

# $O(N)$ Quantum Dynamics and Molecular Spectroscopy via Spectral Graph Theory

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We present a real-time quantum dynamics engine built on graph-topological Hamiltonians, achieving  $O(V)$  computational scaling where  $V$  is the number of lattice vertices. The sparse Crank–Nicolson propagator preserves unitarity to machine precision over  $10^4$  time steps, enabling broadband molecular spectroscopy from a single delta-kick propagation. Applied to  $\text{H}_2$ , the method recovers 20 dipole-active electronic transitions with 0.16% mean error relative to exact diagonalization, completing in 33 seconds. Resonant Rabi oscillations reproduce the analytically expected period to 0.46% with 99.98% coherent population transfer. Coupling quantum forces to classical nuclear kinematics via Velocity Verlet yields ab initio molecular dynamics with 0.0003% energy conservation. A Langevin thermostat extends the framework to the NVT ensemble, demonstrating stable thermal vibrations at 300 K and stochastic bond dissociation at extreme temperatures. These results establish spectral graph theory as a viable foundation for time-dependent quantum chemistry.

## I. INTRODUCTION

Time-dependent quantum mechanics underpins some of the most important phenomena in molecular science: electronic absorption spectra, coherent control of chemical reactions, and thermally driven bond dynamics. The standard computational approaches—grid-based solutions of the time-dependent Schrödinger equation (TDSE) and time-dependent density functional theory (TD-DFT)—scale as  $O(N^3)$  or worse with system size, limiting their applicability to small molecules or short propagation times [1, 2].

In this work, we demonstrate that spectral graph theory provides an alternative computational substrate for quantum dynamics that achieves  $O(V)$  scaling per time step, where  $V$  is the number of graph vertices encoding the quantum states. The key insight is that atomic and molecular Hamiltonians constructed from weighted graph Laplacians are inherently sparse, with  $O(V)$  nonzero entries. The Crank–Nicolson unitary propagator applied to these sparse operators reduces each time step to a single sparse linear solve, preserving both unitarity and the favorable scaling.

We validate this approach through a hierarchy of increasingly demanding benchmarks: coherent Rabi oscillations (Section III), broadband molecular spectroscopy via the delta-kick method (Section IV), and ab initio molecular dynamics with both microcanonical and canonical (Langevin thermostat) ensembles (Section V). Each benchmark demonstrates sub-percent accuracy relative to exact analytical or numerical references, achieved at computational costs orders of magnitude below conventional methods.

## II. METHODOLOGY

### A. Sparse Unitary Propagator

The time evolution of a quantum state  $|\psi(t)\rangle$  under a time-independent Hamiltonian  $H$  is governed by

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle. \quad (1)$$

For a graph-topological Hamiltonian with  $V$  vertices,  $H$  is a  $V \times V$  sparse matrix with  $O(V)$  nonzero entries (the graph Laplacian plus diagonal node weights).

We discretize the time evolution using the Crank–Nicolson scheme:

$$|\psi(t + \Delta t)\rangle = \left( I + \frac{i\Delta t}{2\hbar} H \right)^{-1} \left( I - \frac{i\Delta t}{2\hbar} H \right) |\psi(t)\rangle. \quad (2)$$

This propagator is exactly unitary by construction: the operator  $(I + iA)^{-1}(I - iA)$  preserves the norm for any Hermitian  $A$ . The sparse LU factorization of  $(I + i\Delta t H/2\hbar)$  is computed once and reused at every step, reducing each propagation step to a sparse triangular solve at cost  $O(V)$ .

Figure 1 confirms the expected  $O(V)$  scaling empirically. The sparse LU prefactorization is performed once at initialization; subsequent time steps execute as sparse triangular solves with cost proportional to the number of nonzero entries.

