482  6 C
5      4.68011e-04    6
5      1.438e+18      1.43320  6 C
6      1.29966e-05    6
6      1.705e+15      0.94804  6 C
7      1.43776e-07    6
7      1.884e+21      1.81474  6 C
8      2.24579e-10    (converged)

Contributions to the energy:
=====
term      Value
-----
kin      -0.27650801332
hartree  -1.540122564990
x_hf     0.754861280495
external  0.000000000000
total    -1.030681631827

Print orbital information:
=====
orb_index  Energy[E_h]  Energy[eV]
-----
1          -8.3820795  -18.397
2          -0.3183267  -8.462
HOMO      -0.1919652  -5.224
LUMO      0.6183876  0.283

LUMO-HOMO gap  0.2823529  5.586

=====
orb_index  Energy_hf [E_h]  Energy_hf [eV]  Energy_tb [E_h]  Energy_tb [eV]
-----
1          -8.3820795  -18.397  -0.1427808  -3.883
2          -0.3183267  -8.462  -0.8545095  -1.483
HOMO      -0.1919652  -5.224  0.8545095  1.483
LUMO      0.6183876  0.283  0.1427808  3.883

LUMO-HOMO gap  0.2823529  5.586  0.8881984  2.400

=====
Please, cite the following references:
```

```

#!/usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.model.hamiltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import RCI5, RCI5D
from pybest.wrappers import RHF
from pybest.geminals import RqCCD, R0qCCD
from pybest.cc import RqCOLLCD, RqCOLCCSD
from pybest.ee_eom import REOMqCOLLCD, REOMqCOLCCSD
from pybest.ee_eom import REOMqCCDS
from pybest.cc import RfjCCD, RfjCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fa("test/c0h8.xyz")

# Number of sites represented as a 'LinalgFactory' object (indicating the number of supported atoms).
lf = DenseLinalgFactory(6)

# Define the occupation model where 'nel' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, nel=8) # 8 C-H bond
orb_h = lf.create_orbital()
# t: hopping, u: on-site repulsion, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huckel_output = modelham
parameters = {
    "on_site": 8.0,
    "hopping": 12.4 * electronvolt,
    "u": -5.0 * electronvolt,
    "k": 2.0,
    "hubbard": False,
}

Structure information for: c0h8
Symbols of supported atoms: ['C', 'C', 'C', 'C', 'C', 'C', 'C']
=====
Performing a core Hamiltonian guess.
=====
Starting restricted closed-shell CD115-SCF
-----
Iter      Error      CN      Last nv Method      Energy      Change
-----
0      4.23155e-02      1
0      2.98389e-02      2
0      2.340e+02      2.86472  2 C
1      7.47279e-03      3
2      4.84976e-03      7.863e+02  1.23261  3 C
2      1.219e+04      2.43671  4 C
3      2.33081e-03      5
3      1.477e+05      1.36057  5 C
4      4.12856e-04      6
4      8.518e+07      1.00376  6 C
5      6.80077e-05      6
5      7.898e+07      1.09777  6 C
6      3.03950e-06      6
6      3.150e+09      3.63696  6 C
7      3.27955e-06      6
7      7.560e+08      1.27209  6 C
8      9.18234e-07      6
8      1.286e+08      0.91932  6 C
9      1.08316e-07      6
9      4.585e+09      1.96846  6 C
10     1.75699e-09 (converged)

Contributions to the energy:
-----
term      Value
-----
kin      -0.581186747654
hartree  -1.935286732176
x_hf     0.966682064800
external  0.000000000000
total    -1.467829613742

Print orbital information:
-----
orb_index  Energy[E_h]  Energy[eV]
-----
1      -0.59289099      -10.691
2      -0.3357943      -9.136
3      -0.2010377      -7.520
HOMO     -0.1975734      -5.376
LUMO     0.0083723      0.869
6      0.0408845      1.113

