Mori-Zwanzig: A New Closure To Hedin's Equations For Strongly Correlated Systems

Outline: Solar energy has the momentum to replace fossil fuels in the green transition. To continue this trend, the discovery of more efficient photovoltaic materials is necessary. Core spectroscopy has long been used to elucidate the electronic structure of materials. It is not new, but the ability to do this on an attosecond time scale is, as evidenced by the Nobel Prize in 2023. Such a short time scale lends high resolution to molecular processes, which allows for the design of improved solar materials. Computation can guide these experiments, as exemplified by the classes of Figure 1. Density Functional Theory (DFT) has long served as the computational workhorse of materials science, due to its reasonable accuracy at low expense. However, it treats the repulsive interactions between electrons using an approximate exchange-correlation functional, leading to variable results with a lack of systematic improvability [1]. A potential solution is the application of Green's functions in many-body perturbation theory (MBPT). Central is the Dyson equation,

$$G = G_0 + G_0 \Sigma G, \tag{1}$$

which relates the Green's function of the fully interacting system G to that of the non-interacting system G_0 through the self-energy Σ, which is designed to capture the many-body interactions neglected by G_0. Hedin provided a closed set of 5 equations that can be used to obtain G and Σ. In the common GW approximation of Hedin's framework, the self-energy Σ takes the form iGW, where W is the screened Coulomb interaction. Various levels of self-consistency can be done within GW. The most basic is the one-shot G_0W_0, where the self-energy is calculated using the non-interacting Green's function and the bare Coulomb potential, i.e., $\Sigma = iG_0W_0$. Surprisingly, G_0W_0 has been shown to be quite accurate even at a modest computational cost, due to a fortuitous cancellation of errors. However, it shows a strong starting point dependence on G_0, which again implies the lack of systematic improvability. At the other extreme, we have fully self-consistent GW (scGW). Even at the high computational expense necessitated by full self-consistency, this scheme often does not deliver improved results over G_0W_0. To remedy this, one has to include vertex corrections beyond the GW approximation within Hedin's framework [2], which is computationally intensive. The root of these issues is that Hedin's equations solve for the self-energy Σ through a perturbative expansion in the interaction strength W. The GW approximation is accurate for weakly correlated systems where this expansion is reasonable, but it is not for the strongly correlated, where the interaction is large.

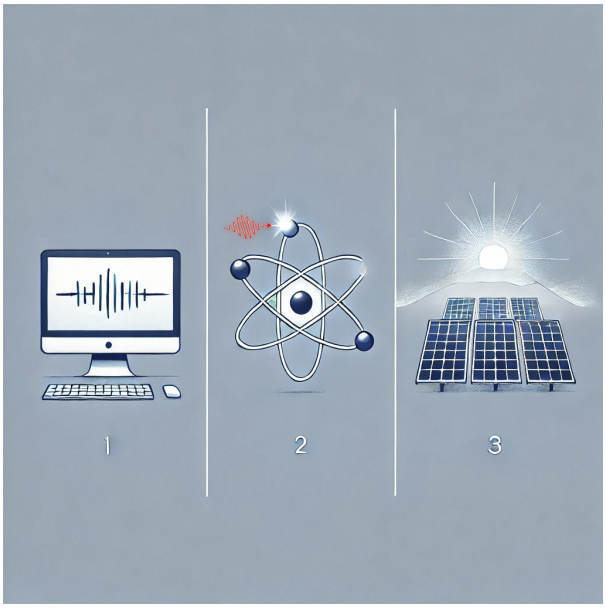

Figure 1: (1) The development of computational methodologies can (2) aid in the spectroscopy of materials to (3) produce more efficient solar cells

The Mori-Zwanzig (MZ) theory offers an alternative. Originating from statistical physics, one starts from a similar Dyson equation 1, but the self-energy Σ is replaced by a memory kernel. This memory kernel is expanded in powers of the evolution time t, whereas in GW the self-energy is expanded in powers of the interaction strength W. This makes the series expansion of Dyson's equation converge faster with MZ for strongly correlated systems. Recently, a diagrammatic theory for MZ has been introduced in the form of tree diagrams [3], as opposed to the Feynman diagrams of GW, suggesting the potential for a computational implementation. However, this has not been done yet and is the goal of the proposed work.