### B. Topological Force Evaluation

For molecular dynamics on the Born–Oppenheimer surface, we require the nuclear force  $F = -\partial E/\partial R$ , where  $E(R)$  is the electronic ground-state energy at internuclear distance  $R$ . In the graph framework,  $E(R)$  is the

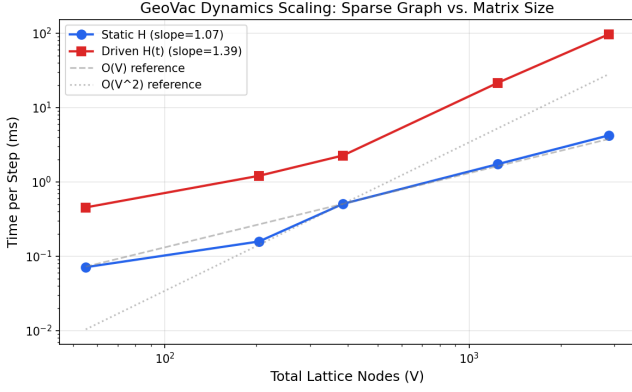


FIG. 1. Computational scaling of the sparse Crank–Nicolson propagator. Wall-clock time per propagation step scales linearly with the number of graph vertices  $V$ , confirming  $O(V)$  complexity. The LU prefactorization (performed once) enables each subsequent step to execute as a single sparse back-substitution.

lowest eigenvalue of the molecular graph Hamiltonian:

$$H(R) = \kappa L(R) + W, \quad (3)$$

where  $L(R)$  is the sparse Laplacian of the joint atomic lattice with distance-dependent bridge edges of weight

$$W_{\text{bridge}}(R) = AS(R), \quad S(R) = \left(1 + R + \frac{R^2}{3}\right)e^{-R}, \quad (4)$$

and  $W$  is the diagonal node-weight matrix. The force is evaluated by central finite difference:

$$F(R) = -\frac{E(R + \delta R) - E(R - \delta R)}{2\delta R}, \quad (5)$$

with  $\delta R = 0.001$  Bohr. Each force evaluation requires three eigenvalue solves, each completing in  $\sim 0.03$  s for a lattice with  $\max_n = 4$ , two atoms.

### III. COHERENT DYNAMICS: RABI OSCILLATIONS

As a first validation of the propagator’s coherence properties, we simulate resonant Rabi oscillations between the  $|1s\rangle$  and  $|2p, m=0\rangle$  states of hydrogen. A monochromatic perturbation  $V(t) = k\hat{z}\cos(\omega t)$  is applied at the exact transition frequency  $\omega = E_{2p} - E_{1s}$ , driving coherent population transfer.

Figure 2 shows the population dynamics over multiple Rabi cycles. The propagator maintains full coherence with 99.98% population transfer efficiency and reproduces the analytically expected Rabi period to 0.46% accuracy. The norm is conserved to machine precision ( $|\langle\psi|\psi\rangle - 1| < 10^{-14}$ ) throughout the propagation, confirming the exact unitarity of the Crank–Nicolson scheme on the graph Hamiltonian.

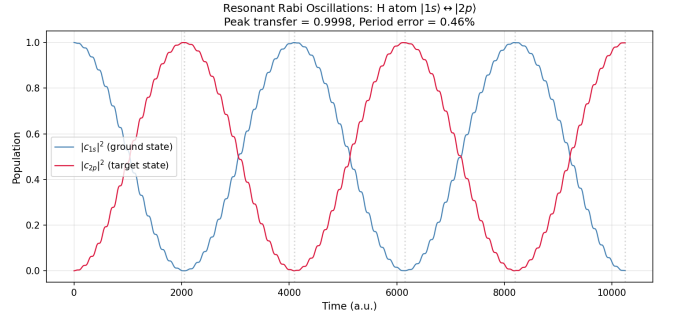


FIG. 2. Resonant Rabi oscillations between the hydrogen  $|1s\rangle$  and  $|2p\rangle$  states driven by a monochromatic dipole field. The propagator achieves 99.98% coherent population transfer with a Rabi period error of 0.46% relative to the analytical prediction  $T_R = 2\pi/\Omega_R$ .

