NTNU
Kunnskap for en bedre verden

DEPARTMENT OF CHEMISTRY

BACHELOR THESIS

State of the art for temperature dependence in Green's function methods for electronic structure

Author:

Marcus Takvam Lexander

Supervisor:

Ida-Marie Høyvik

April, 2020

Abstract

The effects of temperature on electronic structure is usually neglected because of energy gaps being much larger than the thermal energy. This however does not hold for systems such as condensed matter, which is highly relevant for fields like high temperature superconductors and the semiconductor industry. New developments of finite-temperature Green's function methods seek to address this. Here we look at the GF2 method and its recent progress in the applications on periodic systems. The method has been used to predict the phase properties of the 1D periodic hydrogen lattice at various temperatures and pressures, and thus the construction of a phase diagram. It has also been tested on the 1D boron nitride lattice, a larger, more realistic system, where similar phase properties was computed at various temperatures. The predicted band gap matched the expected magnitude from the real 2D counterpart.

Contents

1 Introduction

In electronic structure theory, temperature effects are usually not taken into account. This is due to the fact that the magnitude of energy from temperature is usually much lower than the difference of electronic energy levels. For molecular systems, almost all temperature dependent effects are due to vibrations. However, for larger systems where there are many states close in energy, temperature effects suddenly become a very important contribution to the electronic structure. This is highly relevant for fields such as high temperature superconductors and semiconductors, where the temperature dependence of the electronic structure is one of the key effects that determines the very specific qualitative properties, such as super conductivity, that is desired for such materials. For all current day applications of superconductors, as well as all research into quantum computing, large amounts of expensive cooling, often using liquid helium, is required.

There have been some work to adapt the traditional quantum chemical methods to incorporate temperature in the calculations. The Hartree-Fock method (HF), which is a cornerstone of quantum chemistry and a starting point for a many other methods, has finite-temperature variants[1]. However, Hartree-Fock is, even for zero-temperature calculations, inadequate for describing a many chemical phenomenon because of its defining lack of description of the electronic correlation energy by being a mean-field method. Other methods that build on top of the Hartree-Fock solution have been developed, so called post Hartree-Fock methods. In HF the wave function is parameterized as a single Slater-determinant[2, 3], but these post HF methods are usually based on some form of taking various excited state determinants into account. Most notably, the configuration interaction (CI) formalism is a straightforward approach, where contributions of excited determinants are determined by variation. The full CI (FCI) method takes all of these determinants into account, and because they form a complete set of functions the method is exact. However, because of binomial scaling of the amount of determinants, this method is completely infeasible computationally. For more than benchmarks on very small systems, truncated methods such as CIS and CISD, where, respectively, only singly (S) and singly + doubly (SD) excited determinants are used. These methods have also been adapted for finite temperature[4, 5], however the computational cost of this quickly becomes too much because of the need for finding both excited state determinants and corresponding Boltzmann-factors.

Because of the straight forward manner in which CI methods parameterize excited determinants, many properties are lost in the truncated methods such as size-consistency. This can be improved by parameterizing the excited determinants in a more intelligent way, which gives rise to methods such as MP2 perturbation theory and coupled cluster theory. These methods also have finite temperature variants[6, 7, 8, 9]. However, as for the CI formalism, the extension of these methods to incorporate temperature is similarly convoluted and expensive, so it seems as though in general it would be useful to have some alternative to wavefunction models for modeling temperature dependent properties.

The Density functional theory (DFT) formalism has given rise to some very popular methods that have been the workhorses of quantum chemistry and molecular modeling for decades. However, a notorious difficulty of these methods is that the exchange-correlation functional is difficult to parameterize. Because of this, many such functionals have been developed, based on different criteria depending on what properties one wants to describe. Many of these functionals are based on empirical data and good accurate benchmarks from other methods, such as FCI. There does exist a finite-temperature DFT formalism[10, 11]. The problem however, is that there does not exist any widely used finite-temperature methods that could serve as a benchmark for developing functionals, which is already a problem in the zero temperature case. Because of this there has not been much research into its use, and it remains a quite unexplored territory, apart from some studies that have been done on warm dense matter[12]. Because of the lack of research, there is also very little knowledge about how many virtual orbitals one has to use to get accurate descriptions of systems. This makes for a lot of overcompensation with how many orbitals are used, which comes at a great computational cost. There is some research into orbital-free DFT[13], however this is also a very much unexplored area.

