Numerical Method: Quantum Dynamics Simulation of molecular vibrational wave function with Parallel computing

Schrodinger equation: $i\hbar \frac{d\psi}{dt} = H\psi$

For time-independent Hamiltonian $\psi(t + dt) = e^{-i\hat{H}dt}\psi(t)$

Approximate evolution operator with Chebyshev polynomials $e^{-i\hat{H}dt} \approx \sum_{n=0}^{N} a_n \, T_n(-i\hat{H}dt)$

T_n : nth order Chebyshev polynomials

The error decreases exponentially with increasing order *n*

Reference: J. Chem. Phys. **81**, 3967 (1984)

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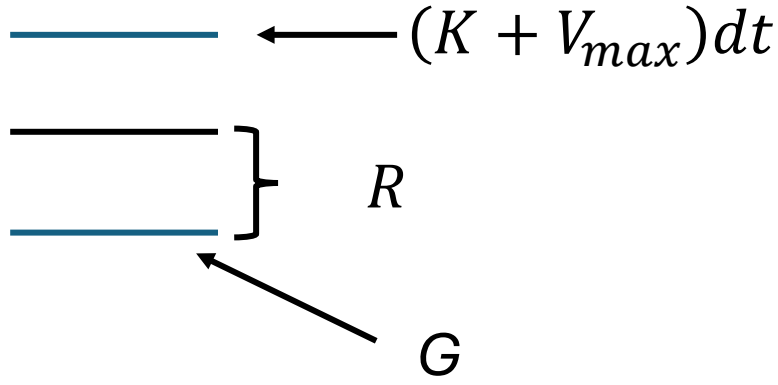
The eigenvalues of Hamiltonian H: $\lambda \in [V_{min}, V_{max} + K]$

Define: $R = \frac{(K+V_{max}-V_{min})}{2} dt, \quad G = V_{min} dt$



$$\omega = \frac{-i[H\,dt-(R+G)]}{R}, \quad \text{eig}(\omega) \in [-i, i]$$

Then: $$e^{-iHdt} \approx \sum_{k=0}^{N} a_k T_k(\omega)$$

$$a_k = e^{i(R+G)} C_k J_k(R)$$

$J_k(R)$: Bessel function, decreases exponentially when $k \geq R$.
Choose dt to make $R \sim O(1)$

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Recursive relation of Chebyshev polynomials:

$$T_k(\hat{\omega})\,\psi = 2\hat{\omega}\,(T_{k-1}(\hat{\omega})\,\psi) + T_{k-2}(\hat{\omega})\,\psi$$

$$T_0(\hat{\omega}) = 1\,,\, T_1(\hat{\omega}) = \hat{\omega}$$

$\hat{\omega}\,\psi$:

- Implemented as matrix – vector multiplication.
- Hamiltonian is a sparse matrix.
- We implement the calculation in C++ using MPI.

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