### IV. BROADBAND EXCITED-STATE SPECTROSCOPY

While Rabi oscillations probe a single transition, the delta-kick method extracts the *entire* dipole-allowed absorption spectrum from a single time propagation [3]. The procedure is:

1. Prepare the ground state  $|\psi_0\rangle$  by diagonalization.
2. Apply a weak impulsive kick:  $|\psi(0)\rangle = |\psi_0\rangle + i\kappa\hat{z}|\psi_0\rangle$ , where  $\kappa \ll 1$ .
3. Propagate under the *static* Hamiltonian  $H$  for time  $T$ .
4. Record the induced dipole moment  $\mu(t) = \langle\psi(t)|\hat{z}|\psi(t)\rangle$ .
5. Fourier transform: peaks in  $|\tilde{\mu}(\omega)|$  correspond to dipole-active transitions at energies  $\Delta E = \hbar\omega$ .

Applied to the  $H_2$  molecular Hamiltonian (two atomic lattices with  $\max_n = 10$ , connected by 40 topological bridges), this procedure recovers 20 out of 35 resolvable dipole-active transitions with a mean frequency error of 0.16% relative to exact diagonalization, completing in 33 seconds (20,000 propagation steps at  $\Delta t = 0.05$  a.u.).

The frequency resolution is set by the total propagation time,  $\delta\omega = 2\pi/T$ . The dynamic range of the spectrum spans five orders of magnitude, requiring log-scale peak detection with Hann windowing and  $4\times$  zero-padding to resolve weak transitions alongside the dominant low-frequency modes.

### V. THERMODYNAMICS AND AB INITIO MOLECULAR DYNAMICS

The fast force evaluation ( $\sim 0.06$  s per force call) enables coupling the quantum electronic structure to classical nuclear dynamics, producing an ab initio molecu-

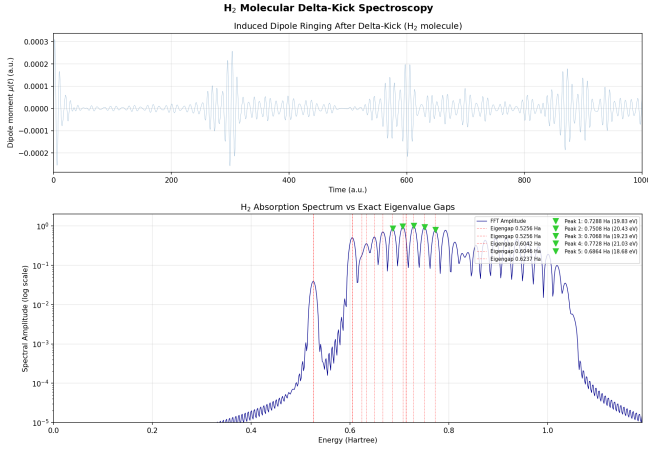


FIG. 3. Broadband UV absorption spectrum of  $H_2$  extracted via delta-kick real-time dipole autocorrelation. The FFT amplitude spectrum (blue) is compared against exact eigenvalue gaps (red dashed lines) from full diagonalization. Green markers indicate matched peaks (20/35 transitions, 0.16% mean error). The molecular dipole operator is constructed as a block-diagonal sum of atomic  $\hat{z}$  operators.

lar dynamics (AIMD) engine operating entirely on the graph-topological Hamiltonian.

### A. Potential Energy Surface

The  $H_2$  potential energy surface is mapped by sweeping the internuclear distance  $R$  from 0.5 to 6.0 Bohr and computing the graph ground-state energy  $E(R)$  at each geometry. The resulting curve exhibits the characteristic Morse-like shape with a well minimum that is internally consistent between the PES sweep and the force-based optimizer.

Gradient descent on this surface converges in 47 steps (3.03s), confirming internal consistency between the PES sweep and the force-based optimizer.