LUMO-HOMO gap      0.1979467      5.386

-----
orb_index  Energy_hf [E_h]  Energy_hf [eV]  Energy_th [E_h]  Energy_th [eV]
-----
1      -0.59289099      -10.691      -0.1589708      -4.325
2      -0.3357943      -9.136      -0.1099616      -2.993
3      -0.2010377      -7.520      -0.0392520      -1.068
HOMO     -0.1975734      -5.376      0.0392520      1.068
LUMO     0.0083723      0.869      0.1099616      2.993
6      0.0408845      1.113      0.1589708      4.325

LUMO-HOMO gap      0.1979467      5.386      0.0787206      1.925

```

```

#!/usr/bin/env python
from pybest import context
from pybest.linalg import DenseLinAlgFactory
from pybest.model.hamiltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import RCIS, RCISD
from pybest.wrappers import RHF
from pybest.globals import RbCCD, RbQCCD
from pybest.cc import RbCCOLCCD, RbCCOLCCSD
from pybest.ee_eom import REOMpCCOLCCD, REOMpCCOLCCSD
from pybest.ee_eom import REOMpCCS
from pybest.cc import RfPCD, RfPCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fat('test/cb18.xyz')

# Number of sites represented as a 'LinAlgFactory' object (indicating the number of supported atoms).
lf = DenseLinAlgFactory(8)

# Define the occupation model where 'n_el' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, n_el=10) # 10 C-H bond
orb_x = lf.create_orbital()

# t: hopping, u: e-e repulsion, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huckel_output = modelham
parameters={
    "on_site": 8.0,
    "hopping": 1.4, electronvolt,
    "u": -8.0 * electronvolt,
    "k": 2.0,
    "hubbard": False,
}
}

1      6.628e+02  1.01956  3 C
2      2.62528e-03  0
3      1.26289e-03  0
4      2.27827e-04  0
5      9.61636e-05  0
6      2.51294e-05  0
7      1.92638e-06  0
8      1.93422e-06  0
9      1.66157e-06  0
10     1.05354e-06  0
11     9.61394e-08  0
12     2.35337e-08  0
13     1.04717e-08  0
14     1.79545e-09 (converged)

Contributions to the energy:
-----
term      Value
-----
kin      -0.735289346627
hartree  -2.317282080594
x_hf     1.186418309297
external  0.000000000000
total    -1.073938376926
-----

Print orbital information:
-----
orb_index  Energy[E_h]  Energy[eV]
-----
1          -0.3908519  -10.627
2          -0.3525680  -9.748
3          -0.3118398  -8.464
4          -0.2739472  -7.464
HOMO      -0.1924976  -5.238
LUMO      -0.0258399  -0.703
7          0.0277818  0.764
8          0.0544588  1.482
-----
LUMO-HOMO gap  0.1666577  4.536
-----

orb_index  Energy_hf [E_h]  Energy_hf [eV]  Energy_tb [E_h]  Energy_tb [eV]
-----
1          -0.3908519  -10.627         -0.1657587        -4.511
2          -0.3525680  -9.748          -0.1351278        -3.677
3          -0.3118398  -8.464          -0.0801984        -2.400
4          -0.2739472  -7.464          -0.0306310        -0.834
HOMO      -0.1924976  -5.238          0.0306310         0.834
LUMO      -0.0258399  -0.703          0.0801984         2.400
7          0.0277818  0.764           0.1351278         3.677
8          0.0544588  1.482           0.1657587         4.511
-----
LUMO-HOMO gap  0.1666577  4.536          0.0575674         1.566
-----

Please, cite the following references:

```

```

#!/usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.model.hamiltonians.ppp_model import PPP
from pybest.cc_model import AufbauCCModel
from pybest.units import electromvolt
from pybest.ci import RCIS, RCISD
from pybest.wrappers import RHF
from pybest.gentials import RqCCD, R0qCCD
from pybest.cc import RqCCOLCCD, RqCCOLCCSD
from pybest.ee_eom import RE0qmpCCOLCCD, RE0qmpCCOLCCSD
from pybest.ee_eom import RE0qmpCCDS
from pybest.cc import RfpcCD, RfpcCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fnl("test/clh11.xyz")

