Following excited molecules in their relaxation journey

Excited state dynamics with deep neural network wave functions

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In Short

- We are developing a method to model how molecules behave after absorbing light, such as during photosynthesis, in solar panels, or in the human eye to initiate vision.
- By combining deep neural networks with Quantum Monte Carlo (QMC) methods, we can simulate these complex processes with high efficiency and accuracy.
- Our approach enables us to track the movement of excited molecules, providing a deeper understanding of energy conversion and transfer mechanisms in materials like solar cells and pigments.
- This method simulates the ultra-fast transitions in molecular systems, revealing how molecules relax after being excited, offering insights into natural processes like photosynthesis and photoprotection mechanisms.

Understanding the behavior of molecules at a fundamental level requires solving the equations of quantum mechanics, which describe how electrons interact within molecules. This is especially important when molecules are excited by light, entering what is called an "excited state". Photoexcitations introduce energy into a molecule leading to an interesting cascade of reactions. These reactions are key to processes like converting sunlight into chemical energy in a leaf during photosynthesis, generating electricity in solar panels, or enabling vision through the isomerization of retinal chromophores in the human eye. They are also critical for photoprotection mechanisms, such as those involving tyrosine, which help protect skin cells from UV damage.

However, studying these ultrafast and intricate processes isn't easy. To accurately capture the interactions of excited electrons, we need to solve complex quantum equations. Traditional methods for doing this are either accurate but slow or fast but inaccurate, especially when studying large molecules or complex systems [1].

Our project aims to overcome this challenge by combining deep learning with advanced quantum simulations, specifically Quantum Monte Carlo (QMC) methods [2]. QMC is a well-established family of methods for solving the Schrödinger equation, which governs the behavior of quantum systems. It uses Monte Carlo sampling to evaluate quantum integrals, solving these equations stochastically. This approach offers a highly accurate description of molecular behavior, especially when paired with neural network wave functions.

As illustrated in Figure 1, our neural network QMC framework encodes positions of electrons and nuclei, solving the Schrödinger equation and thereby determining the quantum states of the molecules. To that end, deep learning methods for iterative optimization of the neural network parameters are employed. From the optimized quantum states properties such as excitation energies and interatomic forces can be calculated. By leveraging DeepQMC [3], an open-source framework that integrates deep neural networks with QMC methods, we can compute precise potential energy surfaces (PES) for ground and excited states across various molecular configurations—an otherwise difficult task for contemporary quantum chemistry methods.

To capture the dynamics of excited states, we integrate DeepQMC results with specialized software that performs surface hopping simulations, such as SHARC [5]. This method allows us to model how excited electrons transition between different states, capturing critical processes like conical intersections and intersystem crossing, as illustrated in Figure 2. These processes are vital for understanding how energy moves through a molecule after it absorbs light, enabling us to create a detailed map of energy pathways.

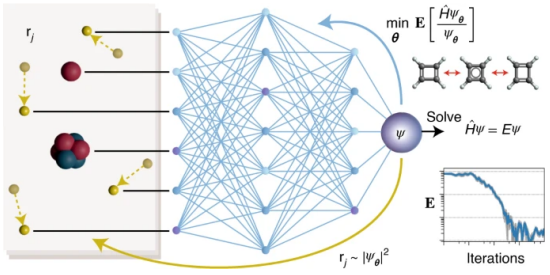

***Figure 1:** Pictorial representation of our neural network Quantum Monte Carlo (QMC) framework. The image illustrates how the positions of electrons and nuclei in a molecule are encoded into a neural network, which then solves the Schrödinger equation to compute the energy of the system. On the left side, the electrons are shown moving around the nuclei, representing the quantum mechanical nature of the problem. The output of the neural network allows for iterative optimization, minimizing the energy until convergence. From Ref. [2].*

