Partial Imaginary Transition State (ITS) Graphs - 2

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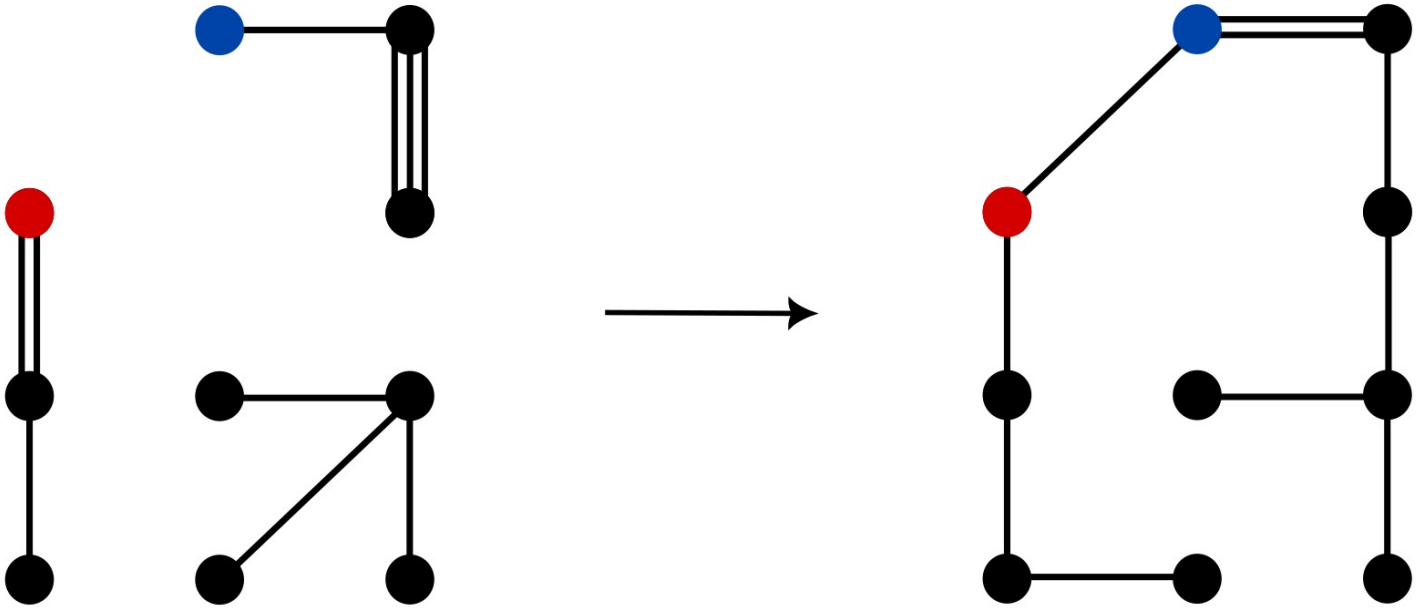
Bundesministerium für Bildung und Forschung

SACHSEN Diese Maßnahme wird gefördert durch die Bundesregierung aufgrund eines Beschlusses des Deutschen Bundestages. Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des von den Abgeordneten des Sächsischen Landtags beschlossenen Haushaltes.

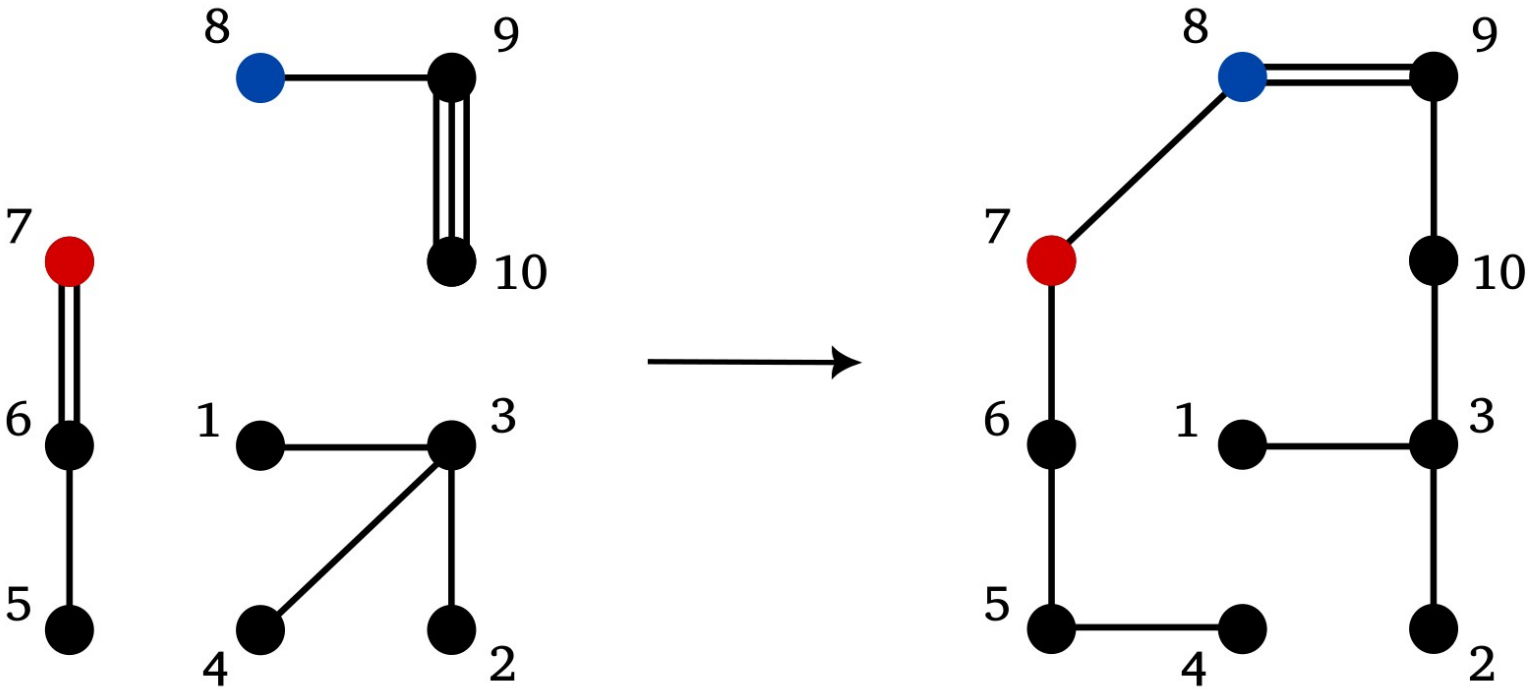
Introduction

Atom-to-atom maps - AAMs



Introduction

Atom-to-atom maps - Definition



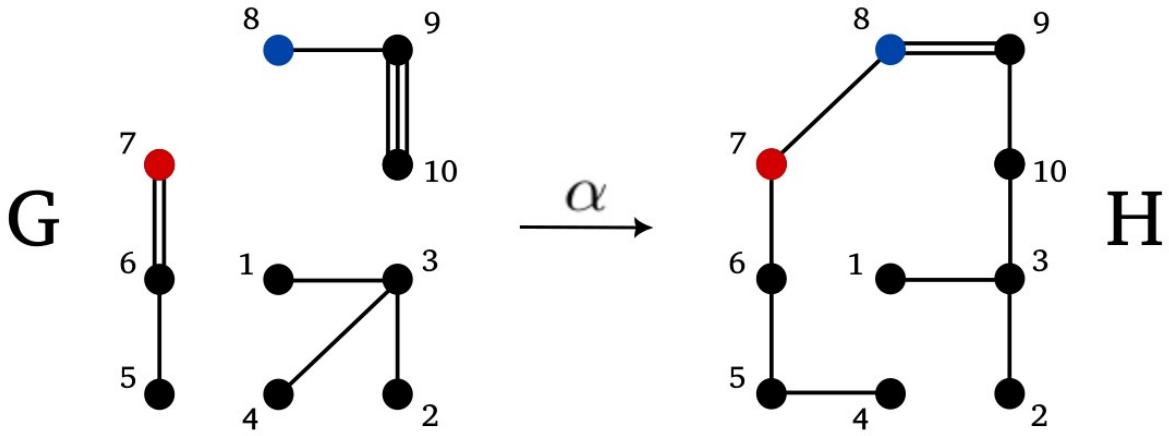
Definition [1] *Let G and H be two labeled graphs. A map $\alpha : V(G) \to V(H)$ is an AAM if it is a bijection and preserves vertex labels, i.e., if $a_H(\alpha(x)) = a_G(x)$ for all $x \in V(G)$.*

[1] González Laffitte, M. E., et al. (2024). *Partial Imaginary Transition State (ITS) Graphs: A Formal Framework for Research and Analysis of Atom-to-Atom Maps of Unbalanced Chemical Reactions and Their Completions*. Symmetry, (9), 1217. Multidisciplinary Digital Publishing Institute. https://www.mdpi.com/2073-8994/16/9/1217