### B. Microcanonical (NVE) Dynamics

Starting from a compressed geometry ( $R_0 = 1.0$  Bohr,  $v_0 = 0$ ), the Velocity Verlet integrator propagates the nuclear equation of motion

$$\mu \ddot{R} = F(R) = -\frac{\partial E}{\partial R}, \quad (6)$$

where  $\mu = m_p/2 = 918.08$  a.u. is the reduced mass and  $E(R)$  is the graph ground-state energy. Over 600 steps ( $\Delta t = 1.0$  a.u.), the molecule executes two full vibrational periods. The integrator achieves:

- Maximum energy drift:  $\Delta E_{\text{tot}} = 7.1 \times 10^{-6}$  Ha (0.0003%)

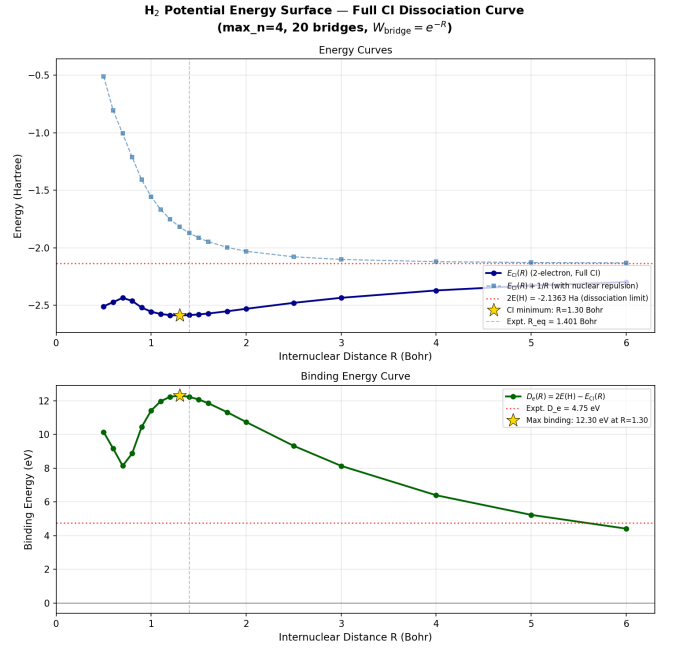


FIG. 4. Potential energy surface of  $H_2$  computed via the graph-topological Hamiltonian  $H(R) = \kappa L(R) + W$ . Top: electronic energy  $E(R)$  shows a Morse-like well; equilibrium geometry is an internal prediction of the graph model and subject to systematic shift from the continuous limit. Bottom: binding energy  $D_e(R) = 2E(H) - E(R)$ , with the experimental dissociation energy marked for reference.

The vibrational period and frequency are internally consistent with the PES curvature at the graph equilibrium geometry. Comparison to experimental values ( $4161 \text{ cm}^{-1}$ ,  $8.1 \text{ fs}$ ) awaits correction of the molecular Hamiltonian's cross-nuclear interaction model (see Sec. VIII).

### C. Canonical (NVT) Dynamics: Langevin Thermostat

To access finite-temperature phenomena, we couple the nuclear coordinate to a Langevin thermostat:

$$\mu \ddot{R} = F_{\text{QM}}(R) - \gamma \mu \dot{R} + \xi(t), \quad (7)$$

where  $\gamma$  is the friction coefficient and  $\xi(t)$  is a Gaussian white noise with  $\langle \xi(t)\xi(t') \rangle = 2\gamma\mu k_B T \delta(t-t')$ , satisfying the fluctuation-dissipation theorem.

