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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 and to keep it going 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 guides these experiments, as exemplified by the workflow 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. The self-energy Σ 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, 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 highest level is fully self-consistent GW (scGW). Even at the high computational expense of scGW, the scheme often does not deliver improved results over the lower levels of self-consistency. To remedy this, one has to include vertex corrections beyond the GW approximation [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.

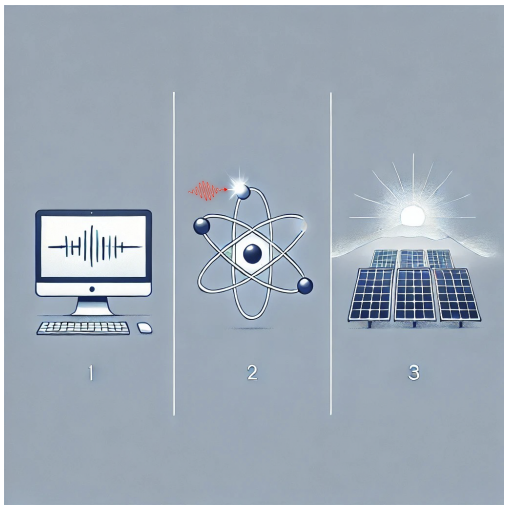

Figure 1: (1) The development of computational methodologies (2) elucidates the core spectroscopy of materials to (3) produce more efficient solar cells.

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 now expanded in powers of the evolution time t, making the Dyson series expansion with MZ converge faster for strongly correlated systems. Recently, a diagrammatic theory for MZ with Green's functions has been introduced in the form of tree diagrams [3], as opposed to the Feynman diagrams of GW. To date, however, no computational implementation has been done and the proposed work will address this gap.

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 am implementing fully self-consistent GW (scGW) for the UEG. Now, I do not have prior experience with the UEG or scGW. However, in past research, I ran quantum chemistry calculations on a periodic system, like the UEG, and completed a senior thesis project on the G_0W_0 method within the same GW approximation that scGW follows. I will first corroborate the

reported result [4], where scGW misses a satellite peak in the frequency spectrum found by highly accurate Quantum Monte Carlo (QMC) simulations.

Aim 2 In the literature, expensive vertex corrections going beyond the GW approximation have been shown to reproduce this satellite peak. I will see if MZ offers a cheaper solution, comparing the number of terms in its perturbative expansion needed to achieve an accuracy on par with vertex-corrected GW for the UEG. I am prepared to work with the MZ theory of open quantum systems from experience with a recent class on quantum many body physics, where I learned to apply matrix product state ideas, culminating in my implementation of the Time Block Evolution Decimation (TEBD) algorithm. More generally, this exploration of MZ on the UEG will enable me to draw connections between MZ and GW for solids, building upon previous work connecting diagrams between GW and wave function-based methods for molecules [5].

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

Motivation and Intellectual Merit: 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.

Broader Impacts: My first research internship was with a spectroscopist, and many of my advanced classes were taught by his kind. I have gained a respect for the spectroscopy community; they use the theoretical chemistry that interests me to discover technologies driving the green energy transition. With my disability inhibiting me from doing experiments, I want to make advances on the computational side, striking up collaborations with them through my novel application of Green's functions in the Mori-Zwanzig theory in their field. As a byproduct of the proposed work, I will gain expertise in photovoltaic materials, which will prepare me to think from the policy perspective of how to efficiently bring solar energy to the consumer.

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.

[5] Malte F. Lange and Timothy C. Berkelbach. On the relation between equation-of-motion coupled-cluster theory and the gw approximation. *Journal of Chemical Theory and Computation*, 14(8):4224–4236, July 2018. ISSN 1549-9626. doi: 10.1021/acs.jctc.8b00455. URL `http://dx.doi.org/10.1021/acs.jctc.8b00455`.