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RPPR Final Report
as of 28-Jun-2022

Agency Code: 21XD

Proposal Number: 75575CHII **Agreement Number: W911NF-19-1-0433**
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Report Date: 14-Feb-2021 Date Received: 19-Jun-2022
Final Report for Period Beginning 15-Aug-2019 and Ending 14-Nov-2020
Title: STIR Proposal: Radiationless Transitions Induced by Natural Incoherent Light
Begin Performance Period: 15-Aug-2019 **End Performance Period:** 14-Nov-2020
Report Term: 0-Other

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STEM Degrees: **STEM Participants:**

Major Goals: The proposed research was to develop and compare various fully dynamics-free quantum methods for nonadiabatic radiationless processes under natural conditions, e.g., when induced by natural light.

Accomplishments: Light harvesting processes are often computationally studied from a time-dependent viewpoint, in line with ultrafast coherent spectroscopy experiments. Yet, natural processes take place in the presence of incoherent light, which induces a stationary state. Such stationary states can be easily described using the eigenbasis of the molecular Hamiltonian, but for realistic systems a full diagonalization is prohibitively expensive. We introduced and computationally compared three efficient computational approaches to obtaining the stationary state which circumvent the system Hamiltonian diagonalization. The connection between the incoherent perturbations, decoherence, and Kraus operators was established and used to discuss the relation between coherent and incoherent quantum yields.

Training Opportunities: All computations and analyses were carried out by Mr. Ignacio Loaiza, a graduate student in Chemical Physics. in addition to training in theoretical methods, he utilized state-o-the-art parallel processing computers. Hence, his training extended over both analytical methods and computational implementation.

Results Dissemination: Manuscript published as :

`Computational Approaches to Efficient Generation of the Stationary State for Incoherent Light Excitation", I. Loaiza, A. Izmaylov and P. Brumer, J. Chem. Phys. 154, 124126/1-10 (2021). ArXiv:2011.03084THe topic

The results were presented in several discussion groups over Zoom.

Honors and Awards: Nothing to Report

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Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Co-Investigator
Participant: Artur Izmaylov
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: PD/PI
Participant: Paul Brumer
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Ignacio Loaiza
Person Months Worked: 9.00 **Funding Support:**
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National Academy Member: N

International Collaboration:

CAN

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Partners

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I certify that the information in the report is complete and accurate:
Signature: Paul BRumer
Signature Date: 6/19/22 10:51PM

In this work, we developed methods for the generation of the system stationary density matrix originating under incoherent light excitations. Such a density matrix can be used for calculating any observable of the system under natural solar light, and it acquires a completely diagonal structure in the energy eigenbasis. Using Kraus operators for modeling a general quantum operation, we showed how this density matrix can be obtained through three different approaches not involving explicit diagonalization.

The first approach performs a dynamical evolution of an initial wavefunction while averaging its associated pure density matrix at different times, recovering a mixed density matrix that approximates the stationary one. We noted how the properties obtained from coherent and incoherent excitations will coincide at short times whenever the linear absorption spectrum is localized over a small energy interval or when the spectrum of the incident light is structureless.

The second approach uses a Lindblad-like equation to induce decoherence in an initially pure state, while the third approach employs a Lanczos shift-and-invert iterative algorithm, building increasingly better guesses to the eigenstates that play a role in the decoherence of the system. The convergence of different seed vectors was studied, showing how an imbalance in their properties might skew the Lanczos process.

The Lindbladian approach suffers from a poor computational efficiency, making it unusable for realistic molecular systems. Both the dynamical averaging and the Lanczos steps behaved more favorably, obtaining accurate approximations of observables with only a fraction of the cost of a full diagonalization. Both the methods offer a computationally efficient and scalable approach for obtaining the stationary density matrix of the system under incoherent light excitations, and the implementation for higher dimensional systems is promising. Scaling of each method with respect to the system size, as well as the case of a continuous spectrum,