AQAlg: Advanced Quantum Algorithms **2024 - 2025**

Lecture 4: Quantum chemistry and simulation

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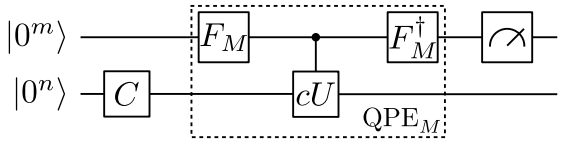
In previous lectures we discussed the use of quantum algorithms for solving essentially "non-quantum" problems such as factoring and optimization. However, the most natural (and maybe most promising) application of quantum computers is the simulation of quantum systems and quantum chemistry.

1 Ground state energy

A canonical problem in quantum chemistry is that of estimating the ground state energy of a molecular or condensed matter Hamiltonian. In full generality, this problem is QMA-hard (see next lectures by A. Grilo), and so we do not expect to solve this efficiently even on a quantum computer. However, there is hope that more "natural" Hamiltonians do allow for efficient quantum algorithms, while still being hard for classical algorithms.

1.1 Quantum phase estimation

There is a very natural quantum algorithm for estimating the ground state energy of an n-qubit Hamiltonian H that is based on quantum phase estimation. It corresponds to the following circuit:



Some details:

1. C is an n-qubit circuit that prepares an "ansatz state" $|\Psi_0\rangle$. Ideally this corresponds to a rough approximation of the ground state $|\phi_0\rangle$ of H.
2. The algorithm then applies quantum phase estimation on $|\Psi_0\rangle$ with operator $U = e^{iH}$ and precision $2^{-m} = 1/M$.
3. Finally, the phase estimation register is measured. The measurement result yields an estimate of the ground state energy.

Assume H has eigenvalue decomposition $H = \sum_{i=0}^{2^n-1} \lambda_i |\phi_i\rangle$, with eigenvalues $\lambda_0 \leq \cdots \leq \lambda_{2^n-1}$, and the ansatz has decomposition $|\Psi_0\rangle = \sum_i \alpha_i |\phi_i\rangle$. We can track the evolution in the circuit:

$$\begin{aligned} |0^m\rangle |0^n\rangle &\xrightarrow{C} |0^m\rangle |\Psi_0\rangle = \sum_i \alpha_i |0^m\rangle |\phi_i\rangle \\ &\xrightarrow{\mathrm{QPE}_M} \sum_i \alpha_i |\tilde{\lambda}_i\rangle |\phi_i\rangle \\ &\xrightarrow{\text{meas.}} |\tilde{\lambda}_i\rangle |\phi_i\rangle \quad \text{with probability} \quad p_i = |\alpha_i|^2. \end{aligned}$$

Here $\tilde{\lambda}_i$ is an estimate such that $|\tilde{\lambda}_i - \lambda_i| \leq 1/M$.

The *complexity* of the circuit is dominated by (i) the complexity of preparing the ansatz (i.e., implementing C), and (ii) the complexity of doing Hamiltonian simulation with Hamiltonian H for time $O(M)$.

Correctness of the algorithm hinges on the overlap $|\alpha_0|^2 = |\langle\Psi_0|\phi_0\rangle|^2$ of our ansatz state $|\Psi_0\rangle$ with the actual ground state $|\phi_0\rangle$. The probability of actually outputting an estimate of the ground state energy is $|\alpha_0|^2$. If this is sufficiently large (e.g., $|\alpha_0|^2$ constant), then after a constant number of iterations, the algorithm will output a correct estimate of the ground state energy. On the other hand, if we have no clue about the ground state $|\phi_0\rangle$, then we could pick as ansatz a uniformly random initial state, but then the overlap would only be $|\alpha_0|^2 = 1/2^n$ in expectation. The algorithm then returns an estimate of a uniformly random energy level of the Hamiltonian, which is typically useless.

Common ansatzes are based on the quantum adiabatic algorithm, classical approximations such as Hartree-Fock, or variational quantum circuits, as we discuss next.

1.2 VQE

Apart from needing a good ansatz, the phase estimation algorithm also requires that we can efficiently simulate the problem Hamiltonian H (i.e., implement e^{iHt}). While this would typically be feasible on a full-fledged quantum computer (see last lecture), there is currently interest in using "near-term" quantum computing devices for which Hamiltonian simulation might be too hard. The "Variational Quantum Eigensolver" (VQE) is a variational quantum algorithm that tries to address both the ansatz and the Hamiltonian simulation problem.

VQE is similar to QAOA, but it is designed to minimize the energy of a general Hamiltonian (rather than a diagonal cost Hamiltonian). I.e., it aims to solve

$$\min_{\langle\psi|\psi\rangle=1} \langle\psi|H|\psi\rangle\,. \tag{1}$$

By the variational principle of quantum mechanics, the minimum equals the ground state energy λ_0 of H, and it is achieved when $|\psi\rangle$ is a ground state of H. Similar to QAOA, VQE uses a parameterized circuit to generate $|\psi\rangle$. The parameters of the circuit are tuned so as to minimize the energy (1).

For QAOA, the Hamiltonian H was diagonal, and so we could easily evaluate the energy of the output state by measuring all qubits and evaluating the cost function $h(z)$ for the resulting bit string z. VQE considers general Hamiltonians, and so evaluating (1) requires more work. One approach is to use quantum phase estimation, as in the previous section, but this requires simulating the Hamiltonian evolution e^{iHt} and this can be expensive. Instead, the Hamiltonian H is decomposed as a linear combination of Pauli operators,

$$H = \sum_{i_1,\ldots,i_n=0}^{3} \alpha_{i_1\ldots i_n}\ \sigma_{i_1}\otimes\sigma_{i_2}\otimes\cdots\otimes\sigma_{i_n}.$$

We can then rewrite the energy as

$$\langle\psi|H|\psi\rangle = \sum_{i_1,\ldots,i_n=0}^{3} \alpha_{i_1\ldots i_n}\ \langle\psi|\sigma_{i_1}\otimes\sigma_{i_2}\otimes\cdots\otimes\sigma_{i_n}|\psi\rangle\,,$$

and so it suffices to estimate the energy of $|\psi\rangle$ with respect to each of the individual Pauli terms. This can be done relatively straightforwardly (see exercises). While there can be 4^n such terms, the sum can often be truncated to poly(n) terms. E.g., assuming 2-body interactions limits the sum to $O(n^2)$ Pauli terms.[1]

[1]The Max Cut Hamiltonian from last lecture is an example of this.