Quantum Graph Approaches to Molecular Vibrations

Second Semester Progress Report

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Project Overview

Goal: Apply quantum graph models to determine vibrational energy levels of fluxional molecules

Key Molecule: CH_5^+ (protonated methane)

- Highly fluxional, scrambles H atoms
- Complex, multidimensional nuclear dynamics
- Simplified using 1D quantum graphs

Semester 1 result: Spectral shortcut $E = \frac{1}{2l^2} \arccos^2(\lambda/d)$ converts adjacency eigenvalues to vibrational energy levels

This Semester: Deeper theory + full web application

Recap: CH_5^+ and the Γ_{60} Graph

Why CH_5^+?

- 3-centre, 2-electron bonding
- Potential energy surface (PES) with very low barriers
- Fluxional behaviour: protons scramble freely
- Traditional rigid-rotor / harmonic-oscillator models fail

Γ_{60} graph

- 60 vertices (configurations of the molecule)
- 4-regular, bipartite, edge length l
- Exactly solvable via adjacency matrix

Key result (Rawlinson et al. 2021):

$$\lambda = d\cos(\kappa l), \quad \kappa = \sqrt{2E}$$

$$\kappa l = \pm \arccos\left(\frac{\lambda}{d}\right) + 2n\pi$$

λ = adjacency eigenvalue
E = vibrational energy level
d = vertex degree (= 4 for Γ_{60})
κ = wavenumber

Theoretical Advance: Vertex Boundary Conditions

Primary mathematical reference: Berkolaiko & Kuchment (2013), *Introduction to Quantum Graphs*

Five vertex condition types formalised:

Type	Condition
Kirchhoff (free / Neumann)	continuity + zero flux sum
δ-type	continuity + flux sum $= \alpha_v \psi(v)$
Vertex Dirichlet	$\psi(v) = 0$ at vertex
Extended δ-type	limiting case bridging Neumann and Dirichlet
δ'-type	dual: flux continuity + sum condition on ψ

Why it matters: the vertex condition decides whether the Hamiltonian is self-adjoint — the guarantee that the computed energy levels come out real and physical. (The CH_5^+ model uses the Kirchhoff condition; the rest form the general framework.)

New Result: Paired Energy Levels Always Sum to a Constant

Key observation: Γ_{60} is bipartite $\Rightarrow$ if λ is an eigenvalue, so is $-\lambda$

Derived closed-form identity:

For *any* d-regular bipartite quantum graph with uniform edge length l, the two energy levels E_1, E_2 corresponding to the eigenvalue pair $(\lambda, -\lambda)$ satisfy

$$\boxed{\sqrt{E_1} + \sqrt{E_2} = \frac{\pi}{\sqrt{2}\, l}}$$

Properties:

- Independent of vertex degree d
- Makes the reflection symmetry noted by Rawlinson et al. (2021) explicit and general
- Explains the Block 1 $\leftrightarrow$ Block 2 pairing seen in variational calculations
- Verified for all 6 eigenvalue pairs of Γ_{60}

Verification: All 6 Eigenvalue Pairs of Γ_{60}

$l = 0.1322, \quad d = 4, \quad$ predicted constant: $\dfrac{\pi}{\sqrt{2}\, l} = 16.804$

λ	$-\lambda$	*deg*	E_1 [cm^{-1}]	E_2 [cm^{-1}]	$\sqrt{E_1} + \sqrt{E_2}$
$+4.000$	-4.000	1	0.0	282.4	16.804
$+3.236$	-3.236	4	11.3	180.7	16.804
$+2.562$	-2.562	5	21.9	146.9	16.804
$+1.562$	-1.562	5	39.1	111.3	16.804
$+1.236$	-1.236	4	45.2	101.6	16.804
$+1.000$	-1.000	11	49.7	95.1	16.804

All 6 pairs satisfy the identity exactly. ✓

Web Application: Architecture

Stack: Flask (Python) backend + vanilla JS / D3.js / Chart.js frontend — no build step required

Dual-solver engine:

- **Path A — Adjacency solver:** fast analytic shortcut for k-regular equilateral graphs
- **Path B — Bond Scattering Matrix (BSM) solver:** general secular determinant $\det(I - e^{ikL}S) = 0$ for arbitrary graphs

Backend endpoints:

- `/api/compute` — energy levels (auto-selects solver)
- `/api/secular-scan` — secular function visualisation
- `/api/eigenfunction` — wavefunction amplitudes
- `/api/eigenstates-bulk` — wavepacket dynamics

Web Application: Features

Interactive graph editor

- D3.js force-directed layout
- Drag nodes, add/remove edges
- Set individual edge lengths

Visualisation panels

- Energy level table (cm^{-1})
- Secular function scan
- Wavefunction $\psi(x)$ per edge
- Wavepacket time evolution

Built-in presets

- Petersen, Icosahedral, Desargues, Γ_{60}

Import / Export (4 formats):
JSON, adjacency matrix, edge list, Graph6

Cross-solver verification:
Path A and Path B produce identical energy levels on all regular presets

Symmetry detection:
Flags bipartite graphs and pairs the eigenvalues $\lambda \leftrightarrow -\lambda$, so the energy-level symmetry is visible at a glance

Manuscript Contributions

Supervisor: A. G. Császár is preparing a paper on quantum graph models of fluxional molecules.

Sections contributed this semester:

- Precise graph-theoretic definitions (vertices, edges, metric graph structure)
- Complete treatment of five vertex boundary condition types
- Derivation of the bipartite pairing identity

Next: continuing to contribute as the manuscript is finalised for submission

Outlook: Rovibrational Extension

Next step: extend from $J = 0$ (vibrational) to $J > 0$ (rovibrational)

Γ_{60}, $J = 0$ **(done)**

- Scalar adjacency eigenvalues
- Spectral shortcut works directly

Γ_{120}, $J > 0$ **(Semester 3)**

- Wigner-D matrix boundary conditions (Rawlinson 2019)
- Planned: rovibrational adjacency operator $A^{(J)}$ (dimension $(2J+1)|V|$)

Goal: extend the algebraic shortcut to $J > 0$

Also planned:

- Apply BSM solver to other fluxional molecules
- Finalise manuscript for submission

Summary

Semester 1	**Semester 2**
Γ_{60} model, $J = 0$	Vertex conditions formalised
Spectral shortcut understood	Bipartite identity derived & verified
SymPy prototype	Full Flask web app, dual solver
—	Manuscript sections contributed

Foundation deepened on all fronts

$\Downarrow$

Semester 3: rovibrational extension to $J > 0$

Use of Artificial Intelligence

Transparency Statement:
AI tools were used in the following aspects of this project:

- **Documentation:** AI generated initial drafts of technical documentation; these required substantial hand-written revisions before reaching their final form
- **Presentation:** These slides were generated by AI based on my project content and requirements
- **Software implementation:** Built iteratively with AI assistance; I reviewed every change, diagnosed the failures, and directed each debugging round

All theoretical understanding, derivations, and interpretation of results were conducted independently through study of the referenced literature.

Thank You!

Questions?

Key References:

- Rawlinson, J. I., Fábri, C., & Császár, A. G. (2021). *Chem. Commun.*, 57, 4827–4830.
- Rawlinson, J. I. (2019). *J. Chem. Phys.*, 151, 164303.
- Fábri, C. & Császár, A. G. (2018). *Phys. Chem. Chem. Phys.*, 20, 16913–16917.
- Berkolaiko, G. & Kuchment, P. (2013). *Introduction to Quantum Graphs*. AMS.