Quantum Graph Approaches to Molecular Vibrational Dynamics

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 dynamics
- Simplified using 1D quantum graphs

This Semester: Theoretical foundations + computational implementation

Theoretical Foundation I: Chemistry

Review of General Chemistry Principles:

- **Atomic Structure**
  - Electron configurations
  - Periodic trends
- **Chemical Bonding**
  - Covalent & ionic bonds
  - Lewis structures
  - VSEPR theory
- **Molecular Orbitals**
  - 3-center-2-electron bonding
  - Delocalized bonding in CH_5^+
- **Potential Energy Surface**
  - Flat PES with low barriers
  - Enables fluxional behavior

Why? Understanding molecular geometry and PES topology essential for defining graph vertices and edges

Theoretical Foundation II: Quantum Mechanics

Studied from Atkins' Physical Chemistry (Chapter 8):
Time-Independent Schrödinger Equation (TISE):

$$\hat{H}\psi(x) = E\psi(x) \tag{1}$$

where $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

Key Concepts:

- Eigenvalue problems in quantum mechanics
- Wave functions and boundary conditions
- Quantization of energy levels
- Foundation for quantum graph theory

The Particle in a Box Model

Central model studied: Infinite potential well (in SI units)
Potential:

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Boundary conditions: $\psi(0) = \psi(L) = 0$

Quantized energies:

$$E_n = \frac{n^2 h^2}{8mL^2}, \quad n = 1, 2, 3, \ldots$$

Inside the box:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

Critical insight: Graph edges behave like 1D "boxes" with complex boundary conditions at vertices

Note: Quantum graph literature uses *mass-scaled coordinates* ($x' = \sqrt{m}x$) or atomic units ($\hbar = m = 1$) to simplify notation

Quantum Graphs: Bridging Topology and QM

Core Idea: Map complex molecular dynamics onto graph structure

Graph Elements:

- **Vertices:** Molecular configurations (versions)
- **Edges:** Transition paths between configurations
- **Particle:** Effective quantum particle moving on edges

Boundary Conditions:

- Wave function continuous
- Zero momentum flux at vertices

Key Result (in mass-scaled coordinates):

For d-regular graphs with edge length l:

$$\lambda = d\cos(kl), \quad k = \sqrt{2E}$$

Spectral condition:

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

where $n = 0, 1, 2, \ldots$ (infinite energy bands)

λ = eigenvalues of adjacency matrix A
E = quantum energy eigenvalues

Source: Rawlinson et al. (2021), *Chem. Commun.*, 57, 4827-4830

The Γ_{60} Model for CH_5^+

Studied from Rawlinson et al. (2021) paper:

Graph Structure:

- **60 vertices:** C_{2v} symmetric transition states
- **4-regular:** Each vertex connected to 4 others
- **Single parameter:** Edge length l
- **Bipartite structure:** Vertices split into sets A and B

Remarkable Property:

Bipartite $\Rightarrow$ if λ is eigenvalue, so is $-\lambda$

Energy pairing:

$$\sqrt{E_1} + \sqrt{E_2} = \text{constant}$$

Explains Block 1 $\leftrightarrow$ Block 2 symmetry observed in variational calculations!

Key insight: Exactly solvable, analytical solutions possible

Computational Implementation

Developed Python software for particle-in-a-box model on quantum graphs

Key Features:

- Analysis of quantum graphs via adjacency matrices
- Input: Adjacency matrix A representing molecular topology
- Output: Combinatorial spectrum (eigenvalues) and quantum energy levels
- Automatic regularity checking (d-regular graphs)
- Numerical eigenvalue computation using power iteration
- Bipartite symmetry detection ($\lambda \to -\lambda$)

Workflow:

1. Define adjacency matrix
2. Compute eigenvalues λ numerically
3. Apply spectral relation to determine energy levels: $E = \frac{1}{2l^2} \arccos^2(\lambda/d)$
4. Analyze symmetry properties

Future Work

Next semester objectives:

1. **Deepen theoretical knowledge**
   - Advanced boundary conditions (Neumann/Kirchhoff)
   - Spectral graph theory
   - Multi-valued energy band structure
2. **Search for new molecular candidates**
   - High permutation symmetry molecules
   - Fluxional systems similar to CH_5^+
   - Test cases for quantum graph approach
3. **Generalize the model**
   - Non-regular graphs (different edge lengths)
   - General spectral relation derivation
   - Complete graph theory $\leftrightarrow$ quantum spectroscopy bridge

Summary

Semester Achievements:

- ✓ Solid foundation in general chemistry and quantum mechanics
- ✓ Mastered particle in a box model and boundary conditions
- ✓ Studied quantum graph theory and the CH_5^+ model from literature
- ✓ Implemented basic software for particle-in-a-box on quantum graphs

Foundation established for quantum graph approach

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Next semester: Extend implementation

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to more complex molecular systems

Use of Artificial Intelligence

Transparency Statement:

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

- **Documentation:** AI generated an initial draft of the technical documentation, which was subsequently revised and modified by me
- **Presentation:** These slides were generated entirely by AI based on my project content and requirements
- **Software Implementation:** AI generated an initial draft of the Python program, which I then reviewed and understood

Note: All theoretical understanding, learning, and interpretation of results were conducted independently through studying the referenced literature and textbooks.

Thank You!

Questions?

Key References:

Rawlinson, J. I., Fábri, C., & Császár, A. G. (2021). *Chem. Commun.*, 57, 4827-4830.

Atkins, P., & de Paula, J. (2006). *Atkins' Physical Chemistry*, 8th ed. Oxford University Press.

Flowers, P., et al. (2015). *Chemistry*. OpenStax.