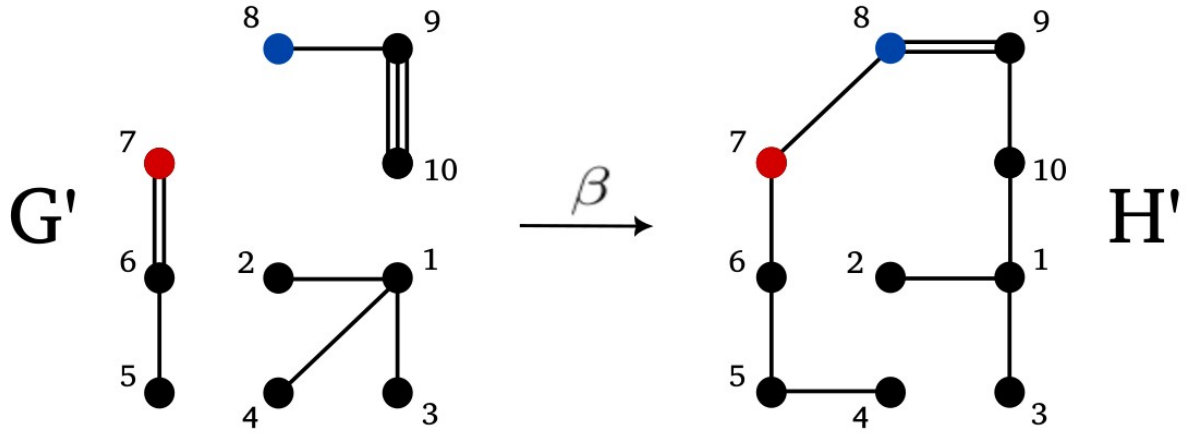
Introduction

Equivalence of AAMs – Are these actually the same?

AAM1

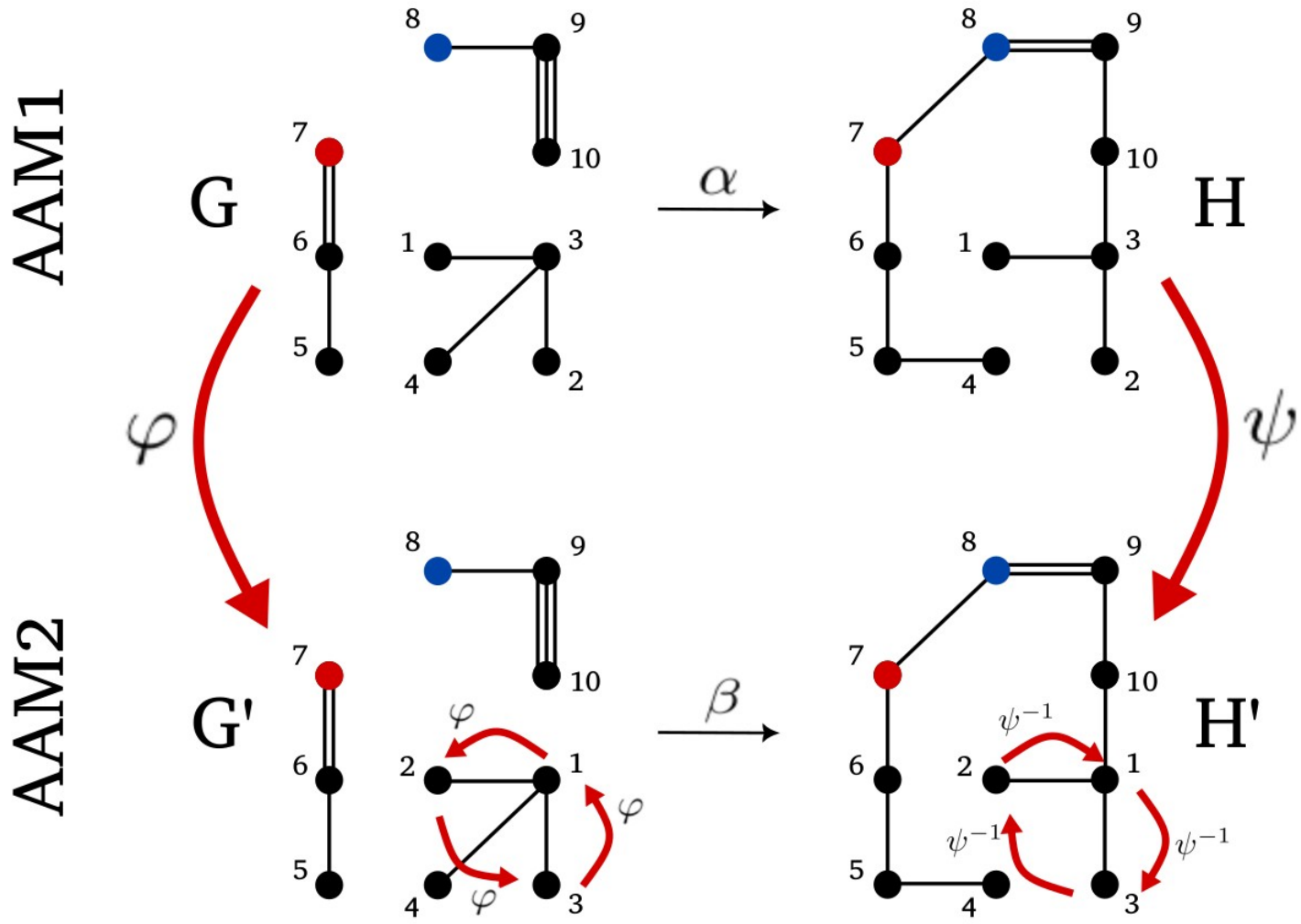


AAM2



Introduction

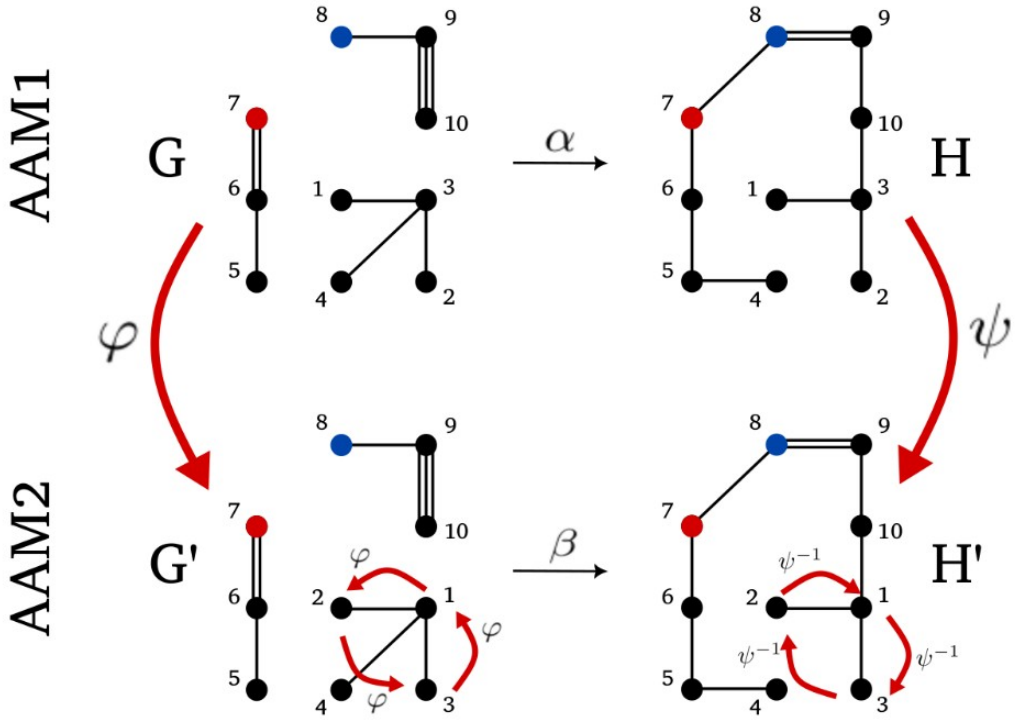
Equivalence of AAMs – “Twisting” the molecules



$$G' \simeq G$$
$$H' \simeq H$$
$$\alpha(x) = \psi^{-1}(\beta(\varphi(x)))$$

Introduction

Equivalence of AAMs – Definition



Definition [2] Two maps $\alpha : V(G) \to V(H)$ and $\beta : V(G') \to V(H')$ are *equivalent*, in symbols $\alpha \equiv \beta$ if there is $\varphi \in \mathrm{GI}(G, G')$ and $\psi \in \mathrm{GI}(H, H')$ such that $\psi \circ \alpha = \beta \circ \varphi$.

