

Quantum chemistry on quantum computers

James Daniel Whitfield¹

Department of Physics and Astronomy
Dartmouth College, Hanover, NH, 03755 USA

Exercises

1. Counting states. Consider M sites and N the number of particles. What is the size of the state space of N bits, N qubits, N fermions and N bosons?

2. Atomic units are often used in the quantum computing literature and software. They are convenient for atomic and molecular energy scales where by $\hbar = e = m_e = a_0 = 1$. This sometimes leads to subtleties in understand the literature and translating back to quantities of interest.

(a) The charge in atomic units does not have the same units as the unit of charge in SI. Why not?

(b) Thermal energy is small compared to the electronic energy scale. Compute what the thermal energy is at 30, 20, -42° C. Compare against often quoted chemical accuracy of $10^{-4} E_h$ and to 1 kJ/mol.

(c) The sensitivity to energy differences in quantum chemistry is seen when considering the temperature dependence of rate reaction rates. The Arrhenius form for the reaction rate is $k = A \exp(-\Delta E/kT)$ dependence of thing on the temperature. If the error in the activation energy ΔE is off by 10^{-3} Hartree, what is the error in the reaction rate?

3. Energy surfaces. The concept of energy has a variety of meanings that you'll explore in this exercise.

Use quantum chemistry software to plot the mean-field potential energy surface of molecular hydrogen and beryllium hydride (vary only one Be-H bond length) as a function of distance. You should see a potential well but only if you include more than just the electronic energy. Both of these potential energy surfaces are featured prominently in the experimental quantum computing for quantum chemistry.

4. Fermions, bosons, and qubits. In ion trap quantum computers, specific electronic states of each ion are used as information degrees of freedom and then phonon modes of the crystal are used to couple these electronic states. Thus it appears that both bosonic and fermionic degrees compose the qubits and their coupling. Yet they still serve as distinguishable, addressable qubits. How can one resolve this seemingly contradictory situation?

¹ james.d.whitfield@dartmouth.edu

5. Entanglement in fermionic systems has additional complications that qubits do not. For qubits there is a single notion of partial trace. For fermions, there are two different ways to perform the partial trace. Consider a density matrix ρ_f with 3 modes and ρ_q over 3 qubits. Assume these state $\Psi_1 = a_1^\dagger a_2^\dagger |\Omega\rangle$ has probability 0.3 and state $\Psi_2 = a_1^\dagger a_3^\dagger |\Omega\rangle$ with probability 0.7. Also assume that $\Phi_1 = |110\rangle$ and $\Phi_2 = |101\rangle$ with probabilities 0.3 and 0.7. Consider the partial trace over 2 fermions, the partial trace over the first 2 fermionic modes. Similarly consider the partial trace over the first two qubits.

6. Field modes and Slater determinants. The translation from second quantization with creation and annihilation operators to coordinate representation is sometimes glossed over even in textbooks. To get from the second quantized expression to a standard coordinate representation called a *Slater determinant* one must use field modes. Evaluate $\langle vac | \hat{\psi}(x_1) \hat{\psi}(x_2) \hat{\psi}(x_3) | \Psi \rangle / \sqrt{(3!)}$ for $|\Psi\rangle = a_i^\dagger a_j^\dagger a_k^\dagger |\Omega\rangle$ expand expression in terms of orbitals $\{\phi_m(x)\}$, then organize your expression into a determinant.

7. First, second quantization. In principle, both formulations do not depend on the underlying basis. However, in practice, first quantization is primarily considered with grid-like localized basis states. Consider a lattice basis with M states and $N < M$ electrons. Consider fixed $N = 5$. At what values of M does the trade off in qubits favor first versus second quantization?

8. LCU and Trotter. Consider the cost of simulation using LCU and the first and second order Trotter approximants as a function of the time step size. Do so explicitly with the tight-binding C_6H_6 benzene molecule (where one only considers the π orbital system): $H = \sum_j t a_j^\dagger a_{j+1} + W a_j^\dagger a_j$. Use $t = 3$ and $W = 1$ for the Hamiltonian parameters and consider the qubit Hamiltonian under JW encoding. How might your answer change if the BK/BKSF were used instead? What about the binary encoding with $M - 1$ qubits?