Parameterizing the PPP Model Hamiltonian
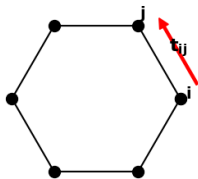
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Outline

Tight Binding Model

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

ϵ_i:onsite energy

t_{ij} hopping parameter between sites i and j.

Hückel model is a specific case of the tight-binding model, tailored for conjugated systems and π-electrons.

Overview of Model Hamiltonians

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

Coulomb Interaction Parameters:

- long-range Coulomb interaction:

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

- 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:**
  - ✓ $U = 11.13\,\text{eV}$,
  - ✓ $\kappa_{i,j} = 1.0\,(i \neq j)$,

HF-Results:

Table: HOMO-LUMO gap[eV]

Molecule	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

pCCD-result for scr and std parameters

✓ for scr and std parameters, the pCCD method failed.

Why?

- Does the pCCD performance depend on parameters in the PPP model?

- Is the performance of the pCCD method dependent on the model Hamiltonian?

- Is the PPP model method-dependent?

Fitting Parameters for Model Hamiltonians

PPP Hamiltonian for polar polycyclic aromatic hydrocarbons

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Abstract. Total energies of charged states and configurations of different spin multiplicity of two polar non-alternant polycyclic aromatic hdrocarbons (PAH), namely, pentaheptafulvalene and azulene, calculated by means of a Multi-Configurational (MCSCF) method which includes correlation only amongst π orbitals, have been fitted by exact solutions of the Pariser-Parr-Pople (PPP) and the Hubbard Hamiltonians for π electrons. As both molecules are planar, such an approach is in principle feasible. As found in our previous analysis of PAH, PPP fittings are significantly better than those attained with the Hubbard Hamiltonian. In addition, parameters for the Hubbard Hamiltonian are around twice those derived for the PPP model, indicating that parameters are not model independent. Fitted PPP parameters are close to those derived from a similar study of the PAH 2, 5, 8-trihydrogenated phenalene and those originally proposed by Pariser et al. providing further support to a wide applicability of the fitted parameters. Fittings obtained for a MCSCF method that also includes σσ and σπ correlations (MCSCF/MP2) are slightly less accurate giving an on-site repulsion 10–15% smaller. The accuracy of the fittings further diminishes when parameters are derived from energies obtained by means of a DFT method (B3LYP) with an additional decrease in U of 5–25%. In the latter two cases, parameters have to be considered as *effective*, accounting for effects of σ orbitals not explicitly included in the model Hamiltonians. Electron affinities, ionization energies and dipole moments, calculated by means of the model Hamiltonians, are compared to those derived from DFT and ab initio methods and, whenever available, to experimental data.

Model Hamiltonian Dependency in Fitting Parameters

✓ **PPP vs. Hubbard Model:** PPP fits the data much better than the Hubbard model.

✓ **Model-Dependent Parameters:** Parameters are not model-independent; different Hamiltonians require different parameter values.

✓ **Method-Dependent Results:** Using different electronic structure methods (e.g., MCSCF/MP2 or DFT instead of MCSCF with π-only) changes the fitted parameters, indicating the results depend on the method used.

parameters in Hubbard model

Orbital entanglement and correlation from pCCD-tailored coupled cluster wave functions

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ABSTRACT

Wave functions based on electron-pair states provide inexpensive and reliable models to describe quantum many-body problems containing strongly correlated electrons, given that broken-pair states have been appropriately accounted for by, for instance, *a posteriori* corrections. In this article, we analyze the performance of electron-pair methods in predicting orbital-based correlation spectra. We focus on the (orbital-optimized) pair-coupled cluster doubles (pCCD) ansatz with a linearized coupled-cluster (LCC) correction. Specifically, we scrutinize how orbital-based entanglement and correlation measures can be determined from a pCCD-tailored CC wave function. Furthermore, we employ the single-orbital entropy, the orbital-pair mutual information, and the eigenvalue spectra of the two-orbital reduced density matrices to benchmark the performance of the LCC correction for the one-dimensional Hubbard model with the periodic boundary condition as well as the N_2 and F_2 molecules against density matrix renormalization group reference calculations. Our study indicates that pCCD-LCC accurately reproduces the orbital-pair correlation patterns in the weak correlation limit and for molecules close to their equilibrium structure. Hence, we can conclude that pCCD-LCC predicts reliable wave functions in this regime.