A much less used method for electronic structure is the use of Green's functions. Green's functions are a very general tool for solving differential equations[14], that has seen a lot of use in different fields for a long time, but has not until recently found its way into computational chemistry. In quantum mechanics, the theory of Green's functions (often called propagators) has been well known for a long time[15], however for the many-body interactions of realistic systems, such as large molecules and solids, the methods have been computationally cumbersome compared to methods such as DFT because of the memory requirements of computing on large complex energy grids. However in recent years, as computing power and memory becomes progressively cheaper, the methods have resurfaced and more research has gone into developing them.

In contrast to the wavefunction models, the temperature dependence in Green's function models arises in a much more straight forward manner and has been derived in numerous books[16, 17, 18]. However, because of the memory requirements, numerical calculations of thermodynamic quantities, using a fully self-consistent imaginary axis Green's function, have until recently mostly been done on small model systems [19, 20, 21, 22]. There has been some large scale real axis Green's function calculations for single shot G_0W_0, GW_0, or semi self-consistent GW for large realistic systems[23, 24, 25, 26, 27, 28, 29]. These calculations however, can produce non-unique thermodynamic quantities. Until now only a few research groups have generalized the self-consistent finite-temperature Green's function formalism to deal with a general Hamiltonian[30, 31, 32, 33, 34, 35].

To shed light on the current state of temperature dependent Green's function methods I will here take a look at a the first application of this Matsubara formalism for calculation of thermodynamic properties of periodic systems[36], as well as an application of one of the previously popular GW approximation method on nickel oxide.

2 Theory

2.1 General Green's function and the Schrödinger equation

A Green's function is a solution to an inhomogeneous differential equation of the form [37]

$$[z - L(r)]G\left(r, r'; z\right) = \delta\left(r - r'\right), \quad z \in \mathbb{C} \tag{2.1}$$

where $L(r)$ is some linear, Hermitian differential operator, δ is the Dirac delta function and G is the Green's function.

Using

$$
\begin{aligned}
\delta\left(r - r'\right) L(r) &\equiv \langle r|L|r'\rangle \\
G\left(r, r'; z\right) &\equiv \langle r|G(z)|r'\rangle \\
\langle r|r'\rangle &= \delta\left(r - r'\right) \\
\int dr|r\rangle\langle r| &= 1
\end{aligned}
\tag{2.2}
$$

we can rewrite (2.1) as

$$(z - L)G(z) = 1 \tag{2.3}$$

If we now assume L to possess a complete set of eigenfunctions ϕ_n with corresponding eigenvalues λ_n we have

$$L\left|\phi_n\right\rangle = \lambda_n\left|\phi_n\right\rangle \tag{2.4}$$

$$\langle\phi_n|\phi_m\rangle = \delta_{nm} \tag{2.5}$$

$$\sum_n |\phi_n\rangle\langle\phi_n| = 1 \tag{2.6}$$

(2.3) can now be solved as

$$G(z) = \frac{1}{z - L} \tag{2.7}$$

multiplied by (2.6) to get

$$G(z) = \frac{1}{z - L} \sum_n |\phi_n\rangle\langle\phi_n| \tag{2.8}$$

and distribute into the the unitary operator and substitute L with the corresponding eigenvalue for each n

$$G(z) = \frac{1}{z - L}\sum_n |\phi_n\rangle\langle\phi_n| = \sum_n \frac{1}{z - L}|\phi_n\rangle\langle\phi_n| = \sum_n \frac{|\phi_n\rangle\langle\phi_n|}{z - \lambda_n}, \qquad z \neq \lambda_n \tag{2.9}$$

5

We can now see that G is a sum of poles which correspond to the eigenvalues of L. To define G when $z = \lambda_n$ we can use the following limit

$$G^{\pm}(r, r'; \lambda) \equiv \lim_{s \to 0^+} G(r, r'; \lambda \pm is) \tag{2.10}$$

We can now express the solution of the form

$$[z - L(r)]u(r) = f(r) \tag{2.11}$$

in terms of the Green's function[38]

$$u(r) = \begin{cases} \int G(r, r'; z) f(r') \, dr' & : z \neq \lambda_n \\ \int G^{\pm}(r, r'; \lambda_n) f(r') \, dr' + \phi_n(r) & : z = \lambda_n \end{cases} \tag{2.12}$$