# Number of sites represented as a 'LinalgFactory' object (indicating the number of supported atoms).
lf = DenseLinalgFactory(18)

# Define the occupation model where 'nel' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauCCModel(lf, nel=12) # 12 C-H bond
orb_e = lf.create_orbital()
# 1 hopping, u1 = revision, k: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_file=coord)

huckel_output = modelham(
    parameters={
        "on_site": 0.0,
        "hopping": 1.4 * electromvolt,
        "u1": -5.0 * electromvolt,
        "k": 2.0,
        "hubbard": False,
    }
)

Starting restricted closed-shell CD119-SCF
=====
Iter      Error      CN      Last nv Method      Energy      Change
=====
0      4.25708e-02      1
0      3.45406e-02      2
0      1.729e+02      3.68172 2 C
1      8.45106e-03      4
1      3.789e+02      1.14295 3 C
2      6.48070e-03      5
2      2.566e+03      2.19429 4 C
3      4.78314e-03      6
3      7.937e+03      1.33883 5 C
4      1.92684e-03      7
4      1.892e+05      2.27453 6 C
5      1.68594e-03      8
5      1.882e+05      1.89577 6 C
6      6.03905e-04      9
6      3.135e+05      1.71115 4 C
7      1.63835e-05      6
7      1.173e+06      1.28522 6 C
8      5.14297e-06      6
8      4.882e+07      1.36890 6 C
9      2.28505e-07      6
9      3.414e+08      1.85863 6 C
10      2.32312e-08      6
10      1.112e+10      1.85880 6 C
11      4.96000e-09 (converged)

Contributions to the energy:
=====
term      Value
-----
Kin      -0.947719423205
hartree      -2.7427043206995
x_hf      1.371392199848
external      0.8088888888888
total      -2.319111623112

Print orbital information:
=====
orb_index      Energy[f_h]      Energy[eV]
-----
1      -0.3919331      -10.665
2      -0.3456877      -9.951
3      -0.3388822      -9.280
4      -0.2918215      -7.941
5      -0.2638542      -7.180
HOMO      -0.1938732      -5.276
LUMO      -0.8336993      -8.917
6      0.6845749      0.124
7      0.8672437      1.286
8      0.8631658      1.719

LUMO-HOMO gap      0.1081739      4.369
=====
orb_index      Energy_hf [e_h]      Energy_hf [eV]      Energy_tb [f_h]      Energy_tb [eV]
-----
1      -0.3919331      -10.665      -0.1092533      -4.686
2      -0.3456877      -9.951      -0.1453944      -4.838
3      -0.3388822      -9.280      -0.1155153      -3.143
4      -0.2918215      -7.941      -0.8732779      -1.994
5      -0.2638542      -7.180      -0.8251839      -0.683
HOMO      -0.1938732      -5.276      0.8251839      0.683
LUMO      -0.8336993      -8.917      0.8732779      1.994
6      0.6845749      0.124      0.1155153      3.143
7      0.8672437      1.286      0.1453944      4.838
8      0.8631658      1.719      0.1092533      4.686