Research Plan

Aim 1 The uniform electron gas (UEG) is a paradigmatic system in condensed matter physics. As part of my rotation project with Prof. Lee, I will implement fully self-consistent GW (scGW) for the UEG. I am interested in whether I can corroborate the result reported in the literature [4], where scGW predicts only one quasi-particle peak in the frequency spectrum, while highly accurate Quantum Monte Carlo (QMC) simulations show an additional satellite peak. In the literature, vertex corrections going beyond the GW approximation have been shown to address this issue within Hedin's framework.

Aim 2 Perform a similar investigation on the UEG in the MZ framework. Assess improvements over GW. Of particular interest is how many terms for the perturbative expansion in the MZ framework need to be included to achieve a similar accuracy to GW and what computational scaling this comes with.

Aim 3 Apply the MZ framework to a realistic condensed matter system. The UEG is known to provide a good description of metallic systems, so the transition should be natural. The eventual goal is to study strongly correlated semiconductors composing photovoltaic systems with the MZ framework.

Aim 4 During my project, I will be using various diagrammatic theories; I have a fine motor impairment resulting from a stroke, so this project will provide the motivation to improve my handwriting through practice. In addition, I will gain experience in how to typeset diagrams, both tree and Feynman, in LaTeX.

Motivation and Intellectual Merit: During my time at Caltech, I analyzed a newly-developed CCSD method for periodic systems in comparison with DFT, as applied to heterogeneous catalysis [1]. In my senior thesis, I implemented G_0W_0 for molecules, with an analytic full frequency integration. In addition, I took a recent course where I learned to apply matrix product state ideas to, among others, implement the time evolution block decimation algorithm (TEBD). This combination of practical experience performing simulations on periodic systems with a theoretical background on GW theory and quantum many-body physics has prepared me to think about alternative formulations to the GW approximation with the MZ of open quantum systems in condensed matter. I will be doing this with Professor Joonho Lee, an expert in applying quantum chemistry to the condensed phase, with a specialty in quantum simulation. In addition, I gave talks on my senior research (Caltech Senior Thesis and Goldwater Symposiums) and attended the BerkeleyGW conference, where I learned about the methodology developments that enable one to track excited state phenomena, such as excitons, in energy materials.

Broader Impacts The proposed research will develop a computational implementation of the theoretical MZ framework. Much thought has been put into improving upon the GW approximation; this will investigate a hitherto unexplored alternative with the potential to upend how MBPT is done for strongly correlated systems. This work will improve upon traditional ab initio core spectroscopy techniques, enabling the design of improved photovoltaic materials.

References

[1] Patryk Kozlowski. Elucidating Catalysis with the "Gold Standard" of Quantum Chemistry. *CURJ*, June 2021. URL `https://curj.caltech.edu/2021/06/29/elucidating-catalysis-with-the-gold-standard-of-quantum-chemistry/`.

[2] A. L. Kutepov and G. Kotliar. One-electron spectra and susceptibilities of the three-dimensional electron gas from self-consistent solutions of Hedin's equations. *Physical Review B*, 96(3):035108, July 2017. doi: 10.1103/PhysRevB.96.035108. URL `https://link.aps.org/doi/10.1103/PhysRevB.96.035108`. Publisher: American Physical Society.

[3] Yuanran Zhu. Combinatorial Mori-Zwanzig Theory, November 2022. URL `http://arxiv.org/abs/2210.08395`. arXiv:2210.08395 [cond-mat, physics:math-ph].

[4] B. Holm and U. von Barth. Fully self-consistent GW self-energy of the electron gas. *Physical Review B*, 57(4):2108–2117, January 1998. doi: 10.1103/PhysRevB.57.2108. URL `https://link.aps.org/doi/10.1103/PhysRevB.57.2108`. Publisher: American Physical Society.