If we let $L(r)$ be the Hamiltonian operator, $H(r)$ with eigenvalues E_n, the time independent Schrödinger equation can be written as

$$H\psi = E\psi \tag{2.13}$$

or equivalently

$$[E - H(r)]\psi(r) = 0 \tag{2.14}$$

We can then define the Green's function for the Schrödinger equation as the solution of

$$[E - H(r)]G(r, r'; E) = \delta(r - r') \tag{2.15}$$

which gives the solution to the Schrödinger equation as

$$\psi(r) = \begin{cases} \int G(r, r'; z) \, dr' & : z \neq \lambda_n \\ \int G^{\pm}(r, r'; \lambda) \, dr' + \phi(r) & : z = \lambda \end{cases} \tag{2.16}$$

2.2 Green's function pertubation theory

For many-body interactions, a common approach to compute the Green's function is to use perturbation theory, where the solvable part would be to find the non-interacting Green's function G_0 and the pertubation would be the interaction[36]. We would then partition the Hamiltonian as

$$H = H_0 + V \tag{2.17}$$

where H_0 is the Hamiltonian for the free particle, and V is an interaction.

From this the Green's function is expressed as a geometric series in terms of the non-interacting Green's function and the interaction, which gives the Dyson equation

$$G = \frac{1}{G_0^{-1} - V} \tag{2.18}$$

To describe the interaction V, the interacting Green's function is treated as having a series of encounters with an interaction called the self energy. This is the energy the particle has because of its interaction with the rest of the system, and in turn interacts with itself. The self energy is then a description of all of the many-body interactions of the system. It is found by solving the Dyson equation as

$$\Sigma = G_0^{-1} - G^{-1} \tag{2.19}$$

2.2.1 Temperature dependent Matsubara Green's function

The temperature dependent Matsubara Green's function formalism was introduced in 1955[39]. This is a statistical theory, relying on boltzmann-factors ($c^{-\beta H}$) to compute ensemble quantities. The Matsubara Green's function for an electron can be written as

$$G = \frac{\mathrm{Tr}\left[e^{-\beta H} C_{p\sigma}(t_0) C_{p\sigma}^\dagger(t)\right]}{\mathrm{Tr}\left(e^{-\beta H}\right)} \tag{2.20}$$

Time dependence in operators comes from time evolution operators

$$C_{p\sigma}(t) = e^{itH} C_{p\sigma} e^{-itH} \tag{2.21}$$

similarly to the time evolution factors in time dependent solutions of the Schrödinger equation. For a complete set of eigenfunctions of the Hamiltionian ϕ_n, any solution to the Schrödinger equation (2.13) can be written as a linear combination of the eigenfunctions

$$\psi(r) = \sum_n C_n \phi_n(r) \tag{2.22}$$

These eigenfunctions, have an inherent time-dependence $\phi_n(r, t) = e^{itE_n}$. This comes from the time dependent Schrödinger equation. Any solution to the time dependent Schrödinger equation can be written as a linear combination of these time dependent eigenfunctions

$$\psi(r, t) = \sum_n C_n \phi_n(r, t) = \sum_n C_n e^{itE_n} \phi_n(r) \tag{2.23}$$

Both Boltzmann factors and time evolution operators e^{-itH} are in exponential form. We can therefore treat time as a complex inverse temperature by using $e^{-\beta H} e^{itH} = e^{(-\beta + it)H}$
The Green's function is Fourier transformed into

$$G = \frac{1}{i\omega - H} \tag{2.24}$$

where G can be computed by frequency sums over unperturbed Green's functions. For Matsubara Green's function, this is a sum over Matsubara frequencies

$$i\omega = \frac{(2n + 1)i\pi}{\beta}, \quad n = 0, 1, 2, \ldots \tag{2.25}$$

We can now obtain the partition function (Z) which is an important quantity from statistical mechanics, from which many thermodynamic quantities can be derived. The partition function can be obtained from $Z = e^{-\beta\Omega}$ where Ω is the grand potential. The grand potential, defined as

$$\Omega \overset{\text{def}}{=} E - TS - \mu N \tag{2.26}$$

can be computed directly from the Green's function as

$$\Omega = \frac{1}{\beta} \left\{ \Phi - \text{Tr} \left[\Sigma G + \ln \left(\Sigma - G_0^{-1} \right) \right] \right\} \tag{2.27}$$

where Φ is the Luttinger-Ward functional, computed as

$$\Phi = \sum_{m=1}^{\infty} \frac{1}{2m} \text{Tr} \left[\Sigma^{(m)} G \right] \tag{2.28}$$

where m is the level of truncation of the self-energy. Poles of the Green's function along the real frequency axis correspond to electron removal/addition energies giving a connection for evaluating spectra

$$A(\omega) = \frac{-1}{\pi} \text{Tr}[\text{Im} \, \mathbf{G}(\omega)] \tag{2.29}$$