LUMO-HOMO gap      0.1081739      4.369      0.8481748      1.311
=====

```

```

7 3.42536e-05 0 1.14237 6 C
7 1.577e+06 0 1.14237 6 C
8 2.61101e-06 0 1.35936 6 C
8 1.386e+08 0 1.35936 6 C
9 3.68782e-07 0 1.86328 6 C
9 3.467e+08 0 1.86328 6 C
10 5.43382e-08 0 1.29976 6 C
10 1.929e+09 0 1.29976 6 C
11 2.00812e-08 0 1.48044 6 C
11 2.955e+09 0 1.48044 6 C
12 1.64521e-08 0 1.11438 6 C
12 6.447e+07 0 1.11438 6 C
13 1.55192e-08 0 1.85962 6 C
13 7.357e+06 0 1.85962 6 C
14 1.55856e-08 0 1.32358 6 C
14 2.365e+06 0 1.32358 6 C
15 1.54980e-08 0 15.62748 6 C
15 5.765e+05 0 15.62748 6 C
16 1.63857e-08 0 1.54546 6 C
16 3.448e+06 0 1.54546 6 C
17 1.36798e-08 0 5.29828 6 C
17 6.181e+06 0 5.29828 6 C
18 8.43816e-09 (converged)

Contributions to the energy:
-----
term Value
-----
kin -1.146584812397
hartree -3.152894512885
x_hf 1.576847860943
external 8.808988888889
total -2.742551873338
-----

Print orbital information:
-----
orb_index Energy[E_h] Energy[eV]
1 -0.3987888 -18.632
2 -0.3718720 -18.119
3 -0.3492677 -16.584
4 -0.3193880 -14.889
5 -0.2792470 -13.099
6 -0.2563618 -11.976
HOMO -0.1925421 -9.239
LUMO -0.8438786 -41.194
9 -0.0068875 -0.185
10 0.0255553 0.696
11 0.0579337 1.576
12 0.0685343 1.865
LUMO-HOMO gap 0.1486635 4.045
-----
orb_index Energy_hf [E_h] Energy_hf [eV] Energy_lb [E_h] Energy_lb [eV]
1 -0.3987888 -18.632 -0.1717718 -4.661
2 -0.3718720 -18.119 -0.1565916 -4.208
3 -0.3492677 -16.584 -0.1328349 -3.593
4 -0.3193880 -14.889 -0.1082848 -2.727
5 -0.2792470 -13.099 -0.0625512 -1.782
6 -0.2563618 -11.976 -0.0212623 -0.579
HOMO -0.1925421 -9.239 0.0212623 0.579
LUMO -0.8438786 -41.194 0.0625512 1.782
9 -0.0068875 -0.185 0.1082848 2.727
10 0.0255553 0.696 0.1328349 3.593
11 0.0579337 1.576 0.1565916 4.208
12 0.0685343 1.865 0.1717718 4.661
LUMO-HOMO gap 0.1486635 4.045 0.8412889 1.124
-----

# /usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.model.halliltonians.ppp_model import PPP
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt
from pybest.ci import RCI5, RCI5D
from pybest.wrappers import RHF
from pybest.geminale import RpCCD, R00pCCD
from pybest.cc import RpCDLCCD, RpCDLCCD
from pybest.ee_eom import RE0mpCCD, RE0mpCCDCCSD
from pybest.ee_eom import RE0mpCCD
from pybest.cc import RfpCCD, RfpCCSD

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fn("test/c12h14.xyz")

# Number of sites represented as a 'LinalgFactory' object (indicating the number of supported atoms).
lf = DenseLinalgFactory(12)

# Define the occupation model where 'n_el' is the number of C-H bonding and lone-pair electrons.
occ_model = AufbauOccModel(lf, n_el=14) # 14 C-H bond
orb_a = lf.create_orbital()

# t: hopping, u: e-e repulsion, v: dielectric constant, hubbard: hubbard term in ppp.
modelham = PPP(lf, occ_model, xyz_filename=coord)

