Insights from Comparing PPP Model Hamiltonian with Tight Binding Model

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Outline

Hamiltonians Overview

Hamiltonian	Hamiltonian Terms
Tight-Binding	$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j$
Hückel-Model	$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j$
Hubbard-Model	$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_i U n_{i\uparrow} n_{i\downarrow}$
PPP-Model	$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_{\langle i,j \rangle} V_{ij} n_i n_j$
PPP+Hubbard term	$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_{\langle i,j \rangle} V_{ij} n_i n_j + \sum_i U n_{i\uparrow} n_{i\downarrow}$

Tight Binding Model

The tight-binding model in second quantization is given by:

$$\hat{H} = \sum_i \epsilon_i \hat{n}_i + \sum_{\langle i,j \rangle} t_{ij} \left(\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i \right)$$

where ϵ_i is the onsite energy and t_{ij} is the hopping parameter between sites i and j.

Hückel Model

The Hückel model is a special case of the tight-binding model, with the onsite energies ϵ_i and the hopping energy t_{ij} being constant.

$$\hat{H} = H_{TB} \tag{1}$$

Hubbard Model

The Hubbard interaction is added to the Hamiltonian to describe electron-electron repulsion on the same site:

$$\hat{H} = \hat{H}_{TB} + \sum_i U n_{i\uparrow} n_{i\downarrow}$$

where U is the Coulomb repulsion and $n_{i\uparrow}$, $n_{i\downarrow}$ are the number operators for spin-up and spin-down electrons at site i.

PPP Model

The PPP model extends the tight-binding model by including distance-dependent electron-electron interactions:

$$\hat{H} = \hat{H}_{TB} + \sum_{\langle i,j \rangle} V_{ij} n_i n_j$$

where V_{ij} represents the long-range columb interaction between site i and j.

PPP + Hubbard term

The final model combines both the PPP model and the Hubbard model:

$$\hat{H} = \hat{H}_{TB} + \sum_{\langle i,j \rangle} V_{ij} n_i n_j + \sum_i U n_{i\uparrow} n_{i\downarrow}$$

This includes both hopping terms, Coulomb interactions, and onsite repulsion.
The Ohno formula is given by:

$$V_{i,j} = \frac{U}{\kappa_{i,j} \sqrt{1 + 0.6117 R_{i,j}^2}}$$

(2)

Coulomb Interaction Parameters:

- U: On-site electron-electron repulsion.
- $\kappa_{i,j}$: Dielectric constant .
- $R_{i,j}$: Distance between i-th and j-th carbon atoms.

Two Types of Coulomb Parameters:

- Screened Parameters:
  - ✓ $U = 8.0\,\text{eV}$,
  - ✓ $\kappa_{i,j} = 2.0\,(i \neq j)$,
- Standard Parameters:
  - ✓ $U = 11.13\,\text{eV}$,
  - ✓ $\kappa_{i,j} = 1.0\,(i \neq j)$,

```python
#!/usr/bin/env python3
from pybest import context
from pybest.linalg import DenseLinalgFactory
from pybest.modelhamiltonians.ppp_hub_model import PPPHub
from pybest.occ_model import AufbauOccModel
from pybest.units import electronvolt

# get the xyz file from pybest/src/pybest/data/test
coord = context.get_fn("test/c36.xyz")

# number of sites
lf = DenseLinalgFactory(36)

# Define the occupation model, expansion coefficients, and overlap
# number of free electrons
occ_model = AufbauOccModel(lf, nel=36)

# t= -1 and epsilon=0 are default hopping and on-site parameters, respectively.
modelham = PPPHub(lf=lf, occ_model=occ_model, xyz_file=coord)

# Output for screen with k_param = 2.
huckel_output = modelham(
    parameters={
        "onsite_param": 0.0,
        "hopping_param": -2.4*electronvolt,
        "u_param": -8.0*electronvolt,
        "k_param": 2.0,
        "pccd": False,
    }
)

# Output for standard with k_param = 1.
huckel_output = modelham(
    parameters={
        "onsite_param": 0.0,
        "hopping_param": -2.4 * electronvolt,
        "u_param": -11.13 * electronvolt,
        "k_param": 1.0,
        "pccd": False,
    }
)
```

Results:

Table: HOMO-LUMO gap[eV]

Molecule	TB	TB	PPP-RHF_scr		PPP-RHF_std	
	Pybest	Paper	Pybest	Paper	Pybest	Paper
Benzo[ghi]perylene	2.11	2.11	3.848	3.85	7.126	7.13
Benzo[a]coronene	2.25	2.25	3.950	3.95	7.138	7.13
Naphtho[2,3a]coronene	1.89	1.89	3.567	3.57	6.71	6.71
Anthra[2,3a]coronene	1.49	1.49	3.141	3.14	6.232	6.23
Naphtho[8,1,2-abc]coronene	1.83	1.83	3.432	3.43	6.478	6.48

Conclusion

- Using Hubbard and Hückel models to demonstrate PPP model implementation:
  - ✓ Validating the approach.
- Extended Tight-Binding to PPP with electron-electron interactions.
- HOMO-LUMO gap results match paper:
  - ✓ Validating the PPP model.

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