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# Calculating Entanglement in Molecules

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## Abstract

Entanglement is the correlation between the state of one particle and the state of another. When two particles are entangled, the transfer of information between them is instantaneous, a surprising result that now serves as the basis for **quantum computing**. Using entangled quantum bits (qubits), which store probabilities represented by wave functions in a superposition of states, quantum computing enables more efficient computations. Quantifying entanglement is essential to utilizing qubits, currently embodied in particles (ions, photons, electrons, etc.), not entire molecules. Our goal was to pioneer a method to **calculate entanglement between electrons in molecules using exact diagonalization**, which can be used to solve the Schrodinger Equation for **molecular Hamiltonians**. We calculated the entanglement of electrons within molecules represented by the **Hubbard Model**, ultimately to be used to rank molecular qubit candidates.

## The Hubbard Model

The Hubbard Model, a benchmark for molecule modelling, describes a lattice of sites containing electrons, where an electron can move, or tunnel, from site to site. We chose this model as the starting point in calculating entanglement in molecules due to its simplicity. Its Hamiltonian boils all interactions down to two components:

$$\hat{H} = \boxed{-t\sum_{i,\sigma}(\hat{\mathbf{c}}^{\dagger}_{i,\sigma}\hat{\mathbf{c}}_{i+1,\sigma} + \hat{\mathbf{c}}^{\dagger}_{i+1,\sigma}\hat{\mathbf{c}}_{i,\sigma})} + \boxed{U\sum_{i} n_{i,\uparrow}n_{i,\downarrow}}$$

$H_t$ : the kinetic energy, describing the movement of an electron from one site to another.

$H_U$ : the interaction energy, representing Coulombic repulsion when a site is occupied by two electrons.

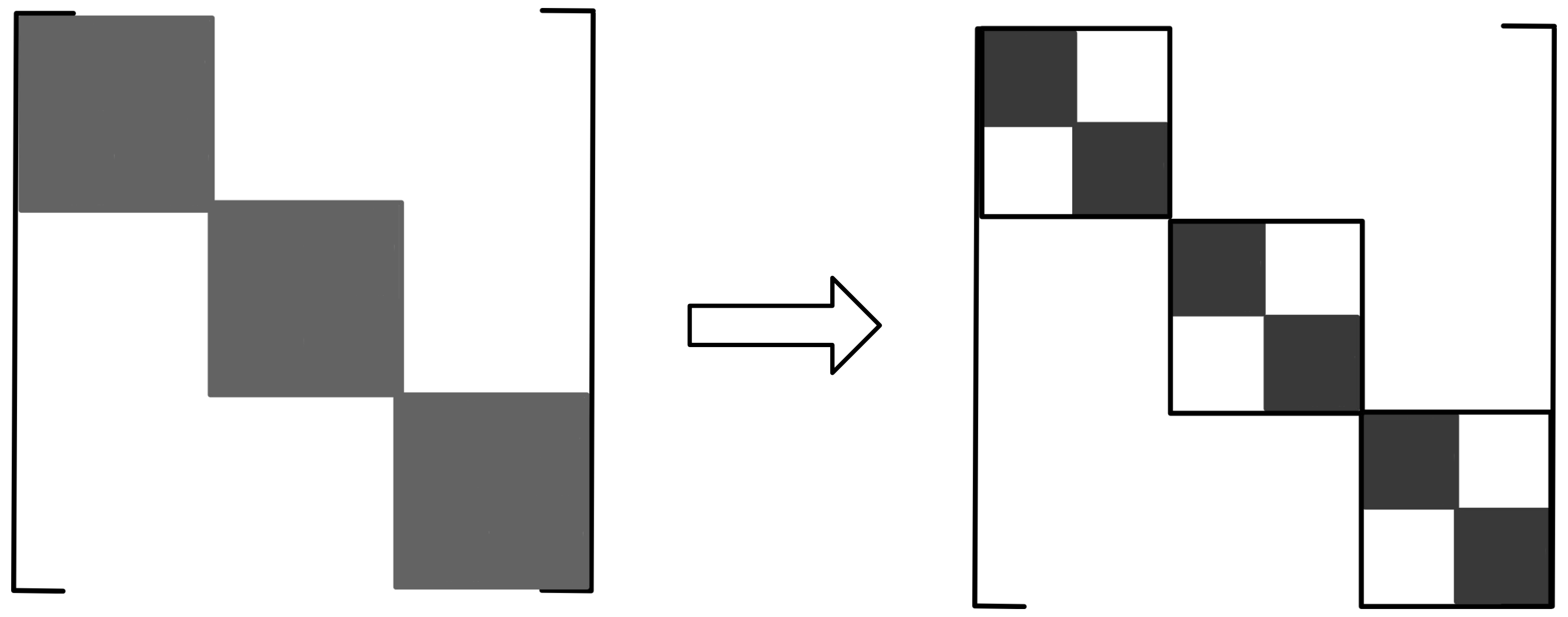
The requirements for this system include: a **total spin of zero** (achieved when the number of up spins equals the number of down spins), adherence to the **Pauli Exclusion principle**, and the electrons must move to adjacent sites when the system is specified to be 2D.