[2] M. E. González Laffitte, N. Beier, N. Domschke, P. F. Stadler, *Comparison of Atom Maps*. MATCH Commun. Math. Comput. Chem. 90 (2023) 75–102.
https://match.pmf.kg.ac.rs/issues/m90n1/m90n1_75-102.html

Introduction

Some general goals of our work

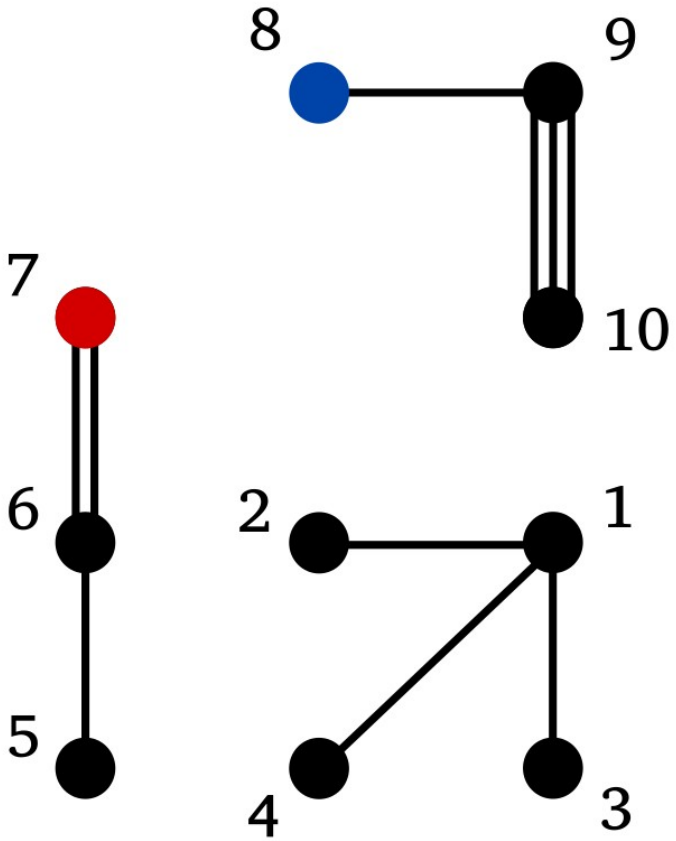
1) Compare and determine equivalent AAMs computationally / in an automatical way

2) Analyze some characteristics of AAMs under “graph alignments”

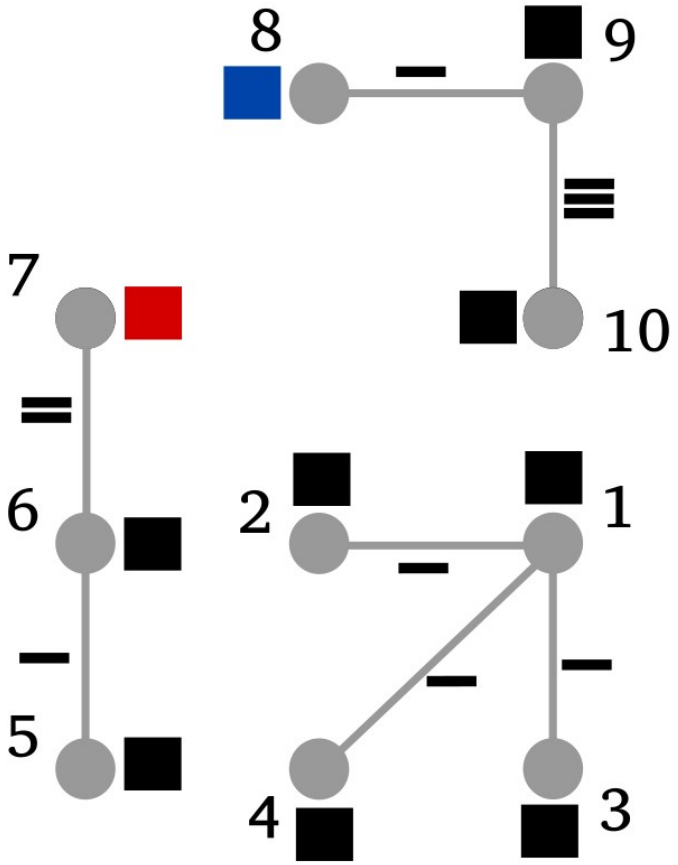
3) Study “partial” AAMs, i.e., AAMs not covering all the atoms in the molecules

Mathematical Framework

Formal and Compuattional Representation of Molecules by Simple Labeled Graphs

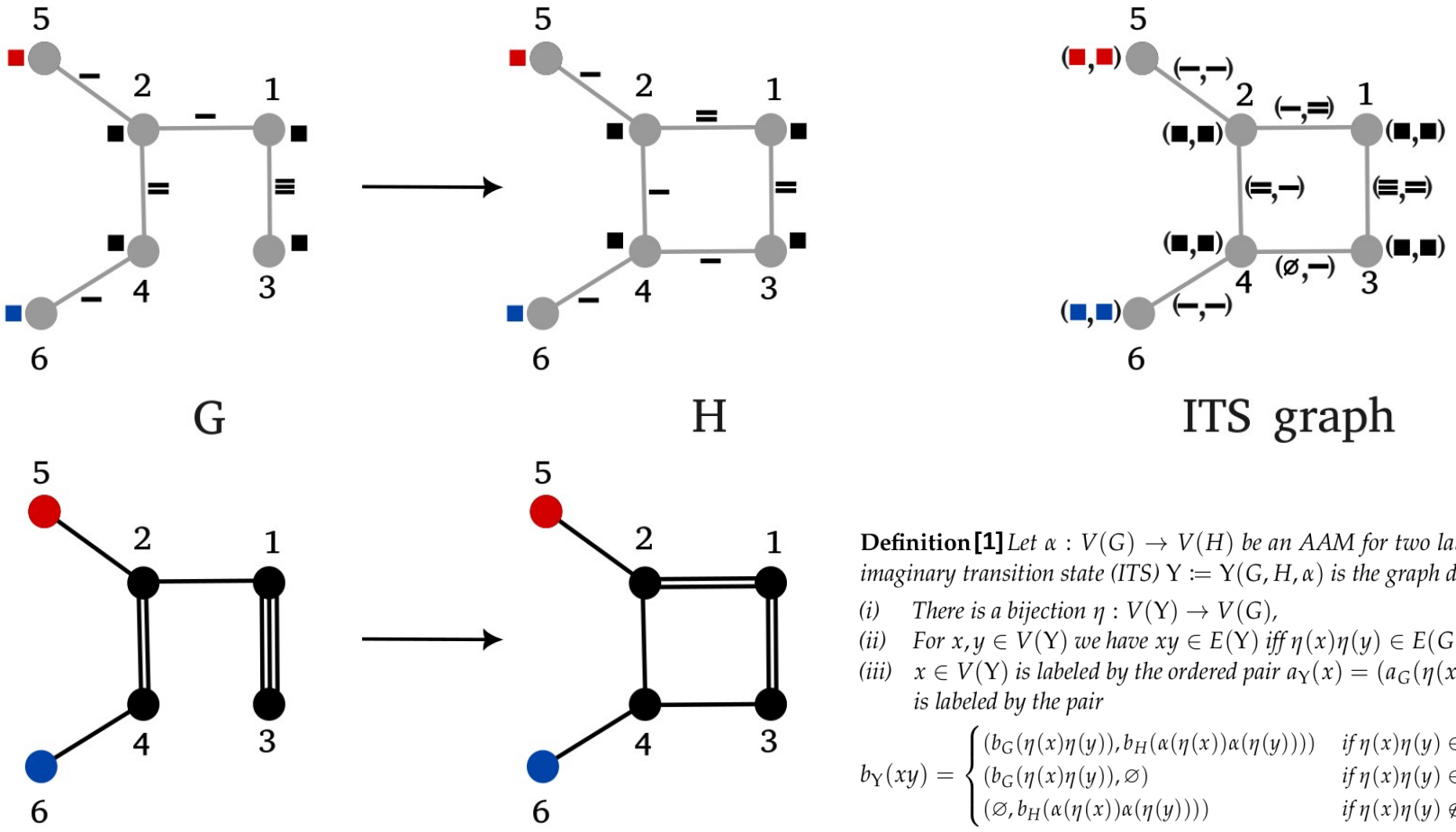


represented as



Mathematical Framework

Imaginary Transition State (ITS) Graphs



Definition [1] *Let $\alpha : V(G) \to V(H)$ be an AAM for two labeled graphs G and H. Then, the imaginary transition state (ITS) $\Upsilon := \Upsilon(G, H, \alpha)$ is the graph defined by all the following:*

