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 its propagation, the discovery of more efficient photovoltaic materials is necessary. Core spectroscopy is used to elucidate the electronic structure of such materials. Experimentalists do this in conjunction with ab initio computations.

Therefore, figure 1 shows how (1) the development of computational methodologies can (2) aid in the spectroscopy of materials to (3) produce more efficient solar cells. Density Functional Theory (DFT) has long served as the go-to computational method in materials science, due to its reasonable accuracy at low computational 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.

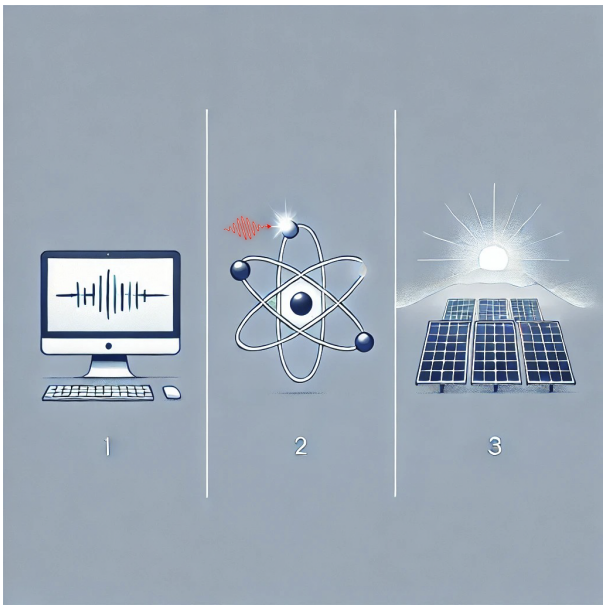

Figure 1: Impact of computational development.

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 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 difficult. 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 systems where this expansion is reasonable, but it is not for strongly correlated systems, where the interaction is large.

The Mori-Zwanzig (MZ) theory offers an alternative. Originating from statistical physics, the role of the self-energy Σ is replaced by a memory kernel. The key difference is that 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 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. However, no computational methodology has been developed for MZ. This 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. Vertex corrections have been shown to address this issue within Hedin's framework.

Aim 2 Perform a similar investigation on the UEG in the Mori-Zwanzig framework. Assess improvements over GW in terms of accuracy, but also computational scaling.

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.

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 performed research and wrote a publication analyzing post-HF wave function-based methods for periodic systems, as applied to heterogeneous catalysis. In my senior thesis, I implemented G_0W_0 for molecules. This combination of practical experience performing simulations on periodic systems with a theoretical background on GW theory has prepared me to think about Green's functions in condensed matter. I will be doing this with Professor Joonho Lee, an expert in applying quantum chemistry to the condensed phase. 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 state of the GW community that I will be a part of in the future.

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. Eventually, this work will enhance the investigation of strongly correlated systems, enabling the design of improved photovoltaic materials.

References

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