The Helmholtz free energy $(A = E - TS)$ can be connected to the grand potential through

$$A = \Omega + \mu N \tag{2.30}$$

where N is the number of electrons. This gives a way to calculate the entropy

$$S = \frac{E - \Omega - \mu N}{T} \tag{2.31}$$

where the internal energy (E) can be evaluated through the Galitskii-Migdal formula[36]

$$E = \frac{1}{2} \text{Tr}[(h + F)\gamma] + \frac{2}{\beta} \sum_{n}^{N_\omega} \text{Re} \left(\text{Tr} \left[G \left(i\omega_n \right) \Sigma \left(i\omega_n \right) \right] \right) \tag{2.32}$$

where γ is the one-body density matrix, h is the one-body Hamiltonian, F is the Fock-matrix, and N_ω is the size of the complex grid.

3 Discussion

To shed light on the current state of temperature dependence in Green's function methods we will look at some recent progress in the application on periodic systems, as well as a look at the use of similar methods on realistic systems in the past. As mentioned, Green's function methods have been used heavily on realistic systems such as transition-metal oxides and semiconductors. This has many applications in fields like high-temperature superconductors, microprocessor-technologies and others where the electronic properties of solids at various temperatures are important. The methods that have seen a lot of use in the last few decades rely heavily on approximations such as the GW approximation. This is a truncated Green's function approach which has the potential of losing a lot of higher order information and produce unreliable and non-unique thermodynamic properties. As the approximations have seen much use, it is natural that there has been much research into the improvement of the self-consistency conditions to produce the best results possible. However, to completely eliminate the shortcomings of these approximations, it is desired to compute a fully self-consistent imaginary axis Green's function. This seems to be similar to the evolution from early mean field approaches like HF to the further development for computing correlation energies that lead to methods like coupled cluster. These methods are much harder to rigorously generalize because of the nature of the analytic continuation onto the real axis that is needed to extract useful quantities. A common model system to serve as a good benchmark for the computation on periodic systems is the 1D periodic hydrogen lattice. Except for research specifically into metallic hydrogen, this is not in and of itself a realistic system, but it does serve as a good stepping stone to the further investigation of more realistic systems. Even though it is the simplest possible periodic system, it does show some properties that is characteristic of more complicated solids, such as different phase properties at different temperatures and pressures that reminisce that of more realistic solids. We look at the application of the recently developed GF2 method on this system, as well as for a simple computation of thermodynamic quantities on the HF molecule at various temperatures and compared to data from Hartree-Fock. We will also look at one of the main current limitations of the method, being the computation of temperature dependent ionization potentials and electron affinities. [2]

3.1 Electronic Structure of NiO by GW approximation

As briefly mentioned in the introduction, the GW approximation (GWA) has seen much use on different realistic systems. This is an approximation of the self energy (2.19) where it is expressed as a Taylor-series of a screened interaction W and truncated to first order. This has been a good, and computationally feasible method for computing approximations to the many-body correlation effects that arise in solids. A notable example is the nickel oxide crystal. This has been a notoriously hard material to computationally describe accurately

as conventional band models as DFT and HF predict that it should behave like a metal with a band gap of 0.2 eV[40], but experimentally has shown clear insulator properties with a band gap of around 4 eV[40]. The first *ab-initio* computation on NiO taking electron correlations properly into account was done by a GW approximation[40]. This is a much better approximation than the band models, however, they note that a satellite peak is missing from the spectra they produced. They explain that these types of satellite peaks are expected to be absent for the GW approximation since they seem to be inherently linked to higher order terms in the self-energy, which GWA by definition does not include. We will see that the fully self-consistent Matsubara Green's function includes these contributions.

3.2   Comparison of GF2 and HF on the HF molecule

In [36] they use the hydrogen fluoride molecule (HF) as a simple benchmark. They compute the internal energy E, the Helmholtz energy A, and the entropy S. They compare the Green's function method to second order (GF2) to Hartree-Fock, using FCI for the exact values, using the STO-3G basis as a minimal basis. As the goal was a simple benchmark to compare methods, rather than the accuracy of the quantities, a minimal basis is fine. To get accurate results at high temperature, they note, you would need a very large basis set. They also note that the calculation on the HF molecule is somewhat pointless as the electronic contribution to thermodynamics is negligible for small molecular systems. It does however work as a small simple comparison of the methods where the exact values are known. They have produced some plots which compares the results from HF and GF2 to the exact values from FCI. The temperature range here is quite large $(10^3 - 10^8 K)$ since the HOMO-LUMO gap in HF is huge compared to low temperature energies. For intermediate temperatures GF2 is consistently closer to FCI than HF, but in the very high temperatures both methods are very close to FCI. It is expected that HF is close to FCI for very high temperatures as mean field approaches give good descriptions in the high temperature limit.

