

Thermochemistry of Hydrocarbons: MTB/2

Dulce Torres & Sabrina Temesghen



Introduction

Problem

Experimental data is difficult to obtain and often missing

Previous Work

ab initio and DFT techniques not applicable for extended hydrocarbons

Our approach

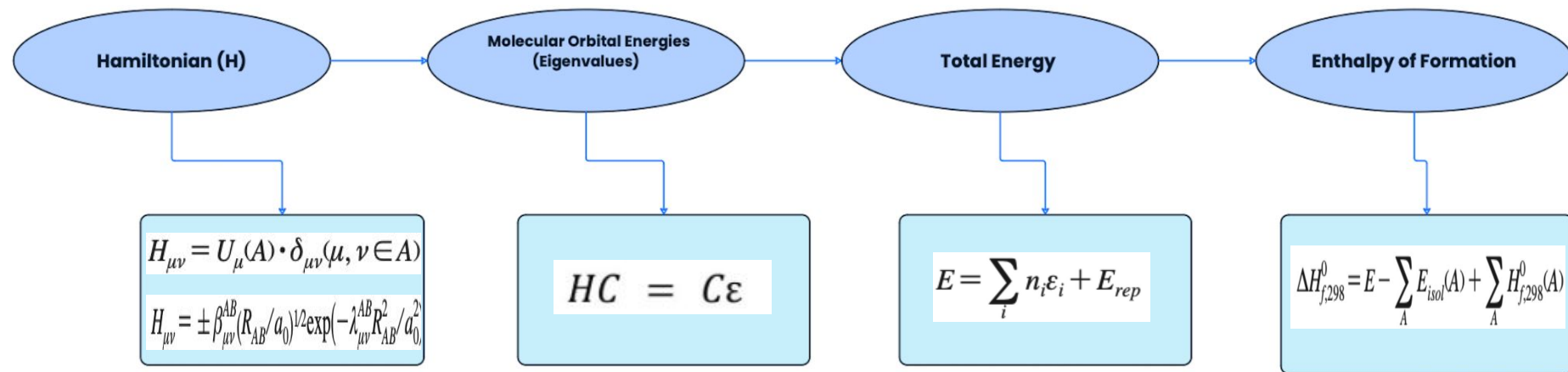
Apply MTB/2, a less computationally intensive method



Methodologies

The background of the slide is decorated with a pattern of overlapping hexagons. These hexagons are rendered in three-dimensional, isometric styles, giving them the appearance of cubes or prisms. The colors used are various shades of blue and cyan, ranging from light, almost white, to deep, vibrant blues. The hexagons are scattered across the slide, with some appearing in the foreground and others receding into the background, creating a sense of depth and a modern, geometric aesthetic.

Standard Heat of Formation Workflow



Compare the computed relative energies and heat of formations to experimental values

Hamiltonian Matrix

Diagonal

Energy of electron on
AO ϕ

One-center off diagonal

$$H_{\mu\nu} = U_{\mu}(A) \cdot \delta_{\mu\nu} (\mu, \nu \in A)$$

Two-center off diagonal

$$H_{\mu\nu} = \pm \beta_{\mu\nu}^{AB} (R_{AB}/a_0)^{1/2} \exp(-\lambda_{\mu\nu}^{AB} R_{AB}^2/a_0^2)$$

Table 1. Parameters of the MTB/2 Model

Atomic Parameters			
parameter	H	C	
U_s^A (eV)	-13.605	-21.559	
U_p^A (eV)		-13.507	
Bond-Type Parameters			
parameter	H-H	C-H	C-C
λ_{ss}	0.280	0.275	0.086
λ_{sp}		0.218	0.180
$\lambda_{pp\sigma}$			0.186
$\lambda_{pp\pi}$			0.282
β_{ss} (eV)	-4.442	-8.574	-5.969
β_{sp} (eV)		-6.813	-6.160
$\beta_{pp\sigma}$ (eV)			-8.420
$\beta_{pp\pi}$ (eV)			-7.403
α_{AB} (\AA^{-1})	2.823	2.831	3.401
γ_{AB} (eV)	12.612	99.370	658.659
ω_{AB} (eV)	-0.0791	-0.0340	0.0312
r_{AB} (\AA)	2.279	2.843	3.044