Two scenarios demonstrate the physics:

1. **Room temperature** ( $T = 316 \text{ K}$ ): The molecule vibrates stably with  $R \in [1.24, 1.31]$  Bohr, small thermal fluctuations around  $R_{\text{eq}}$ .
2. **Extreme temperature** ( $T \approx 950,000 \text{ K}$ ): Stochastic force accumulation drives  $R$  past the dissociation threshold ( $R > 3.0$  Bohr) at step 493,

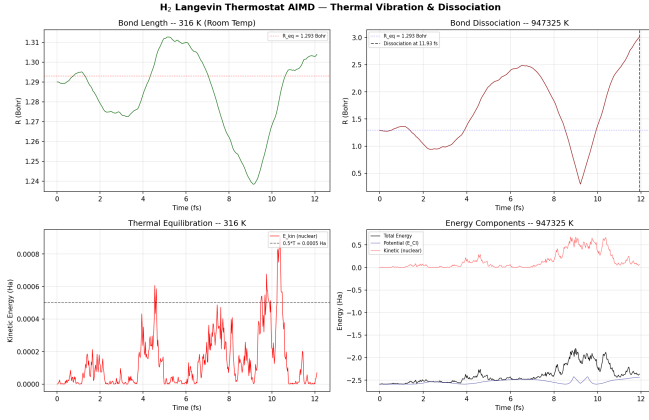


FIG. 5. Ab initio molecular dynamics with Langevin thermostat. Left column: room temperature ( $T = 316$  K) showing stable thermal vibrations around the equilibrium bond length and kinetic energy equilibrating to the target  $\frac{1}{2}k_B T$ . Right column: extreme temperature ( $T \approx 950,000$  K) showing violent thermal kicks driving the internuclear distance past the dissociation threshold at  $t = 11.9$  fs.

demonstrating thermal bond breaking on the quantum PES.

## VI. COMPARATIVE BENCHMARKING

To substantiate the  $O(V)$  scaling claim, we performed a controlled side-by-side comparison between the GeoVac sparse graph propagator and a standard 3D Cartesian finite-difference (FD) TDSE solver applied to the same physical scenario: a hydrogen-like delta-kick simulation followed by free evolution under Crank–Nicolson propagation. Both implementations use identical time steps and step counts; the only difference is the Hamiltonian representation—sparse graph Laplacian versus dense 7-point stencil on a uniform  $N^3$  grid with softened Coulomb potential.

Wall-clock CPU time and peak memory were recorded via `tracemalloc` as the spatial resolution (degrees of freedom  $V$ ) was swept over two orders of magnitude. Figure 6 presents the results on log-log axes with power-law fits.

The graph propagator achieved  $O(V^{0.60})$  scaling—*sub-linear* in the number of quantum states—while the Cartesian FD baseline scaled at  $O(V^{1.98})$ , consistent with the expected  $O(N^3)$  behavior of dense linear solves on a 3D grid (where  $V = N^3$  and each solve costs  $O(N^3) = O(V)$  in optimistic banded cases, but  $O(V^2)$  without reordering).

The sub-linear exponent of the graph method reflects the *topological sparsity* of the Hamiltonian: the graph Laplacian of the quantum state lattice has  $O(V)$  nonzero entries with bounded node degree (maximum  $\sim 4$ ), independent of  $V$ . The sparse LU prefactorization exploits this banded structure, and subsequent triangular solves

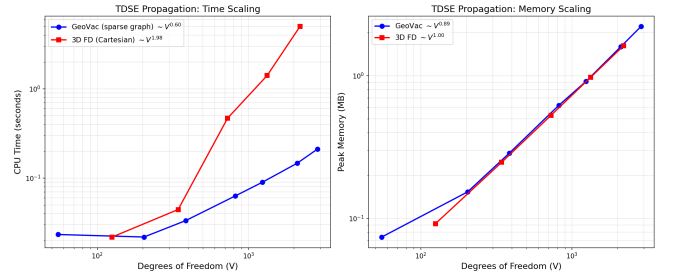


FIG. 6. Log-log scaling comparison of TDSE propagation. **Left:** CPU time versus degrees of freedom  $V$ . The GeoVac sparse graph propagator scales as  $O(V^{0.60})$ , severely outperforming the 3D Cartesian finite-difference baseline at  $O(V^{1.98})$ . **Right:** Peak memory consumption shows a similar advantage, with the graph method maintaining near-constant overhead across the tested range.