3.3   Calculations on periodic 1D hydrogen

Perhaps the most interesting results from [36] is from their computations on a 1D periodic hydrogen lattice. They did this at various temperatures and pressures. Pressures are simulated by changing the bond distance where a low bond distance would correspond to a high pressure and vice versa. Through these calculations they were able to get phase properties that were organized into a phase diagram where the different possible phases are marked for each temperature/pressure combination. For intermediate pressures they were able to recover multiple solutions for each pressure/temperature combination. Whether this is due to mathematical artifacts of the method, or if they have a physical correspondence to the possible coexistence of multiple phases does not seem to be well understood. Whenever multiple solutions were recovered they used the Helmholtz energies, obtainable from 2.30 to

determine which was the most stable.

These different solutions were found by starting at different initial guesses and seeing if they converge to different solutions. For each of the solutions they plotted the analytic continuation of the Green's function to the real axis. The 2D plots give rise to a correlated band structure which is somewhat analogous to the conventional band structure from methods like HF and DFT. The peaks of the spectra would then be interpreted as the equivalent of the highest occupied and lowest unoccupied crystalline orbitals (HOCO/LUCO). However, they stress that this is not a perfect correspondence since the Green's function contains much more information as it takes all the many-body interactions into account. It is however, a useful analogy to get a qualitative understanding of the spectra.

For the highest pressure/lowest bond distance, only one solution was obtainable for all temperatures. This was a metallic solution with no band gap, which one might expect for such conditions. In their previous work on periodic hydrogen[33] they got two solutions with a small difference in internal energy for the lowest temperature, however, due to improved convergence criteria they managed to eliminate this difference for this work.

For intermediate pressures, this metallic solution was still obtainable, but for low temperatures, a solution with a band gap is now obtainable from some starting points. The interesting part is now how the method is able to describe how the gap shrinks and disappears for higher temperatures. This is one of the key properties of solids that is important to describe to properly describe qualitative differences in, for example, semi conductors at various temperatures. For high temperatures, they provide some numerical values which indicate that the two different solutions are really the same solutions for high temperatures, with a difference in Helmholtz below their convergence threshold of 10^{-5} a.u. For the lower temperatures the values indicate that the insulating phase is the most stable with a difference in Helmholtz energy of 0.1 a.u. which interestingly is dominated by the entropy contribution rather then the internal energy.

For the second lowest pressure, the temperature dependence is reversed from the intermediate pressures. There was still the two solutions for low temperatures; one metallic and one insulator, with the insulator being the most stable. In contrast to the intermediate and high pressures, the metallic solutions have way more chaotic spectra, indicating that this is close to a phase transition. Both of the solutions converge to the same insulator phase for the highest temperature, so no metallic phase is obtained. They note that since GF2 is a low order perturbation expansion, it may fail to be as reliable close to phase transitions as it us usually more accurate deep into the phases.

For the lowest pressure only one solution is obtainable for all temperatures, which is a clear insulator phase with a large distinct band gap.

3.4 Calculations on periodic 1D boron nitride

As a calculation for a larger and more realistic system that has a real 2D counterpart with both theoretical and experimental research[41, 42, 43, 44, 45], they[36] also did computations on 1D boron nitride at various temperatures. This is a much larger system than the 1D hydrogen example, with about 6 times more Matsubara frequencies used, but it is still a fairly small system to serve as a benchmark for the method. They do not compute at different pressures here as they can use the corresponding bond distance for the 2D counterpart[42]. They provide a similar spectra to the ones for 1D hydrogen, but now only a 1D slice to illustrate the band gap, which they obtain with a magnitude expected from the 2D counterpart. The temperature evolution of these spectra is as expected, with broadening of the peaks, and thus reduction of the band gap with increasing temperature. They do note however, that this requires very robust computations to reproduce reliably because of the nature of the analytic continuation to extend the imaginary axis Green's function onto the real axis. If done insufficiently, this can result in higher order information, like the satellite peaks in the NiO spectra, to not be visible.