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Dependence of pCCD Results on Model Parameters

✓ **Weak Correlation Limit:** For $U/t < 2$, pCCD works well and predicts electron correlation accurately. This range is good for reliable modeling.

✓ **Moderate Correlation:** When U/t gets close to 4, pCCD becomes less accurate. Around $U/t = 4$, the method's reliability drops.

✓ **Strong Correlation Limit:** For $U/t \geq 4$, pCCD fails. It overcorrelates the system and cannot model it correctly.

Highlighted Parameter Region Matching Experimental Excitation Energy for c28

Contour Plot of First-Excitation Energy for C28 (k=2, 3, 4, 5) with Continuous Highlighted Region
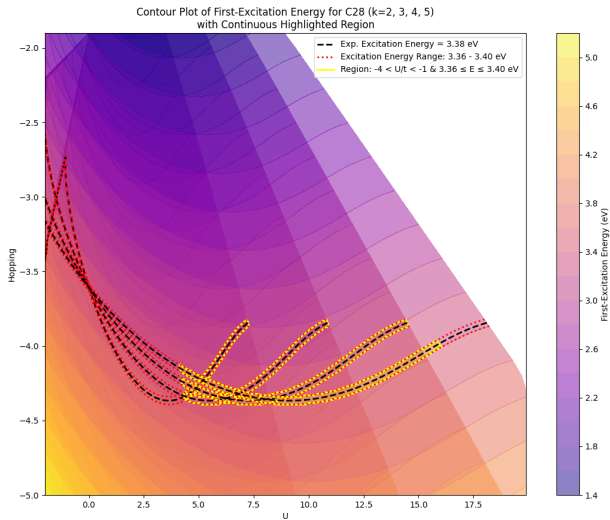
Highlighted Parameter Region Matching Experimental Excitation Energy for c30
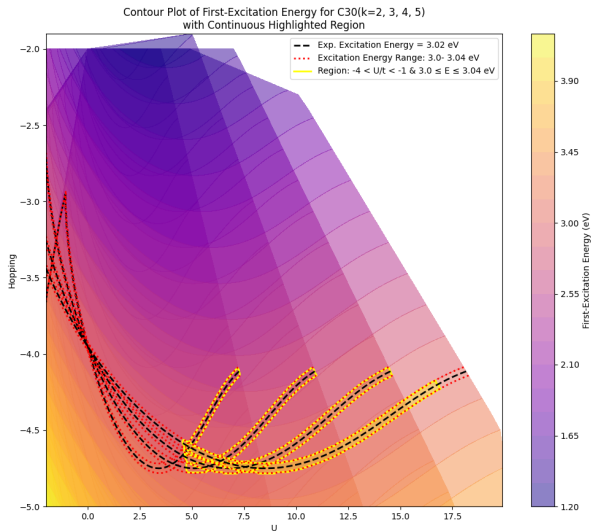
Overlapping Parameter Space Matching Experimental Data

Combined Contour Plot of First-Excitation Energy for C28 & C30 with Highlighted Regions
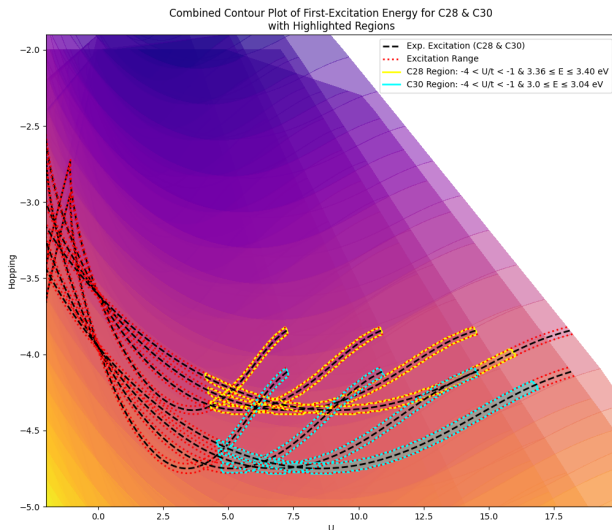
Optimal Parameter Range for C28 and C30

- ✓ **Overlap Region:** A common parameter region exists for $5 < U < 15$ eV and $-4.5 < t < -4$ eV.

- ✓ **Consistency Across Structures:** This region satisfies the experimental excitation energies for both C28 and C30.