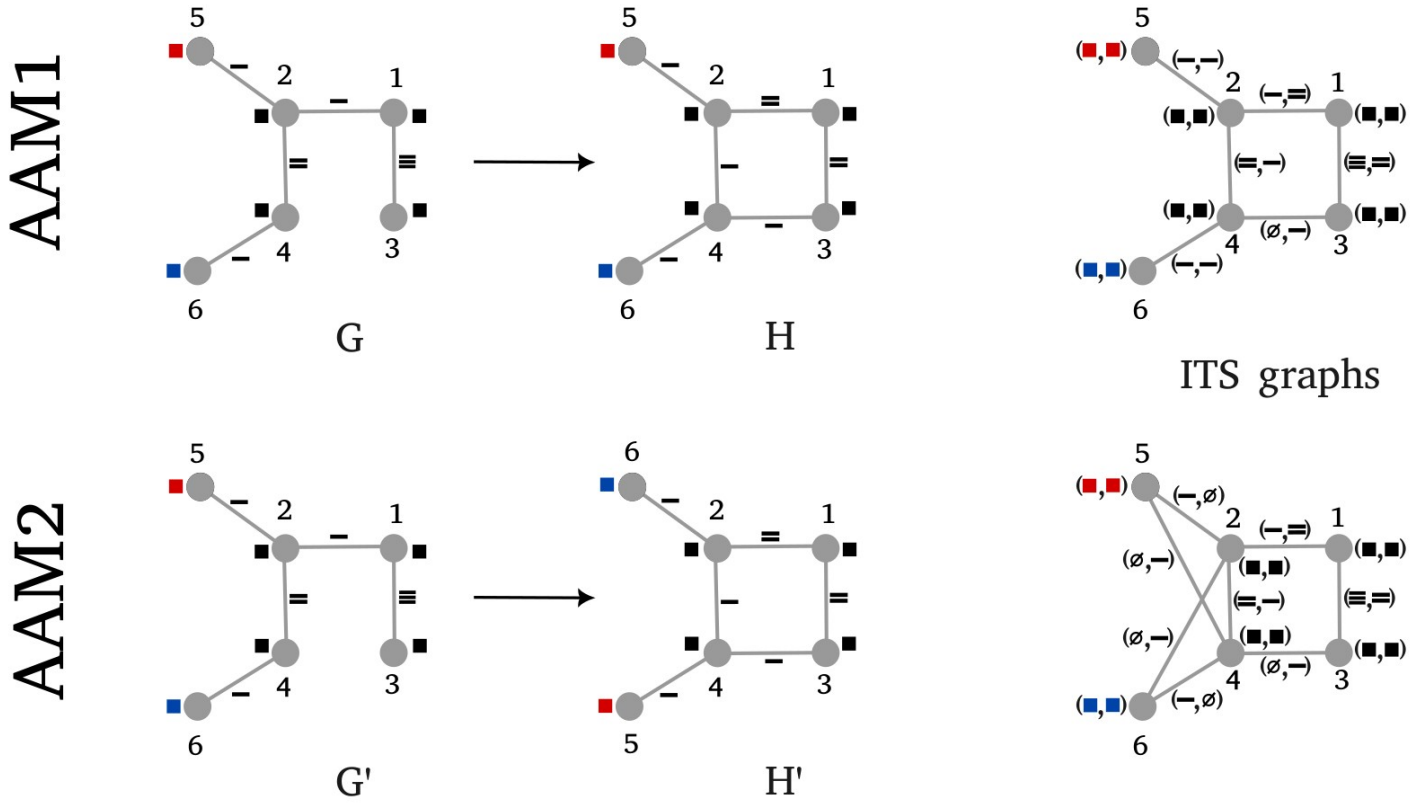
(i) *There is a bijection $\eta : V(\Upsilon) \to V(G)$,*
(ii) *For $x, y \in V(\Upsilon)$ we have $xy \in E(\Upsilon)$ iff $\eta(x)\eta(y) \in E(G)$ or $\alpha(\eta(x))\alpha(\eta(y)) \in E(H)$,*
(iii) *$x \in V(\Upsilon)$ is labeled by the ordered pair $a_\Upsilon(x) = (a_G(\eta(x)), a_H(\alpha(\eta(x))))$ and $xy \in E(\Upsilon)$ is labeled by the pair*

$$b_\Upsilon(xy) = \begin{cases} (b_G(\eta(x)\eta(y)), b_H(\alpha(\eta(x))\alpha(\eta(y)))) & \text{if } \eta(x)\eta(y) \in E(G) \text{ and } \alpha(\eta(x))\alpha(\eta(y)) \in E(H) \\ (b_G(\eta(x)\eta(y)), \varnothing) & \text{if } \eta(x)\eta(y) \in E(G) \text{ and } \alpha(\eta(x))\alpha(\eta(y)) \notin E(H) \\ (\varnothing, b_H(\alpha(\eta(x))\alpha(\eta(y)))) & \text{if } \eta(x)\eta(y) \notin E(G) \text{ and } \alpha(\eta(x))\alpha(\eta(y)) \in E(H) \end{cases}$$

[1] González Laffitte, M. E., et al. (2024). *Partial Imaginary Transition State (ITS) Graphs: A Formal Framework for Research and Analysis of Atom-to-Atom Maps of Unbalanced Chemical Reactions and Their Completions*. Symmetry, (9), 1217. Multidisciplinary Digital Publishing Institute. https://www.mdpi.com/2073-8994/16/9/1217

Mathematical Framework

Characterization of Equivalence of AAMs by ITS Graphs

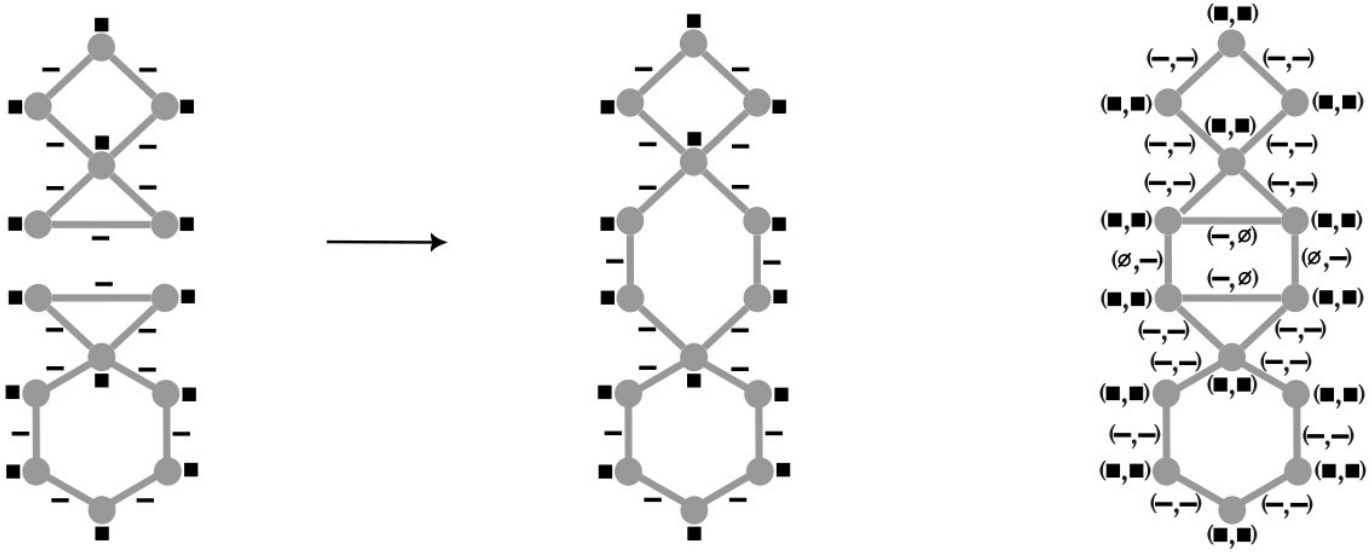


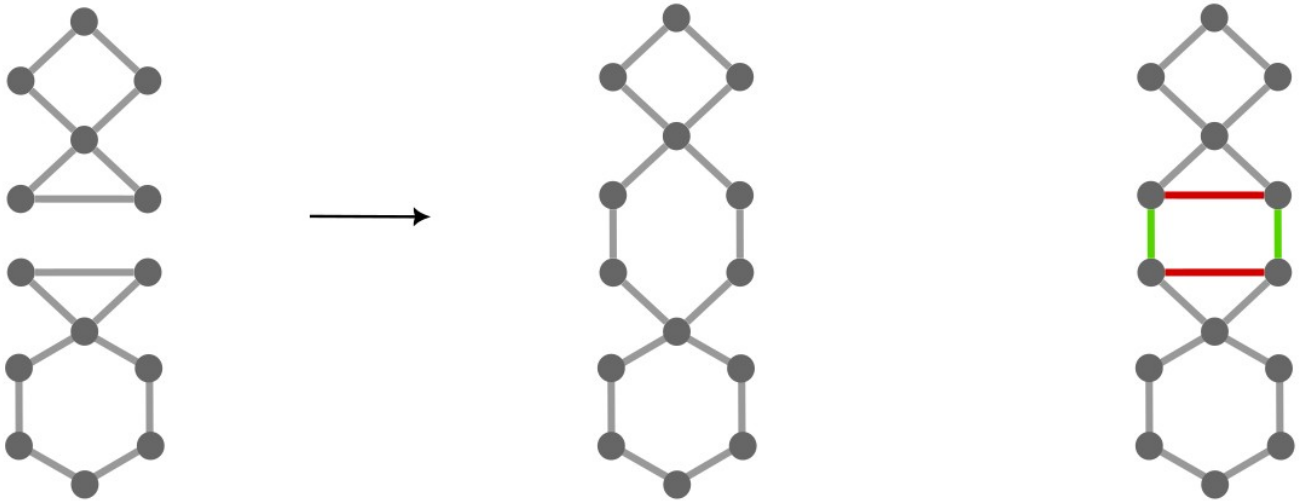
Corollary [2] *Let $G \simeq G'$, $H \simeq H'$ and suppose $\alpha : V(G) \to V(H)$ and $\beta : V(G') \to V(H')$ are atom maps. Then $\alpha \equiv \beta$ if and only if the ITSs $\Upsilon(G, H, \alpha)$ and $\Upsilon(G', H', \beta)$ are isomorphic.*

[2] M. E. González Laffitte, N. Beier, N. Domschke, P. F. Stadler, *Comparison of Atom Maps*. MATCH Commun. Math. Comput. Chem. 90 (2023) 75–102.
https://match.pmf.kg.ac.rs/issues/m90n1/m90n1_75-102.html