## Exact Diagonalization

**Exact diagonalization:** the process of formatting a Hamiltonian in matrix form, to then diagonalize using a computer.

**Diagonalization:** a method that converts a square matrix into a diagonal matrix that conveys the same foundational information.

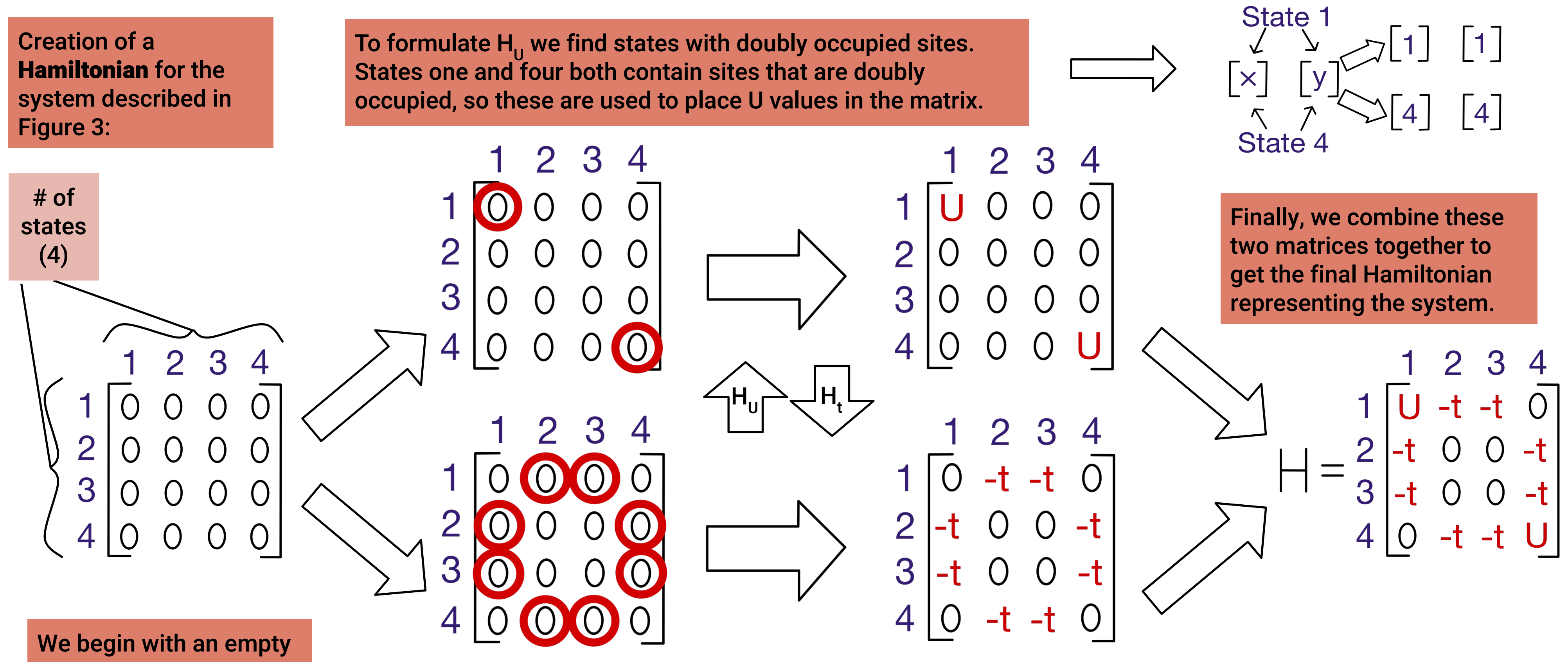
**Figure 1**: The process of exact diagonalization in action. The white space represents zeros, and the gray squares represent the information of the matrix, with the darker squares showing how this process condenses information onto the diagonal.