Energy Calculation

Standard eigenvalue problem

$$E = \sum_i n_i \varepsilon_i + E_{rep}$$

$$E_{rep} = \sum_{A>B} G_{AB}$$

$$G_{AB} = \gamma_{AB} \exp(-\alpha_{AB} R_{AB}) + \omega_{AB} \exp[-6(R_{AB} - r_{AB})^2]$$

Table 1. Parameters of the MTB/2 Model

Atomic Parameters			
parameter	H	C	
U_s^A (eV)	−13.605	−21.559	
U_p^A (eV)		−13.507	
Bond-Type Parameters			
parameter	H–H	C–H	C–C
λ_{ss}	0.280	0.275	0.086
λ_{sp}		0.218	0.180
$\lambda_{pp\sigma}$			0.186
$\lambda_{pp\pi}$			0.282
β_{ss} (eV)	−4.442	−8.574	−5.969
β_{sp} (eV)		−6.813	−6.160
$\beta_{pp\sigma}$ (eV)			−8.420
$\beta_{pp\pi}$ (eV)			−7.403
α_{AB} (Å ^{−1})	2.823	2.831	3.401
γ_{AB} (eV)	12.612	99.370	658.659
ω_{AB} (eV)	−0.0791	−0.0340	0.0312
r_{AB} (Å)	2.279	2.843	3.044

Heat of Formation

$$\Delta H_{f,298}^0 = E - \sum_A E_{isol}(A) + \sum_A H_{f,298}^0(A)$$

1) Total energy

$$E_{isol}(A) = n_s U_s(A) + n_p U_p(A)$$

2) Isolation energy

3) Atom specific heat formation

Results & Discussion



Results

Large over predictions:

- **Alkanes** (ex: pentane: +249 kcal/mol)
- **Branched/Substituted alkenes** (ex: trimethylethane +203, isobutene +172)
- **Strained Rings with Saturation** (ex: Cyclopropane(tris)...: +132)

Better performance:

- **Simple Alkenes & Alkynes** (Diacetylene, ethylene, cyclopropene)
- **Aromatics & Cross-Conjugated Systems**

	Molecule	Experimental	Predicted	Difference	Absolute_Error	Bias
4	pentane	-35.1	214.14300	-249.243	249.24300	Over
3	butane	-30.1	173.63300	-203.733	203.73300	Over
10	trimethylethene	-9.9	179.78700	-189.687	189.68700	Over
9	isobutene	-4.0	168.63100	-172.631	172.63100	Over
2	propane	-25.0	133.21600	-158.216	158.21600	Over
20	benzene	19.7	153.86200	-134.162	134.16200	Over
27	cyclopropane, tris(methylene)	74.8	207.19800	-132.398	132.39800	Over
25	fulvelene	33.8	-58.54170	92.3417	92.34170	Under
12	vinylacetylene	70.4	149.89000	-79.49	79.49000	Over
7	acetylene	54.5	-12.31000	66.81	66.81000	Under
18	cubane	148.7	81.95710	66.7429	66.74290	Under
16	cyclobutene	37.5	-26.56910	64.0691	64.06910	Under
15	cyclopropene	66.2	8.04425	58.15575	58.15575	Under
26	2,4-hexadiyne	70.4	114.87200	-44.472	44.47200	Over
17	fulvene	53.5	95.32050	-41.8205	41.82050	Over
11	diacetylene	111.0	82.01010	28.9899	28.98990	Under
8	propene	6.7	23.08040	-16.3804	16.38040	Over
14	cyclopropane	12.7	28.92750	-16.2275	16.22750	Over
6	ethylene	12.5	20.23880	-7.7388	7.73880	Over
24	benzene	0.0	0.00000	0	0.00000	Under
0	H2	0.0	0.00000	NaN	0.00000	Under