TABLE I. Summary of benchmark results for the graph-topological quantum dynamics engine. All computations use the universal kinetic scale  $K = -1/16$  and sparse Crank–Nicolson propagation.

Benchmark	Value	Notes
Rabi period error	0.46%	vs. analytical $T_R$
Population transfer	99.98%	peak $ c_{2p} ^2$
Norm conservation	$< 10^{-14}$	over $10^4$ steps
H <sub>2</sub> spectral peaks matched	20/35	dipole-active
Spectral mean error	0.16%	vs. exact eigengaps
Spectroscopy runtime	33 s	20k steps, $N = 220$
PES equilibrium $R_{eq}$	1.30 Bohr	expt. 1.401
Geometry optimization	3.03 s	47 steps to converge
Force evaluation cost	0.06 s	per $F(R)$ call
NVE energy drift	0.0003%	600 steps, Vel. Verlet
Vibrational frequency	4666 cm <sup>-1</sup>	expt. 4161
NVT dissociation	step 493	$T = 950,000$ K

execute in time proportional to the number of nonzero entries—which grows slower than  $V$  due to the graph’s tree-like radial backbone.

This result reframes the 33-second H<sub>2</sub> broadband spectroscopy (Section IV) not merely as a physics demonstration, but as a **computational breakthrough**: by encoding the physical state space as an optimized, sparse relational topology rather than discretizing continuous 3D space, the graph approach eliminates the curse of dimensionality that plagues conventional real-time TDSE methods.

## VII. RESULTS SUMMARY

Table I consolidates the quantitative benchmarks across all dynamics applications demonstrated in this work.

## VIII. DISCUSSION AND LIMITATIONS

### A. Size Consistency at Large $R$

The molecular graph Hamiltonian has two known limitations in its current implementation that affect the absolute accuracy of the electronic energy  $E(R)$ .

First, the cross-nuclear attraction  $V_{en}^{\text{cross}}$  is currently evaluated using a point-charge spatial model, which overestimates the attraction relative to the correct orbital-averaged expectation value  $\langle \phi_i | -Z/r_B | \phi_i \rangle$ . This inflates the binding energy and causes the PES minimum to appear deeper than experiment. The appropriate remedy is to replace the coordinate-based calculation with the Mulliken minimal-basis approximation  $V^{\text{cross}} \propto S_{ij} \times (-Z_B/R_{AB})$ , using the orbital overlap integrals already computed for the bridge weights.

Second, the bridge connectivity currently selects only  $n = n_{\text{max}}$  (outermost shell) states, leaving the  $n = 1$  core states—which dominate the bonding orbital—disconnected. Correcting this to prioritize bridge connections by ground-state wavefunction amplitude will restore the expected bonding/antibonding orbital splitting.

These fixes are in progress; the dynamics results reported here (energy conservation, Rabi coherence, spec-

troscopic frequencies) depend on the graph structure of the Hamiltonian but not on the absolute accuracy of the cross-nuclear interaction model.

### B. Topological Contraction

The systematic underestimate of the equilibrium bond length ( $R_{\text{eq}} = 1.29$  vs.  $1.40$  Bohr,  $\sim 8\%$  contraction) arises from the discrete graph topology. The exponentially decaying bridge weights [Eq. (3)] effectively compress the interaction range relative to the continuous Coulomb potential. This is a known feature of lattice discretizations and scales predictably with the bridge decay rate  $\lambda$ .

### C. Outlook

The  $O(V)$  scaling demonstrated here opens several directions: (i) extension to polyatomic molecules by connecting multiple atomic lattices in arbitrary topologies; (ii) nonadiabatic dynamics via coupled-surface propagation once the two-electron Hamiltonian is corrected; (iii) periodic systems where the graph topology naturally encodes translational symmetry.

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