- ✓ **No Universal k Parameter:** There is no single k value that fits both structures simultaneously.

- • **Chosen Parameters:** Based on the overlap, we selected $U = 6$ eV, $t = -4.1$ eV, and $k = 2$ for further analysis.

RCI on top of RHF Results:

Table: RCI on top of RHF-Hubbard_term = False

Molecule	CIS First e-e [eV]	CID First e-e [eV]	CISD First e-e [eV]	Exp First e-e [eV]
Benzo[ghi]perylene-c22	2.29	2.86	2.61	-
Benzo[a]coronene-c28	2.98	2.56	3.35	3.38
Naphtho[8,1,2-abc]coronene-c30	2.47	1.31	2.86	3.02
Naphtho[2,3a]coronene-c32	2.05	0.22	2.51	-
Anthra[2,3a]coronene-c36	1.11	0.73	0.58	-

RCI on top of pCCD Results:

Table: RCI on top of pCCD-Hubbard_term = False

Molecule	CID	CISD	Exp	EOM-pCCD+S
	First e-e [eV]	First e-e [eV]	First e-e [eV]	First e-e [eV]
Benzo[ghi]perylene-c22	2.96	2.55	-	2.76
Benzo[a]coronene-c28	2.56	3.30	3.38	3.40
Naphtho[8,1,2-abc]coronene-c30	1.56	2.81	3.02	2.88
Naphtho[2,3a]coronene-c32	0.65	2.47	-	2.41
Anthra[2,3a]coronene-c36	0.10	1.14	-	1.44

Optimized Parameters for OOpCCD with Maximum U Value, k=2

Table: OOpCCD Parameters: t=-4.1, k=2-`Hubbard_term` = True

Molecule	maximum u-value	OOpCCD First e-e [eV]	Exp First e-e [eV]
Benzo[ghi]perylene-c22	6.0	2.41	-
Benzo[a]coronene-c28	5.1	2.57	3.38
Naphtho[8,1,2-abc]coronene-c30	3.3	2.32	3.02
Naphtho[2,3a]coronene-c32	0.60	3.03	-
Anthra[2,3a]coronene-c36	0.2	2.48	-

Optimized OOpCCD Parameters for All Structures, k=2

Table: OOpCCD Parameters: u=0.2, t=-4.1, k=2-Hubbard_term = True

Molecule	OOpCCD	Exp
	First e-e [eV]	First e-e [eV]
Benzo[ghi]perylene-c22	3.53	-
Benzo[a]coronene-c28	3.77	3.38
Naphtho[8,1,2-abc]coronene-c30	3.07	3.02
Naphtho[2,3a]coronene-c32	3.16	-
Anthra[2,3a]coronene-c36	2.48	-

Optimized Parameters for OOpCCD with Maximum U Value, k=3

Table: OOpCCD Parameters: t=-4.1, k=3-Hubbard_term = True

Molecule	maximum u-value	OOpCCD First e-e [eV]	Exp First e-e [eV]
Benzo[ghi]perylene-c22	6.0	3.0	-
Benzo[a]coronene-c28	6.0	3.10	3.38
Naphtho[8,1,2-abc]coronene-c30	6.0	2.47	3.02
Naphtho[2,3a]coronene-c32	2.3	2.80	-
Anthra[2,3a]coronene-c36	0.2	2.50	-

Optimized OOpCCD Parameters for All Structures, k=3

Table: OOpCCD Parameters: u=0.2, t=-4.1, k=3-Hubbard_term = True

Molecule	OOpCCD First e-e [eV]	Exp First e-e [eV]
Benzo[ghi]perylene-c22	3.56	-
Benzo[a]coronene-c28	3.80	3.38
Naphtho[8,1,2-abc]coronene-c30	3.10	3.02
Naphtho[2,3a]coronene-c32	3.19	-
Anthra[2,3a]coronene-c36	2.50	-

Optimized OOpCCD Parameters for All Structures, k=1

Table: OOpCCD Parameters: u=0.65, t=-4.1, k=1-Hubbard_term = True

Molecule	OOpCCD	Exp
	First e-e [eV]	First e-e [eV]
Benzo[ghi]perylene-c22	3.15	-
Benzo[a]coronene-c28	3.38	3.38
Naphtho[8,1,2-abc]coronene-c30	2.71	3.02
Naphtho[2,3a]coronene-c32	2.77	-
Anthra[2,3a]coronene-c36	2.05	-

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