Quick Parenthesis

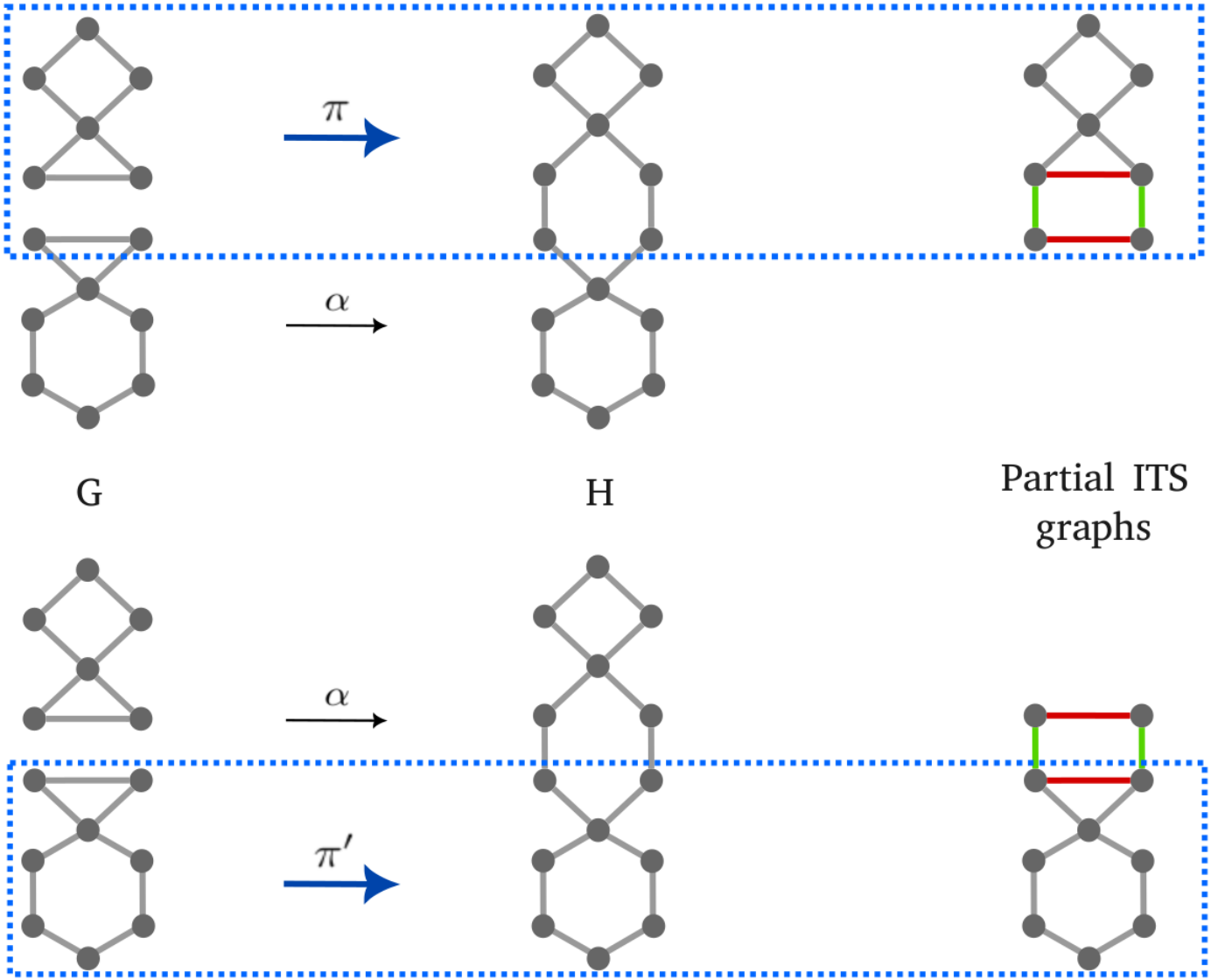
For the sake of the presentation ...