Misclassification of σ (Sigma) and π (Pi) Bonding

- **What we did:** Applied a hard threshold (`unit_vec_component > 0.9`) to decide σ vs. π alignment between orbital axis and the bond vectors.
 - **However:** “The electron/charge transfer via the orbital overlap has a direction or several competing directions in the chemical reactions... the ideal reactivity indexes should be computed with the identification of the orbital overlap direction (Shi et al., 2025).”
 - Real systems exhibit varying orbital overlaps due to continuous bond angle deformations, and classification based only on a static threshold ignores this directional nuance.
- **Effects:**
 - β pp σ vs. β pp π
 - Parameters for β pp σ are larger than β pp π
 - Overestimate the orbital coupling
 - Make H matrix too large
 - Cause the eigenvalues (orbital energies) to be too low
- **Results:**
 - Overstabilization of bonding orbitals
 - Total energy estimation is affected
 - Heat of Formation (ΔH_f) is too negative

$$H_{\mu\nu} = \pm \beta_{\mu\nu}^{AB} (R_{AB}/a_0)^{1/2} \exp(-\lambda_{\mu\nu}^{AB} R_{AB}^2/a_0^2)$$

Phase Factor:

$$H_{\mu\nu} = \pm \beta_{\mu\nu}^{AB} (R_{AB}/a_0)^{1/2} \exp(-\lambda_{\mu\nu}^{AB} R_{AB}^2/a_0^2)$$

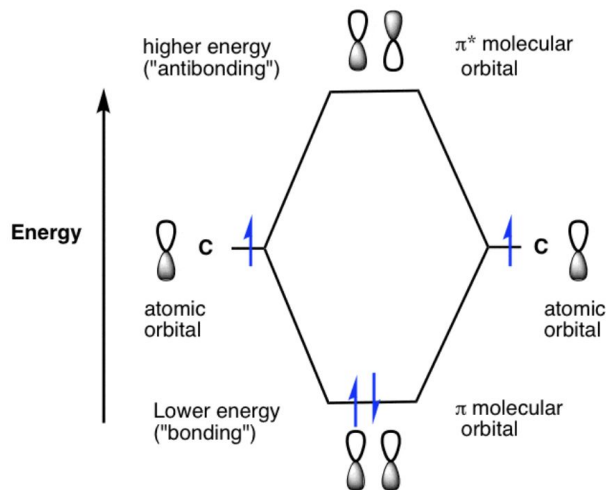
Positive Phase Factor Only

- **What we did:** Assumed +1 phase factor and thereby, ignored sign inversion (\pm) in AO overlaps for bonding vs. antibonding orientation.
 - a. Bonding orientation $+\beta$ (what we are doing)
 - b. Antibonding orientation $-\beta$ (what's not being accounted for)
- **Effects:**
 - a. This affects the sign and magnitude of $H_{\mu\nu}$ (off-diagonal Hamiltonian elements).
- **Result:** energy levels (eigenvalues) are shifted
 - a. especially when antibonding contributions are incorrectly treated as bonding.
 - b. Overestimate bonding
 - c. Underestimating antibonding
 - d. Heat of Formation (ΔH_f) skewed

In a π bond, the sideways overlap of p orbitals leads to two types of molecular orbitals: bonding (π) and antibonding (π^*)

The orientation of the p orbitals is crucial for this overlap. If the lobes are out of phase, the interaction becomes antibonding.