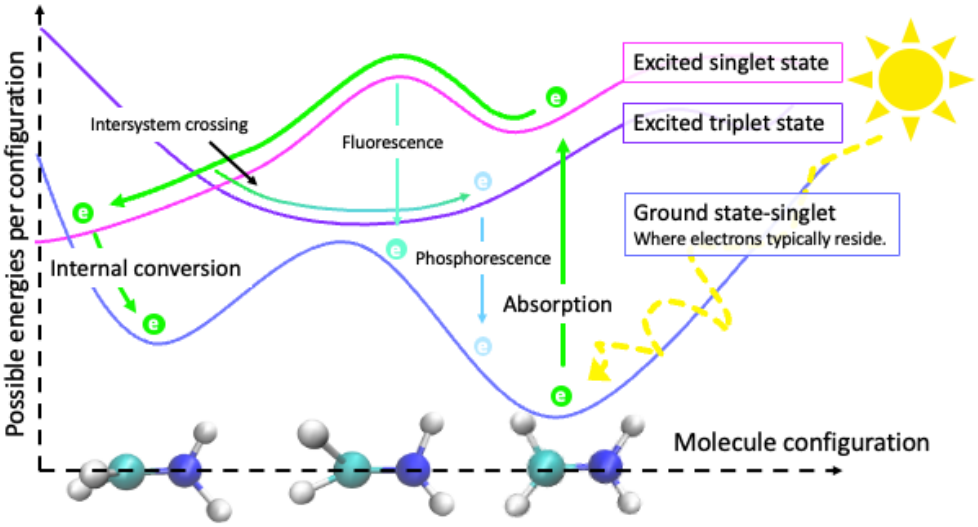

Figure 2: *Energy diagram illustrating the excitation and relaxation pathways of a molecule. This diagram shows the potential energy surfaces for a ground state-singlet (blue curve), an excited singlet state (pink curve), and an excited triplet state (violet curve). When a photon is absorbed (yellow arrow), the electron is excited from the ground state to an excited state. Various relaxation processes are illustrated, including internal conversion (green arrow), where the molecule transitions between states without emitting light, and intersystem crossing (light blue arrow), a transition between singlet and triplet states. Radiative processes such as fluorescence and phosphorescence are also depicted they are pathways where the molecule emits light while returning to a lower energy state. The molecular structures along the bottom axis represent changes in molecular configuration as the molecule moves along these energy pathways.*

The diagram in Fig. 2 further illustrates, how an electron, upon absorbing a photon, transitions from the ground state to an excited state and then follows various pathways to relax back.We depict both radiative processes, such as fluorescence and phosphorescence, where light is emitted, as well as non-radiative transitions like internal conversion and intersystem crossing, which dissipate energy through molecular vibrations and interactions.

One of the key advantages of our approach is its ability to model not just a single molecular configuration at a time, but how the same molecule behaves across different geometries. For instance, when a molecule bends or twists after absorbing light, altering its geometry, our neural network models can adapt to these changes. This versatility allows us to better understand how molecules return to their stable states, providing insights into phenomena like fluorescence, where a molecule emits light as it releases energy, or energy transfer processes within plant pigments.

In summary, our project aims to explore the hidden world of excited molecules, providing a clearer picture of how they capture, transfer, and release energy. By combining the accuracy of QMC methods with the expressiveness of neural networks and the dynamical modeling provided by surface hopping, we hope to contribute to the development of more efficient solar energy technologies and deepen our understanding of the natural processes that power life on Earth.

WWW

https://www.mi.fu-berlin.de/en/math/groups/ai4s/index.html

More Information

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[2] J. Hermann, Z. Schätzle, F. Noé *JCTC* **20**, 7922 (2024). doi:10.1021/acs.jctc.4c00678

[3] J. Hermann, Z. Schätzle, P. B. Szabó, M. Mezera DEEPQMC open source package https://github.com/deepqmc/deepqmc

[4] P. B. Szabó, Z. Schätzle, M. T. Entwistle, F. Noé *Nat. Chem.* **12**, 891 (2020). doi: 10.1021/acs.jctc.4c00678

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Project Partners

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DFG Subject Area

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