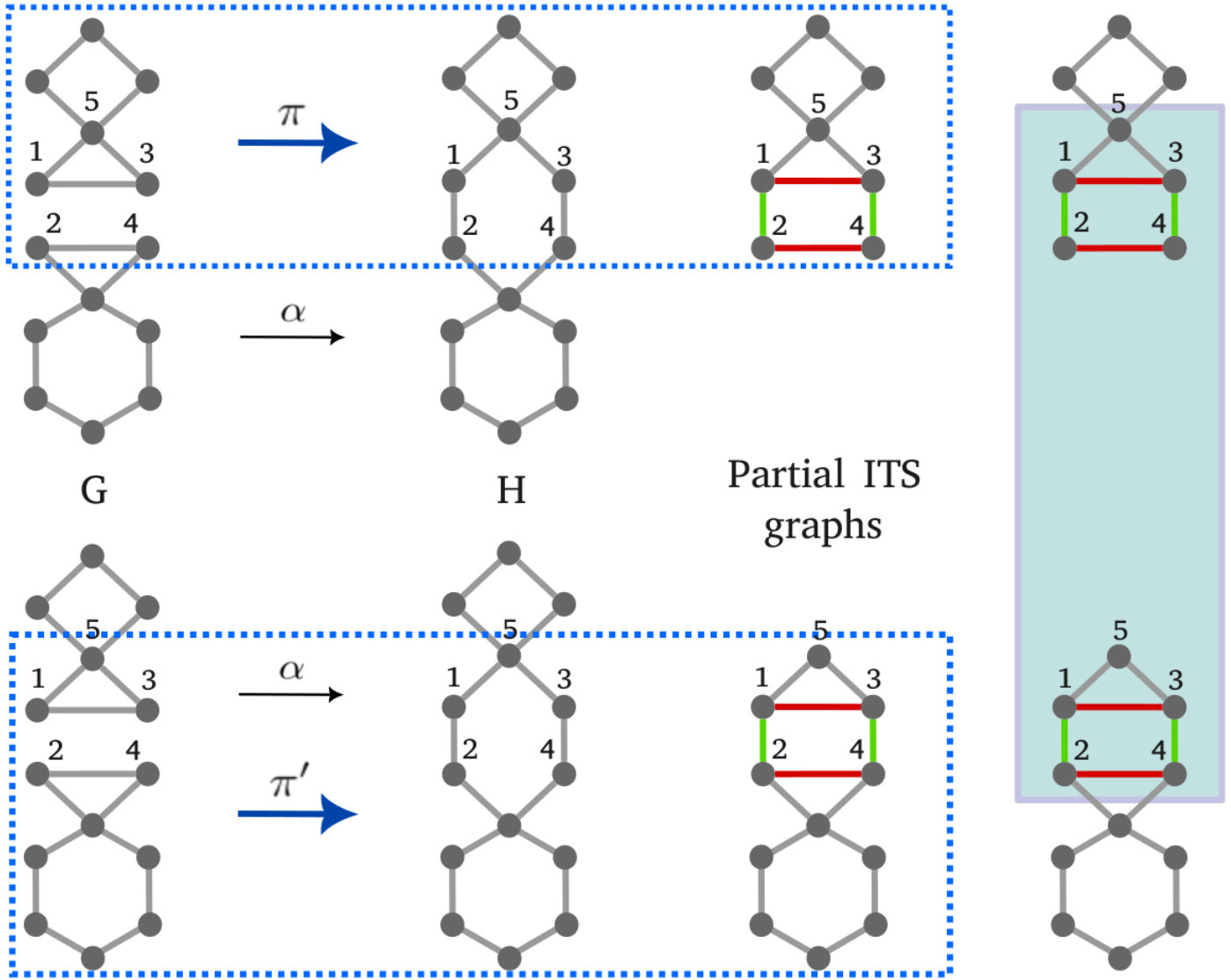
Extending the Mathematical Framework

Partial ITS Graphs, Reaction Centers, Good and Bad Partial AAMs



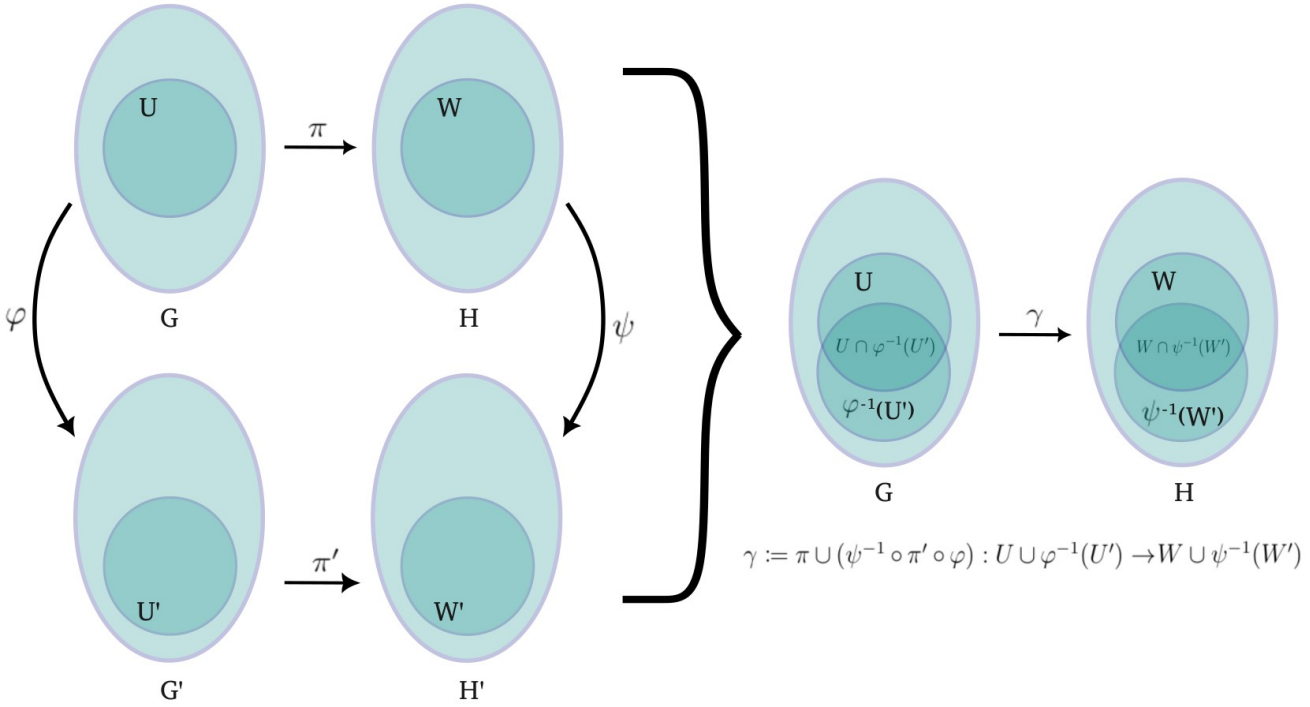
Some results on Partial ITS Graphs

Consistency of AAMs – A notion of “local equivalence” for partial AAMs



Some results on Partial ITS Graphs

Consistency of AAMs - Definition

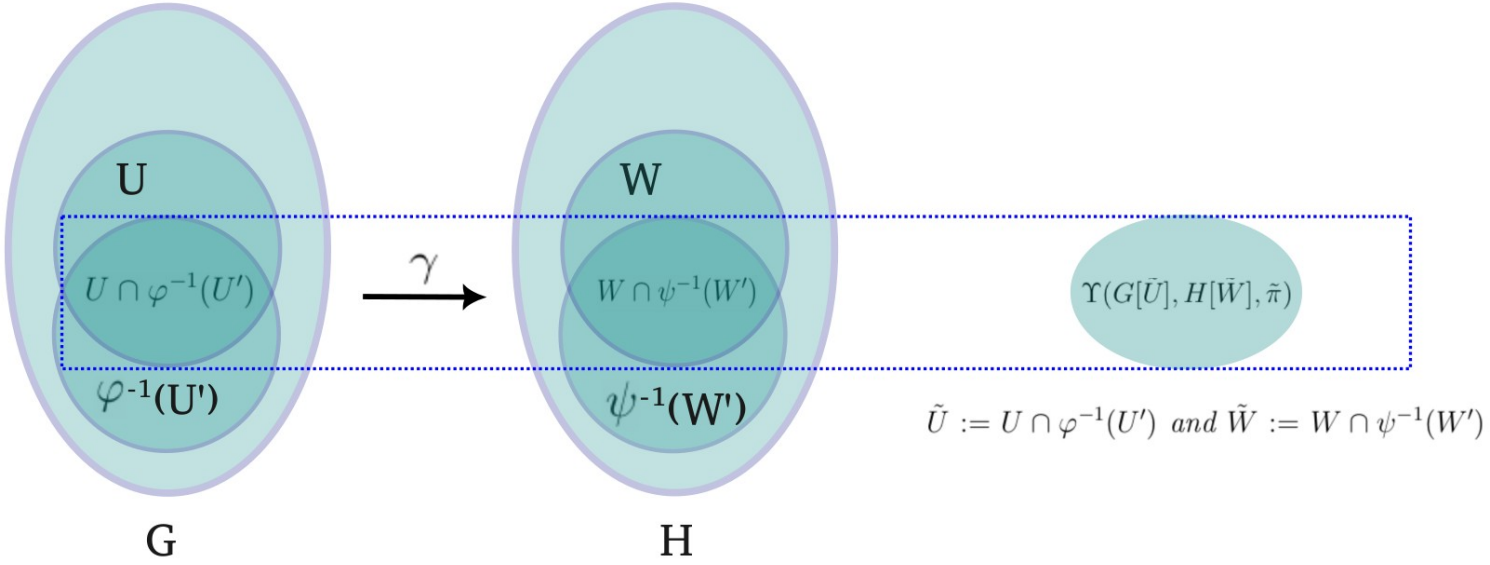


Definition [3] *For two reactions $G \longrightarrow H$ and $G' \longrightarrow H'$, two partial AAMs $\pi : U \to W$ with $U \subseteq V(G)$ and $W \subseteq V(H)$, and $\pi' : U' \to W'$ with $U' \subseteq V(G')$ and $W' \subseteq V(H')$, are said to be* consistent, *if there are isomorphisms $\varphi : V(G) \to V(G')$ for $G \cong G'$ and $\psi : V(H) \to V(H')$ for $H \cong H'$, such that the union $\gamma := \pi \cup (\psi^{-1} \circ \pi' \circ \varphi) : U \cup \varphi^{-1}(U') \to W \cup \psi^{-1}(W')$ is well-defined and bijective.*

[3] Phan, T.-L., Weinbauer, K., **Gonzalez Laffitte, M. E.**, Pan, Y., Merkle, D., Andersen, J. L., Fagerberg, R., et al. (2024). *SynTemp: Efficient Extraction of Graph-Based Reaction Rules from Large-Scale Reaction Databases*. American Chemical Society (ACS). https://chemrxiv.org/engage/chemrxiv/article-details/66f677b751558a15ef4cf5f7

Some results on Partial ITS Graphs

Consistency of AAMs – The Overlap Graph

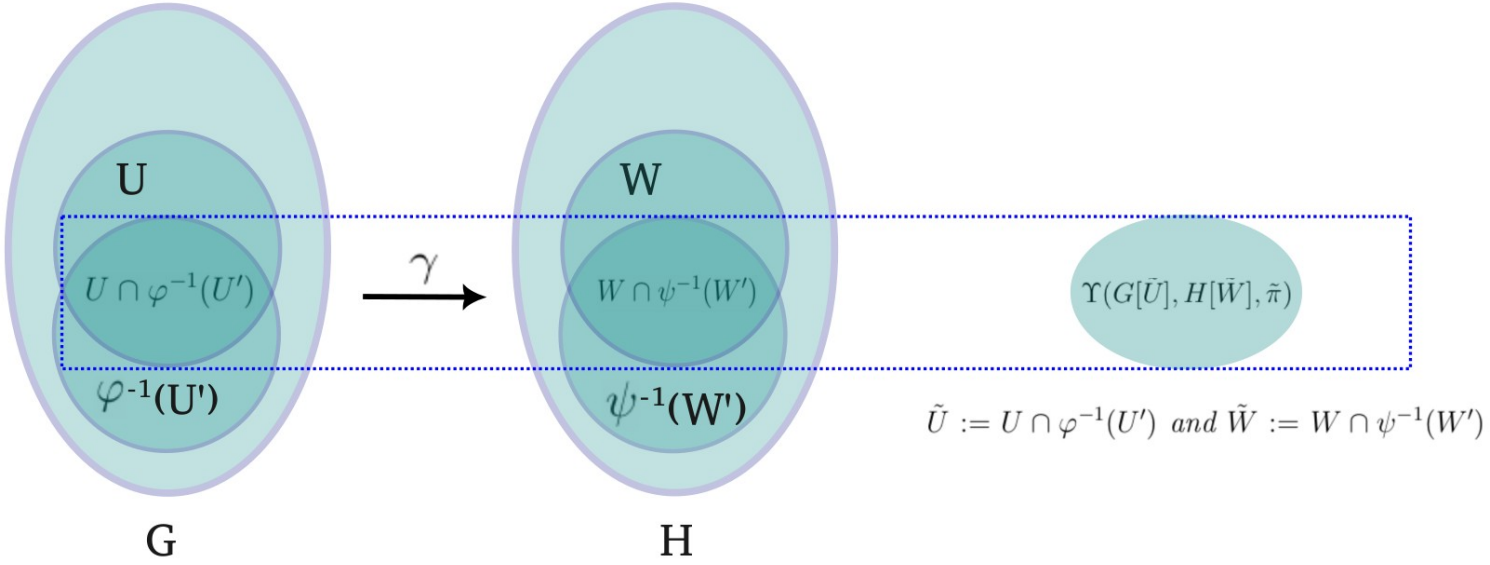


$\tilde{U} := U \cap \varphi^{-1}(U')$ *and* $\tilde{W} := W \cap \psi^{-1}(W')$

$$\gamma := \pi \cup (\psi^{-1} \circ \pi' \circ \varphi) : U \cup \varphi^{-1}(U') \to W \cup \psi^{-1}(W')$$