huckel_output = modelham(
    parameters={
        "n_site": 8.0,
        "hopping": 2.4 * electronvolt,
        "u": -8.0 * electronvolt,
        "v": 12.0,
        "hubbard": False,
    }
)

```

- we have HF results for all molecules- pCCD fail in all cases.

7 Standard parameters(t=2.4, u=-11.13, k=1, hubbard=True)

- Same result as standard parameters. (all conditions not complete yet)

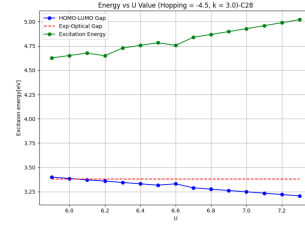
7.1 Conclusion:

The pCCD method does not work for both standard and screened parameters. We investigated other structures, such as all-trans polyenes. Previously, we attempted pCCD for coronene derivative molecules, but it did not converge. The results indicate that the performance of the pCCD method in the PPP model Hamiltonian case does not depend on the type of molecule but rather on the choice of parameters, specifically U and t . Since pCCD is suitable for weak correlation, meaning a small U/t ratio, it is not effective for standard and screened parameters where U/t is large.

8 Parameter Selection Based on Experimental Data

Therefore, we are now trying to find a suitable range for our parameters by comparing them with experimental optical gap data.

Comparison of Calculated and Experimental HOMO-LUMO Gaps and first excitation energy for C28 with Varying Parameters						
hopping	U	K	HOMO energy	LUMO energy	H-L gap	first excitation energy
-4.5	5.9	3.0	4.209	7.900	3.690	4.626140e+00 [eV]
-4.5	6.0	3.0	4.307	7.993	3.686	4.609910e+00 [eV]
-4.5	6.1	3.0	4.414	7.786	3.372	4.676164e+00 [eV]
-4.5	6.2	3.0	4.321	7.879	3.558	4.646340e+00 [eV]
-4.5	6.3	3.0	4.608	7.972	3.364	4.726209e+00 [eV]
-4.5	6.4	3.0	4.734	8.066	3.331	4.755140e+00 [eV]
-4.5	6.5	3.0	4.841	8.159	3.317	4.784864e+00 [eV]
-4.5	6.6	3.0	4.734	8.066	3.331	4.755140e+00 [eV]
-4.5	6.7	3.0	5.065	8.240	3.175	4.826751e+00 [eV]
-4.5	6.8	3.0	5.102	8.038	3.276	4.805570e+00 [eV]
-4.5	6.9	3.0	6.031	8.269	3.202	4.897067e+00 [eV]
-4.5	7.0	3.0	5.076	8.024	3.249	4.827061e+00 [eV]
-4.5	7.1	3.0	5.483	8.717	3.235	4.957520e+00 [eV]
-4.5	7.2	3.0	5.580	8.811	3.231	4.986010e+00 [eV]
-4.5	7.3	3.0	5.686	8.904	3.217	5.030313e+00 [eV]



Comparison of Calculated and Experimental HOMO-LUMO Gaps for C30 with Varying Parameters						
hopping	U	K	HOMO energy	LUMO energy	H-L gap	first excitation energy
-4.5	3.7	4.0	2.159	5.241	3.082	3.719184e+00 [eV]
-4.5	3.8	4.0	2.264	5.336	3.072	3.731108e+00 [eV]
-4.5	3.9	4.0	2.369	5.431	3.062	3.750850e+00 [eV]
-4.5	4.0	4.0	2.474	5.526	3.053	3.771536e+00 [eV]
-4.5	4.1	4.0	2.578	5.622	3.043	3.791665e+00 [eV]
-4.5	4.2	4.0	2.683	5.717	3.034	3.813320e+00 [eV]
-4.5	4.3	4.0	2.788	5.812	3.024	3.835424e+00 [eV]
-4.5	4.34	4.0	2.893	5.890	3.000	3.844150e+00 [eV]
-4.5	4.4	4.0	2.998	6.002	3.005	3.896504e+00 [eV]
-4.5	4.6	4.0	3.103	6.097	2.996	3.904140e+00 [eV]
-4.5	4.7	4.0	3.207	6.193	2.986	3.928171e+00 [eV]
-4.5	4.8	4.0	3.312	6.288	2.976	3.957716e+00 [eV]
-4.5	4.9	4.0	3.417	6.383	2.966	3.977704e+00 [eV]
-4.5	5.0	4.0	3.522	6.478	2.956	4.003630e+00 [eV]

