Lecture 6: Second quantization
Reading: Ostlund and Szabo Chap 2, or other documents online like this one.

1 Review of second quantization

Before we discuss using quantum computers for quantum simulation, we need to review the formalism of second quantization. This discussion is very abbreviated and is mainly to motivate the form of the second-quantized Hamiltonian we will use throughout the course. A more detailed description of second-quantization can be found in Chapter 2 of Ostlund and Szabo or other references online.

First, let's review a generic electronic structure problem specified in second quantization. Consider a fermionic, nonrelativistic Hamiltonian under the Born-Oppenheimer approximation which in first-quantization is generically of the form:

$$H = T_e + U_{e,n} + U_{e,e} + U_{n,n} = -\sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2}\sum_{i,j\neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{I,J\neq I} \frac{1}{|\vec{R}_I - \vec{R}_J|} \quad (1.1)$$

This Hamiltonian is to be understood as an operator that acts on an N-particle state vector $|\psi\rangle$. For fermions, such a state needs to anti-symmetric with respect to the interchange of any two particles. The usual way to ensure that the state is indeed anti-symmetric is to take N single-particle orbitals and construct a determinant - a Slater determinant. A determinant naturally changes sign if we switch two columns. If we have N single-particle orbitals ϕ_j, we have a Slater determinant $|\phi_1 ... \phi_N\rangle$ where $|,,,\rangle$ is understood to indicate the Slater determinant, not a product! The full expression for the Slater determinant in terms of single-particle orbitals was given in class.

Now, we generally have to compute the action of H on our Slater determinant state. The rules about how to carry out this action are known as the Slater-Condon rules. An alternate approach to enforce these rules is to encode them into operators that act on a Fock space - a symmetrized or anti-symmetrized direct sum of single-particle Hilbert spaces tensored together N times (for N particles). These operators can add or subtract particles to the Fock space via operators $a^\dagger$ and a (just like you learned for the harmonic oscillator problem). A state in this Fock space is given as:

$$|\psi\rangle = |f_{n-1}...f_0\rangle = a^\dagger_{n-1}...a^\dagger_1 |vac\rangle \quad (1.2)$$

where $f_j \in \{0, 1\}$ indicates whether state j is empty or occupied. Note the canonical order of the Fock space is orbital $n-1$ is left-most and orbital 0 is right-most in the ket state. $|vac\rangle$ denotes the state with no particles.

The creation and annihilation operators operate on the Fock space in the following way:

$$\begin{aligned}
a^\dagger_j |f_{n-1}...f_{j+1}0f_{j-1}...f_0\rangle &= (-1)^{\sum_{s=0}^{j-1} f_s} |f_{n-1}...f_{j+1}1f_{j-1}...f_0\rangle & (1.3)\\
a^\dagger_j |f_{n-1}...f_{j+1}1f_{j-1}...f_0\rangle &= 0 & (1.4)\\
a_j |f_{n-1}...f_{j+1}1f_{j-1}...f_0\rangle &= (-1)^{\sum_{s=0}^{j-1} f_s} |f_{n-1}...f_{j+1}0f_{j-1}...f_0\rangle & (1.5)\\
a_j |f_{n-1}...f_{j+1}0f_{j-1}...f_0\rangle &= 0 & (1.6)\\
& & (1.7)
\end{aligned}$$

In this way the required anti-symmetry of the fermionic wavefunction is enforced. Thinking about these requirements in turn implies the creation and annihilation operators obey the following commutation relations:

$$\{a_i, a_j\} = a_i a_j + a_j a_i = 0 \tag{1.8}$$
$$\{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \tag{1.9}$$
$$\{a_j, a_k^\dagger\} = \delta_{jk} \tag{1.10}$$
$$\tag{1.11}$$

where {} indicate anti-commutator.

To translate the Hamiltonian from first-quantization to second quantization, consider that we have a first-quantized operator O and we want $\langle\psi|O|\psi\rangle$ where $|\psi\rangle$ is understood to be a Slater determinant. One can show that exactly the same overlap term will be produced in second-quantization if we let:

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \tag{1.12}$$
$$\tag{1.13}$$

where h_1 are the one-body terms (kinetic energy, electron-nuclear attraction) and h_2 are the two-body terms (from electron-electron repulsion). We won't worry much about the h one and two-electron tensors for now - just assume that they are tensors of numbers that will be provided when needed. If you are curious, they are the matrix elements of the various operators like kinetic energy and two-electron repulsion in the basis of the spin-orbitals.

There is a lot of detail we have skimmed over but at least you have a general idea of where the second quantized fermionic Hamiltonian comes from. An approach to find the ground state of this Hamiltonian is to solve the problem in a mean-field approximation (e.g. Hartree-Fock theory), and then apply a perturbation theory (such a coupled-cluster on a classical computer or unitary coupled-cluster on a QC) to that state to add in the correlation that is not present in HF (correlation energy being defined as $E_C = E_0 - \varepsilon_0$, where ε_0 is the exact energy and E_0 is the basis-set-converged HF energy. Classically, there are many approaches to recover this correlation energy. In this course, we will examine quantum algorithms to accomplish this task and others.