Some results on Partial ITS Graphs

The Overlap Graph is a well-defined Partial ITS Graph



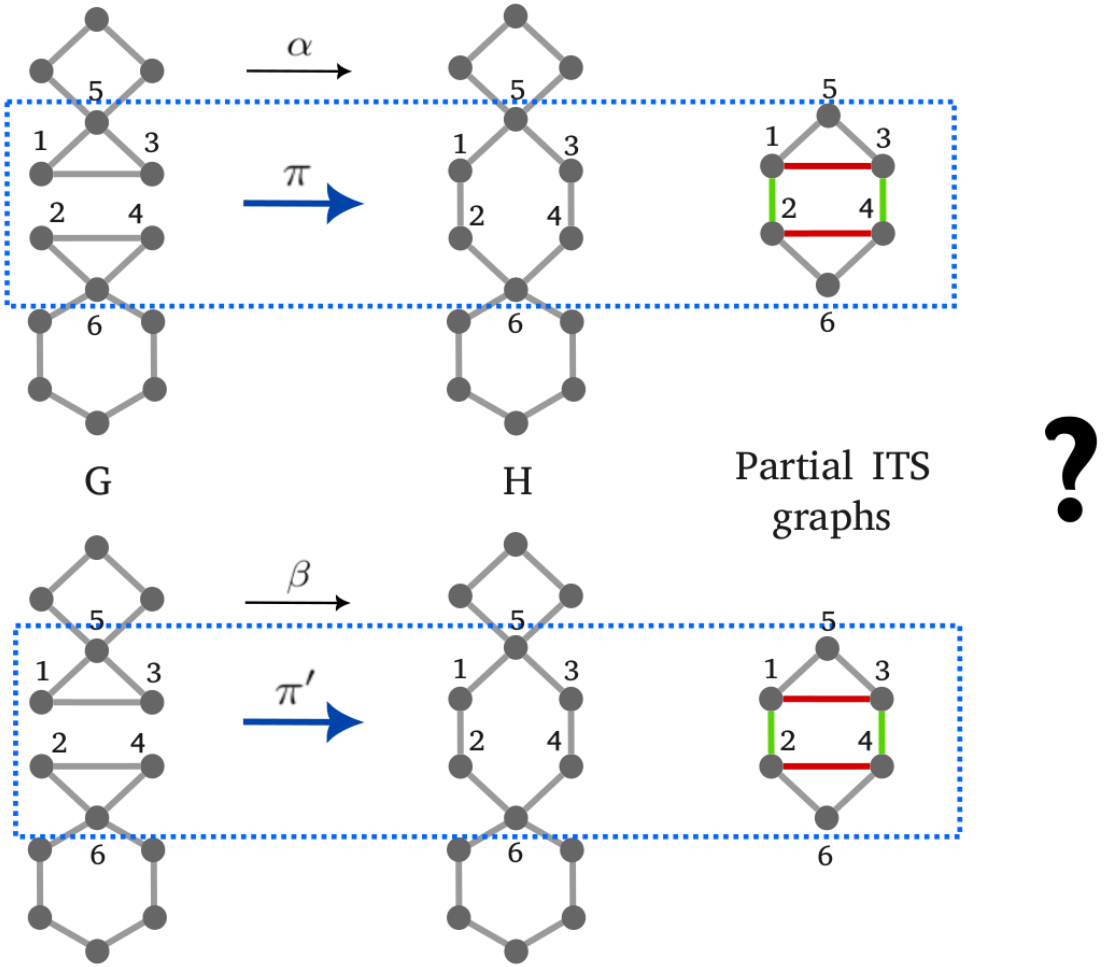
$$\gamma := \pi \cup (\psi^{-1} \circ \pi' \circ \varphi) : U \cup \varphi^{-1}(U') \rightarrow W \cup \psi^{-1}(W')$$

Proposition [3] *Let $\pi : U \rightarrow W$ and $\pi' : U' \rightarrow W'$ be consistent partial AAMs, and set $\tilde{U} := U \cap \varphi^{-1}(U')$ and $\tilde{W} := W \cap \psi^{-1}(W')$. Let $\tilde{\pi}$ be the restriction of π to $\tilde{U}$. Then the partial ITS graph $\Upsilon(G[\tilde{U}], H[\tilde{W}], \tilde{\pi})$ is well-defined and isomorphic to a common induced subgraph of $\Upsilon(G[U], H[W], \pi)$ and $\Upsilon(G'[U'], H'[W'], \pi')$.*

[3] Phan, T.-L., Weinbauer, K., **Gonzalez Laffitte, M. E.**, Pan, Y., Merkle, D., Andersen, J. L., Fagerberg, R., et al. (2024). *SynTemp: Efficient Extraction of Graph-Based Reaction Rules from Large-Scale Reaction Databases*. American Chemical Society (ACS). https://chemrxiv.org/engage/chemrxiv/article-details/66f677b751558a15ef4cf5f7

Some results on Partial ITS Graphs

Extended Reaction Centers at radius r >= 0 – An idea



[3] Phan, T.-L., Weinbauer, K., **Gonzalez Laffitte, M. E.**, Pan, Y., Merkle, D., Andersen, J. L., Fagerberg, R., et al. (2024). *SynTemp: Efficient Extraction of Graph-Based Reaction Rules from Large-Scale Reaction Databases*. American Chemical Society (ACS). https://chemrxiv.org/engage/chemrxiv/article-details/66f677b751558a15ef4cf5f7

Some results on Partial ITS Graphs

Extended Reaction Centers – A counterexample to the idea

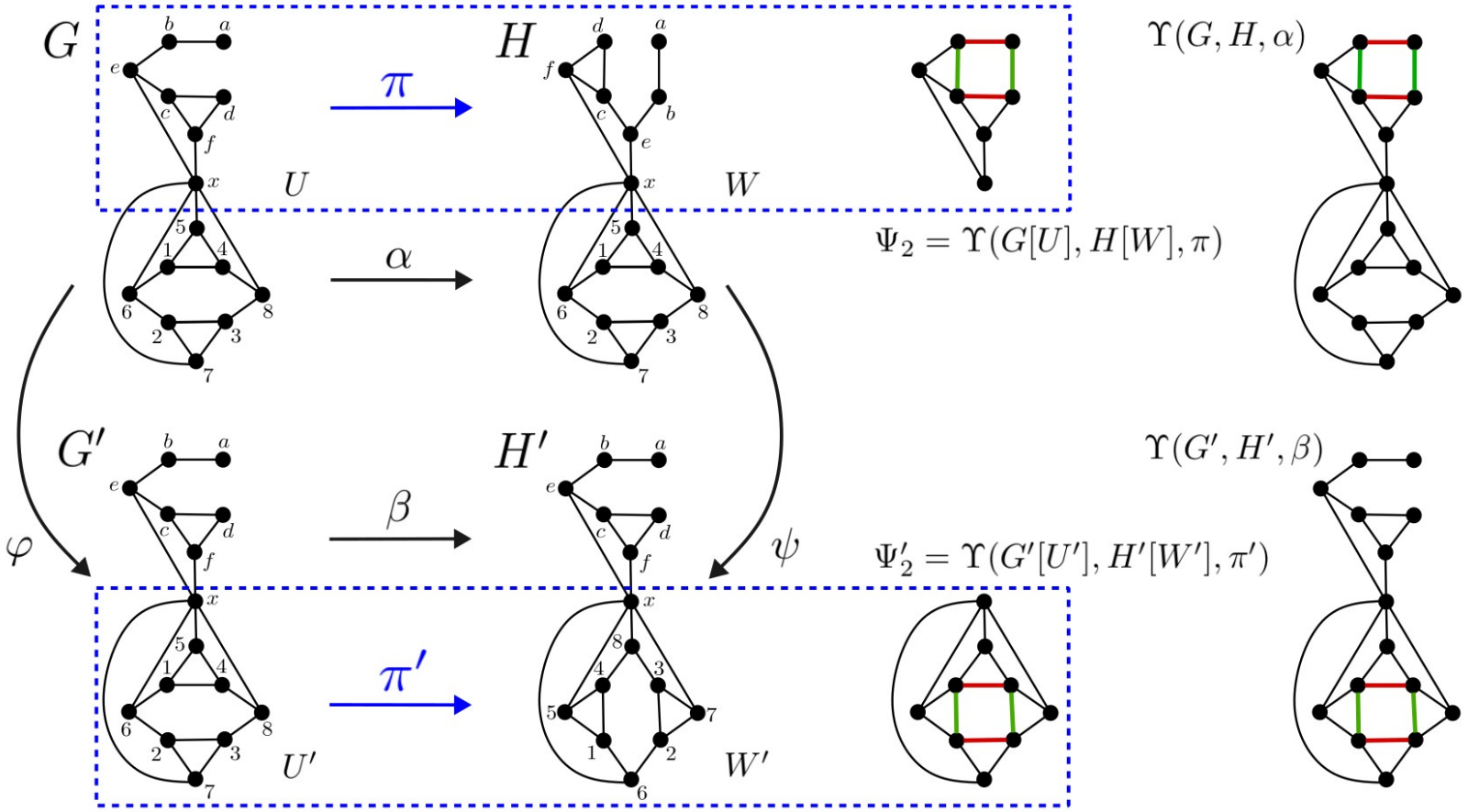


Figure taken from [3]

[3] Phan, T.-L., Weinbauer, K., **Gonzalez Laffitte, M. E.**, Pan, Y., Merkle, D., Andersen, J. L., Fagerberg, R., et al. (2024). *SynTemp: Efficient Extraction of Graph-Based Reaction Rules from Large-Scale Reaction Databases*. American Chemical Society (ACS). https://chemrxiv.org/engage/chemrxiv/article-details/66f677b751558a15ef4cf5f7

Some results on Partial ITS Graphs

Extended Reaction Centers – But at least now we know that ...