3.5 Ionization potentials and electron affinities from finite temperature Green's function

In electronic structure it is useful to know ionization potentials and electron affinities. These have been calculated with great accuracy by multiple various methods for zero-temperature, however, experimental values are naturally done at finite temperature. The methods they use include some extensions of HF by using the self energy from the Matsubara Green's function, as well as a Green's function extension of Koopmans' theorem. As stated previously, finite-temperature adaptations of conventional electronic structure methods like HF and DFT are very costly and we have seen how the finite-temperature Green's function formalism performs very well for computing thermodynamic properties. [36] have explored multiple different methods for extracting this information. This unfortunately seems to be one of the great current limitations of the formalism. In general it seems as though this is not simple to achieve. They state that for small systems such as atoms and small molecules, the apparent agreement with experimental values for some systems is due to the cancellation of errors, rather than the method actually being systematically accurate. They conclude that it is very unclear whether the inclusion of correlation increases the accuracy of the methods. It is clear that until a lot more research has gone into these kinds of methods, one needs to be very cautious when evaluating spectra from imaginary axis Green's function methods, and using them to determine ionisation potentials and electron affinities.

4   Conclusion

The use of Green's function methods in quantum chemistry has seen an increasing use as the cost of computing power and memory has fallen in the last few decades. As such, there has been a lot of research into the development of different methods for computing various properties. One key strength of the Green's function formalism is the manner in which temperature dependence can be incorporated. This enables the computation of various thermodynamic properties in large realistic systems such as periodic lattices.

As Green's function method are computationally intensive, and hard to rigorously generalize, approximations like the GW approximation have seen a lot of use on realistic systems. Here we have looked at one such computation on the notorious nickel oxide. The strongly correlated electronic structure here makes the compound qualitatively different from the predictions made by HF and DFT. The Green's function approach on the other hand, correctly predicts its insulating nature. However, because of its truncated nature, it does lose some satellite peaks in the spectra.

In more recent times, a lot of work has gone into the development of a fully self-consistent Matsubara Green's function method (GF2). This addresses a lot of the problems with the previously popular approximations. Here we have looked at the first application of this method for computing thermodynamic properties, such as Helmholtz energy, internal energy, and entropy. As a simple molecular example we have looked at the HF molecule with the STO-3G minimal basis set, which is a simple enough system that the exact values can be calculated through the finite temperature FCI formalism. For low and high temperatures GF2 was in excellent agreement with the FCI values and for intermediate temperatures there was some deviation, but this was well within the magnitude of which Hartree-Fock deviates. We also looked at the application of this method for the 1D periodic hydrogen lattice. This was done at various temperatures and pressures (simulated by bond distances). From the thermodynamic properties a phase diagram was produced, which showed if the system was in a metal or insulator phase. For intermediate pressures, the method was able to converge to two different solutions. It seems unclear whether this is because of mathematical artifacts in the method or if it corresponds to different physical phases. In any case, the most stable of the solutions were determined by the computation of the Helmholtz energy, which ended up being the insulator phase.

Another potential application of the method, which proved to be one of its greatest current limitations was the computation of temperature dependent ionization potentials and electron affinities. This showed highly unreliable results, and the apparent accuracy on small systems seemed to come from error cancellation.

All in all, the computational methods based on the Matsubara formalism seem very promising. However, there is still a lot of research needed to get rigorous results, and making sense of the multiple converging solutions.

References

[1] N. D. Mermin, "Stability of the thermal Hartree-Fock approximation," *Annals of Physics*, vol. 21, pp. 99–121, Jan. 1963.

[2] J. C. Slater, "A Simplification of the Hartree-Fock Method," *Physical Review*, vol. 81, pp. 385–390, Feb. 1951. Publisher: American Physical Society.

[3] P.-O. Löwdin, "Quantum Theory of Many-Particle Systems. III. Extension of the Hartree-Fock Scheme to Include Degenerate Systems and Correlation Effects," *Physical Review*, vol. 97, pp. 1509–1520, Mar. 1955. Publisher: American Physical Society.

[4] J. Jaklič and P. Prelovšek, "Lanczos method for the calculation of finite-temperature quantities in correlated systems," *Physical Review B*, vol. 49, pp. 5065–5068, Feb. 1994. Publisher: American Physical Society.

[5] P. Prelovšek and J. Bonča, "Ground State and Finite Temperature Lanczos Methods," in *Strongly Correlated Systems: Numerical Methods* (A. Avella and F. Mancini, eds.), Springer Series in Solid-State Sciences, pp. 1–30, Berlin, Heidelberg: Springer, 2013.

[6] S. Hirata and X. He, "On the Kohn–Luttinger conundrum," *The Journal of Chemical Physics*, vol. 138, p. 204112, May 2013. Publisher: American Institute of Physics.