## Creating a System Hamiltonian

Creation of a **Hamiltonian** for the system described in Figure 3:

To formulate $H_U$ we find states with doubly occupied sites. States one and four both contain sites that are doubly occupied, so these are used to place U values in the matrix.



$$\begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & 0 \end{array}$$

$$\begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & U & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & U \end{array}$$

$$\begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & 0 & -t & -t & 0 \\ 2 & -t & 0 & 0 & -t \\ 3 & -t & 0 & 0 & -t \\ 4 & 0 & -t & -t & 0 \end{array}$$

Finally, we combine these two matrices together to get the final Hamiltonian representing the system.

$$H = \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & U & -t & -t & 0 \\ 2 & -t & 0 & 0 & -t \\ 3 & -t & 0 & 0 & -t \\ 4 & 0 & -t & -t & U \end{array}$$

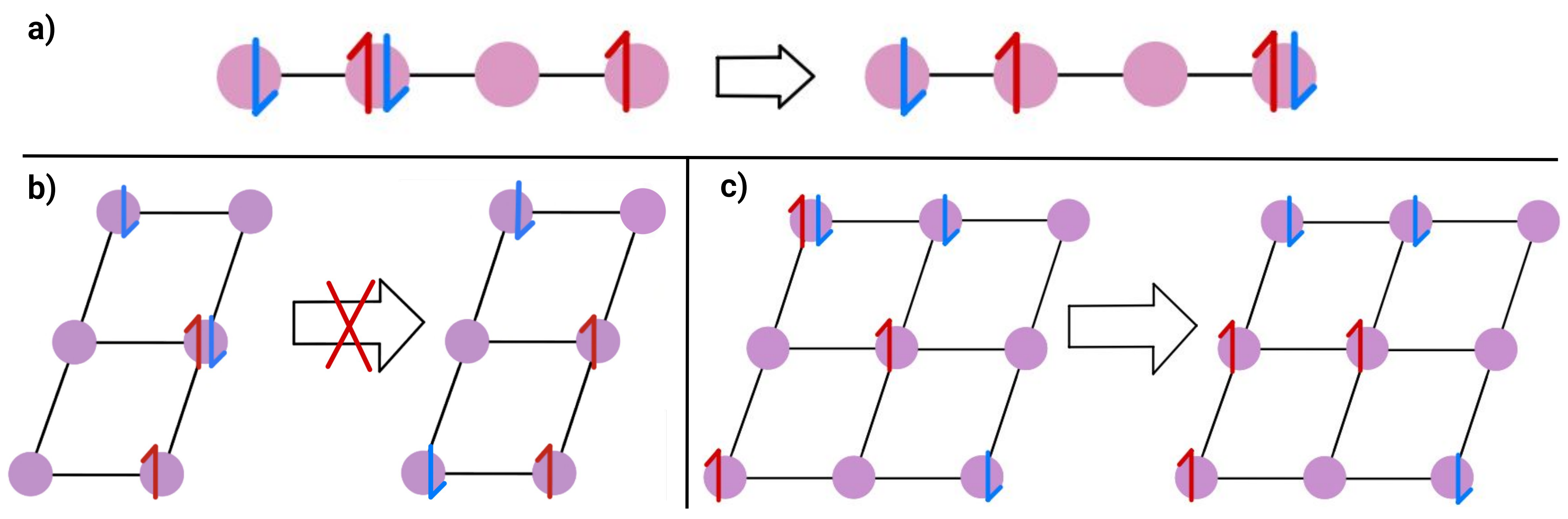
We begin with an empty 4 x 4 matrix, where 4 is the amount of possible states for the system.