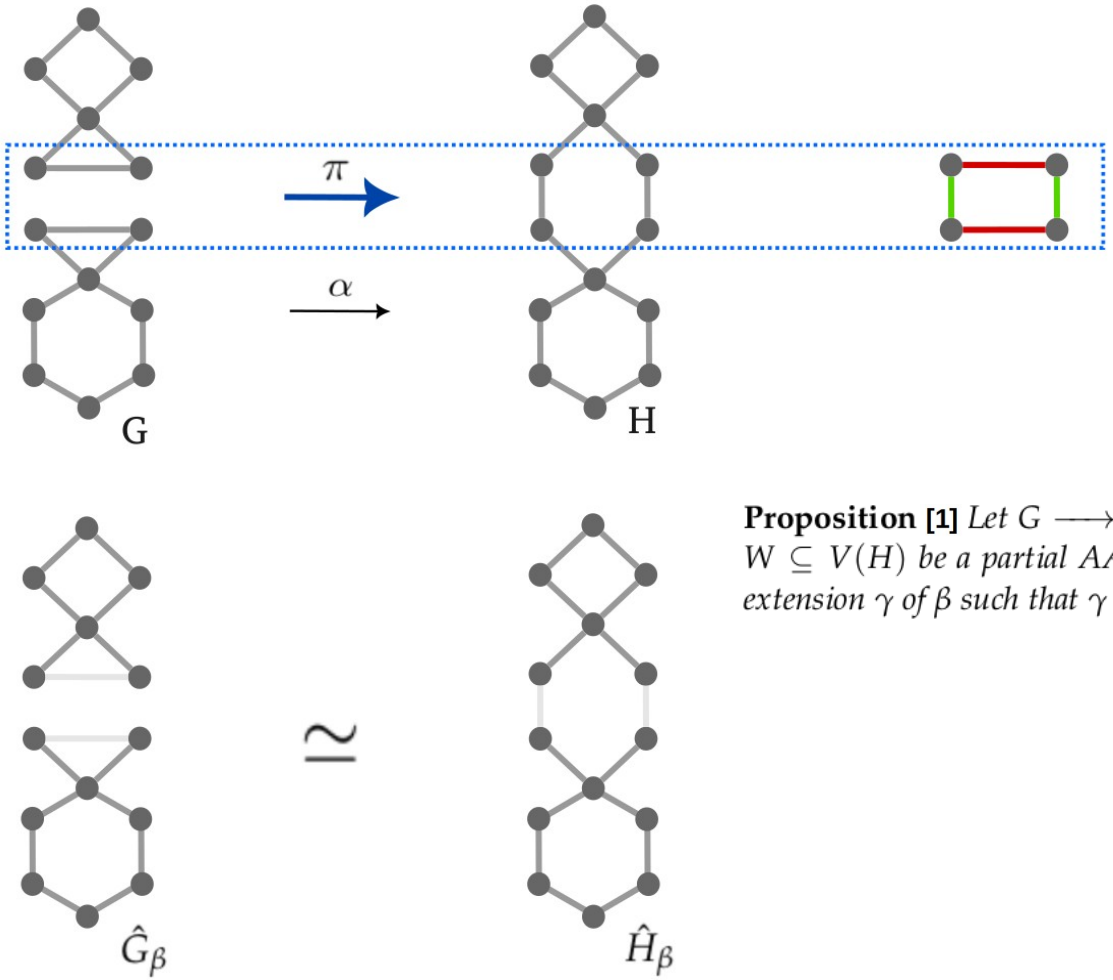
Lemma [3] *Let $\alpha : V(G) \to V(H)$ and $\beta : V(G') \to V(H')$ be complete AAMs for a balanced reaction $G \longrightarrow H$. Then, α and β are consistent if and only if α and β are equivalent AAMs.*

Proposition [3] *Let $\alpha : V(G) \to V(H)$ and $\beta : V(G') \to V(H')$ be two consistent complete atom maps. Then the extended reaction centers Ψ_r and Ψ'_r are isomorphic for every radius $r \geq 0$.*

[3] Phan, T.-L., Weinbauer, K., **Gonzalez Laffitte, M. E.**, Pan, Y., Merkle, D., Andersen, J. L., Fagerberg, R., et al. (2024). *SynTemp: Efficient Extraction of Graph-Based Reaction Rules from Large-Scale Reaction Databases*. American Chemical Society (ACS). https://chemrxiv.org/engage/chemrxiv/article-details/66f677b751558a15ef4cf5f7

Future Work

Extending Good AAMs – Balanced Reactions

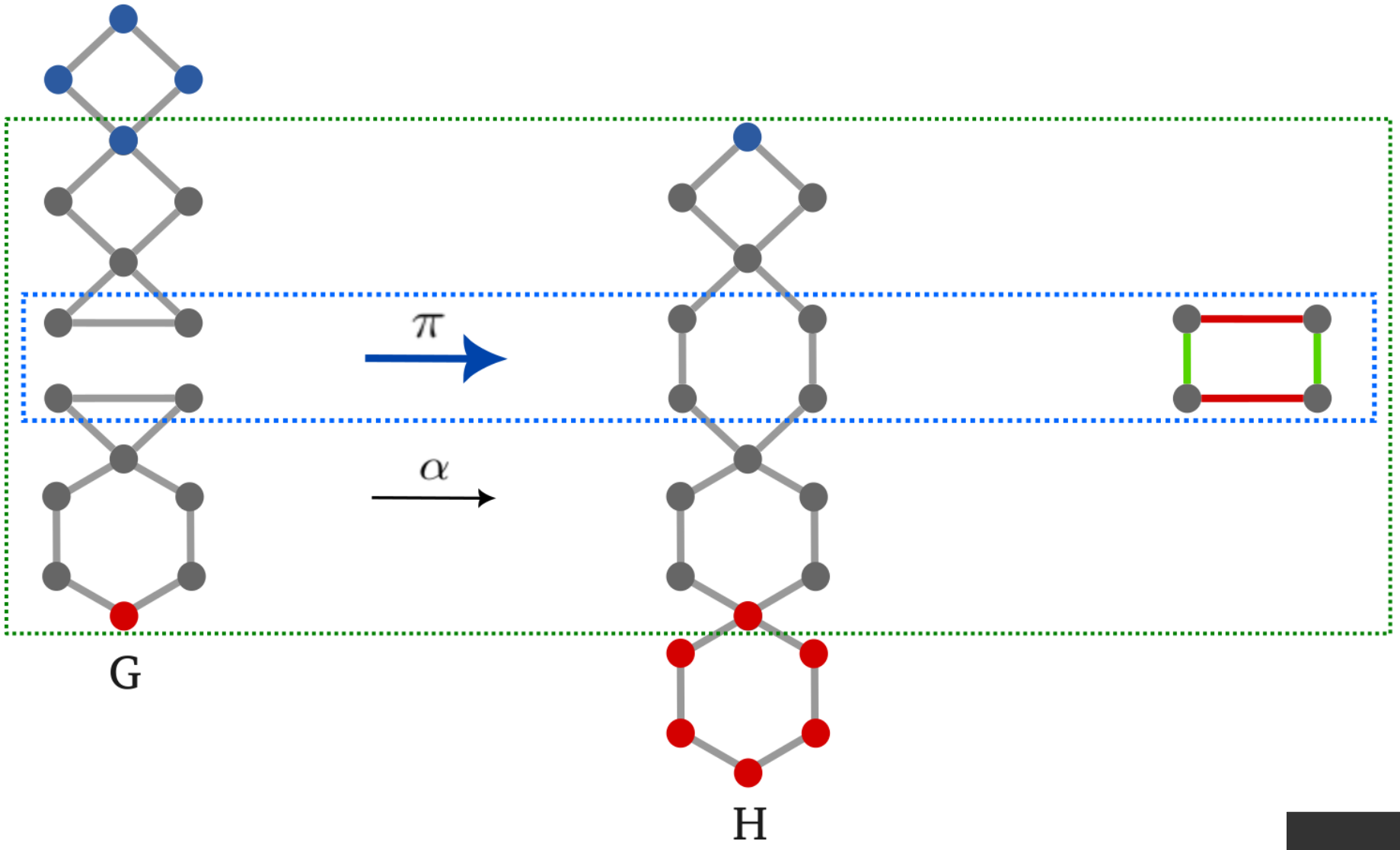


Proposition [1] *Let $G \longrightarrow H$ be a balanced reaction and let $\beta : U \to W$ with $U \subseteq V(G)$ and $W \subseteq V(H)$ be a partial AAM. Then, β is a good partial AAM if and only if there is a proper extension γ of β such that γ is an isomorphism for $\hat{G}_\beta$ and $\hat{H}_\beta$.*

[1] González Laffitte, M. E., et al. (2024). *Partial Imaginary Transition State (ITS) Graphs: A Formal Framework for Researc**[1]**h and Analysis of Atom-to-Atom Maps of Unbalanced Chemical Reactions and Their Completions*. Symmetry, (9), 1217. Multidisciplinary Digital Publishing Institute. https://www.mdpi.com/2073-8994/16/9/1217

Future Work

Extending Good AAMs – Unbalanced Reactions



Thank you for your attention

References

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[*4] González Laffitte, M. E., & Stadler, P. F. (2024). *Progressive Multiple Alignment of Graphs*. Algorithms, 17(3). https://www.mdpi.com/1999-4893/17/3/116

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Thanks

Extra Slide

Notation