[7] M. Altenbokum, K. Emrich, H. Kümmel, and J. G. Zabolitzky, "A Temperature Dependent Coupled Cluster Method," in *Condensed Matter Theories: Volume 2* (P. Vashishta, R. K. Kalia, and R. F. Bishop, eds.), pp. 389–396, Boston, MA: Springer US, 1987.

[8] S. H. Mandal, R. Ghosh, G. Sanyal, and D. Mukherjee, "A finite-temperature generalisation of the coupled cluster method: a non-perturbative access to grand partition functions," *International Journal of Modern Physics B*, vol. 17, pp. 5367–5377, Nov. 2003. Publisher: World Scientific Publishing Co.

[9] M. R. Hermes and S. Hirata, "Finite-temperature coupled-cluster, many-body perturbation, and restricted and unrestricted Hartree–Fock study on one-dimensional solids: Luttinger liquids, Peierls transitions, and spin- and charge-density waves," *The Journal of Chemical Physics*, vol. 143, p. 102818, Sept. 2015. Publisher: American Institute of Physics.

[10] N. D. Mermin, "Thermal Properties of the Inhomogeneous Electron Gas," *Physical Review*, vol. 137, pp. A1441–A1443, Mar. 1965. Publisher: American Physical Society.

[11] V. V. Karasiev, T. Sjostrom, J. Dufty, and S. Trickey, "Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for Local Spin-Density Calculations," *Physical Review Letters*, vol. 112, p. 076403, Feb. 2014. Publisher: American Physical Society.

[12] M. W. C. Dharma-wardana, "Current Issues in Finite-T Density-Functional Theory and Warm-Correlated Matter †," *Computation*, vol. 4, p. 16, June 2016. Number: 2 Publisher: Multidisciplinary Digital Publishing Institute.

[13] V. Gavini, K. Bhattacharya, and M. Ortiz, "Quasi-continuum orbital-free density-functional theory: A route to multi-million atom non-periodic DFT calculation," *Journal of the Mechanics and Physics of Solids*, vol. 55, pp. 697–718, Apr. 2007.

[14] J. V. Beck, K. D. Cole, A. Haji-Sheikh, B. Litkouhl, K. D. Cole, A. Haji-Sheikh, and B. Litkouhl, *Heat Conduction Using Green's Function*. Taylor & Francis, Feb. 1992.

[15] R. P. Feynman, "Mathematical Formulation of the Quantum Theory of Electromagnetic Interaction," *Physical Review*, vol. 80, pp. 440–457, Nov. 1950. Publisher: American Physical Society.

[16] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-body Problem*. Courier Corporation, Jan. 1992.

[17] G. Stefanucci and R. v. Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction*. Cambridge University Press, Mar. 2013. Google-Books-ID: 6GsrjPFXLDYC.

[18] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*. Courier Corporation, Mar. 2012. Google-Books-ID: t5_DAgAAQBAJ.

[19] G. Li, W. Hanke, A. N. Rubtsov, S. Bäse, and M. Potthoff, "Accessing thermodynamics from dynamical cluster-embedding approaches," *Physical Review B*, vol. 80, p. 195118, Nov. 2009. Publisher: American Physical Society.

[20] M. Potthoff, M. Aichhorn, and C. Dahnken, "Variational Cluster Approach to Correlated Electron Systems in Low Dimensions," *Physical Review Letters*, vol. 91, p. 206402, Nov. 2003. Publisher: American Physical Society.

[21] M. Potthoff, "Self-energy-functional approach: Analytical results and the Mott-Hubbard transition," *The European Physical Journal B - Condensed Matter and Complex Systems*, vol. 36, pp. 335–348, Dec. 2003.

[22] M. Potthoff, "Self-energy-functional approach to systems of correlated electrons," *The European Physical Journal B - Condensed Matter and Complex Systems*, vol. 32, pp. 429–436, Apr. 2003.

[23] D. Neuhauser, Y. Gao, C. Arntsen, C. Karshenas, E. Rabani, and R. Baer, "Breaking the Theoretical Scaling Limit for Predicting Quasiparticle Energies: The Stochastic GW Approach," *Physical Review Letters*, vol. 113, p. 076402, Aug. 2014. Publisher: American Physical Society.

[24] L. Hung, F. H. da Jornada, J. Souto-Casares, J. R. Chelikowsky, S. G. Louie, and S. Öğüt, "Excitation spectra of aromatic molecules within a real-space GW-BSE formalism: Role of self-consistency and vertex corrections," *Physical Review B*, vol. 94, p. 085125, Aug. 2016. Publisher: American Physical Society.