U values range from 2 to 5, and t typically equals 1.

To formulate $H_t$, we find states with doubly occupied sites, i.e. states one and four. We then move one of the doubly occupied electrons (either the down spin or the up spin) and see if it matches any other states. This matching provides the coordinates for locations of t.

State one can transition into states two and three, and state four can transition into states three and two, meaning in the one column and row, the second and third positions will be locations for t. The Hubbard model Hamiltonian is written to incorporate symmetry in the matrix, explaining why values go in both the columns and rows of doubly occupied states.

**Figure 2**: **(a)** A four-site, four-electron 1D system. **Electron movement from a doubly occupied site** is not influenced by the site's location in the lattice. **(b)** A six-site, four-electron 2D system. The electron movement is diagonal, so the resulting state is invalid. **(c)** A 9-site, four-electron 2D system. Electron movement is limited to the sites immediately adjacent to the doubly occupied site.



## Automate

To automate, **we chose to represent states as binary strings**, using the Pauli Exclusion Principle and a total spin of zero to filter out unwanted states.

| | |
|---|---|
| 0101 | 1001 |
| 0110 | 1010 |

| | | |
|---|---|---|
| 001001 | 001010 | 001100 |
| 010001 | 010010 | 010100 |
| 100001 | 100010 | 100100 |

<u>States</u>: 2 sites, 2 electrons

As the number of sites grows, the number of states grows exponentially. Automation is limited to 10 sites.

<u>States</u>: 3 sites, 2 electrons

Using these strings, we automated the formation of $H_U$ and $H_t$, and subsequently H. By diagonalizing H, we received the energies and wavefunctions of the system.

To calculate the Renyi entropy of the system using the energies and wave functions, we used the following steps:

$$G = \frac{e^{-\beta H}}{\mathbb{I} + e^{-\beta H}}\,,\quad \beta = \frac{1}{k_B T}$$

$$\Downarrow$$

$$\rho_{B,\mathbb{I}} = G(\mathbb{I} - G)^{-1}\det(\mathbb{I} - G)$$

$$\Downarrow$$

$$\begin{bmatrix} 0.03824601 & 0.06792543 & 0.06792543 & 0.03198333 \\ 0.06792543 & 0.19989752 & 0.07410811 & 0.06792543 \\ 0.06792543 & 0.07410811 & 0.19989752 & 0.06792543 \\ 0.03198333 & 0.06792543 & 0.06792543 & 0.03824601 \end{bmatrix}$$

