Estimation of Ro-Vibrational Eigenphases Using Gaussian Processes and Bayesian Quantum Phase Estimation

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Abstract

Ro-vibrational Eigenvlaue Problem Formulation

To analyze molecular characteristics, chemists often solve the following eigenvalue equation:

$$\mathbf{H}_{RV}\Psi(\vec{\theta}) = E_0\Psi(\vec{\theta}) \tag{1}$$

In this equation, $\mathbf{H}_{RV}$ represents the Hamiltonian that accounts for the molecule's total ro-vibrational energy. The wavefunction Ψ, parameterized by the vector $\vec{\theta}$, serves as the eigenvector. The energy level E_0 corresponds to the lowest ground state energy that electrons can occupy. While simpler molecules like H_2 allow for straightforward single vector decompositions, larger molecules present computational challenges due to the increased size of $\mathbf{H}_{RV}$. Asnaashari et al. employed a hybrid quantum-classical computing approach to address this eigenvalue problem, using a greedy induced point sampling algorithm to compute an expectation in their respective basis[1]. However, they encountered significant scalability issues related to the time complexity of quantum circuit generation, denoted by $\mathcal{O}(\sum_k n \cdot M_k)$, where M represents the time required to generate an expectation value per iteration over n samples, and k denotes the iteration index. To overcome this scaling issue, this work implements a phase estimation algorithm enhanced by Bayesian Optimization to solve the eignevalue problem instead. This method was evaluated on a dichromium gas (Cr_2) model, using data from a discrete variable representation of the Hamiltonian. ## Background {-} \ Taking the ro-vibrational Hamiltonian $\mathbf{H}_{RV}$ and performing the following operation to form a matrix $\mathcal{U}$ gives $\mathcal{U} = e^{i\mathbf{H}_{RV}t}$. The expression above allows for the application of the phase estimation algorithm, which estimates the eigenvalues of the unitary operators. The algorithm then uses these eigenvalues to approximate the eigenvalues of the original Hamiltonian. A matrix is denoted to be unitary if it follows the spectral theorem which is listed below.

Spectral Theorem: Let U be a normalized $K \times K$ complex matrix. There exists an orthonormal basis of K-dimensional complex vectors $\{|\psi_1\rangle, \dots, |\psi_K\rangle\}$, along with complex numbers $\lambda_1, \dots, \lambda_K$, such that $U = \lambda_1|\psi_1\rangle\langle\psi_1| + \cdots + \lambda_K|\psi_K\rangle\langle\psi_K|$. This matrix U can be diagonalized in an orthonormal basis consisting of its eigenvectors, with the corresponding eigenvalues on the diagonal.

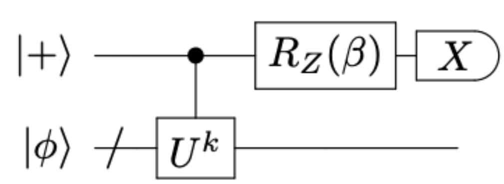
The main implementation of the phase estimation algorithm is shown below:

Quantum Phase Estimation Algorithm:

- **Input:** An n-qubit quantum state $|\psi\rangle$ and a unitary quantum circuit for an n-qubit operation U.
- **Promise/Assumptions:** $|\psi\rangle$ is an eigenvector of U.
- **Output:** An approximation to the number $\theta \in [0, 1)$ satisfying $U|\psi\rangle = e^{2\pi i\theta}|\psi\rangle$.

Bayesian QPE

Quantum phase estimation also takes a probablistic approach in the form of Bayesian optimization. Termed Bayesian Quantum Phase Estimation by Weibe and Granade in 2016[2]. It was made efficient in a highly noisy environment by Yamamoto et al. (2024)[3]. This method uses a quantum circuit to represent the posterior distribution of the phase estimation algorithm[2,3]. For a two qubit circuit, the authors used a quantum circuit which is an acyclic network of



quantum gates connected by wires. The quantum gates are matrices that represent quantum operations while the wires represent the **qubits** (see appendix) on which the gates act. The pictoral representation of the circuit is shown in Figure 1 (on the right).

Minim

underline{Results}

References

[1] Asnaashari, K.; Krems, R. V. Compact quantum circuits for variational calculations of ro-vibrational energy levels of molecules on a quantum computer. *arXiv.org* **2023**,

[2] Wiebe, N.; Granade, C. Efficient Bayesian Phase Estimation. *Phys. Rev. Lett.* **2016**, *117*, 010503.

[3] Yamamoto, K.; Duffield, S.; Kikuchi, Y.; Muñoz Ramo, D. Demonstrating Bayesian quantum phase estimation with quantum error detection. *Phys. Rev. Res.* **2024**, *6*, 013221.