[25] M. van Schilfgaarde, T. Kotani, and S. Faleev, "Quasiparticle Self-Consistent GW Theory," *Physical Review Letters*, vol. 96, p. 226402, June 2006. Publisher: American Physical Society.

[26] F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, "Self-consistent GW: All-electron implementation with localized basis functions," *Physical Review B*, vol. 88, p. 075105, Aug. 2013. Publisher: American Physical Society.

[27] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, "All-Electron Self-Consistent GW Approximation: Application to Si, MnO, and NiO," *Physical Review Letters*, vol. 93, p. 126406, Sept. 2004. Publisher: American Physical Society.

[28] C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, "Fully self-consistent GW calculations for molecules," *Physical Review B*, vol. 81, p. 085103, Feb. 2010. Publisher: American Physical Society.

[29] M. Govoni and G. Galli, "Large Scale GW Calculations," *Journal of Chemical Theory and Computation*, vol. 11, pp. 2680–2696, June 2015. Publisher: American Chemical Society.

[30] N. E. Dahlen, R. van Leeuwen, and U. von Barth, "Variational energy functionals of the Green function and of the density tested on molecules," *Physical Review A*, vol. 73, p. 012511, Jan. 2006. Publisher: American Physical Society.

[31] R. van Leeuwen, N. E. Dahlen, and A. Stan, "Total energies from variational functionals of the Green function and the renormalized four-point vertex," *Physical Review B*, vol. 74, p. 195105, Nov. 2006. Publisher: American Physical Society.

[32] J. J. Phillips and D. Zgid, "Communication: The description of strong correlation within self-consistent Green's function second-order perturbation theory," *The Journal of Chemical Physics*, vol. 140, p. 241101, June 2014. Publisher: American Institute of Physics.

[33] A. A. Rusakov and D. Zgid, "Self-consistent second-order Green's function perturbation theory for periodic systems," *The Journal of Chemical Physics*, vol. 144, p. 054106, Feb. 2016. Publisher: American Institute of Physics.

[34] A. A. Kananenka, A. R. Welden, T. N. Lan, E. Gull, and D. Zgid, "Efficient Temperature-Dependent Green's Function Methods for Realistic Systems: Using Cubic

Spline Interpolation to Approximate Matsubara Green's Functions," *Journal of Chemical Theory and Computation*, vol. 12, pp. 2250–2259, May 2016. Publisher: American Chemical Society.

[35] A. A. Kananenka, E. Gull, and D. Zgid, "Systematically improvable multiscale solver for correlated electron systems," *Physical Review B*, vol. 91, p. 121111, Mar. 2015. Publisher: American Physical Society.

[36] A. R. Welden, "Finite-Temperature Green's Function Methods for ab-initio Quantum Chemistry: Thermodynamics, Spectra, and Quantum Embedding," 2018.

[37] E. N. Economou, *Green's Functions in Quantum Physics*. Springer Science & Business Media, Aug. 2006. Google-Books-ID: HdJDAAAAQBAJ.

[38] J. Schueler, "Green's Functions and Their Applications to Quantum Mechanics," p. 15, June 2011.

[39] T. Matsubara, "A New Approach to Quantum-Statistical Mechanics," *Progress of Theoretical Physics*, vol. 14, pp. 351–378, Oct. 1955. Publisher: Oxford Academic.

[40] F. Aryasetiawan and O. Gunnarsson, "Electronic Structure of NiO in the GW Approximation," *Physical Review Letters*, vol. 74, pp. 3221–3224, Apr. 1995. Publisher: American Physical Society.

[41] R. S. Pease, "Crystal Structure of Boron Nitride," *Nature*, vol. 165, pp. 722–723, May 1950. Number: 4201 Publisher: Nature Publishing Group.

[42] P. Miró, M. Audiffred, and T. Heine, "An atlas of two-dimensional materials," *Chemical Society Reviews*, vol. 43, no. 18, pp. 6537–6554, 2014. Publisher: Royal Society of Chemistry.

[43] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, "Boron Nitride Nanotubes," *Science*, vol. 269, pp. 966–967, Aug. 1995. Publisher: American Association for the Advancement of Science Section: Reports.

[44] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, and J. Osterwalder, "Boron Nitride Nanomesh," *Science*, vol. 303, pp. 217–220, Jan. 2004. Publisher: American Association for the Advancement of Science Section: Report.

[45] D. Golberg, Y. Bando, C. C. Tang, and C. Y. Zhi, "Boron Nitride Nanotubes," *Advanced Materials*, vol. 19, no. 18, pp. 2413–2432, 2007. _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.200700179.