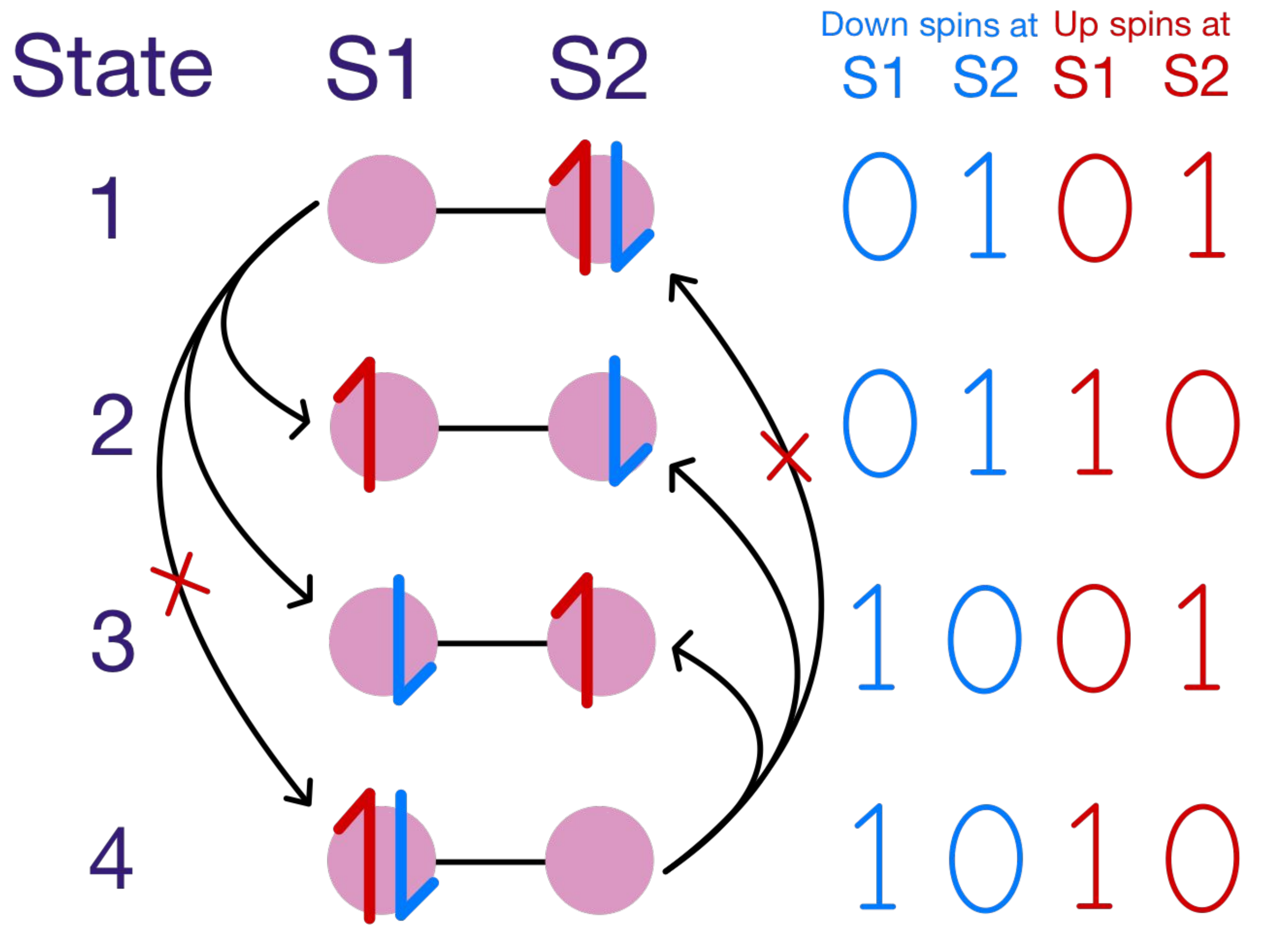


**Figure 3:** A two-site, two-electron system where each combination of electron orientations is a state, totalling four states. The arrows point from doubly occupied states to states where an electron may have transitioned to another site. Only one can move at a time, so state 1 cannot become state 4 in one movement, and vice versa.

## Conclusion

We created the Hubbard model Hamiltonian, a benchmark for molecules and more complex systems. By writing a program we automated the exact diagonalization process of creating a system-specific Hamiltonian for all 1D and 2D systems. The model cannot exceed 10 sites, a limitation created by the need for huge amounts of computer memory as the number of sites increases. **We were then able to extract energies (eigenvalues) and wavefunctions (eigenvectors)** from this Hamiltonian, and further work with these values in our program to **output the Renyi entropies of the system**. Our immediate next step is to use these Renyi entropies to calculate the entanglement of the electrons in a system, using the following equation:

$$\rho_B = \det(\mathbb{I} - G)(\exp\sum_{i,j}[\ln G(\mathbb{I} - G)^{-1}]_{i,j}\, c_i^{\dagger}c_j)$$

Using the values for entanglement calculated with this method, we will **rank molecular qubit candidates based on the strength of their entanglements**.

## Future Work

Our future work will focus on automating the creation of the molecular Hamiltonian:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{U}_{en} + \hat{U}_{ee} + \hat{U}_{nn}$$

This Hamiltonian more accurately represents a molecule and its electrons. With this Hamiltonian, we plan to write another program that performs exact diagonalization to extract the energies and wavefunctions of the system, which will require more nuance due to its complexity. We will also use Quantum Monte Carlo Methods to achieve our goals. Our end goal is to calculate the entanglement of molecules, and then rank current molecular candidates using these values. Discuss further relevance to quantum computing here.

## References

1. S Akbar Jafari, *Introduction to Hubbard model and Exact Diagonalization*, Iranian Journal of Physics Research (2008).

2. Siew-Ann Cheong, Christopher L. Henley, *Many-body density matrices for free fermions,* American Physical Society (2004)