Project Progress Report:
Quantum Graph Approaches to Molecular Vibrations

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1 Project Overview

This project has been inspired by recent successes in modeling the low-energy rovibrational quantum states of quasistructural molecules [3], such as protonated methane (CH_5^+) [4, 5, 8–10], using the theory of quantum graphs [2, 7].

This novel approach avoids the use of complex multidimensional potential energy surfaces (PES), and greatly simplifies the solution of the time-independent multidimensional rovibrational Schrödinger equation, as it replaces the complex motion of the nuclei by the motion of an effective particle along the edges of a metric graph.

The primary objectives of this project are (a) to systematically investigate small quantum graphs that are potentially useful for chemists, and (b) identify new molecular candidates whose low-energy vibrations can be accurately modeled using quantum graphs.

This report summarizes (a) the theoretical foundations established in chemistry and quantum mechanics, (b) the mathematical derivations studied, and (c) the current state of the computational implementation using symbolic algebra.

2 Theoretical Foundations

2.1 Chemical principles

To understand the structural basis of the molecules we intend to model, I have completed a comprehensive review of some of the principles of modern chemistry [6]. Key areas of focus included:

- **Atomic structure and periodicity:** Understanding electron configurations and periodic trends to predict molecular shapes and geometry.
- **Chemical bonding:** Studying covalent and ionic bonding, Lewis structures, and VSEPR (Valence-Shell Electron-Pair Repulsion) theory, concepts crucial for determining the vertices of our quantum graphs.
- **Molecular orbitals:** Understanding how atomic orbitals combine, which provides the physical justification for the electron delocalization often seen in fluxional molecules.

2.2 Quantum mechanics and the Schrödinger equation

A significant portion of the research phase was dedicated to Chapters 8 and 9 of Atkins' textbook *Physical Chemistry* [1]. The central focus was mastering the Time-Independent Schrödinger Equation (TISE), which governs the energy states of our molecular quantum systems.

The general form of the TISE is given by the following eigenvalue equation:

$$\hat{H}\psi_i(x) = E_i\psi_i(x) \tag{1}$$

where $\hat{H}$ is the Hamiltonian (the energy operator), $\psi_i(x)$ is a set of wave functions, and E_i represents the energy eigenvalues. For a single particle of mass m moving in one dimension under the influence of a potential $V(x)$, the Hamiltonian takes the form

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x). \tag{2}$$

3 The Quantum Graph Model

Based on previous studies [5, 9, 10], we are transitioning from standard quantum chemistry to a topological graph model when attempting to describe the low-energy vibrational motions of certain systems, like CH_5^+.

3.1 Graph topology and energy

In this model, the molecule is represented as a graph Γ, where vertices represent equilibrium versions of the molecule and edges represent transition paths between the versions. In the simplest models, which assume that there is no potential hindering the motion of the particles ($V(x) = 0$), the particle moves freely along edges of length L (where $V = 0$).

For a d-regular graph (where every vertex connects to d other vertices), the energy levels are not solved by differential equations directly, but by the spectral properties of the graph's adjacency matrix **A**. The relationship derived is:

$$\lambda = d\cos\left(\sqrt{2E}L\right), \tag{3}$$

where λ are the eigenvalues of the adjacency matrix **A**. This formula allows us to map the combinatorial geometry of the molecule directly to its vibrational spectrum.

3.2 The particle in a box model

To understand how confinement leads to quantized energy levels—the fundamental concept behind quantum theory—I studied the "particle in a box" (sometimes also called the infinite potential well) model [1] in detail.

In this simple model, we define a potential $V(x)$ for a one-dimensional (1D) box of length L such that:

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases} \tag{4}$$

Thus, inside the box, the TISE simplifies to an equation that is similar to the motion of a "free" particle :

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \Longrightarrow \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{5}$$

where $\hbar = h/(2\pi)$ is the reduced Planck constant and $k = \frac{\sqrt{2mE}}{\hbar}$. The general, analytical solution of this second-order differential equation is

$$\psi(x) = A\sin(kx) + B\cos(kx). \tag{6}$$

Applying the boundary conditions required by quantum mechanics, $\psi(0) = 0$ and $\psi(L) = 0$, forces $B = 0$ and $kL = n\pi$ (for $n = 1, 2, 3...$, where n is a "quantum number"). This quantization of k leads to the following simple formula for the exact energy levels of the particle in a box:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}. \tag{7}$$

The corresponding normalized wave functions, sometimes called standing waves, can be written as

$$\psi_n = \sqrt{2/L}\,\sin\frac{n\pi x}{L}. \tag{8}$$

This derivation is critical for the project because the edges of our quantum graphs behave similarly to these one-dimensional (1D) “boxes”, but the boundary conditions at the vertices are significantly more complex. Nevertheless, the particle in a box is the simplest quantum graph.

4 Computational Implementation

4.1 Current status

I have begun developing a Python-based simulation tool to automate the quantum-graph calculations. Recognizing the need for exact analytical solutions, the software utilizes `sympy` for symbolic algebra.

The program currently performs the following tasks:

1. Accepts an adjacency matrix representing the molecular graph.
2. Checks for graph regularity.
3. Computes the combinatorial spectrum (eigenvalues λ) of the graph symbolically.
4. For regular graphs, it inverts the cosine relation to solve for the energy levels E.

5 Future Work

The next phase of the project will focus on three key objectives:

1. **Deepening theoretical knowledge:** I intend to further study the time-independent Schrödinger equation, specifically focusing on Neumann/Kirchhoff boundary conditions at graph vertices, which govern how wave functions split at molecular transition states.
2. **Searching for molecular candidates:** I will research other fluxional molecules, similar to CH_5^+, that exhibit high permutation-inversion symmetry to serve as test cases for our quantum-graph model.
3. **Generalizing the Spectral Relation:** The ultimate goal is to find the precise mathematical relation between the graph eigenvalues and energy levels for arbitrary (non-regular) molecular graphs, completing the link between graph theory and high-resolution molecular spectroscopy.

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