Energy diagram for two Pi molecular orbitals in a typical pi bond

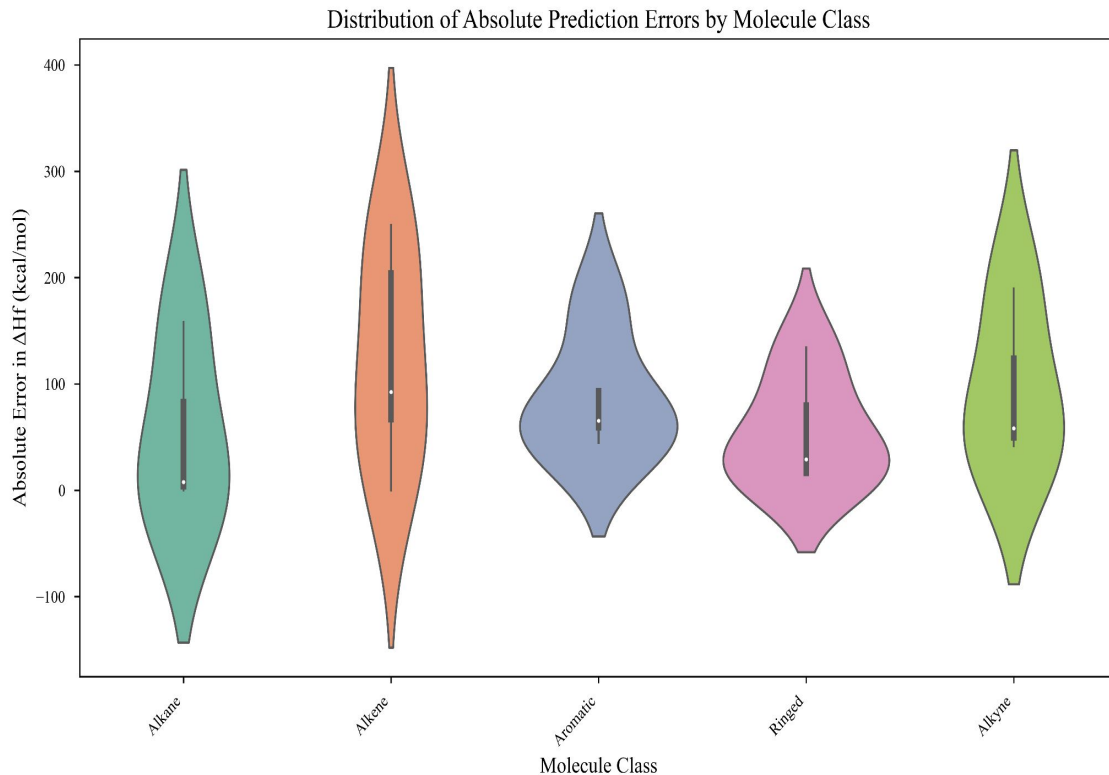


Error Distribution by Molecule Type

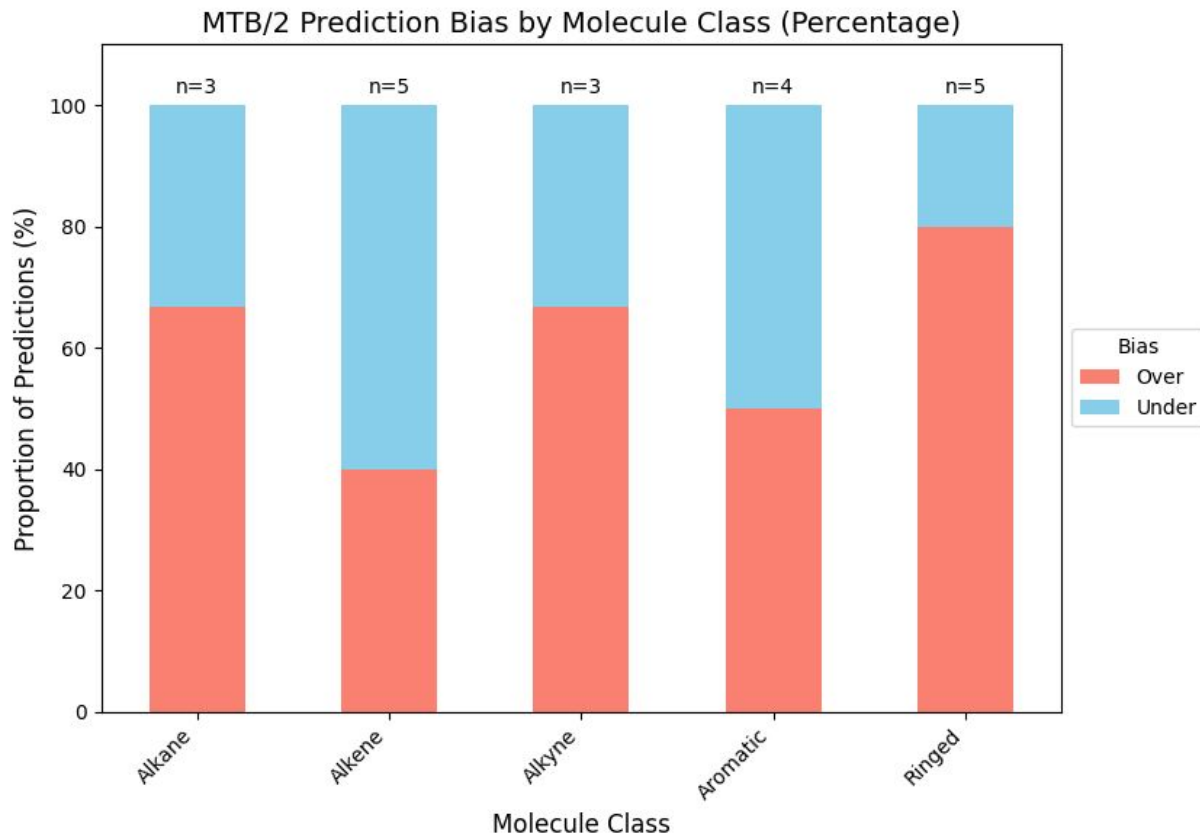
- **Alkanes & Alkenes:**
 - Widespread error
- **Aromatics and Alkynes:**
 - Tighter distribution = fewest error
- **Ringed Compounds**
 - Intermediate Performance

Potential Bias:

- Sigma vs. Pi Classification
- Phase Factor



Bond Type Distribution



Suggests possible systematic issues in bond-type recognition

- Alkanes and Ringed compounds: majority overpredicted
- Aromatics and Alkenes: more balanced predictions
- Overestimating π character

Potential Bias:

- Sigma vs. Pi Classification
- Phase Factor

Conclusion

- MTB/2 method is based on the orthogonal model and thus is even simpler than EHM... (Voityuk, 2008)."
- MTB/2 captures general thermochemical trends, but large errors persist in:
 - Saturated/branched alkanes and substituted alkenes (strong overprediction bias)
 - Misclassified σ/π bonds in distorted or mixed bonding systems
 - Overstabilization due to assuming a constant +1 phase factor
- Aromatics and π -delocalized systems are predicted with better accuracy

Next Steps (Future Work)

- Implementing proper orbital phase handling to distinguish bonding vs. antibonding
- Refining σ/π classification with flexible directional thresholds

Citations

Ashenhurst, J. (2023b, January 8). *Bonding and antibonding pi orbitals*. Master Organic Chemistry.
<https://www.masterorganicchemistry.com/2017/02/14/molecular-orbital-pi-bond/#notefour>

Kolb, M.; Thiel, W. "Calculation of Two-Center One-Electron Integrals." *J. Comput. Chem.* 1993, 14, 775.

Shi, X., Song, J., & Wei, D. (2025). An analysis method including orbital overlap directions for predicting π electron properties and reactivity vectors. *Nature Communications*, 16(1). <https://doi.org/10.1038/s41467-025-58281-9>

Voityuk, A. A. "Thermochemistry of Hydrocarbons. Back to Extended Hückel Theory." *J. Chem. Theory Comput.* 2008, 4, 1877-1885.